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Design, Fabrication and Mechanical Characterization of Fused Silica Microstructures by Two-Photon Polymerization

TESI DI LAUREA MAGISTRALE IN
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Abstract

This thesis focuses on the fabrication and mechanical characterization of **fused silica micropillars** produced by **Two-Photon Polymerization (2PP)** using the silica-loaded **GP-Silica** resin, followed by thermal conversion through **debinding** and **sintering**. All experimental activities were carried out at EMPA – Swiss Federal Laboratories for Materials Science and Technology (Thun, Switzerland). The objective is to strengthen the reliability and comparability of microscale mechanical measurements by improving the **reproducibility** of geometry, surface condition, and defect population across printing and post-processing conditions.

A systematic experimental campaign was conducted to: (i) establish a stable **process window** for printing pillars suitable for mechanical testing; (ii) quantify the impact of **time-dependent** process drift and **relative humidity** on print fidelity and defect formation; and (iii) clarify how thermal treatments affect **shrinkage**, final geometry, and mechanical response. A reference conversion condition of 1300 °C for 4320 s was selected, enabling the production of dense and sufficiently uniform glass pillars for quantitative testing on a consistent substrate population.

Mechanical characterization combines **microcompression** and **pillar splitting** tests performed on the same material state, providing complementary insight into elastic response, strength, and defect sensitivity, including a microscale metric related to **fracture toughness**. The results show that, at micrometer dimensions, the mechanical behavior does not simply replicate that of bulk glass: measured strengths can shift toward significantly higher values, consistent with the reduced probability of sampling a critical flaw (the *smaller is stronger* concept). At the same time, the experiments demonstrate that even minor variations in geometry, contact conditions, and surface state leave measurable signatures in the mechanical curves and contribute to scatter among nominally identical specimens. Overall, the work establishes a clear process–structure–property relationship for 2PP-derived fused silica micropillars and provides practical guidance on how fabrication variability translates into variability in microscale mechanical response.

Keywords: fused silica micropillars; Two-Photon Polymerization (2PP); GP-Silica;

debinding; sintering; reproducibility; process window; process drift; relative humidity; shrinkage; microcompression; pillar splitting; fracture toughness; size effect; smaller is stronger.

Abstract in lingua italiana

Il lavoro di tesi riguarda la realizzazione e la caratterizzazione meccanica di **micropilastri in silice fusa** ottenuti mediante **Two-Photon Polymerization (2PP)** a partire dalla resina caricata in silice **GP-Silica**, con successiva conversione termica tramite **debinding** e **sintering**. Le attività sperimentali sono state svolte presso EMPA – Swiss Federal Laboratories for Materials Science and Technology (Thun, Svizzera). L’obiettivo è rendere più solide e confrontabili le misure meccaniche su microscala, migliorando la **riproducibilità** di geometria, stato superficiale e difettosità al variare delle condizioni di stampa e post-processo.

Viene presentata una campagna sperimentale mirata a: (i) definire una **finestra di processo** stabile per la stampa di pilastri idonei alle prove meccaniche; (ii) quantificare l’impatto della **deriva temporale** del processo e dell’**umidità relativa** su fedeltà di stampa e formazione di difetti; (iii) chiarire come i trattamenti termici influenzino **shrinkage**, geometria finale e risposta meccanica. Come condizione di riferimento è stata selezionata una conversione a 1300 °C per 4320 s, che consente di ottenere pilastri in vetro denso e sufficientemente uniformi per una caratterizzazione quantitativa sulla stessa popolazione di substrato.

La caratterizzazione meccanica combina prove di **microcompressione** e test di **pillar splitting** sullo stesso stato di materiale, così da descrivere in modo complementare risposta elastica, resistenza e sensibilità alla presenza di difetti locali, includendo anche una metrica legata alla **tenacità a frattura** (*fracture toughness*) su microscala. I risultati mostrano che, a queste dimensioni, il comportamento non ricalca semplicemente quello del vetro su scala macroscopica: le proprietà misurate possono spostarsi verso valori più elevati, in linea con l’idea che riducendo il volume sollecitato diminuisca la probabilità di intercettare un difetto critico (concetto alla base del *smaller is stronger*). Allo stesso tempo, emerge con chiarezza che su microscala anche variazioni minime di geometria, contatto e stato superficiale lasciano una firma misurabile nelle curve e contribuiscono alla dispersione tra campioni nominalmente identici. Nel complesso, il lavoro stabilisce un collegamento processo-struttura-proprietà per micropilastri in silice fusa ottenuti via 2PP e fornisce indicazioni operative su come la variabilità di fabbricazione si traduca in

variabilità della risposta meccanica su microscala.

Parole chiave: micropilastri in silice fusa; Two-Photon Polymerization (2PP); GP-Silica; debinding; sintering; riproducibilità; finestra di processo; deriva temporale; umidità relativa; shrinkage; microcompressione; pillar splitting; *fracture toughness*; effetto di scala; smaller is stronger.

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1 | Introduction and State of the Art

1.1. Motivation, scope, and thesis contribution

Fused silica is a model amorphous ceramic: it combines outstanding thermal, chemical, and optical stability with an intrinsically brittle mechanical response. At the macroscopic scale, its strength is rarely an intrinsic property and is instead affected by the statistics of surface and volume flaws. When the characteristic dimensions shrink to the micrometer range, the likelihood of sampling a critical defect decreases and the apparent strength can move closer to intrinsic limits, while the test outcome becomes extremely sensitive to geometry, surface condition, and processing-induced imperfections. [1]

In parallel, materials research is increasingly shifting toward micro- and nano-architected solids, where performance is engineered through geometry as much as through chemistry. However, translating ceramic and glass materials into micro-architected forms remains substantially harder than for polymers or metals, because brittle materials are less tolerant to defects and their manufacturing routes at small scale are typically multi-step and variability-prone. This makes the manufacturing process chain not a background detail, but a first-order design variable that ultimately controls reliability and mechanical performance. [2]

Two-Photon Polymerization (2PP) combined with silica-filled photopolymer resins and subsequent debinding/sintering offers a practical route to fabricate micrometer-scale fused silica with high design freedom. In this workflow, the final specimen is not “printed glass” in a single step: it is the emergent result of an integrated chain that includes exposure conditions, development, binder removal, viscous densification, shrinkage, and environmental variability. Consequently, even small deviations in printing parameters, resin state, cleanroom conditions, or thermal history can translate into geometric artifacts, residual porosity, and surface flaws. These effects directly bias stress estimation, complicate comparisons across specimens, and may change the apparent deformation and

failure modes observed during microscale tests. [2]

This thesis is motivated by a simple but impactful gap: despite the rapid growth of 2PP-derived glass microfabrication, systematic mechanical datasets on *fully converted* fused silica produced *end-to-end* via the 2PP–nanocomposite–debinding/sintering route are still scarce and often difficult to compare across studies. In particular, the literature contains limited and heterogeneous data on well-controlled micropillar compression and pillar splitting for specimens whose geometry, process history, and post-processing are documented in a way that enables a meaningful process–structure–property interpretation.

For this reason, the first core objective of the work is not to demonstrate the most complex geometry that can be fabricated, but to build a robust and reproducible *process playbook*. The thesis develops and optimizes a sequence of practical steps that leads from setup choices (materials, substrates, mounting strategy, and tool selection), through printing (process parameters and scan strategy), development (handling-sensitive steps and defect mitigation), environmental control (time effects, temperature/humidity sensitivity, and resin aging), and thermal conversion (debinding and sintering schedules, shrinkage, and geometry retention). The rationale is deliberately engineering-oriented: each step is treated as a lever that can be tuned, diagnosed, and stabilized, so that a future user can reproduce simple fused silica microstructures while understanding *what to do*, *why it matters*, and *what failure modes to expect* along the chain.

The second objective is mechanical: once a stable fabrication route is established, the thesis performs microscale mechanical characterization of 2PP-derived fused silica in a regime where data are still limited. While the mechanical properties of fused silica are well established at the macro-scale, transferring those expectations to micrometer-sized specimens is non-trivial because the measured response couples intrinsic glass behavior with specimen geometry, surface state, and process-induced defects. In this work, cylindrical micropillars are intentionally used as a controlled reference geometry to enable quantitative stress–strain extraction and to support clear comparisons across specimens printed and converted under the same reference thermal state.

The experimental program combines (i) identification of stable fabrication conditions and quality criteria, (ii) quantitative evaluation of shrinkage, geometry retention, and reproducibility after thermal conversion, and (iii) mechanical testing through micropillar compression (stress–strain response) and pillar splitting with cube-corner indentation (fracture toughness). The overarching goal is to clarify to what extent a “smaller is stronger” trend can be observed for fused silica produced via this additive microfabrication

route, and to connect strength and failure signatures to the underlying process-dependent defect population and geometric fidelity.

A key thesis contribution is therefore the explicit coupling between mechanical characterization and manufacturing reproducibility. Instead of treating micropillars as ideal test coupons, the interpretation is anchored to the real process chain and to its dominant sources of variability. This enables the definition of practical limits of interpretability (for example when geometry departs from the nominal design), and it frames mechanical results as an outcome of a controlled, traceable workflow rather than as isolated measurements.

Finally, while this thesis focuses on simple pillars as the necessary foundation for quantitative mechanics, the broader context is the longer-term development of architected fused silica microstructures. Complex lattices and functional micro-architectures are discussed as a natural continuation once the process chain is stabilized and the mechanical response of reference geometries is understood. In that sense, this work aims to provide the solid baseline that future studies can leverage to move from “can we fabricate it?” to “can we design it for performance and reliability?”.

The remainder of this chapter provides the background required to interpret the experimental results. It reviews the brittle mechanical response of glasses and the relevance of fused silica as a model amorphous material, introduces size effects in brittle solids from both statistical and mechanistic viewpoints, and summarizes the state of the art in 2PP-based fabrication and thermal conversion of silica-filled resins, highlighting the specific challenges of reproducibility and geometry-sensitive microscale mechanical testing.

1.2. Ceramics and Glasses: Structure and Mechanical Behavior

Ceramic materials are characterized by predominantly ionic and covalent bonding, which gives rise to high elastic stiffness, excellent thermal stability, and high compressive strength [3]. These strong and directional bonds also limit the mobility of dislocations, strongly restricting the availability of plastic deformation mechanisms. As a result, most ceramics exhibit intrinsically brittle mechanical behavior, with failure typically governed by the nucleation and unstable growth of cracks originating from pre-existing defects [4].

Within this broad class, glasses represent a distinct category of ceramics in which the atomic structure lacks long-range periodic order. Despite the absence of crystallinity,

glasses retain many of the characteristic features of ceramic materials, including high stiffness and limited plasticity, while displaying mechanical responses that are strongly influenced by their amorphous nature [5].

Mechanical behavior of glasses. The mechanical behavior of glasses is dominated by their amorphous atomic structure and the absence of conventional dislocation-mediated plasticity. In oxide glasses, such as silicate-based systems, the atomic network is composed of corner-sharing tetrahedra linked through strong covalent bonds. Under mechanical loading, deformation is therefore accommodated almost exclusively through elastic bond stretching and bending, with negligible irreversible strain prior to failure [1].

As a consequence, glasses often display a predominantly linear elastic stress–strain response up to fracture at the macroscopic scale, with limited macroscopic plasticity. At small length scales and under highly confined stress states (e.g., microcompression), deviations from strict linearity may emerge due to mechanisms such as densification or shear-assisted rearrangements of the amorphous network [6].

Because plastic deformation is essentially absent, stresses cannot be redistributed around local heterogeneities. Instead, stress concentrations develop at surface or volume flaws, such as microcracks, scratches, or inclusions, which act as preferential sites for crack initiation. The measured strength of glass components is therefore governed by fracture mechanics rather than by the intrinsic strength of the atomic bonds, leading to pronounced scatter even among nominally identical specimens [4].

The influence of loading mode further reflects this behavior. Under tensile and bending loads, crack opening is promoted and surface flaws dominate the failure process, resulting in relatively low strengths and significant variability. Under compressive loading, crack opening is suppressed and the apparent strength is higher; however, failure remains controlled by localized fracture or shear-related mechanisms rather than by stable plastic flow [4].

Fused silica as a model glass. Among oxide glasses, fused silica occupies a unique position due to its exceptionally high chemical purity, structural homogeneity, and fully amorphous nature. Its atomic structure consists of a continuous random network of SiO_4 tetrahedra, which confers outstanding optical transparency, chemical inertness, and thermal stability over a wide temperature range [7].

These properties have led to the widespread use of fused silica in optical components, microelectronic substrates, and high-temperature applications, where dimensional

stability and resistance to chemical and thermal degradation are critical [7].

From a mechanical perspective, fused silica represents an ideal model system for studying the fundamental behavior of brittle amorphous solids. The absence of grain boundaries, crystallographic anisotropy, or secondary phases eliminates many of the microstructural variables that complicate the interpretation of mechanical response in polycrystalline ceramics. As a result, deformation and failure can be analyzed primarily in terms of elastic behavior, stress concentration, and fracture processes within a chemically and structurally uniform material [8].

At the macroscopic scale, the strength of fused silica is well known to be limited by surface and volume flaws introduced during fabrication, processing, or handling. Typical fracture strengths at the millimeter-to-centimeter scale are on the order of 1–1.5 GPa and exhibit significant statistical scatter, reflecting the stochastic nature of flaw populations [9].

At the same time, the simplicity and reproducibility of its amorphous structure make fused silica particularly well suited for probing how mechanical response evolves when characteristic dimensions are reduced. For this reason, fused silica has been extensively adopted as a reference material in microscale mechanical testing studies and serves as the primary material system investigated in this work [6].

1.3. Size Effects in Brittle Materials

The mechanical behavior of brittle materials is strongly influenced by defects and their statistical distribution. In ceramics and glasses, fracture typically initiates at pre-existing flaws such as surface microcracks, pores, or inclusions, which act as stress concentrators under applied loads. As a result, the apparent strength and deformation behavior depend not only on the intrinsic properties of the material, but also on the characteristic dimensions of the stressed volume. [10] This section first introduces the theoretical framework commonly used to describe size effects in brittle materials and subsequently reviews experimental evidence of how mechanical properties evolve when dimensions are reduced to the microscale.

Theoretical Framework for Size Effects The size dependence of strength in brittle materials is commonly interpreted within the framework of fracture mechanics and statistical models. Since failure is governed by the most critical flaw present in the stressed volume or surface, the probability of fracture increases with increasing specimen size. Weibull-type statistical approaches formalize this concept by linking the probability of failure to the distribution of flaws and the stressed volume [11].

Within Weibull theory, the probability of failure P_f under an applied stress σ can be expressed as in Equation (1.1).

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \frac{V}{V_0} \right], \quad (1.1)$$

where σ_0 is a characteristic strength, m is the Weibull modulus describing the scatter in strength, and V is the stressed volume relative to a reference volume V_0 . According to this formulation, larger specimens have a higher probability of containing a strength-limiting flaw, leading to lower average strengths and increased variability [4].

This statistical nature of fracture explains why bulk glass components typically exhibit relatively low and scattered strength values, despite the high intrinsic strength of atomic bonds. Conversely, when specimen dimensions are reduced, the likelihood of sampling large critical flaws decreases, resulting in higher measured strengths and reduced scatter. This effect is often summarized by the expression “smaller is stronger” and represents a fundamental consequence of flaw-controlled fracture in brittle materials [12].

Experimental Evidence of Size-Dependent Mechanical Behavior Experimental investigations at reduced length scales confirm the predictions of statistical fracture models and reveal additional features of brittle material behavior that are not accessible at the macroscale. In micro- and nanoscale testing, glasses and ceramics have been shown to sustain significantly higher stresses than their bulk counterparts, with measured strengths approaching the intrinsic limits of the atomic network [1]. For fused silica in particular, compressive strengths in the range of 8–10 GPa have been reported for micrometer-scale pillars, compared to typical macroscopic strengths on the order of 1–1.5 GPa [13].

Beyond strength scaling, size reduction also influences the shape of the stress–strain response. While bulk glasses are commonly described as purely elastic up to catastrophic fracture, microscale experiments indicate the emergence of nonlinear deformation prior to failure. In compression, the suppression of crack opening combined with highly confined stress states can activate additional deformation mechanisms, such as localized densification, shear-assisted rearrangements of the amorphous network, and time-dependent viscous flow [14].

The influence of specimen geometry and boundary conditions becomes increasingly pronounced at small length scales. In micropillar compression, the local stress distribution is strongly affected by pillar aspect ratio, taper, surface quality, and contact conditions with the indenter tip [15]. As a result, failure may occur through shear localization

or splitting mechanisms rather than classical tensile crack propagation [16]. While size reduction reduces the influence of material flaws, it simultaneously imposes stricter requirements on geometric control and test alignment in order to obtain reliable and reproducible mechanical data.

Overall, microscale experiments demonstrate that size effects in brittle materials involve not only an increase in strength, but also qualitative changes in deformation and failure behavior. These observations provide the necessary context for interpreting mechanical tests on microscale fused silica structures and form the basis for the experimental analysis presented in this work.

1.4. Fabrication route: 2PP-derived fused silica and thermal conversion

The fabrication of glass microstructures has traditionally relied on subtractive approaches such as precision machining, laser ablation, and wet or dry etching. While effective for planar or moderately complex geometries, these techniques become increasingly constrained when targeting truly three-dimensional microstructures with high aspect ratios and tight dimensional tolerances [17]. In brittle materials, machining-induced surface damage, microcracking, and residual stresses can further dominate the strength of the final component, which is particularly critical when mechanical characterization at small length scales is required [8].

To overcome these limitations, additive manufacturing (AM) routes have attracted significant interest as an alternative pathway toward complex glass geometries. Several strategies have been explored, including laser powder bed fusion (LPBF), extrusion-based approaches such as direct ink writing, and photopolymerization-based processes combined with post-processing [18]. However, most AM routes for glass face a fundamental trade-off between achievable resolution, geometric complexity, and final material quality. In particular, producing fully dense amorphous silica with high optical transparency remains challenging due to residual porosity, devitrification risks, and thermal stresses arising from steep temperature gradients during processing [19].

Within this landscape, photopolymerization-based shaping followed by thermal conversion has emerged as a promising route for high-quality fused silica microstructures. In these approaches, a silica-loaded photopolymer is first shaped into a green body and subsequently converted into glass through debinding and sintering [2]. By decoupling shape generation from high-temperature densification, this strategy enables complex

three-dimensional geometries while preserving the amorphous nature of silica when thermal schedules are properly controlled [20]. Among photopolymerization techniques, Two-Photon Polymerization offers the highest spatial resolution and design flexibility, making it particularly suited for microscale test geometries and micro-architected designs.

1.4.1. Two-Photon Polymerization of silica-loaded resins

Two-Photon Polymerization (2PP) is a laser-based microfabrication technique that enables the direct writing of three-dimensional structures with sub-micrometer resolution. Polymerization is initiated only within the focal volume of a tightly focused femtosecond laser beam through nonlinear two-photon absorption, which confines curing to a small voxel inside a photosensitive resin [21]. This nonlinear exposure mechanism enables true three-dimensional patterning without the need for layer-by-layer stacking, providing exceptional geometric flexibility and spatial precision as shown in Figure 1.1.

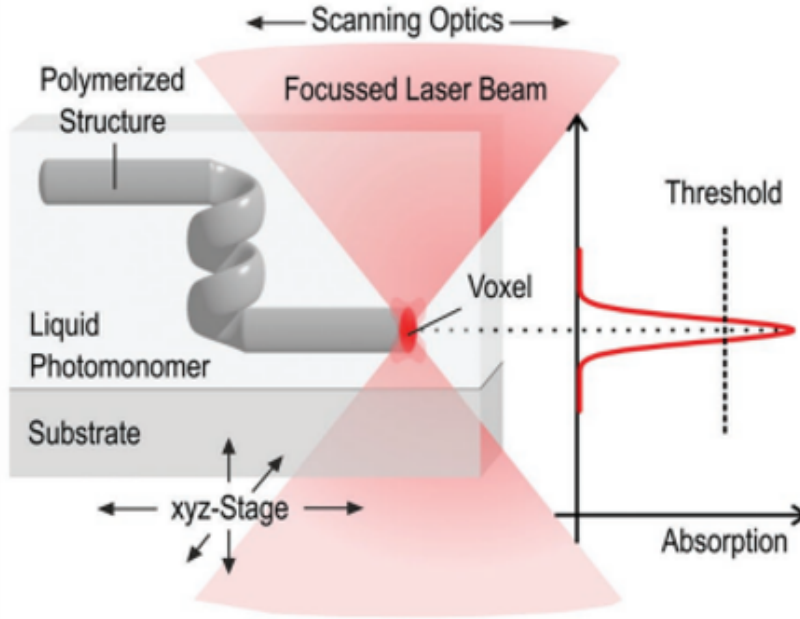


Figure 1.1: Schematic of Two-Photon Polymerization (2PP) and voxel-threshold concept. Adapted from [22].

Compared to conventional stereolithography, 2PP offers superior resolution and the ability to fabricate well-defined microscale test geometries (e.g., pillars) with tightly controlled dimensions, while still enabling more complex three-dimensional designs when required [23]. The effective voxel size and shape are governed by the numerical aperture of the objective lens, laser power, scan speed, and the photochemical properties of the resin, making the process highly sensitive to optical configuration and processing

parameters [24]. As a result, careful optimization of printing conditions is required to achieve reproducible and dimensionally accurate microstructures.

The extension of 2PP to ceramic and glass fabrication has been enabled by nanoparticle-loaded photopolymer resins. In these nanocomposite systems, inorganic particles are dispersed within a polymerizable organic matrix, allowing the fabrication of green bodies that can be converted into dense materials through thermal post-processing [17]. GP-Silica is a commercial nanocomposite resin designed for fused silica fabrication via 2PP. It contains a high volume fraction of silica nanoparticles embedded in an organic binder matrix [2]. After printing, the organic phase is removed during debinding and the silica network is densified during sintering, resulting in transparent fused silica components; with optimized thermal treatment, optical and mechanical properties can approach those of conventional fused silica [20].

Despite these advantages, GP-Silica introduces additional constraints compared to standard polymeric photoresists. High particle loading and viscosity lead to increased light scattering, narrower processing windows, and heightened sensitivity to exposure conditions [25]. These effects can produce geometric distortions such as axial voxel elongation, base overgrowth, and surface roughness, particularly for tall or slender structures. In addition, the subsequent thermal conversion induces substantial shrinkage, requiring the printing step to be understood as the first stage of a coupled process chain rather than an independent shaping operation [26].

For the objectives of this thesis, these considerations highlight that fabrication is not solely a printing problem, but rather a coupled process involving green-body formation, polymer removal, and sintering-driven densification. Nevertheless, 2PP combined with GP-Silica remains one of the most powerful approaches for fabricating micrometer-scale fused silica specimens with high geometric fidelity, which is a prerequisite for quantitative microscale mechanical testing [6].

1.4.2. Thermal conversion: debinding and sintering

Photopolymerization-based routes for fused silica microstructures rely on a multi-step thermal post-processing sequence to convert printed green bodies into dense, transparent glass. After printing, the structures consist of a composite in which silica nanoparticles are embedded in an organic polymer matrix. Achieving final glass properties requires complete removal of the organic binder (debinding), followed by high-temperature sintering to densify the silica network [19]. At the microscale, this conversion is not a purely material-transformation step: it strongly influences dimensional accuracy, surface

quality, internal defect population, and ultimately mechanical behavior, due to the high surface-to-volume ratio and the large shrinkage associated with densification [17].

Debinding Debinding refers to the thermal removal of the organic binder from the printed nanocomposite green body. In silica-loaded photopolymer resins, the binder is a crosslinked polymer network formed during exposure, which must be decomposed and volatilized without damaging the fragile inorganic skeleton [2]. Incomplete or non-uniform binder removal can generate residual porosity, cracking, or distortion that subsequently amplifies during sintering.

From a thermal standpoint, debinding involves overlapping degradation and oxidation reactions occurring over several hundred degrees Celsius [19]. The release of gaseous products can create internal pressure, making heating rate and atmosphere control essential: if gas evolution is too rapid, stresses may exceed the strength of the partially consolidated silica network and cause defects or delamination [2]. For microscale features, limited permeability and narrow channels further constrain outgassing, so schedules optimized for bulk parts may be unsuitable and typically require slower ramps or tailored profiles. Successful debinding yields a porous “brown body” that retains the printed geometry but has very low mechanical strength.

Sintering After debinding, sintering densifies the silica nanoparticle network into transparent fused silica. Densification proceeds mainly by viscous flow and diffusion-driven mechanisms, promoting neck growth, pore shrinkage, and progressive consolidation as temperature increases [26]. For silica, full densification generally requires peak temperatures above 1200–1300 °C, depending on particle size, purity, and thermal history [19].

Densification is accompanied by substantial volumetric shrinkage (typically 20–30% for nanocomposite-derived structures). While shrinkage can be close to isotropic in bulk specimens, microscale geometries are more prone to non-uniform densification and shape changes due to constrained sintering, density gradients in the green body, and local thermal non-uniformities, which can lead to tapering or localized distortions in high-aspect-ratio pillars [17]. Residual porosity or incomplete neck growth can act as stress concentrators and reduce strength even when the external shape appears intact, whereas optimized schedules can yield elastic modulus and hardness values approaching those of conventionally produced fused silica [20]. Understanding these competing effects is therefore essential for interpreting the mechanical response of 2PP-derived fused silica micropillars.

1.5. Microscale Mechanical Testing of Fused Silica

Microscale mechanical testing techniques are essential for probing the intrinsic mechanical behavior of brittle materials while minimizing the influence of macroscopic defects. By restricting the probed material volume, these methods reduce the probability of encountering critical flaws and enable access to deformation and fracture mechanisms that are otherwise masked at larger length scales [12].

Among the available approaches, micropillar compression and pillar splitting induced by sharp indentation have emerged as particularly powerful techniques for the quantitative characterization of fused silica at the microscale [27]. In the present work, these two methods are employed to investigate, respectively, the compressive stress–strain response and the fracture toughness of fused silica microstructures fabricated by Two-Photon Polymerization.

1.5.1. Micropillar compression: stress–strain response

Micropillar compression involves the uniaxial loading of freestanding micro-scale pillars using a flat punch indenter. Compared to conventional sharp-tip nanoindentation, this geometry allows a more direct interpretation of the mechanical response, as it reduces the influence of highly localized stress and strain gradients beneath the indenter [15].

The engineering stress is commonly defined as in Equation (1.2).

$$\sigma = \frac{F}{A_0}, \quad (1.2)$$

where F is the applied load and A_0 is the initial cross-sectional area of the pillar. The nominal axial strain is estimated as in Equation (1.3).

$$\varepsilon = \frac{\Delta h}{h_0}, \quad (1.3)$$

with Δh the measured axial displacement and h_0 the initial pillar height.

These definitions implicitly assume homogeneous deformation and a constant cross-sectional area during loading. While these assumptions introduce systematic uncertainties, they provide a consistent framework for comparing specimens with similar geometries and for identifying trends in strength and deformation behavior [28]. Finite element simulations have shown that deviations from ideal pillar geometry, such as taper angle or base filleting, can significantly modify the local stress distribution, particularly

near the pillar–substrate interface [29].

For fused silica, micropillar compression experiments have reported compressive strengths in the range of several gigapascals, significantly exceeding macroscopic values and approaching the intrinsic strength of the silicate glass network ($Si - O$ backbone) [13]. Failure typically occurs through shear localization, splitting, or densification-assisted collapse rather than classical tensile crack propagation [16]. Localized inelastic deformation mechanisms, including stress-induced densification and time-dependent viscous flow, may precede catastrophic failure and modify the apparent stress–strain response.

In-situ mechanical testing inside the scanning electron microscope enables direct correlation between load–displacement data and deformation or fracture events [30]. However, for amorphous silica, electron-beam irradiation has been shown to promote enhanced viscous flow and crack-tip blunting, potentially altering the measured mechanical response. These effects must therefore be carefully considered when interpreting microscale compression data obtained under electron exposure [14].

1.5.2. Pillar splitting: fracture toughness

While micropillar compression primarily probes compressive strength and deformation mechanisms, pillar splitting provides access to the fracture toughness of brittle materials at small length scales [31]. In this approach, a sharp cube-corner indenter is driven into the top surface of a cylindrical pillar, generating a highly concentrated stress field that promotes the nucleation and stable propagation of radial cracks.

At a critical load, the pillar splits into distinct fragments, typically along three radial planes dictated by the indenter geometry. The fracture toughness K_c can be related to the critical splitting load P_c through a scaling relationship as shown in Equation (1.4)

$$K_c = \gamma \frac{P_c}{R^{3/2}}, \quad (1.4)$$

where R is the pillar radius and γ is a dimensionless factor that depends on pillar geometry and boundary conditions [32]. This formulation allows fracture toughness to be extracted from microscale experiments without relying on long crack geometries or large test volumes.

Compared to conventional indentation cracking on bulk specimens, pillar splitting offers improved control over crack geometry and reduced sensitivity to residual stresses and surface damage [8]. For fused silica, fracture toughness values obtained by pillar splitting

are generally consistent with macroscopic measurements, while exhibiting reduced scatter due to the limited flaw population sampled at the microscale [4].

As with micropillar compression, testing conditions play a critical role. In particular, in-situ SEM experiments have shown that electron-beam exposure can suppress crack propagation and increase the apparent fracture resistance of amorphous silica [33]. This highlights both the potential and the limitations of microscale fracture experiments and underscores the need for careful control and interpretation of testing environments.

Overall, the combined use of micropillar compression and pillar splitting provides a complementary framework for probing strength and fracture behavior in fused silica microstructures. Together, these techniques enable a quantitative investigation of size effects, deformation mechanisms, and failure modes at length scales relevant for micro-architected glass components fabricated by Two-Photon Polymerization.

1.6. Reproducibility at the Microscale

At the microscale, fabrication reproducibility becomes a critical factor in determining the reliability and interpretability of mechanical measurements. Unlike macroscopic specimens, microscale structures are highly sensitive to small variations in geometry, surface quality, and defect distribution [13].

In Two-Photon Polymerization, geometric imperfections may arise from voxel discretization, focus drift, resin aging, light scattering, and environmental fluctuations [21]. For nanoparticle-loaded resins such as GP-Silica, these effects are further amplified by variations in particle dispersion, viscosity, and local polymerization kinetics [34]. As a result, even nominally identical structures printed under similar conditions can exhibit measurable differences in shape, surface roughness, and dimensional accuracy.

Small geometric deviations have been shown to significantly affect microscale mechanical measurements. In micropillar compression, variations in taper angle, aspect ratio, base filleting, and sidewall roughness modify the local stress distribution and can shift the dominant failure mode, leading to scatter even for nominally identical specimens [13].

In brittle materials, where fracture is governed by extreme-value statistics, the presence of a single critical defect can dominate the mechanical response [11]. At small length scales, the reduced flaw population increases the average strength, but it also makes the results more sensitive to subtle geometric irregularities. Consequently, microscale mechanical testing often exhibits significant scatter, even when specimens are fabricated on the same

substrate under nominally identical conditions [35].

For GP-Silica structures, reproducibility is further affected by the multistep nature of the fabrication process. Printing, debinding, and sintering each introduce potential sources of distortion, residual porosity, and surface defects [2]. The cumulative effect of these stages can lead to measurable differences in mechanical response between nominally identical specimens.

Therefore, mechanical properties extracted from microscale experiments should be interpreted as effective values that incorporate both intrinsic material behavior and process-induced imperfections [15]. Careful control of fabrication parameters, environmental conditions, and specimen geometry is essential to ensure meaningful and reproducible mechanical characterization.

1.7. Outlook: Toward robust 2PP-derived fused silica microstructures

The long-term motivation behind 2PP-derived fused silica is not limited to demonstrating geometric freedom, but to enable *reliable* microscale glass components whose mechanical performance can be predicted and engineered with a level of confidence comparable to mature manufacturing routes. In this framework, micropillars play a strategic role as a reference geometry: they reduce design complexity and provide a controlled test vehicle to isolate how the coupled printing–debinding–sintering process modifies geometry, surface state, and defect population, and how these factors propagate into measurable strength and fracture behavior. Establishing a robust process–structure–property link on pillars is therefore a necessary prerequisite before extending the approach to more complex three-dimensional architectures, where the number of stress concentrators, feature-to-feature variability, and cumulative distortions are expected to increase.

Looking forward, a natural research direction is the transition from simple pillars to *architected* fused silica geometries (e.g., lattices or cellular microstructures) fabricated by 2PP and converted to glass. In such systems, mechanical response is governed not only by the base material, but also by the architecture and by the local variability of strut thickness, node curvature, and surface condition. When feature sizes reach the micrometer and sub-micrometer regime, size effects may reduce the likelihood of sampling critical defects, potentially enabling higher specific strength than bulk glass. However, these potential advantages can be easily offset by process-driven imperfections: small geometric deviations, residual porosity, and surface defects can dominate performance

and may be amplified by architecture-induced stress localization [13, 22]. In this sense, the pillar baseline established in this thesis can be viewed as a prerequisite dataset and workflow for future architected designs, rather than as an endpoint.

To illustrate typical 2PP-enabled architected geometries and the relevant feature-size regime, examples from the literature are reported in Figure 1.2.

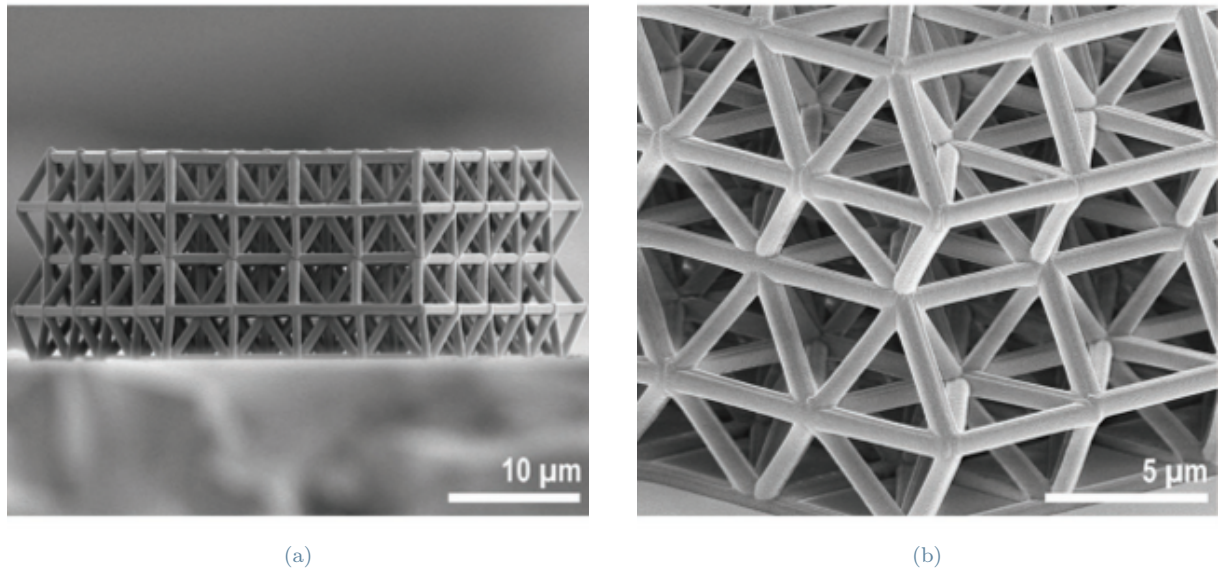


Figure 1.2: Example of micro-architected metamaterials fabricated by Two-Photon Polymerization: (a) three-dimensional lattice geometry and (b) high-resolution detail highlighting sub-micrometer feature size. Adapted from [22].

A second direction concerns *process robustness and standardization*. For nanoparticle-filled resins such as GP-Silica, the print outcome is sensitive to optical and environmental boundary conditions, including focus stability, local exposure dose, resin aging, and humidity-driven variability in printability and defect formation. Improved process monitoring, tighter control of exposure strategies (e.g., contour/core parameter decoupling), and standardized metrics for geometry fidelity (taper angle, base filleting, top-distortion descriptors) would improve comparability across studies and reduce ambiguity in interpreting mechanical datasets. In parallel, further optimization and mechanistic understanding of thermal conversion protocols remain essential. Shrinkage and densification are not merely geometric scaling factors: non-uniform debinding, constrained sintering, or density gradients can generate anisotropic shape changes and residual defect populations that directly influence fracture initiation and apparent strength [17, 26].

A third direction is the development of *testing methodologies* that are both quantitative and transferable. Micropillar compression and pillar splitting provide

powerful tools for probing strength and fracture toughness at small scales, yet the extracted properties remain sensitive to geometry, alignment, frictional constraints, and data-reduction assumptions (e.g., constant cross section, homogeneous stress) [28]. Mechanical interpretability can be strengthened by integrating systematic geometry metrology (pre- and post-test), refined stress estimation (including taper corrections or finite-element-assisted calibration), and statistically meaningful sample sizes to separate intrinsic scatter from process-induced variability. Where feasible, extending fracture measurements beyond single-load splitting events toward protocols that better constrain crack initiation and propagation would further increase confidence in microscale toughness values and their dependence on processing history [31].

Finally, once reproducible fabrication and validated testing are established, the next step is convergence toward *functional micro-devices* and application-driven geometries. Fused silica combines optical transparency, chemical inertness, and high-temperature stability, making it attractive for micro-optics, photonics, MEMS, and microfluidic environments where polymeric 2PP structures are limited by temperature or aging. In these contexts, reliable microscale mechanical datasets are not merely descriptive: they become a quantitative basis for design rules, safety factors, and lifetime prediction strategies for additively manufactured glass microstructures.

Overall, the research trajectory suggested by this thesis is a staged progression: from simple, well-controlled pillars to more complex architectures; from qualitative printability to quantified process windows and reproducibility metrics; and from isolated mechanical tests to standardized, geometry-aware mechanical characterization. Advancing along this path is essential to transform 2PP-derived fused silica from a powerful prototyping platform into a reliable materials-and-process toolbox for next-generation glass microdevices.

2 | Materials and Methods

2.1. Overview of the Experimental Workflow

This overview is placed at the beginning of the chapter because the experimental methodology is not a single fabrication step, but an integrated sequence in which early choices (substrate preparation, objective selection, and exposure parameters) propagate into post-processing outcomes and ultimately into the mechanical response of the final fused silica pillars. In particular, GP-Silica processing requires treating printing, development, and thermal conversion as a coupled pipeline rather than independent operations.

A key feature of the workflow is the use of SEM-based “checkpoints” (dashed boxes in Figure 2.1). These checkpoints were implemented as quality gates to verify structural integrity and adhesion, document defect formation, and quantify geometry (height, diameter, taper) at the stage where it becomes relevant for later data reduction. SEM inspection was therefore used repeatedly throughout the workflow, not only as a final characterization step.

The remainder of this chapter follows the same structure as Figure 2.1. Each section describes in detail the corresponding stage of the process, including the cleanroom and Nanoscribe setup, substrate and resin handling, digital preparation and printing execution (Describe/NanoWrite), development and thermal post-processing, SEM metrology, mechanical testing (microcompression and pillar splitting), and the associated data reduction methods used to obtain stress-strain curves and fracture-toughness values.

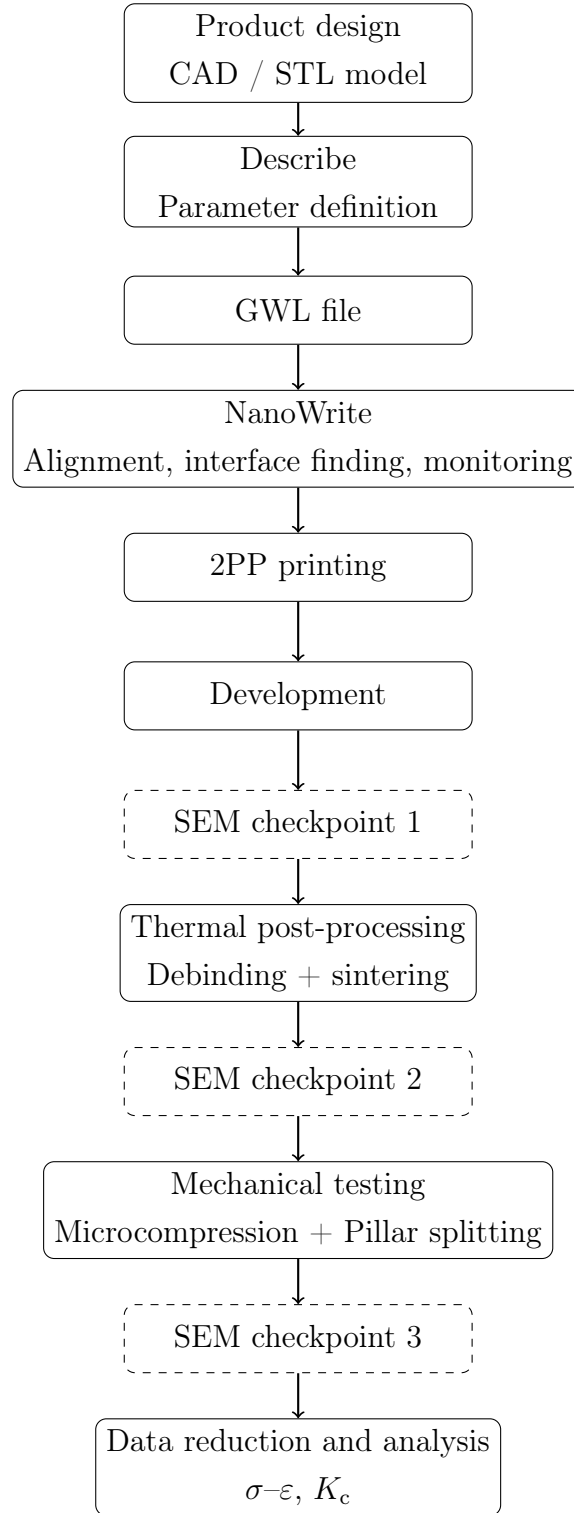


Figure 2.1: End-to-end experimental workflow adopted in this work, from digital design and print execution (Describe/NanoWrite) to development, thermal conversion to fused silica, SEM-based metrology checkpoints, mechanical testing (microcompression and pillar splitting), post-test SEM inspection, and data reduction. Dashed boxes indicate SEM quality-gate checkpoints used to track the evolution of geometry and defect formation across stages.

2.1.1. Experimental campaign and sample set overview

The experimental work was structured as a progressive fabrication campaign comprising 40 samples produced over multiple iterations, as summarized in Table 2.1. Early samples were primarily used to build process familiarity and map sensitivity using polymeric resins and non-pillar motifs, while later iterations converged toward downscaled micropillars and a reproducible fabrication window. Samples #31–#40 correspond to the final micropillar design and constitute the mechanically relevant set used in this thesis.

Sample range	Phase focus	Main structures / materials	Goal and key outputs
#0–#14	Familiarization + scouting	Polymeric resins; non-pillar motifs (e.g., honeycomb / honeyflower); larger pillars	Map basic process sensitivity, print fidelity, and qualitative defect modes; identify failure points along development/handling/thermal steps.
#15–#30	Downscaling + robustness screening	Micropillars with progressively reduced dimensions (toward final geometry)	Converge on a printable/convertible pillar geometry; screen sensitivity to time drift and RH; refine print and handling strategies.
#31–#40	Reproducible window + mechanical-ready set	Final micropillar design used for testing; subset used for microcompression and pillar splitting	Establish the most reproducible condition; generate mechanically testable specimens; enable geometry–property correlations.

Table 2.1: Overview of the fabrication campaign (samples #1–#40) and role of each phase in the process convergence.

2.1.2. Data management, traceability, and experimental metadata

Given the multi-variable nature of the campaign (printing parameters, environmental conditions, thermal schedules, and specimen-level mechanical outcomes), a structured

data-management strategy was implemented to ensure full traceability from fabrication to final analysis.

Sample-wise folder structure. All experimental outputs were stored in a dedicated repository organized by sample ID (#1–#40). For each sample, the corresponding folder contains the complete set of microscopy images acquired along the workflow, including representative SEM micrographs pre- and post-sintering. For specimens that were mechanically tested, the same folder also includes post-test SEM images documenting the fracture morphology (microcompression failure and pillar splitting), enabling direct linkage between mechanical response and observed damage mechanisms.

Master logbook and parameter registry. In parallel, a master Excel logbook was maintained to consolidate experimental metadata for each sample. For each substrate/sample, the log includes: (i) the printing parameter set (objective, laser power, scan speed, hatching/slicing distances, base/contour strategies, and writing settings), (ii) session-level boundary conditions (relative humidity, temperature, and elapsed time within the printing session), (iii) SEM acquisition notes relevant for metrology (e.g., viewing/tilt angle used for height reconstruction when applicable), and (iv) the applied thermal conversion program (peak temperature, holding time, and any relevant furnace settings).

Linking images, geometry, and mechanical datasets. For mechanically characterized pillars, the associated load–displacement datasets and derived stress–strain curves were stored using a consistent naming convention that includes the sample ID and pillar identifier. This convention enables unambiguous cross-referencing between (a) the raw mechanical signals, (b) the SEM-based geometrical measurements used for data reduction, and (c) the corresponding pre-/post-test microscopy documentation. Overall, this approach provides a coherent view of the full pipeline and supports reproducible re-analysis of the dataset.

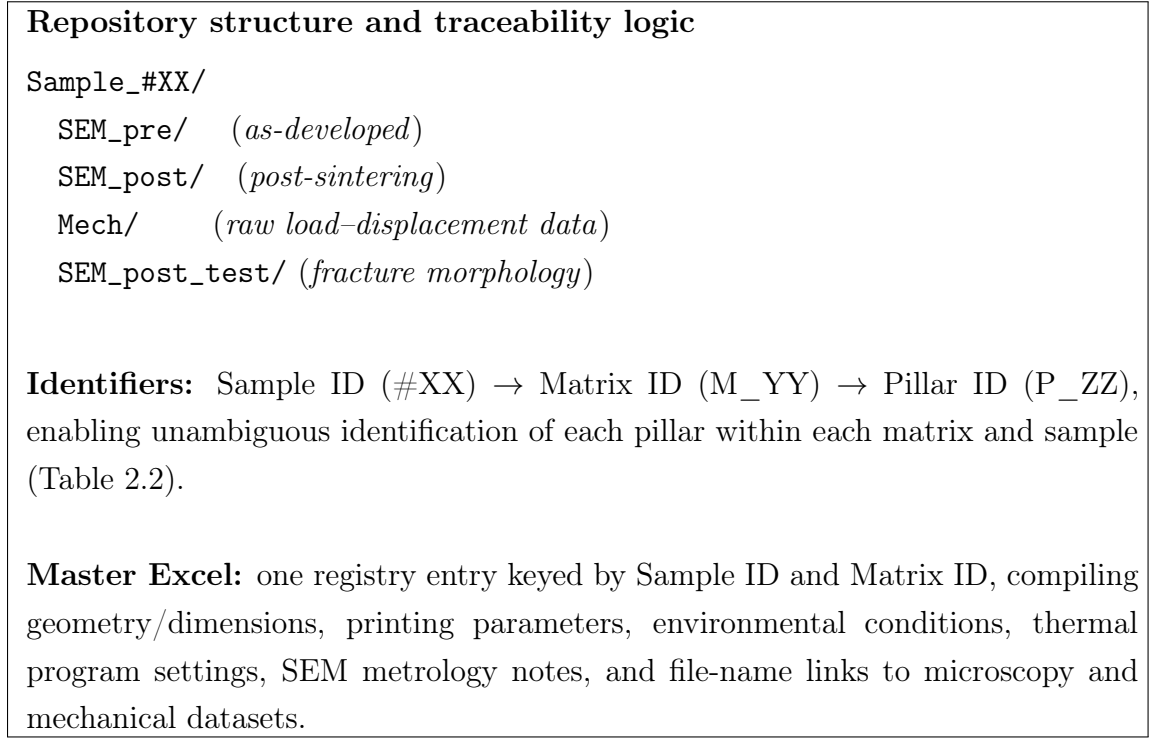


Figure 2.2: Schematic of the data-management strategy used to ensure traceability across microscopy, thermal processing, and mechanical datasets.

Field	Example / meaning
Sample ID	S31 = substrate/sample #31
Matrix ID	M04 = matrix #4 on that sample
Pillar ID	P12 = pillar #12 within the matrix

Table 2.2: Naming convention used to identify the structures across different samples.

2.2. Cleanroom and Nanoscribe System

All fabrication was performed in the EMPA Thun cleanroom. For Two-Photon Polymerization (2PP), cleanliness matters because (i) particles can disturb the resin droplet and the substrate–resin interface, affecting adhesion and interface detection, and (ii) contamination of the objective front lens and nearby mechanics degrades imaging contrast and exposure stability, which is critical when printing close to the resolution limits of a low-NA configuration.

The working area comprised three consecutive rooms: an infrastructure room (e.g., vacuum pumps and nitrogen supply), a gowning room, and the main fabrication room. Access required a full cleanroom suit, shoe covers, head cap, and gloves; adhesive floor

mats further limited particle transfer.

2.2.1. Environmental Conditions and Monitoring

Temperature and relative humidity (RH) were monitored and nominally controlled at facility level. Environmental stability is beneficial in 2PP because temperature/RH influence resin viscosity and wetting, oxygen availability near the resin surface, and, for nanoparticle-loaded photoresists, the effective optical response.

In the first months, fluctuations in both temperature and RH were observed. Conditions were therefore logged at least daily, and for critical sessions also immediately before and after printing. This monitoring was essential, because variations in temperature—and especially RH—were found to systematically affect the printability and geometric reproducibility of small GP-Silica features. Large structures were generally tolerant to moderate variations, whereas printing close to the process limits (e.g., pillars of $\sim 15\ \mu\text{m}$ diameter and $\sim 30\ \mu\text{m}$ height) was markedly more sensitive. Environmental conditions are thus reported as boundary conditions and were considered when defining the operational envelope for reproducible printing (see also Section 2.3).

2.2.2. Nanoscribe Photonic Professional GT2: System Overview

Fabrication was carried out with a Nanoscribe Photonic Professional GT2, integrating an inverted microscope, a hierarchical positioning architecture (motorized stage, piezo stage, objective z -drive), and a femtosecond laser at 780 nm. Operation was performed via NanoWrite, coordinating motion, laser exposure, autofocus routines, and live optical imaging.

2PP confines polymerization to the focal volume of a tightly focused femtosecond beam, enabling true 3D microfabrication [21]. The underlying physics is discussed in Chapter 1; here, the emphasis is on the system workflow for reproducible manufacturing.

Geometries were prepared in Describe and executed in NanoWrite. The effective voxel size and resolution were primarily governed by the objective lens and the exposure regime (laser power, scan speed, voxel overlap). Figure 2.3 summarizes the system setup; the open chamber (Figure 2.4) highlights the motorized stage (1) and piezo stage (2).



Figure 2.3: Photonic Professional GT2 setup used in this work: printer enclosure, control electronics, and workstation for job preparation and monitoring. Adapted from [36]

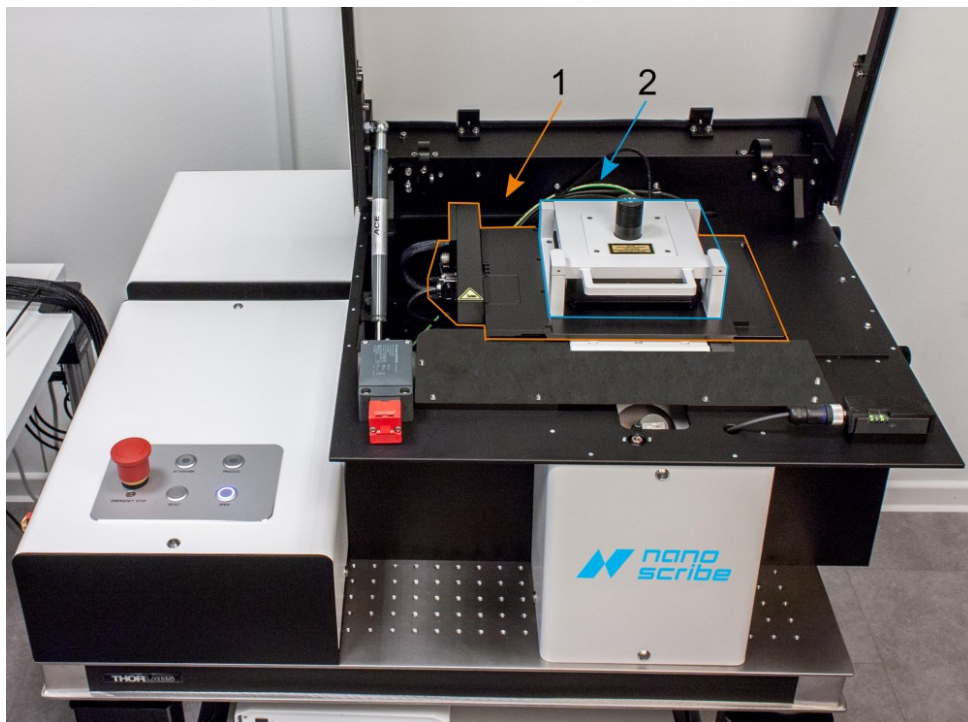


Figure 2.4: Open print chamber showing the motorized stage (1) and piezo positioning stage (2) for coarse and fine substrate alignment. Adapted from [37]

2.2.3. Motion and Positioning Architecture

The GT2 uses a hierarchical motion architecture, with each subsystem covering a distinct length scale. The motorized stage provides centimeter-scale travel for substrate addressing, long-range moves, and block placement during large-area fabrication. Fine positioning is provided by the piezo stage, offering high-resolution motion over a limited travel range and ensuring stable layer stacking; when printing near the process limits, its stability is critical because small deviations alter local energy density and voxel overlap.

Figure 2.5 summarizes the coordinate systems and origins of the motorized stage (Stage Origin, SO) and the piezo stage (Piezo Origin, PO). Coarse positioning is defined in the stage coordinate system, whereas writing trajectories are defined relative to the piezo origin.

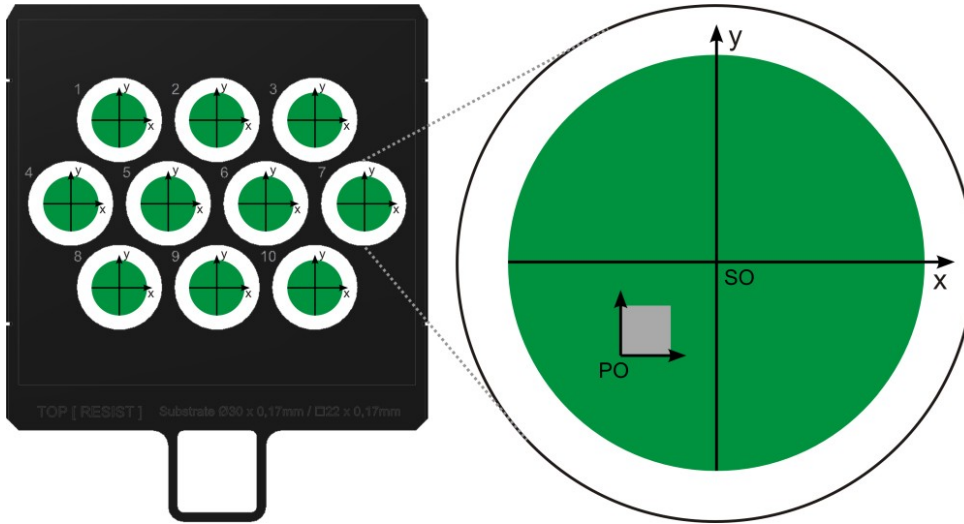


Figure 2.5: Coordinate systems and origins for the motorized stage (SO) and piezo stage (PO), shown from top view. Adapted from [37]

The objective z -drive is used for interface detection and coarse focal positioning before writing, but it does not participate in high-resolution layer stacking. In this work, galvo scanning was used for lateral motion in the x - y plane, while the piezo stage controlled fine positioning along z .

2.2.4. Laser Source and Beam Delivery

The integrated femtosecond laser (780 nm) is guided to galvanometric mirrors that steer the beam in the x - y plane (Figure 2.6), defining the in-plane writing trajectories.

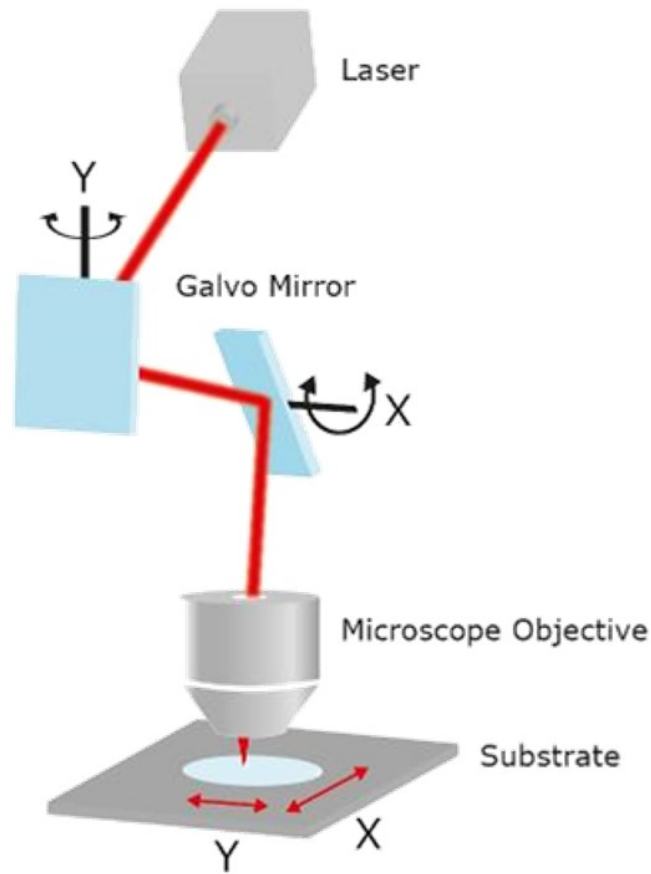


Figure 2.6: Simplified optical path within the galvo scanner. Adapted from [37]

The galvo scan field is objective-dependent and spans positive and negative coordinates around an optical origin, whereas the piezo scan range is objective-independent and defined in positive coordinates relative to the piezo origin. Figure 2.7 compares the galvo fields for the objectives used in this work with the piezo range (live-view window: dashed lines).

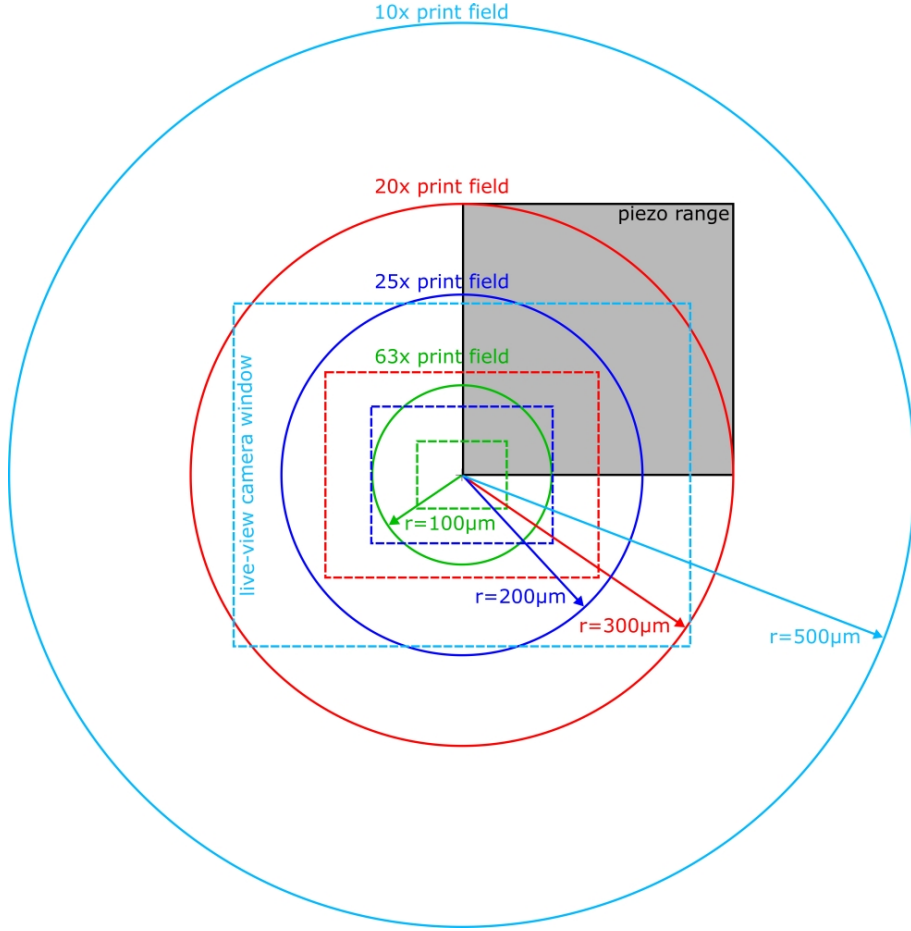


Figure 2.7: Comparison of the objective-dependent galvo scan fields (63x, 25x, 20x, 10x) relative to the piezo scan range; the live-view window is indicated by dashed lines. Adapted from [37]

For highly curved paths, galvo accuracy can decrease at high scan speeds, particularly near the scan-field edges. For structures exceeding the objective-specific galvo field, galvo steering is therefore combined with stage/piezo repositioning between writing blocks.

2.2.5. Optical Microscope and Imaging System

The system is built around a Carl Zeiss Axio Observer inverted microscope, used for beam focusing and real-time monitoring. Transmission or reflection illumination is selected depending on substrate transparency, and live imaging supports alignment and in-situ inspection.

Interface detection is performed via the integrated Definite Focus system, which identifies the resin–substrate interface and sets the vertical reference for writing. The microscope can be operated via touchscreen or NanoWrite routines; the touchscreen interface is shown in Figure 2.8.

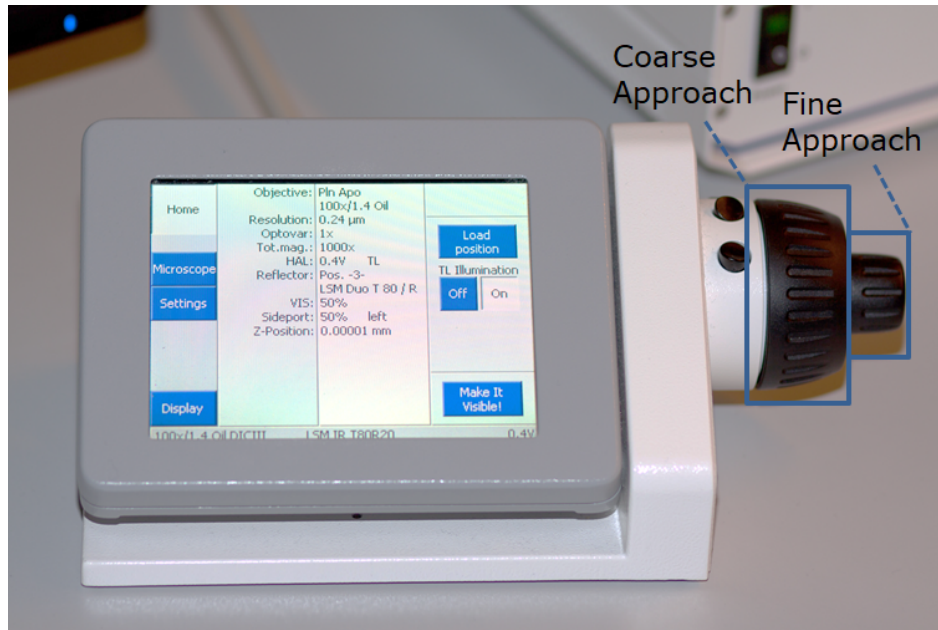


Figure 2.8: Microscope touchscreen with fine and coarse z-drive controls (coarse and fine approach). Adapted from [37].

2.3. Protocols to Isolate Time- and Humidity-Dependent Effects

During the fabrication of small GP-Silica structures close to the process stability threshold, variability was observed that could not be explained by printing parameters alone. To prevent time- and environment-driven drift from being conflated with exposure settings or geometry, two external variables were explicitly treated as experimental boundary conditions: (i) elapsed time within a printing session and (ii) relative humidity (RH) in the cleanroom.

To address this, I designed and implemented two dedicated protocols to isolate, document, and compare these effects in a controlled and reproducible manner. Rather than attempting to eliminate drift through active control, the protocols kept geometry and printing parameters fixed and systematically varied only the boundary condition of interest, enabling quantitative discussion in later chapters without confounding factors.

Time-Dependence Protocol

To isolate within-session time-dependent effects, a controlled repetition strategy was adopted. On a single substrate, the same micropillar geometry was fabricated repeatedly at regular intervals while keeping all printing parameters, objective configuration, and

writing strategy constant. The typical interval between successive prints was ~ 10 minutes, matching the practical cadence of fabricating small pillar arrays.

By using a single substrate and identical exposure settings (laser power, scan speed, hatching/slicing distances, base/contour strategy, and writing order), substrate-to-substrate variability was minimized. Any changes in geometry, defect formation, or print fidelity could therefore be primarily attributed to temporal evolution within the session. Plausible contributors include resin evolution after droplet deposition (e.g., rheological changes or partial pre-polymerization), progressive contamination of optical components, and slow drift in imaging or interface-detection conditions.

After development, all time-separated prints were evaluated by SEM using a consistent set of metrics (pillar height, top-surface morphology, intra-array dispersion, and occurrence of local defects in the surrounding area), acquired under consistent imaging conditions and processed using the same measurement procedure.

Humidity-Dependence Protocol

To isolate the influence of RH independently from within-session temporal degradation, humidity-dependent comparisons were performed using prints executed within a short and controlled elapsed time after resin deposition and system setup. For each RH condition, pillar arrays were fabricated within a restricted time window (typically within ~ 30 minutes), using the same geometry, identical printing parameters, and the same objective configuration.

Relative humidity and temperature were recorded for each session using the cleanroom monitoring system. Although RH was not actively controlled, the natural variability of the cleanroom over the experimental campaign provided access to a broad range of RH conditions. Following development, SEM-based evaluation was performed using the same geometric and qualitative metrics adopted for the time-dependence protocol, enabling direct comparison of print outcomes across different RH levels under otherwise comparable conditions.

Selection Rules for Mechanically Testable Specimens

Because the primary objective of this work was mechanical characterization, specimen selection was treated as an explicit methodological step rather than an informal screening. In practice, only micropillars fabricated under conditions shown—by the two protocols above—to preserve geometric fidelity and limit defect formation were forwarded to thermal conversion and mechanical testing.

Candidate specimens were therefore required to satisfy both of the following conditions: (i) fabrication within the time-stability window identified through the time-dependence protocol, and (ii) fabrication under RH conditions that did not visibly compromise geometric uniformity or surface integrity. Operationally, this translated into prioritizing the mechanically relevant geometry (typically $\sim 15\mu\text{m}$ diameter and $\sim 30\mu\text{m}$ height) within the first ~ 30 minutes after droplet deposition and system setup, and in any case within approximately 1 hour. Sessions characterized by very high RH were avoided when possible, since they were associated with a higher likelihood of defects and reduced reproducibility.

Selection decisions were documented for each specimen and supported by SEM images acquired after development and prior to thermal treatment, ensuring traceability from fabrication history to final mechanical response. While thermal processing can partially smooth surface roughness through viscous-flow-driven mechanisms during sintering, it cannot compensate for major geometric distortions, missing features, or severe defects originating in the green state. For this reason, the time- and RH-related selection rules were primarily imposed to guarantee geometric fidelity and repeatability of the as-printed structures, rather than to optimize surface finish alone.

2.4. Post-Processing Procedures

After fabrication, all samples underwent development to remove unpolymerized resin and stabilize the printed microstructures. This step is critical in Two-Photon Polymerization (2PP), because residual resin trapped between or around polymerized voxels can compromise dimensional fidelity, introduce local inhomogeneities, and reduce mechanical stability during handling and subsequent processing.

In this work, post-processing was primarily optimized for the GP-Silica nanocomposite resin used to fabricate fused silica microstructures. Compared to standard polymeric photoresists, GP-Silica requires a more conservative handling and development approach due to its high viscosity, nanoparticle loading, and the mechanical fragility of the as-printed “green parts” intended for thermal conversion.

General handling immediately after printing. Immediately after printing, the structures exist as polymerized “green parts” embedded in unpolymerized resin. At this stage, the microstructures are mechanically weak and particularly sensitive to external perturbations; furthermore, effective adhesion to the substrate can be limited when printing close to the process window, where polymerization at the interface may be

marginal. For this reason, post-print handling was treated as an integral part of the fabrication workflow. After removal from the Nanoscribe sample holder, the substrate was kept horizontal to prevent resin flow across the printed region, and the printed area was never contacted. All handling steps were performed at the solvent bench in the same cleanroom environment. Substrates were manipulated using dedicated fine tweezers and transferred using a rigid metallic support to avoid direct mechanical loading of the printed region.

2.4.1. Development of GP-Silica Nanocomposite

Development of GP-Silica aims to remove unpolymerized fractions without damaging the mechanically weak green-state microstructures and without leaving residues that could later interfere with thermal processing. A conservative solvent sequence and gentle, reproducible handling were therefore adopted.

Solvent sequence and timing

The development sequence used for GP-Silica consisted of:

- immersion in methanol for approximately 10–15 minutes;
- a short rinse in isopropanol (IPA), typically ~ 2 –3 minutes;
- air drying under ambient conditions.

A schematic view of the development setup is shown in Figure 2.9: panel (a) illustrates the two-beaker arrangement (methanol and IPA) together with the metallic holder used to support the substrate; panel (b) shows the holder during immersion in the methanol bath.

Methanol was selected because it effectively penetrates the polymerized network and extracts unpolymerized resin fractions while minimizing swelling and damage. The rigid metallic support enabled controlled insertion and retrieval from the solvent, reducing fluid-induced loads and accidental contact that could otherwise promote detachment of fragile microstructures. After methanol treatment, the sample was transferred to IPA to remove methanol residues and accelerate evaporation. More aggressive drying methods (e.g., nitrogen blow-drying) were avoided to reduce the risk of cracking, deformation, or detachment.

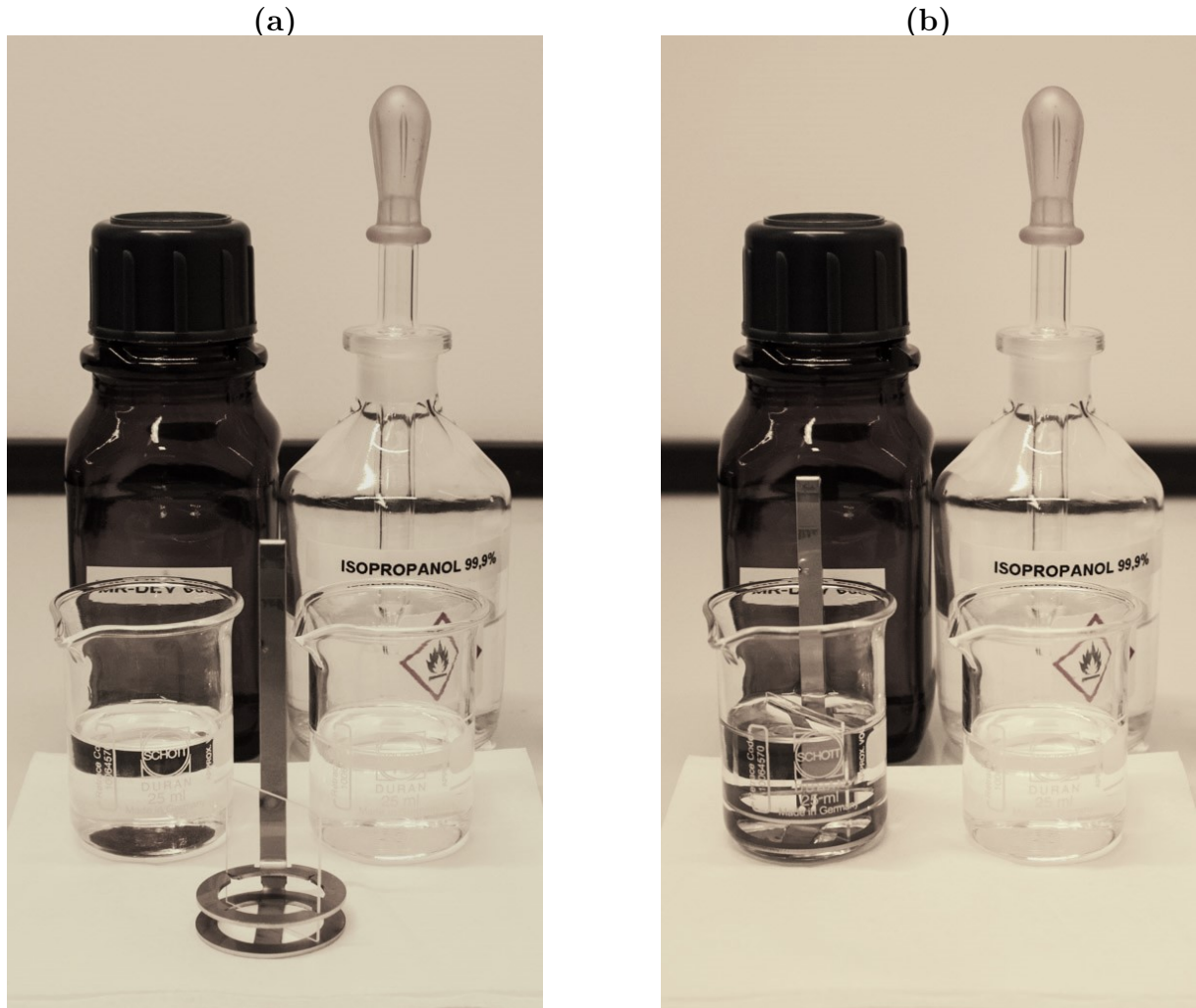


Figure 2.9: Development setup for GP-Silica. (a) Methanol and IPA beakers with the metallic holder used to support the substrate during handling. (b) Holder immersed in the methanol bath during the first development step. Adapted from [37]

Controlled manual agitation to remove residues

During methanol immersion, handling was performed using the metallic holder (Figure 2.9(a)) to avoid contact with the printed region. After a few minutes—once most unpolymersed resin had dispersed into the solvent—the holder was gently moved up and down with a slow, small-amplitude vertical motion. This controlled agitation helped dislodge persistent residues, which often appeared as concentric ring-like deposits around the printed features, and promoted their diffusion into the solvent. The motion was intentionally minimal and reproducible (slow speed, limited stroke), because excessive fluid-induced forces can detach pillars or bend high-aspect-ratio microstructures. Nevertheless, residue removal was important to achieve cleaner surfaces and to mitigate

artifact formation during subsequent thermal treatment.

Drying and green-part stability

After the methanol and IPA steps, samples were left to dry naturally under ambient conditions without mechanical or thermal assistance. At this stage, the printed parts are still hybrid polymer–silica networks and remain sensitive to shocks and handling. Samples were therefore stored in clean containers and the printed region was not contacted prior to microscopy inspection.

2.4.2. Objective and System Cleaning After GP-Silica Printing

In addition to sample development, the optical system was cleaned at the end of each printing session. This step was particularly important when working with GP-Silica, because resin residues and silica nanoparticles can progressively accumulate and partially solidify on optical surfaces within hours, degrading image contrast and exposure stability if not removed promptly.

Two different consumables were used, depending on the optical surface. Lint-free optical tissues were employed for general cleaning around the objective front area and to manage solvent droplets, while ultra-soft lens wipes were reserved exclusively for direct contact with the front lens element, which is the most delicate component. As shown in Figure 2.10(a), the objective was gently rotated while the tissue was kept close to the lens center to collect residues without applying pressure on the glass. Figure 2.10(b) illustrates the subsequent step, where the objective was wrapped to safely capture solvent run-off during rinsing.

For GP-Silica, the cleaning media were lightly wetted with methanol, which effectively dissolved uncured resin and helped remove nanoparticle-containing residues while evaporating rapidly. When visible contamination remained on the lens, an ultra-soft lens wipe moistened with a small amount of methanol was passed over the lens surface multiple times using very light strokes until the lens appeared completely clean. In some cases, a final IPA rinse was applied to remove methanol traces and accelerate drying. Throughout the procedure, motions were kept slow and gentle to reduce the risk of scratching or damaging the front lens element.

Overall, the methanol–IPA sequence combined with immediate post-print cleaning was treated as a standard end-of-session protocol to maintain stable optical performance across consecutive fabrication runs.



Figure 2.10: Objective cleaning procedure after GP-Silica printing. (a) Tissue-assisted cleaning around the lens by gently rotating the objective while keeping the tissue close to the lens center. (b) Wrapping the objective to collect solvent run-off during rinsing and prevent redeposition on the lens. Adapted from [37]

2.5. Thermal Post-Processing

After development, the polymerized GP-Silica microstructures—hereafter referred to as “green parts”—were converted into fused silica through thermal post-processing. All thermal treatments were carried out in a DEKEMA AUSTROMAT 674 furnace equipped with the extra-vacuum option [38]. The availability of a vacuum-assisted furnace allowed debinding and sintering to be performed within a single continuous thermal cycle, minimizing handling of intermediate fragile structures and reducing the risk of damage or contamination.

Thermal post-processing was treated as an experimental variable rather than a fixed finalization step. For this reason, a baseline furnace program was defined and then systematically modified by varying peak temperature and holding time, while keeping all other parameters constant.

2.5.1. Baseline Furnace Program

The manufacturer provides two standard thermal protocols for GP-Silica: a slow cycle (approximately 60 h) recommended for millimeter-scale components, and a fast cycle (less than 20 h) optimized for microscale structures. In this work, the fast cycle was adopted as the baseline program due to the characteristic dimensions of the printed pillars (tens of micrometers), which facilitate efficient out-diffusion of decomposition products during binder removal.

The baseline furnace program consisted of:

- heating rate: $3\text{ }^{\circ}\text{C min}^{-1}$;
- peak temperature: $1300\text{ }^{\circ}\text{C}$;
- holding time at peak temperature: 2 h;
- atmosphere: vacuum maintained below 70 mbar;
- controlled cooling to $100\text{ }^{\circ}\text{C}$ prior to venting.

A simplified schematic of the baseline thermal profile is reported in Figure 2.11, showing the temperature ramp ($3\text{ }^{\circ}\text{C min}^{-1}$), the $1300\text{ }^{\circ}\text{C}$ holding step (2 h), and the subsequent controlled cooling to $100\text{ }^{\circ}\text{C}$. The pressure history is reported on the secondary axis to indicate the vacuum level ($<70\text{ mbar}$) maintained during the high-temperature stage and the venting to ambient pressure after cool-down.

This program served as the reference condition against which all deliberate variations were compared.

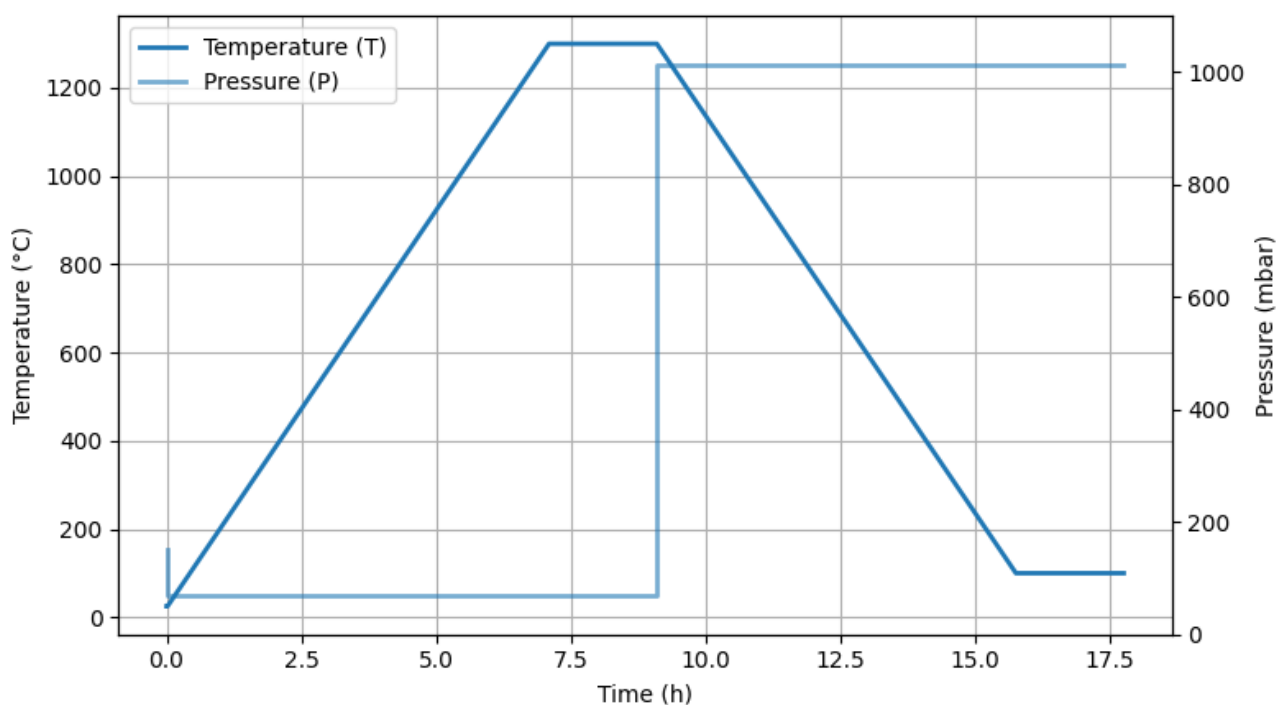


Figure 2.11: Baseline GP-Silica fast furnace program used as reference in this work. Temperature profile (primary axis) and pressure history (secondary axis) highlight the main process parameters: heating rate ($3\text{ }^{\circ}\text{C min}^{-1}$), peak temperature ($1300\text{ }^{\circ}\text{C}$), holding time at peak (2 h), vacuum level ($<70\text{ mbar}$), and controlled cooling to $100\text{ }^{\circ}\text{C}$ prior to venting.

2.5.2. Strategy for Thermal Parameter Variation

To isolate the influence of individual thermal parameters, peak temperature and holding time were varied independently following a one-factor-at-a-time strategy. All samples were printed using identical geometries and printing parameters prior to thermal treatment.

Holding Time Variation at Fixed Peak Temperature

To investigate the effect of sintering time, the peak temperature was fixed at 1300 °C, corresponding to the baseline condition, while the holding time was varied across different substrates. Each substrate was processed using a single holding time, ensuring that no sample experienced multiple thermal histories.

Holding times were varied in the range 0.5 h to 4 h. This approach allowed the effect of time at constant temperature to be evaluated independently from temperature-related effects.

Peak Temperature Variation at Fixed Holding Time

To investigate the influence of peak temperature, the holding time was fixed at 2 h, corresponding to the baseline program, while the maximum temperature was varied. Separate substrates were processed at peak temperatures of 1100 °C, 1200 °C, and 1300 °C.

All other parameters of the thermal cycle, including heating rate, atmosphere, and cooling procedure, were kept constant. This strategy enabled a direct comparison of thermal outcomes as a function of peak temperature alone.

2.5.3. Summary of Thermal Conditions and Sample Groups

Table 2.3 summarizes the thermal programs applied to the different sample groups. Each condition corresponds to a distinct set of printed pillar arrays, processed on separate substrates and later evaluated by SEM prior to mechanical testing.

Table 2.3: Summary of thermal post-processing conditions applied to GP-Silica samples.

Sample group	Peak temperature (°C)	Holding time (min)	Purpose
Baseline	1300	120	Reference condition
T1	1100	120	Temperature variation
T2	1200	120	//
t1	1300	40	Holding time variation
t2	1300	53	//
t3	1300	72	//
t4	1300	160	//
t5	1300	215	//

2.6. Microscopy and Visual Characterization

A combination of microscopy techniques was employed to evaluate the quality, morphology, and structural integrity of the fabricated microstructures at different stages of the workflow, both before and after thermal processing. These techniques provided complementary information, ranging from rapid qualitative inspection to high-resolution morphological analysis and quantitative metrology of pillar dimensions. Geometrical measurements were treated as a critical part of the methodology because the stress-strain reconstruction in microcompression and the fracture-toughness evaluation in pillar splitting depend directly on pillar height and diameter.

2.6.1. Optical Microscopy: Rapid Screening and Process Feedback

Optical microscopy was used for the initial inspection of printed arrays immediately after development. This technique enabled rapid identification of missing structures, printing defects, misalignment, or gross deformations across large areas of the substrate. Although the limited depth of field and resolution prevented a full three-dimensional assessment of the micropillars, optical microscopy proved valuable for high-throughput screening and real-time feedback during printing sessions. In practice, arrays presenting obvious defects (e.g., incomplete development, merged pillars, severe tilt, or extensive residue rings) were excluded from further processing to maximize downstream efficiency.

2.6.2. Confocal Profilometry: Exploratory Height Mapping

Confocal imaging was evaluated as a potential tool for obtaining height profiles and surface maps of the fabricated micropillars. However, due to the small lateral dimensions and limited aspect ratio of the structures, the measurements were strongly affected by optical scattering and edge-related artifacts. These effects distorted the reconstructed profiles and prevented robust quantitative analysis. As a result, confocal profilometry was not used systematically in this work and was limited to exploratory tests.

2.6.3. Scanning Electron Microscopy (SEM): Morphology and Metrology

Scanning Electron Microscopy (SEM) was the primary technique used for detailed morphological characterization and dimensional measurements. Imaging was performed using a Philips XL30 system operated under high vacuum [39]. SEM imaging was primarily carried out in secondary-electron (SE) mode at low accelerating voltage (3 kV to 5 kV) and short working distances to mitigate charging, enabling operation without conductive coating. This approach allowed stable imaging of the insulating silica-based structures while preserving fine surface details.

Samples were mounted on aluminum stubs. For post-print characterization, mounting was typically achieved using conductive carbon tape, whereas samples prepared for mechanical testing were later rigidly bonded using a high-strength adhesive (see Section 2.7.1).

SEM analysis was systematically performed after each major processing step:

- after development, to verify voxel integrity, structural continuity, surface residues, and adhesion to the substrate;
- after thermal post-processing, to assess shrinkage, edge rounding, surface smoothing, base swelling, and the presence of cracks or distortions;
- after mechanical testing, to document fracture modes, splitting behavior, and damage morphology.

2.6.4. Geometrical Measurements from SEM Images

Quantitative SEM-based metrology was required to convert the measured load–displacement data into stress–strain curves and to extract fracture-related quantities from pillar splitting tests. For each mechanically tested pillar, geometrical parameters were measured from SEM images acquired prior to testing.

The mechanical data reduction used the pillar height h and the top diameter d_{top} . These parameters enter the definitions of engineering strain ($\varepsilon = \Delta h/h$) and engineering stress ($\sigma = F/A$, with $A = \pi(d_{\text{top}}/2)^2$), and they also provide the effective radius required by the analytical relations adopted for pillar splitting. Although diameters were measured at multiple heights to capture shape variations, d_{top} was selected as the reference value for mechanical calculations to remain consistent with the microcompression contact geometry, where load transfer is governed by the cross-sectional area at the top surface of the pillar [35].

Diameter measurements were extracted from tilted SEM images (typically 45° – 70° relative to the substrate normal). Measurements were taken perpendicular to the pillar axis so that the extracted values correspond to the true cross-sectional dimensions; therefore, no tilt correction was required. For each pillar, diameters were measured at three locations (near the base, mid-height, and near the top) to quantify axial variations such as tapering, base swelling, and top rounding.

Height Measurement Using Tilted Views and Sine Correction

Height measurements were performed using SEM images acquired at a tilted stage configuration, in which the pillar axis is projected onto the imaging plane and becomes directly measurable.

Depending on the sample geometry and field of view, different tilt angles were employed in this work, typically $\theta = 55^\circ$ or $\theta = 70^\circ$. The specific angle was selected to ensure that the full pillar height was visible within a single frame, avoiding truncation or shadowing effects. To keep the formulation general, the tilt angle is here denoted by θ .

In a tilted configuration, the measured pillar length corresponds to an apparent height h_{app} , which represents the projection of the true vertical height h onto the imaging plane. The geometric relationship between the apparent and true height is illustrated schematically in Figure 2.12, where h , h_{app} , and the stage tilt angle θ are defined.

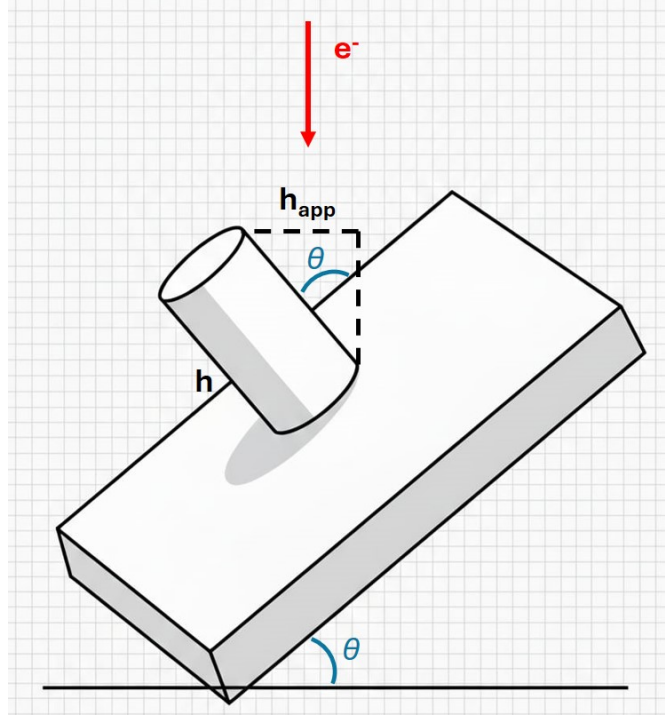


Figure 2.12: Schematic representation of the geometric relationship used to extract the true pillar height from tilted SEM images. The sample stage is tilted by an angle θ with respect to the horizontal plane. The apparent height h_{app} measured in the tilted view corresponds to the projection of the true pillar height h onto the imaging plane.

Assuming that the pillar axis is perpendicular to the substrate, the true height can be recovered through a simple trigonometric correction based on the sine of the tilt angle:

$$h = \frac{h_{app}}{\sin \theta}. \quad (2.1)$$

This correction was systematically applied to all pillars whose height was extracted from tilted SEM views. Pillars exhibiting a visible inclination relative to the substrate normal were excluded from subsequent mechanical testing, as such misalignment could compromise the assumption of uniaxial loading conditions and lead to ambiguous interpretation of the mechanical response.

Measurement Consistency and Error Sources

To ensure internal consistency, height and diameter measurements were performed using the same SEM calibration and magnification settings within each session. The main sources of uncertainty were: (i) manual selection of the pillar top and base reference points in tilted images, particularly when the top region exhibited excessive rounding or after sintering, and (ii) slight deviations from perfect verticality, which can introduce

projection errors not captured by a simple cosine correction.

Nevertheless, the sine-based tilt correction provides a robust first-order correction for vertical dimensions, and it was sufficient for the purposes of stress reconstruction, given that geometric variability between pillars (often on the order of $1\text{ }\mu\text{m}$) dominated the overall scatter in calculated stress levels. For this reason, geometrical metrology was treated as an integral methodological step and explicitly documented for each tested pillar.

2.6.5. Specimen Selection Criteria Based on SEM

Only pillars meeting minimal geometrical and morphological quality criteria were selected for thermal treatment and mechanical testing. The selection criteria were based on SEM inspection and included:

- intact pillar geometry with continuous sidewalls and no visible cracks after sintering;
- limited taper and absence of extreme top rounding that would compromise flat-punch contact;
- clean surrounding area, without large residual rings or particulate contamination likely to interfere with the indenter approach;
- stable adhesion to the substrate, with no visible detachment at the base.

This pre-selection reduced the number of available specimens but improved the reliability of subsequent mechanical characterization by minimizing failure modes dominated by gross fabrication defects rather than intrinsic material behavior.

2.7. Mechanical Testing: Experimental Procedure

Mechanical characterization of the sintered fused silica micropillars was performed using an Alemnis nanoindenter integrated inside the chamber of a Philips XL30 scanning electron microscope (SEM). This in situ configuration enabled accurate positioning of the indenter tip with respect to individual micropillars and allowed direct SEM observation of the structures before and after mechanical loading. During mechanical tests, however, the SEM electron beam was deliberately switched off, as discussed later in this section.

2.7.1. System Preparation and Sample Loading

The mechanical testing setup consists of three main elements: (i) the SEM chamber housing the nanoindenter head, sample, and indenter tip; (ii) the external Micro-Controller System (MCS) and EcoBox controlling force and displacement; and (iii) the control computer running the Alemnis software. The MCS, EcoBox, and control electronics remain outside the SEM chamber and are not affected by the vacuum environment.

At the beginning of each experimental session, the SEM chamber was vented to atmospheric pressure to allow safe access to the internal components. All handling operations inside the chamber were performed while wearing clean gloves in order to minimize contamination of both the indenter tip and the sample.

The appropriate indenter configuration was then mounted on the dedicated mechanical stage inside the SEM chamber. This stage accommodates both the sample holder and the indenter head in a fixed relative geometry, ensuring mechanical stability during testing. Depending on the experiment, the following diamond tips were installed:

- a flat punch tip for microcompression tests;
- a cube-corner tip for pillar splitting experiments.

The sample, previously mounted on an aluminum stub using a rigid adhesive and allowed to cure for at least 24 hours, was fixed onto the sample holder facing the indenter tip. Tip mounting and sample positioning were carried out with particular care to avoid mechanical shock, misalignment, or contamination.

Once the tip and sample were securely installed, the SEM chamber was closed and pumped down to the operating vacuum. After vacuum stabilization, electrical and mechanical connections between the nanoindenter head, the MCS, and the EcoBox were verified, and the system was initialized through the control software.

2.7.2. Controller Configuration and Stage Referencing

After vacuum stabilization, stage calibration and reference positioning were performed using the Micro-Controller System (MCS). Reference positions for the indenter stage were defined along the x , y , and z directions to establish a consistent coordinate framework for subsequent manual positioning.

During this phase, the indenter tip was kept at a safe distance from the sample surface. Vertical motion was controlled via the MCS, while the force signal was simultaneously

monitored in real time using the Alemnis software on the external computer. The force readout was used as a safety indicator: deviations from a zero-load condition indicated unintended contact and required immediate correction of the tip position.

Only after successful stage referencing was the system considered ready for manual approach and fine alignment of the indenter tip relative to individual micropillars.

2.7.3. Manual Approach and Tip–Pillar Alignment

Fine positioning of the indenter tip relative to the micropillars was performed manually using the joystick-controlled motion system. This step represents one of the most critical phases of the experiment, as accidental contact or excessive approach speed can damage either the indenter tip or the fragile micropillars. For context, a SEM overview of the indenter tip positioned above a micropillar array is shown in Figure 2.13, which illustrates the typical geometry used for navigation and target selection prior to final centering.

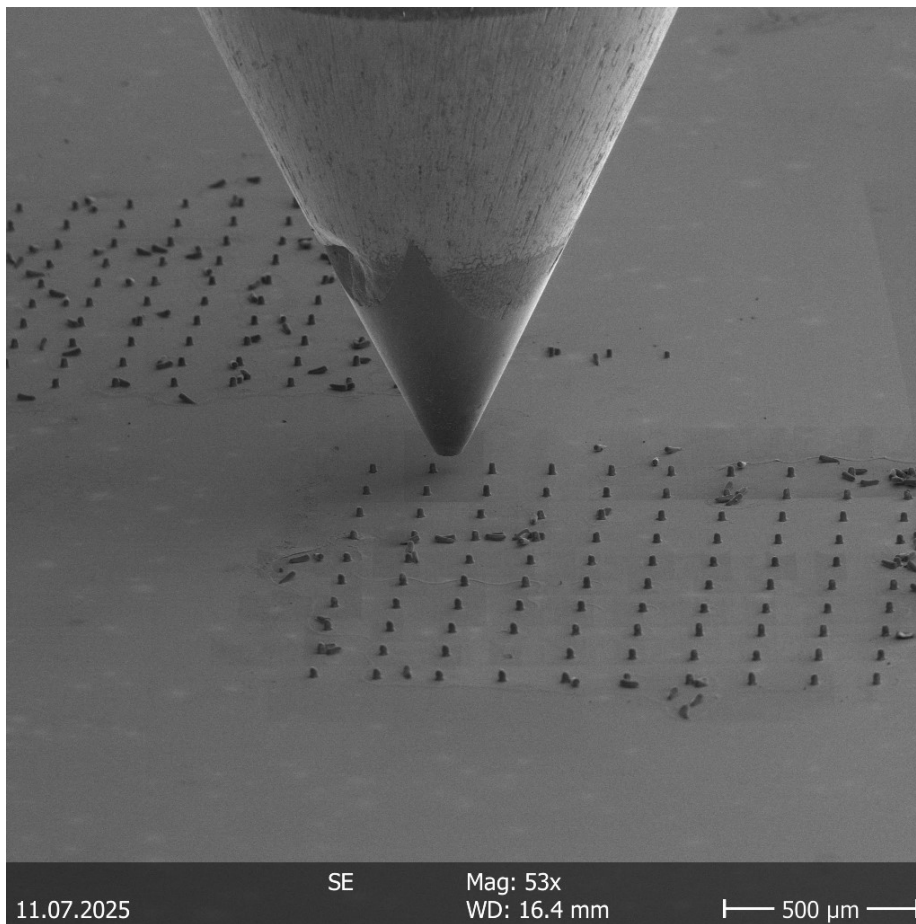


Figure 2.13: SEM overview of the indenter tip positioned above a micropillar array prior to microcompression. The low-magnification view was used to navigate across the array and select individual pillars before fine centering and final approach.

The approach was carried out incrementally, using very small displacement steps along the vertical direction. The step size could be adjusted by the operator and was progressively reduced as the tip approached the pillar top. This cautious procedure minimized the risk of uncontrolled contact and ensured safe positioning even when operating close to the surface.

Once the tip was at a suitable height above the sample, lateral alignment was performed to center the indenter exactly above the selected pillar. This centering operation was initially challenging, particularly during the first experimental sessions, due to the small pillar dimensions and limited depth perception in SEM imaging. However, with increasing familiarity with the joystick control and visual cues provided by the SEM, the procedure became significantly faster and more reliable. After this learning phase, accurate centering of the indenter tip above individual pillars could be achieved routinely and reproducibly.

Correct alignment was verified visually by ensuring that the indenter tip apex (or flat punch center) was concentric with the pillar top surface when viewed under SEM at appropriate magnification.

2.7.4. Pre-Test Calibration and Signal Stabilization

Before initiating each mechanical test, a calibration and stabilization routine was executed through the control software. This procedure included zeroing of load and displacement signals and verification of baseline stability. In practice, this step served to eliminate residual drift, mechanical backlash, and low-frequency vibrations that could otherwise distort the initial portion of the load–displacement curve.

This calibration routine was performed before *every* individual test, rather than once per session, to ensure that each dataset was acquired under well-defined and comparable initial conditions. Only after confirming stable zero-load and zero-displacement baselines was the loading sequence initiated.

2.7.5. SEM Beam Management During Testing

Although the nanoindenter is integrated within the SEM chamber, the electron beam was deliberately switched off during mechanical loading. This choice was motivated by well-documented beam–material interaction effects in brittle and semi-brittle materials at small scales. Electron irradiation can locally modify material behavior by inducing charging, localized heating, or beam-stimulated defect mobility, potentially promoting enhanced apparent plasticity or altering crack initiation and propagation mechanisms

[13].

Since the objective of the present work was to characterize the intrinsic mechanical response of fused silica micropillars, mechanical tests were conducted with the SEM beam off. The beam was reactivated only after completion of the loading sequence, in order to image the deformed or fractured pillar and document the failure morphology. This approach ensured that the measured mechanical response was not influenced by concurrent electron irradiation.

2.7.6. Microcompression Testing Protocol

Microcompression tests were performed using a flat punch indenter under displacement-controlled loading (Figure 2.14). The displacement rate was selected to achieve a nominal engineering strain rate of approximately $1 \times 10^{-3} \text{ s}^{-1}$, corresponding to quasi-static loading conditions commonly adopted in micropillar compression experiments. For pillars with post-sintering heights of approximately $25 \mu\text{m}$, this resulted in a displacement rate on the order of 25 nm s^{-1} .

The loading sequence consisted of a monotonic displacement ramp until either fracture or a predefined displacement limit was reached. Load and displacement signals were recorded continuously throughout the test. The evolution of force as a function of time was monitored in real time via the software interface. This live feedback allowed the operator to identify characteristic features of the mechanical response, such as the onset of nonlinearity, sudden load drops, or catastrophic failure.

Upon observing a clear load drop associated with fracture, the test was terminated and an unloading ramp was executed to retract the indenter safely from the pillar. This prevented secondary damage and facilitated subsequent SEM imaging of the fractured structure.

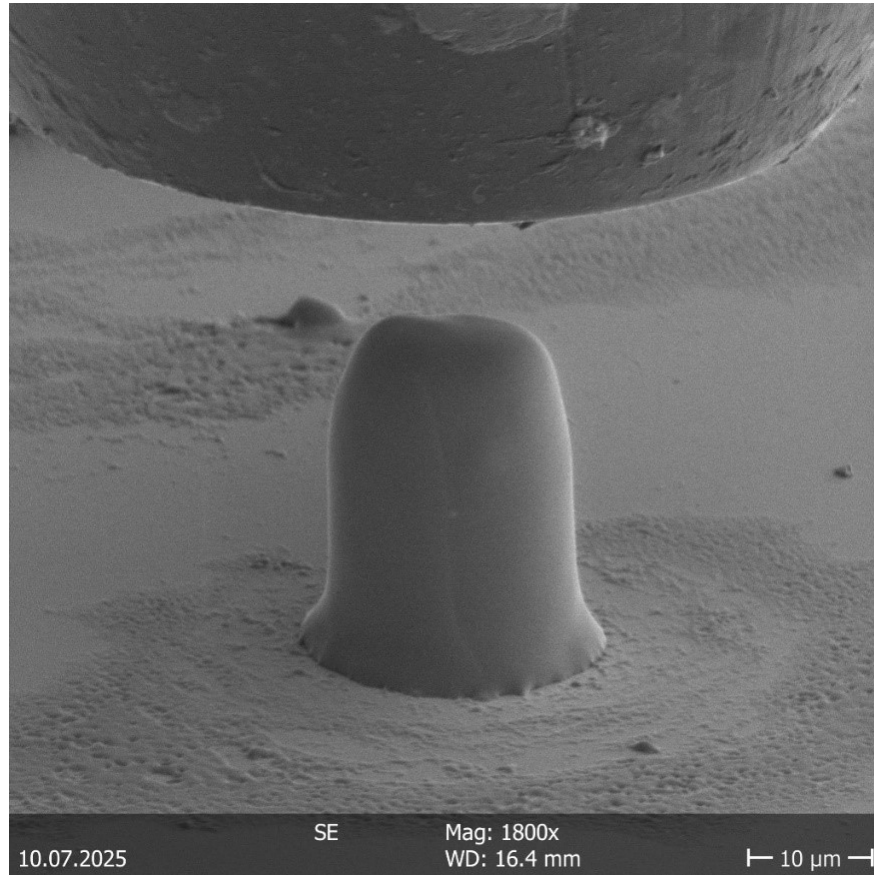


Figure 2.14: SEM image illustrating the flat punch tip aligned above a micropillar prior to microcompression testing.

2.7.7. Pillar Splitting Testing Protocol

Pillar splitting experiments were performed using a cube-corner diamond indenter to promote localized stress concentration and controlled crack initiation (Figure 2.15). As in microcompression, tests were conducted under displacement control. The loading velocity was set to approximately 20 nm s^{-1} , while the unloading velocity was increased (typically to 100 nm s^{-1}) to rapidly disengage the indenter after crack initiation.

The maximum displacement was limited (on the order of $10 \mu\text{m}$) and a conservative force limit was imposed to avoid saturation of the 2 N load cell. Due to the abrupt nature of crack initiation in pillar splitting, the data acquisition rate was increased relative to microcompression tests in order to capture the critical load drop with sufficient temporal resolution.

During the test, the force–time signal was monitored in real time. The critical load P_c associated with crack initiation was identified by a sudden and irreversible drop in the measured force. Immediately after detecting this event, the loading was stopped and the

indenter was retracted through the unloading ramp.

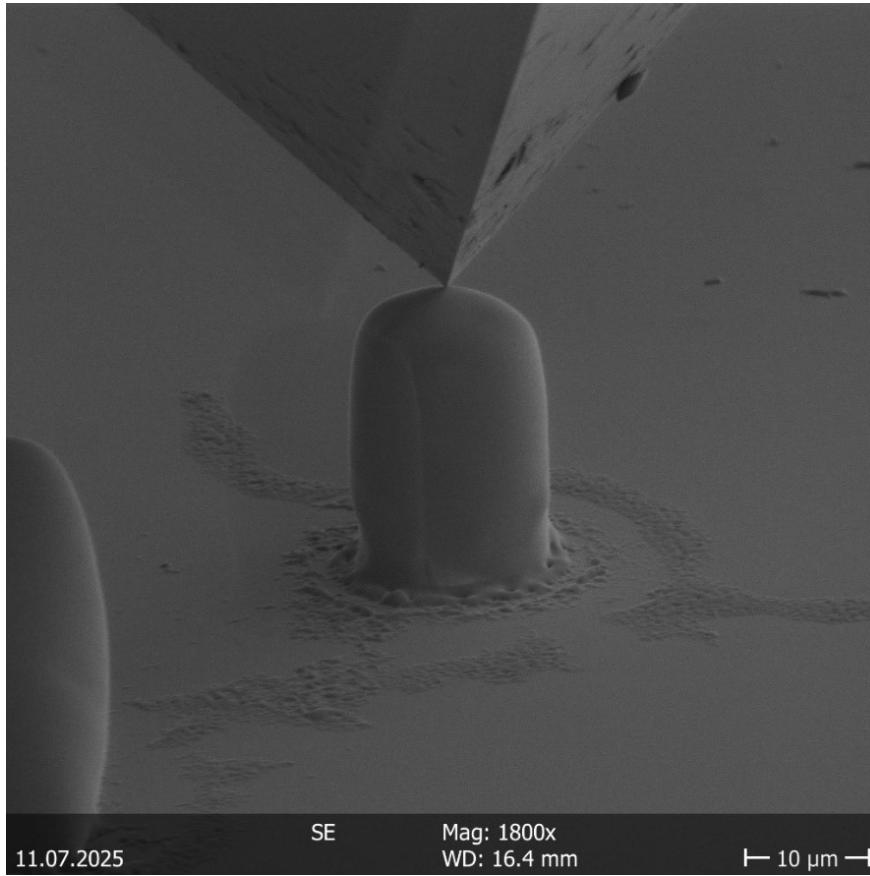


Figure 2.15: SEM image illustrating the cube-corner indenter positioned above a micropillar prior to pillar splitting, enabling localized stress concentration and crack initiation.

2.7.8. Post-Test Imaging and Sequential Testing

After completion of each test, the SEM beam was reactivated and high-resolution images of the tested pillar were acquired. These images were used to document deformation mechanisms, fracture paths, and splitting morphologies, providing direct visual correlation with the mechanical data.

Once imaging was completed, the indenter tip was repositioned laterally using the joystick, and the procedure was repeated for the next pillar. This sequential approach allowed multiple pillars to be tested on the same substrate under comparable conditions, while maintaining full control over alignment, calibration, and beam exposure for each individual experiment.

2.7.9. Experimental Workflow Summary

In summary, each mechanical test followed a well-defined sequence:

1. mounting of the sample and indenter tip;
2. careful manual approach and centering of the tip above the selected pillar;
3. pre-test calibration and stabilization of signals;
4. execution of the loading protocol with SEM beam off;
5. real-time monitoring of force evolution and identification of fracture events;
6. controlled unloading and tip retraction;
7. post-test SEM imaging with beam on;
8. lateral repositioning and repetition on the next pillar.

This procedure ensured that each dataset was acquired under controlled and reproducible conditions, while minimizing the risk of experimental artifacts related to misalignment, beam effects, or uncontrolled contact events.

2.7.10. Data acquisition and export of raw signals

For each micropillar test (microcompression and pillar splitting), the instrument software recorded the time series of load $F(t)$ and displacement $u(t)$ throughout the full loading–unloading cycle. Prior to exporting, the standard AMICS processing tools were applied to improve the consistency of the raw signals, including compliance calibration and displacement correction. The corrected datasets were then exported and organized in a dedicated Excel workbook, where each pillar corresponded to a pair of columns (displacement and load). In the same file, representative SEM images of each pillar were stored (before and after testing) to keep the mechanical signal and the observed failure morphology linked at the specimen level.

2.7.11. Geometrical measurements from SEM images

Pillar geometries were quantified from SEM micrographs to convert the raw F – u signals into engineering stress–strain curves. As schematically indicated in Figure 2.16, the top diameter D_{top} was measured at the contact surface with the indenter. This choice reflects the fact that the initial contact and the highest stress concentrations are expected at the upper surface during loading. Pillar height H was measured from side-view SEM images;

when images were acquired with a tilted stage (tilt angle θ), the apparent height H_{app} measured on the micrograph (Figure 2.16) was corrected as:

$$H = \frac{H_{\text{app}}}{\sin \theta}. \quad (2.2)$$

Diameter and height measurements were performed using the microscope PC software during SEM sessions; for offline measurements on a personal laptop, Fiji (ImageJ) was used. In both cases, the pixel-to-length conversion was set by calibrating the scale using the reference scale bar embedded in each SEM image.

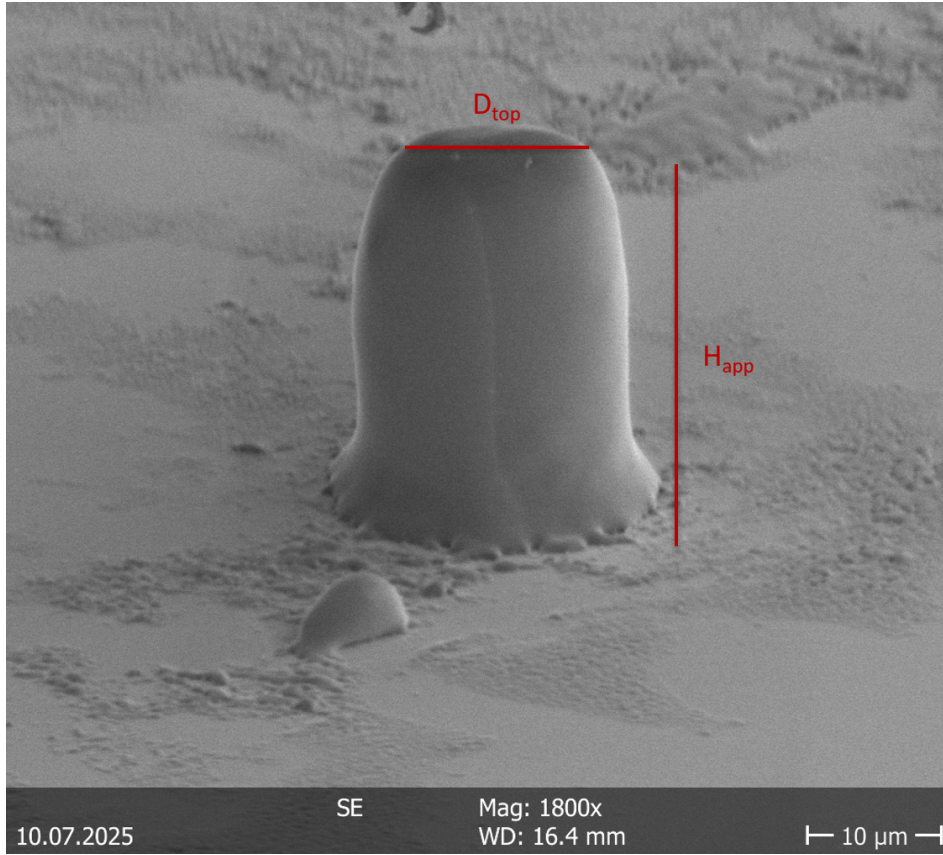


Figure 2.16: Schematic definition of the geometric quantities extracted from SEM images for stress–strain data reduction: top diameter D_{top} at the indenter contact surface, apparent height H_{app} measured on a tilted SEM view (tilt angle θ), and the corresponding corrected pillar height $H = H_{\text{app}}/\sin \theta$.

2.7.12. Engineering stress–strain conversion

For microcompression, the corrected displacement u was converted to engineering strain as:

$$\varepsilon = \frac{u}{H}, \quad (2.3)$$

where H is the pre-test pillar height obtained as described in Section 2.7.11 (Figure 2.16). The engineering stress was obtained from the measured force using the cross-sectional area at the top surface, computed from D_{top} (Figure 2.16):

$$\sigma = \frac{F}{A_{\text{top}}}, \quad A_{\text{top}} = \pi \left(\frac{D_{\text{top}}}{2} \right)^2. \quad (2.4)$$

This definition is consistent with the indenter–pillar load-transfer region and provides a conservative, physically meaningful estimate of the stress level for pillars exhibiting slight tapering. For each specimen set, individual $\sigma(\varepsilon)$ curves were plotted together, and an average response was computed on a common strain grid. At each strain value, the mean curve and the $\pm 1\sigma$ scatter band were calculated while ignoring missing values outside the individual curve ranges.

2.7.13. Piecewise evaluation of the apparent Young’s modulus

To identify the elastic regime and quantify the stiffness evolution, an apparent Young’s modulus was computed as the local slope of the stress–strain curve within small strain intervals. Each curve was segmented into strain windows (typically $\Delta\varepsilon = 0.01$), and within each window the modulus was extracted by linear regression:

$$E_k = \left. \frac{d\sigma}{d\varepsilon} \right|_{\varepsilon \in [\varepsilon_k, \varepsilon_{k+1}]} . \quad (2.5)$$

This piecewise approach provides a robust visualization of how the slope increases, stabilizes (approximately elastic response), and then decreases as the curve departs from linearity. For each pillar, the maximum value E_{max} among the valid windows was retained as a representative stiffness metric to support subsequent analysis.

2.7.14. Yield stress by the 0.2% offset method

The yield point was determined using the 0.2% offset method, adapted to microscale compression data. For each pillar, a linear fit $\sigma = E_{\text{fit}}\varepsilon + b$ was performed over a user-defined strain interval selected around the region where the modulus transitions from approximately constant to decreasing. The fitted line was then translated by an offset strain $\varepsilon_0 = 0.002$:

$$\sigma_{\text{off}}(\varepsilon) = E_{\text{fit}}(\varepsilon - \varepsilon_0) + b. \quad (2.6)$$

The yield strain ε_y was taken as the first intersection between the measured curve $\sigma(\varepsilon)$ and $\sigma_{\text{off}}(\varepsilon)$, and the corresponding yield stress was defined as $\sigma_y = \sigma(\varepsilon_y)$. This procedure was repeated for all pillars, producing a distribution of σ_y values that was summarized using mean and standard deviation.

2.7.15. Gauge factor γ estimation for pillar splitting

The pillar splitting fracture toughness formulation requires a dimensionless gauge factor γ that depends on indenter geometry and on the elastic–plastic response of the pillar material. In this work, γ was estimated from a literature correlation linking γ to the ratio E/H (with H denoting hardness). Specifically, hardness was approximated from the compressive yield stress using:

$$H \approx 1.5 \sigma_y, \quad (2.7)$$

and γ was obtained from the linear interpolation proposed in the literature:

$$\gamma = 0.021 \left(\frac{E}{H} \right) + 0.392, \quad (2.8)$$

where E is taken as the pillar-specific E_{max} extracted from the piecewise modulus analysis. A pillar-wise γ_i was computed for each microcompression curve and then averaged to obtain a representative $\bar{\gamma}$ used for the subsequent pillar splitting analysis. [16, 32]

2.7.16. Pillar splitting data reduction and extraction of the critical load

For each pillar splitting test, the primary signal used for fracture toughness evaluation was the load–displacement curve $F(u)$. The critical load was identified as the maximum load associated with the splitting event. Operationally, P_{max} was taken as the maximum force preceding the main irreversible load drop that marks crack initiation and unstable propagation [16]. In some cases, secondary peaks appeared before or after the main event due to partial fragment instability or progressive chipping; these features were not used to define P_{max} . As for microcompression, the ensemble of curves was visualized together and summarized by computing a mean curve with a $\pm 1\sigma$ band.

2.7.17. Fracture toughness calculation and treatment of tapered pillars

Mode-I fracture toughness was computed using the pillar splitting relation:

$$K_c = \gamma \frac{P_{\max}}{R^{3/2}}, \quad (2.9)$$

where R is the pillar radius. Because the tested pillars were slightly tapered, R is not strictly constant along the height. Therefore, the radius was treated as an interval $R \in [R_{\text{top}}, R_{\text{base}}]$ estimated from SEM measurements. The fracture toughness was consequently reported as a bounded range:

$$K_c^{\min} = \bar{\gamma} \frac{P_{\max}}{R_{\text{base}}^{3/2}}, \quad K_c^{\max} = \bar{\gamma} \frac{P_{\max}}{R_{\text{top}}^{3/2}}, \quad (2.10)$$

reflecting the geometrical uncertainty due to tapering. For comparison with literature, a representative value was obtained by averaging either the two bounds or by using a mid-radius $R_{\text{mid}} = (R_{\text{top}} + R_{\text{base}})/2$, while keeping the interval as the primary uncertainty descriptor.

A worked example illustrating the full data-reduction workflow (single-pillar stress-strain, piecewise modulus, 0.2% offset construction, and γ estimation) is provided in Appendix A.1.

3 | Results and Discussion

This chapter reports the experimental results on fused silica micropillars produced by Two-Photon Polymerization (2PP), covering fabrication, thermal conversion, and mechanical testing.

The work culminates in microcompression and pillar splitting on thermally converted pillars, used to extract Young's modulus, compressive strength, and fracture-related metrics.

Figure 3.1 outlines the decision pathway used to define the reference mechanical state: polymeric resins (IP-S/IP-Dip) were first used to tune exposure, then GP-Silica highlighted adhesion and height-driven instabilities. The geometry was progressively downscaled until stable printing and compatibility with the 2 N load cell were achieved.

Workflow overview

1. **Baseline printing (IP resins):** tune exposure settings and build process intuition.
2. **Transition to GP-Silica:** identify the main printability constraints and select a stable pillar geometry.
3. **Parameter refinement:** narrow the process window and verify short-range reproducibility on pillar arrays.
4. **Environmental sensitivity:** assess time-dependent drift and relative-humidity effects to define robust operating conditions.
5. **Thermal conversion:** screen thermal schedules and define a reference conversion state for mechanical testing.
6. **Mechanical testing:** microcompression and pillar splitting on the same reference state to extract E , σ_y , $\sigma_{\max}$, and $K_{c,\text{eff}}$.

Figure 3.1: Schematic overview of the experimental pathway leading from process development to the reference mechanical dataset.

3.1. Process Familiarization and Parameter Exploration with Polymeric Resins

Preliminary experiments with IP-S and IP-Dip provided a controlled baseline to interpret parameter sensitivity before transitioning to GP-Silica. Although polymeric resins have wider processing windows than nanoparticle-loaded photoresists, they enabled systematic identification of exposure regimes associated with incomplete polymerization, stable feature formation, and over-exposure defects for a fixed pillar geometry.

3.1.1. Coupled Effects of Laser Power and Scan Speed

A strong interdependence between laser power (LP) and scan speed (SS) emerged across the explored conditions, as summarized in Figure 3.2. Increasing scan speed required progressively higher laser power to maintain stable polymerization, consistent with reduced exposure time per unit length at higher writing velocities. Conversely, at low scan speeds, stable pillar fabrication was achieved at lower power values, albeit with a reduced margin to over-exposure.

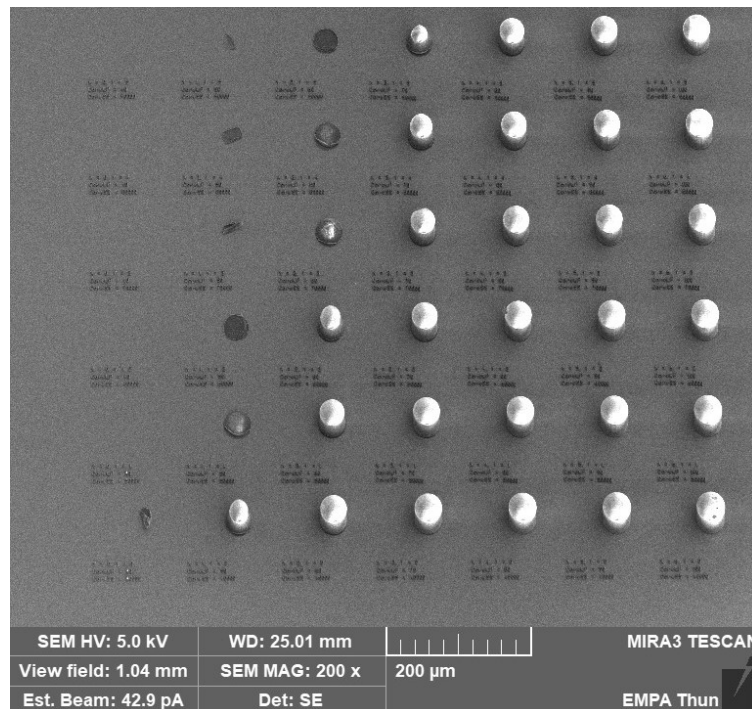


Figure 3.2: SEM-based pillar matrix summarizing the combined effect of laser power (x-axis) and scan speed (y-axis) on print outcome. The upper-left region corresponds to low-dose conditions (low LP and high SS), while the lower-right region indicates progressively higher delivered energy.

In the low-dose regime (upper-left region of Figure 3.2), pillars frequently exhibited

incomplete development or strongly reduced height relative to the target geometry. In several cases, only a small polymerized base remained near the substrate, while the upper part of the pillar was absent, consistent with insufficient polymerization in the bulk. Partial solidification at the base can still occur due to locally enhanced effective exposure in the first layers close to the substrate. A representative example is shown in Figure 3.3, where the initial layers appear more robust despite the overall low-dose condition, consistent with substrate-related optical contributions (e.g., reflection) increasing local energy deposition near the interface.

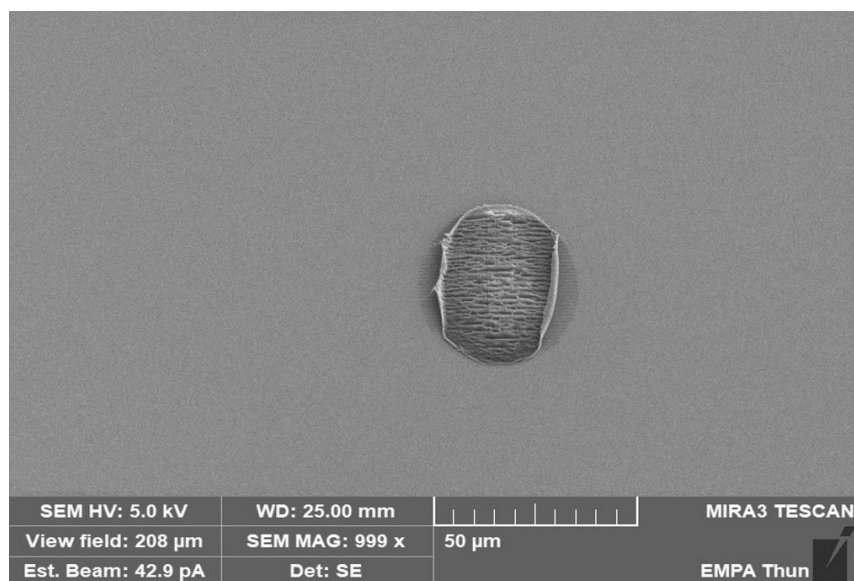


Figure 3.3: Representative low-dose pillar showing preferential polymerization of the first layers close to the substrate, resulting in a solidified base while the upper part of the structure is incomplete.

Moving along the matrix diagonal toward intermediate dose, a region of stable printing was identified where pillars exhibited uniform height and smooth sidewalls (Figure 3.2). At the opposite extreme, excessive energy input led to swelling and localized defects that become progressively more evident toward the high-dose corner. Although extremely high LP values were deliberately avoided to limit air-bubble formation, early signatures of over-exposure were already apparent, confirming that stable fabrication occurs within a bounded process window.

3.1.2. Influence of Hatching and Slicing Distance

Hatching distance (HD) and slicing distance (SD) were found to critically affect morphological quality and structural integrity. The coupled effect of laser power and hatching distance is summarized in Figure 3.4. For moderate-to-small HD values, sufficient lateral voxel overlap ensured good inter-line bonding and lateral continuity, yielding smooth sidewalls and uniform structures over a relatively broad power range.

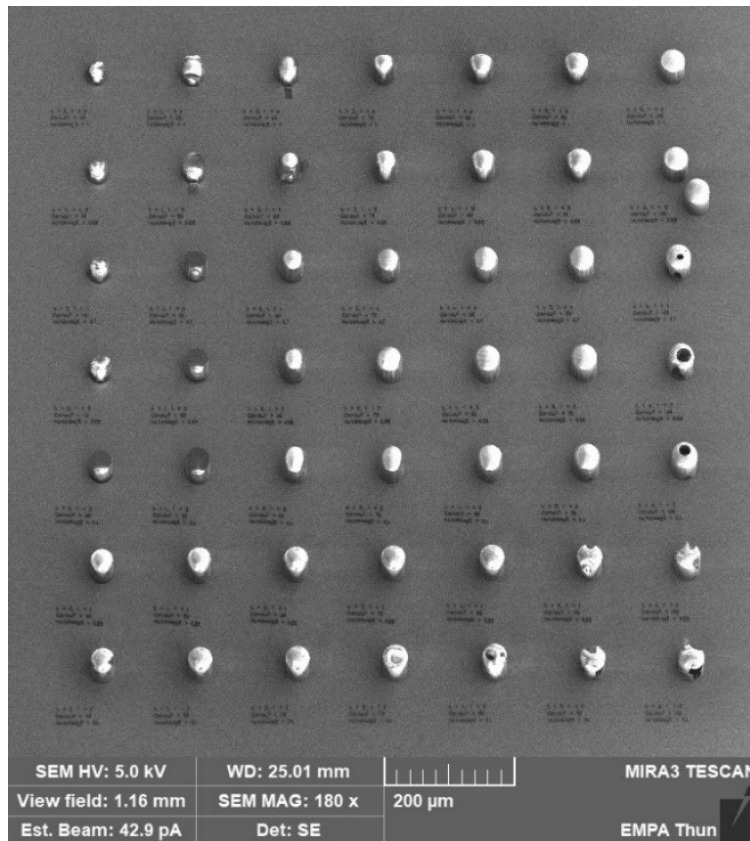


Figure 3.4: SEM-based pillar matrix showing the coupled effect of laser power ($LP = 40\text{--}100\text{ mW}$) and hatching distance ($HD = 0.1\text{--}1.0\text{ }\mu\text{m}$) on pillar morphology and print integrity. Scan speed was fixed at $SS = 40\text{ mm/s}$ and slicing distance at $SD = 0.4\text{ }\mu\text{m}$.

As HD increased, the stable operating window shifted toward higher LP, reflecting reduced overlap between adjacent scan lines. At low LP, insufficient lateral bonding produced underexposed or mechanically weak structures, whereas at high LP combined with small HD, excessive overlap promoted swelling and surface irregularities. When HD exceeded a critical value, SEM inspection revealed increased surface roughness with scan-line ridges and, in extreme cases, partial delamination of the pillar sidewalls (Figure 3.5).

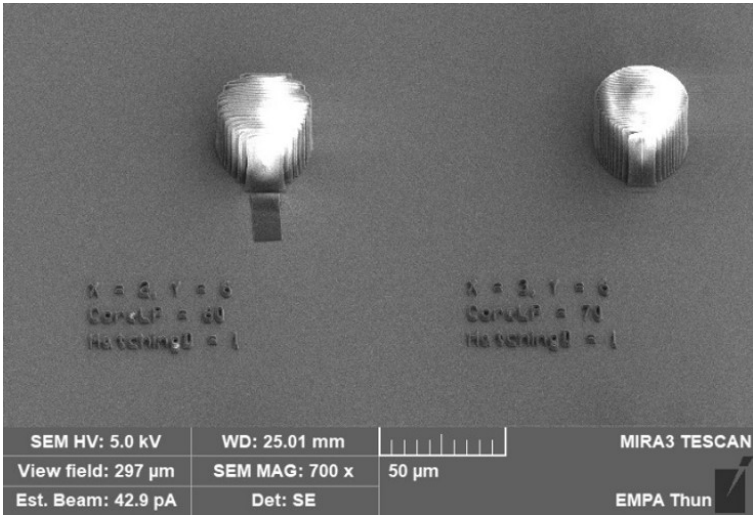


Figure 3.5: Representative pillar printed with high hatching distance, showing pronounced scan-line ridges and partial sidewall delamination due to insufficient lateral voxel overlap.

A complementary trend was observed when varying slicing distance at fixed hatching distance (Figure 3.6). Increasing SD shifted the polymerization threshold only slightly toward higher laser power, but the upper boundary linked to damage and over-exposure moved faster. As a result, the operating window expanded with increasing SD.

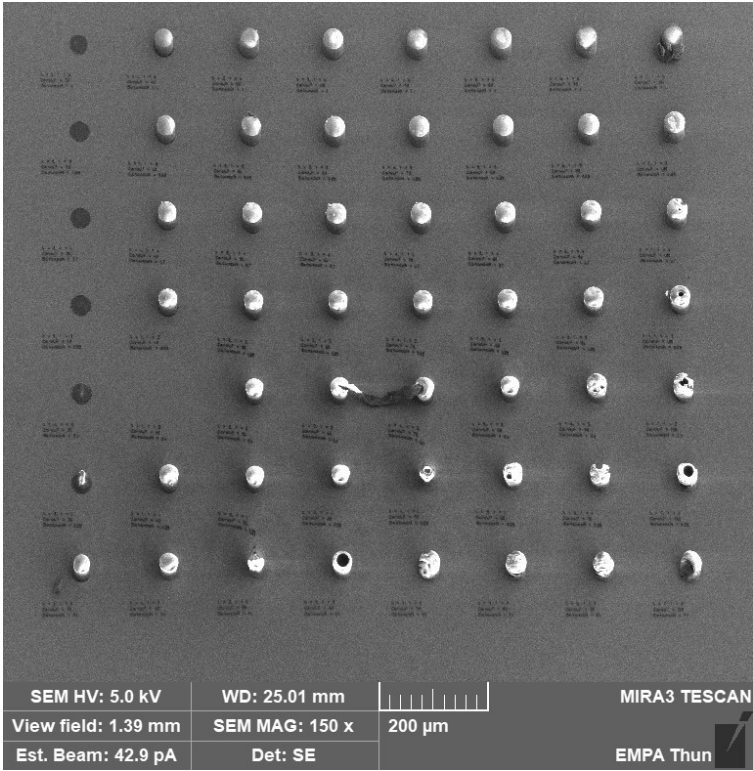


Figure 3.6: SEM-based pillar matrix showing the coupled effect of laser power (40–100 mW) and slicing distance (0.1–1.0 µm) at fixed scan speed (40 mm/s) and fixed hatching distance (0.4 µm).

This behavior is consistent with distinct roles of lateral and vertical voxel overlap. While the onset of polymerization remains strongly coupled to lateral energy distribution and thus to HD, excessive vertical overlap increases repeated laser passes through the same volume. This cumulative exposure promotes over-polymerization and defect formation, including bubble nucleation and local deformation. Representative defects observed at low slicing distance are shown in Figure 3.7.

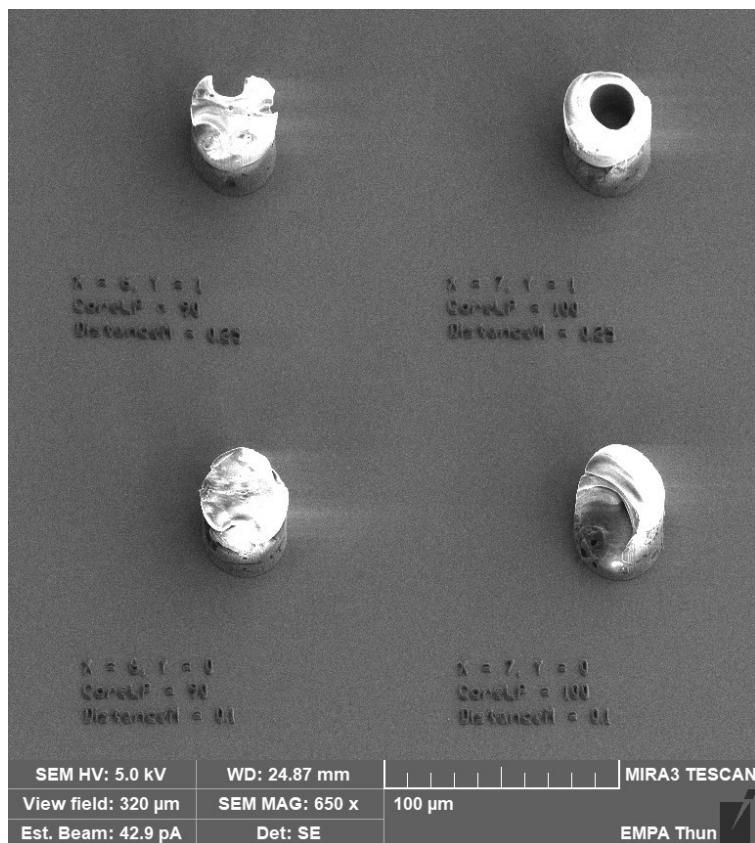


Figure 3.7: Representative defects observed at low slicing distance, including voids and shape distortions attributed to excessive vertical overlap and cumulative exposure.

3.1.3. Process Windows and Implications for GP-Silica

Overall, the polymeric-resin campaigns indicated that stable fabrication is achieved only within finite process windows defined by coupled combinations of laser power, scan speed, hatching distance, and slicing distance. Within these windows, compensation effects (e.g., higher scan speed offset by higher power) support an energy-density interpretation, where printability is governed by combined dose and voxel overlap rather than by any single parameter.

These findings motivated a conservative exploration strategy for GP-Silica. Compared to polymeric resins, the viscosity and nanoparticle loading of GP-Silica impose a narrower

stability window and higher sensitivity to boundary conditions (time after dispensing and relative humidity), which are addressed next.

3.2. Scaling effects and printability limits in GP-Silica

Transitioning from polymeric resins to GP-Silica introduced a different limiting regime. Rather than a broad under/overexposure window, printability became dominated by (i) adhesion at the substrate interface and (ii) height-dependent instabilities that amplify axial growth under high-dose conditions. The following subsections show how these constraints drove a progressive geometry downscaling toward mechanically testable $15 \times 30 \text{ }\mu\text{m}$ pillars.

3.2.1. Exploratory complex geometries: honeycomb and “honeyflower”

Before focusing on pillars, thin-walled honeycomb-like architectures were printed as qualitative probes of GP-Silica limitations. After thermal processing, these structures frequently showed cracking, wall inclination, and local collapse (Figure 3.8), indicating strong shrinkage-driven stress sensitivity in slender features. A reduced seven-cell “honeyflower” was also tested; most specimens detached during processing, consistent with insufficient anchoring area, while surviving parts still exhibited pronounced wall collapse (Figure 3.9).

Since the thesis objective is quantitative mechanics, the study was subsequently narrowed to pillar geometries, which provide a controlled and repeatable basis for process optimization and mechanical testing.

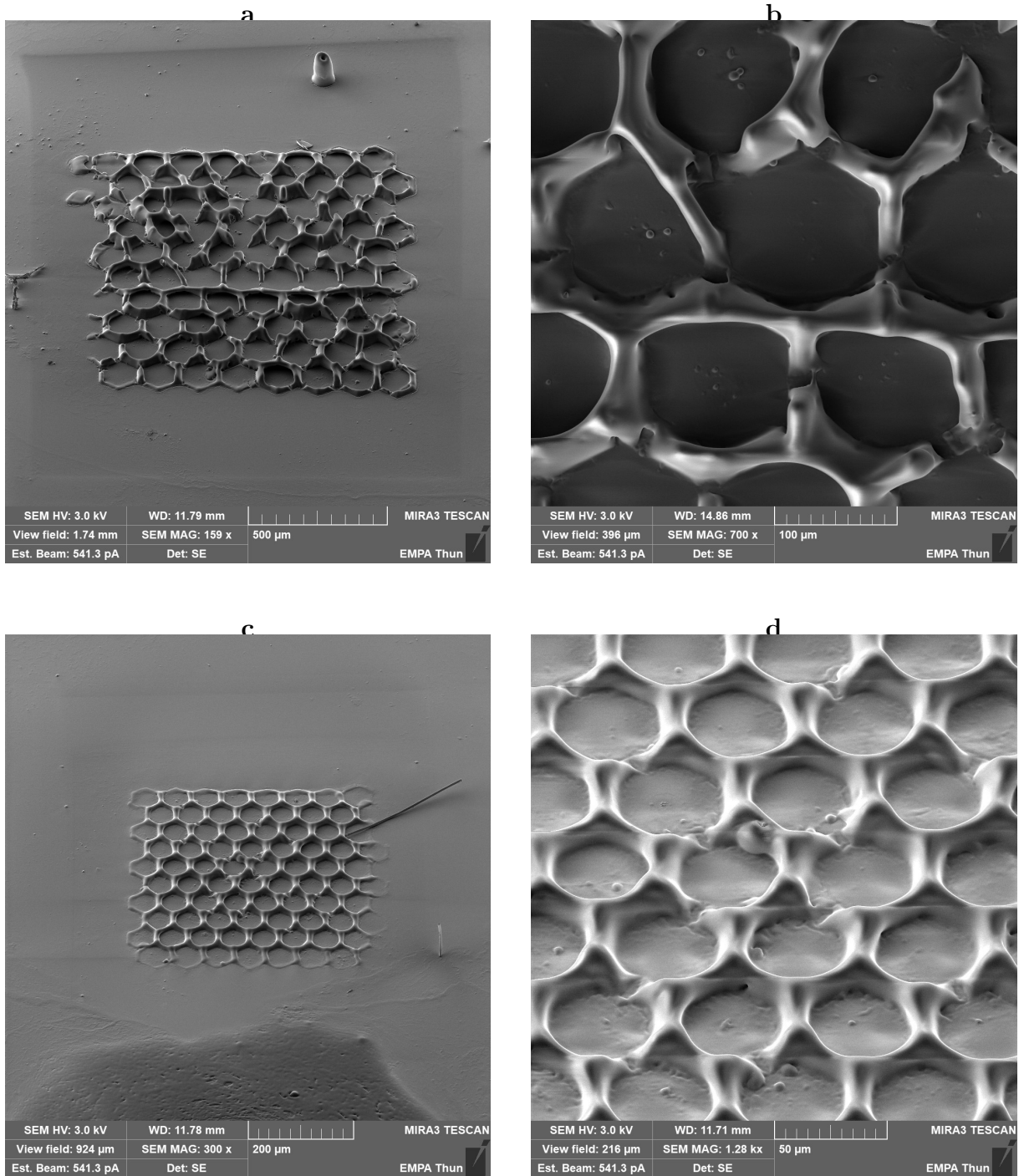


Figure 3.8: Exploratory GP-Silica honeycomb architectures after thermal processing. (a,c) Overview SEM images of two honeycomb prints, while (b,d) provide the corresponding higher-magnification views. Shrinkage-driven damage includes multi-site cracking, wall inclination, and local collapse/flattening consistent with internal stress development during thermal treatment.

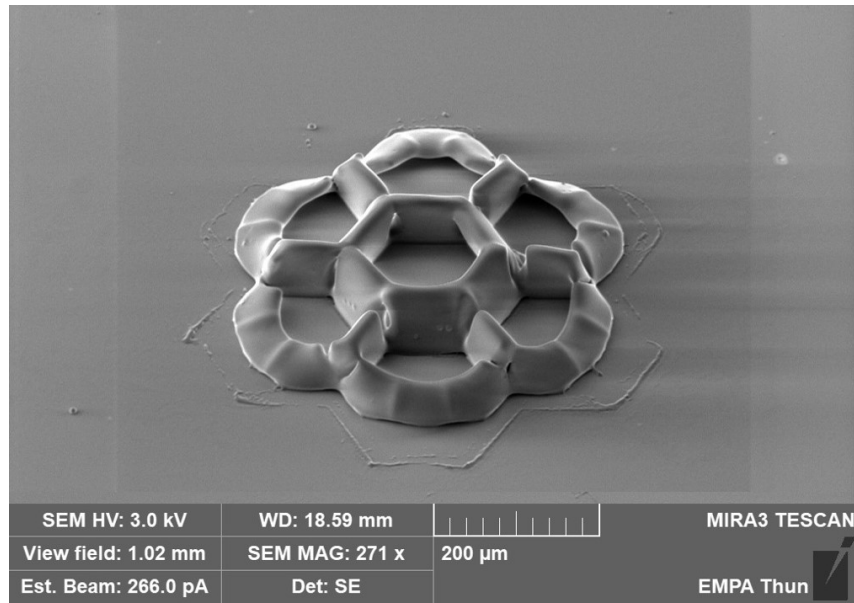


Figure 3.9: Exploratory GP-Silica “honeyflower” geometry (seven hexagonal cells) after thermal processing. The reduced footprint decreases the number of anchoring points, increasing the likelihood of detachment, while the taller thin walls exhibit pronounced shrinkage-driven collapse.

3.2.2. Adhesion versus base overgrowth

To mitigate detachment during development, pillars were initially printed with an enlarged base. This improved survival, but it also introduced a systematic geometric penalty: the base region became highly dose-sensitive and progressively merged into the pillar body at higher exposure, leading to rounded fillets, local bulging, and loss of a well-defined cylindrical gauge section (Figure 3.10–3.11). In addition, the added support geometry reduced dimensional fidelity and increased the occurrence of process-induced distortions near the substrate, which would directly bias stress conversion and compromise specimen-to-specimen comparability.

Decision. Support-like bases and more elaborate adhesion-aid geometries were therefore abandoned. To keep the mechanical dataset interpretable, the study converged on a simple cylindrical pillar geometry with a clearly defined top diameter and gauge section. Adhesion was then addressed through process control (first-layer exposure strategy and printing parameters) rather than through sacrificial geometrical features that introduce uncontrolled shape changes.

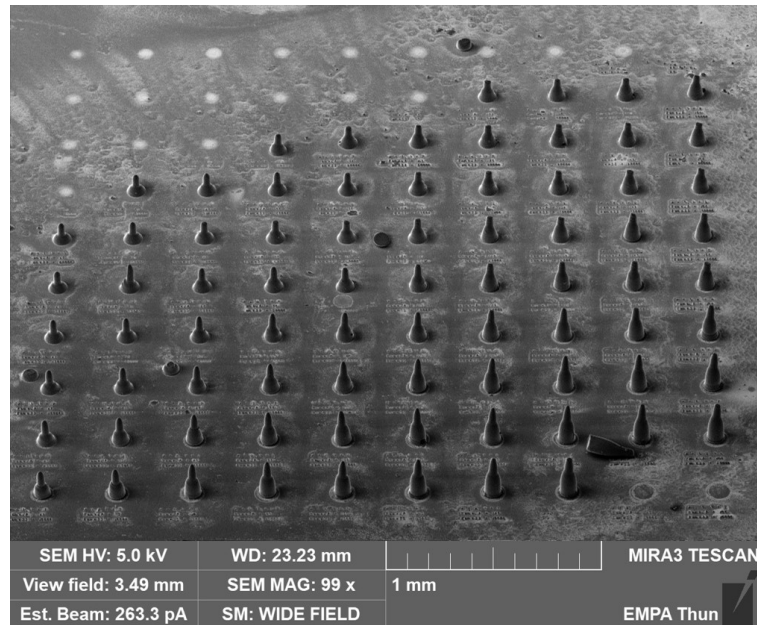


Figure 3.10: LP–SS parameter matrix (10×10) for pillars printed with an enlarged base. Hatching and slicing distances were fixed at $HD = SD = 1 \mu\text{m}$, while laser power and scan speed were varied from 10 to 100 (as defined in the matrix). Missing pillars occur in the low-dose region (upper-left), whereas high LP/low SS conditions (lower-right) promote strong height overgrowth and pronounced base enlargement.

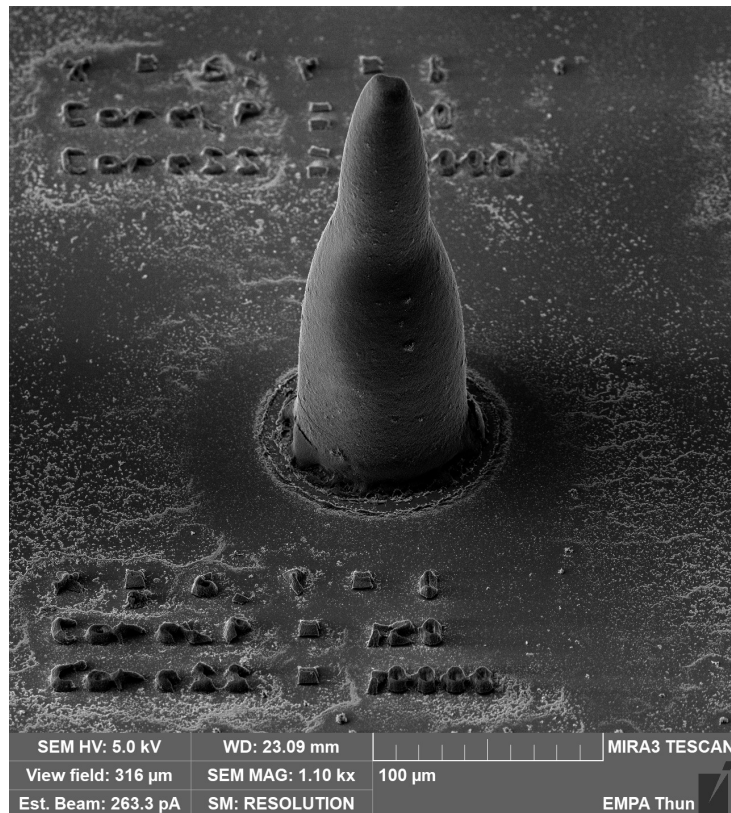


Figure 3.11: Close-up SEM image of a representative pillar printed at high LP and low SS, showing substantial base overgrowth. The base (nominal length $20 \mu\text{m}$) extends upward and progressively merges with the pillar body, resulting in a nearly continuous geometry.

3.2.3. Axial overgrowth and height-dependent instability

A dominant limitation in GP-Silica was a height-amplified axial overgrowth: for nominally tall pillars, the green-state height could exceed the design value by a factor of ~ 2 – 3 . The LP–SS screening on $40 \times 80 \mu\text{m}$ arrays (Figure 3.12) highlights a clear trade-off. Low-dose conditions lead to widespread detachment during development, whereas only high-dose settings yield a surviving pillar. However, the survivor is strongly overgrown in height (e.g., $\sim 120 \mu\text{m}$ vs. a nominal $80 \mu\text{m}$), indicating that the exposure conditions required for adhesion simultaneously activate the axial instability.

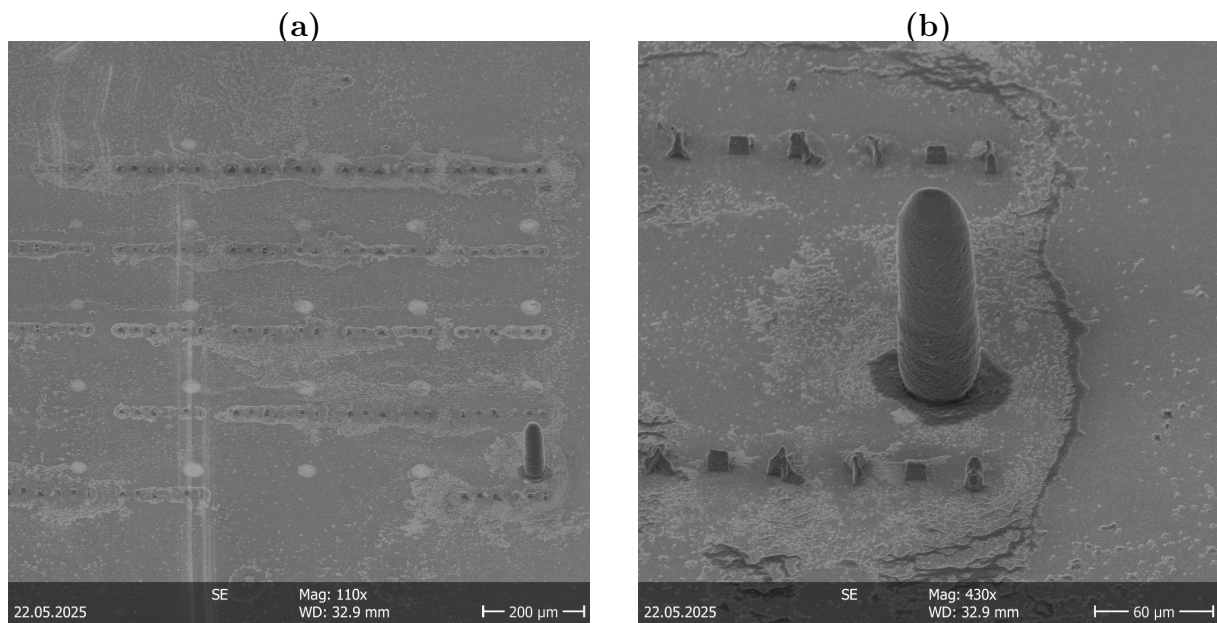


Figure 3.12: $40 \times 80 \mu\text{m}$ pillars ($\text{HD} = 1.5 \mu\text{m}$, $\text{SD} = 2 \mu\text{m}$) printed while varying LP (30–70 mW) and SS (10–50 mm/s). (a) LP–SS matrix showing extensive pillar loss after development, with survival mainly in the high-dose corner. (b) Close-up of the surviving pillar at high LP/low SS, showing near-target diameter but pronounced axial overgrowth in the green state ($\sim 120 \mu\text{m}$ vs nominal $80 \mu\text{m}$).

To decouple adhesion from axial growth, a two-step exposure strategy was introduced using pre-exposed base layers (Figure 3.13). By fixing a high-dose condition for the first layers at the substrate interface and independently scanning the LP–SS window for the pillar core, stable pillars could be obtained in a wider portion of the matrix and with closer-to-target heights. This confirms that survival is governed primarily by the exposure state of the first layers, while the axial overgrowth is driven by dose accumulation in the pillar body.

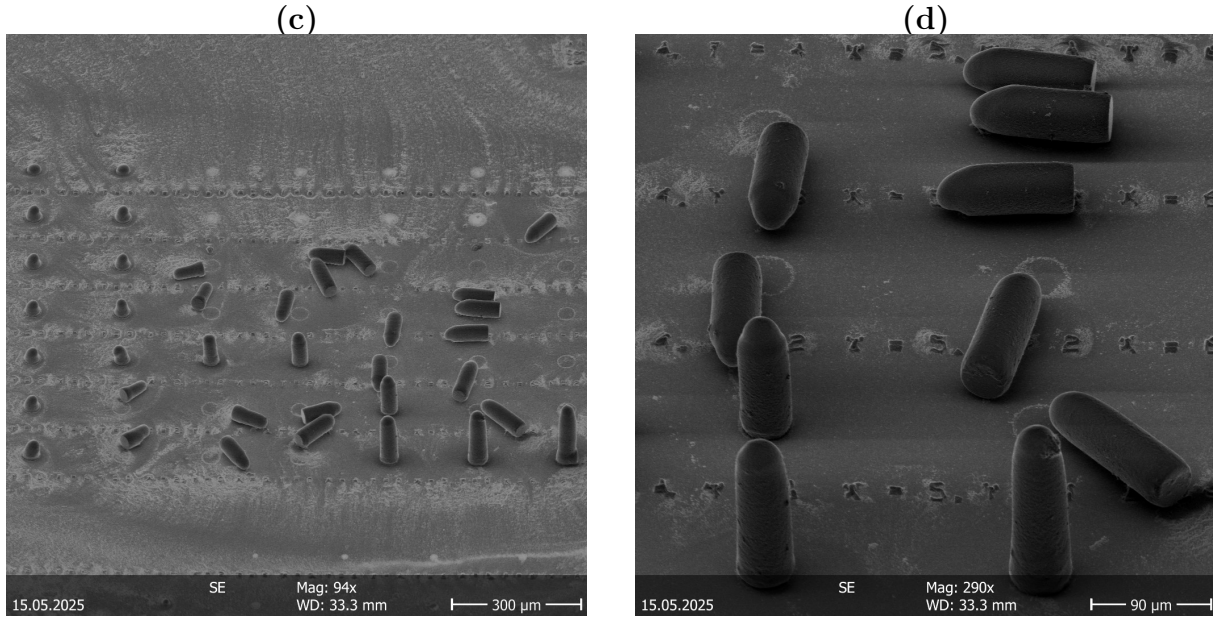


Figure 3.13: $40 \times 80 \mu\text{m}$ pillars printed with a pre-exposed base-layer stack (base layers: LP = 100 mW, SS = 15 mm/s) prior to the core exposure. (c) LP-SS matrix showing improved survival compared to Figure 3.12; at low core dose (left) only short, uniform features are visible, corresponding to the base-layer stack alone, indicating insufficient energy to polymerize the pillar core. (d) Close-up illustrating the resulting pillar population: base layers improve adhesion and enable near-design heights in the central region ($\sim 80 \mu\text{m}$) despite occasional fallen pillars, whereas high-dose conditions (lower-right) still promote pronounced axial overgrowth (up to $\sim 140 \mu\text{m}$).

In contrast, attempting to increase adhesion by reducing voxel spacing (smaller HD/SD) did not suppress the instability and could even amplify it (Figure 3.14). In general, decreasing hatching and slicing distance increases voxel overlap and reduces the effective spacing between adjacent scan lines and layers. This promotes more continuous polymerization, improves lateral and vertical bonding, and typically enhances adhesion at the substrate interface—an effect already observed in the polymeric-resin screening, where tighter overlap produced more robust structures.

For GP-Silica, however, the same overlap-driven strategy has a clear downside: the increased overlap also raises the accumulated energy density within the pillar volume, effectively shifting the exposure toward a higher-dose regime. As a result, polymerization is not only strengthened at the base (beneficial for survival), but also intensified along the pillar core, where the axial overgrowth mechanism is triggered and reinforced. In this case, pillars designed at $60 \mu\text{m}$ height reached $\sim 160 \mu\text{m}$, consistent with cumulative exposure and overlap effects increasing the effective dose throughout the entire volume and therefore exacerbating the height-dependent instability.

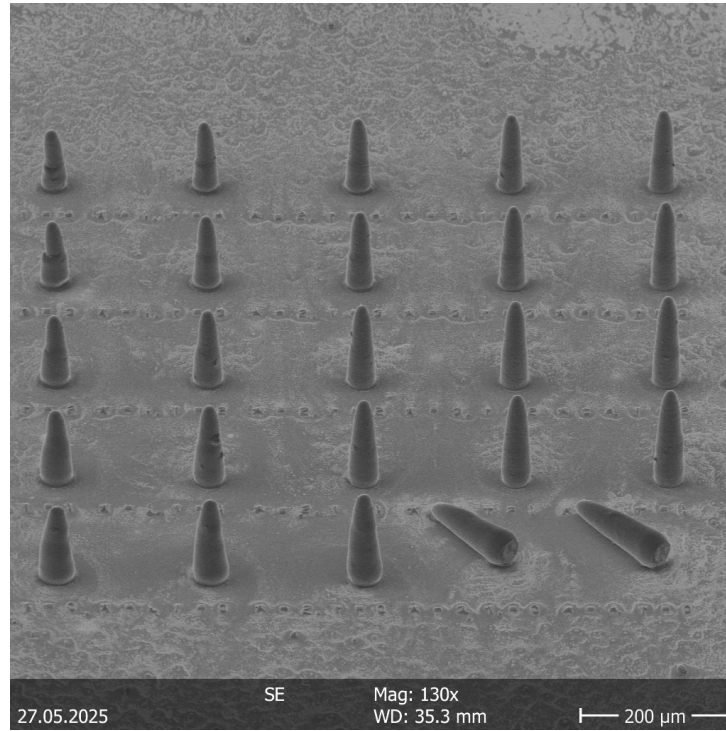


Figure 3.14: Representative $30 \times 60 \mu\text{m}$ pillar printed under high-dose conditions ($LP = 70 \text{ mW}$, $SS = 10 \text{ mm/s}$) with reduced voxel spacing. The green-state height can exceed $\sim 160 \mu\text{m}$, showing that decreasing overlap distances does not suppress the instability and may intensify axial growth.

Decision. Because axial overgrowth scales strongly with pillar height and is exacerbated by global high-dose settings (and by excessive overlap), the geometry was progressively downscaled. The base-layer strategy was retained as the preferred adhesion lever, while the core exposure (LP/SS and HD/SD) was tuned to limit dose accumulation and obtain near-target pillars compatible with the 2 N load cell.

3.2.4. Downscaling to $15 \times 30 \mu\text{m}$: optimization and reproducibility

The previous analysis established two key constraints: (i) complex or support-assisted geometries introduced distortions and dose-driven artifacts that compromised dimensional fidelity, and (ii) axial overgrowth and adhesion were tightly coupled to exposure dose and voxel overlap. For this reason, the strategy was simplified to cylindrical pillars only, and the geometry was progressively downscaled. Reducing the height mitigated axial overgrowth, while operating at smaller hatching and slicing distances ensured sufficient voxel overlap to maintain polymerization continuity and substrate adhesion. In addition, pre-exposed base layers were retained as a controlled means to enhance adhesion without excessively increasing the core dose.

At the $15 \times 30 \mu\text{m}$ scale, gross failures (missing pillars or extreme overgrowth) were largely suppressed (Figure 3.15). The limiting factor shifted from survival to reproducibility and geometric fidelity: small variations in laser power, scan speed, and overlap parameters produced measurable differences in taper, top rounding, and effective height. The optimization therefore proceeded in three steps: overlap screening (HD–SD), dose refinement (repeated LP–SS matrices), and an intra-sample reproducibility check using a 10×10 array.

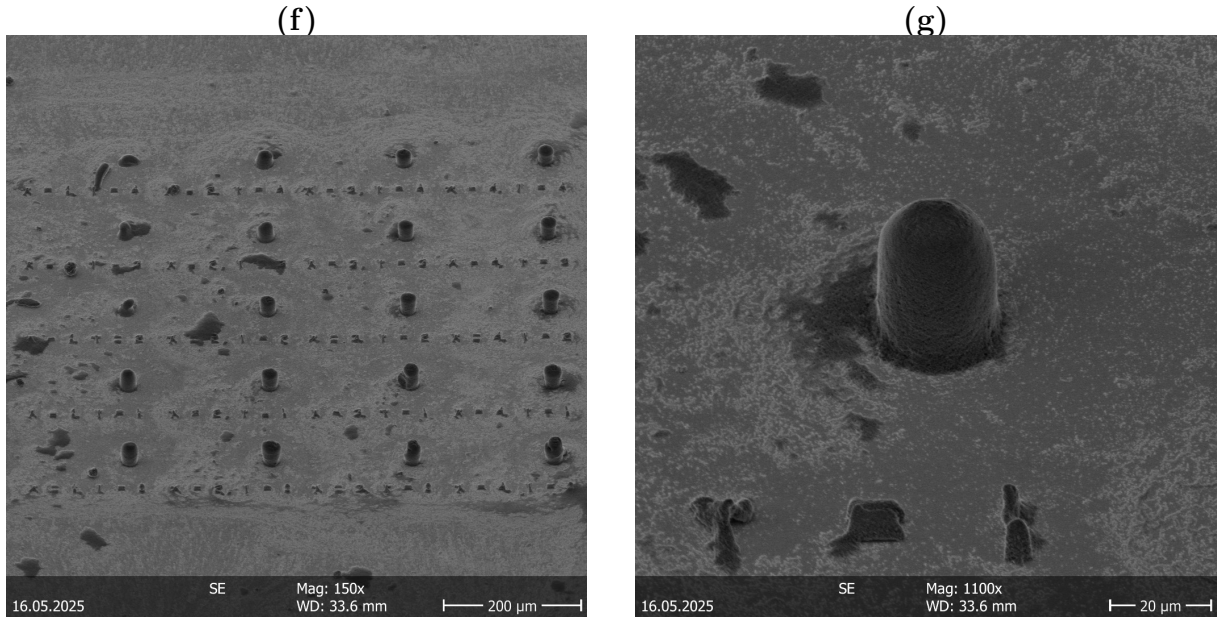


Figure 3.15: $15 \times 30 \mu\text{m}$ pillars printed at $\text{HD} = 0.2 \mu\text{m}$ and $\text{SD} = 2 \mu\text{m}$ while varying LP (30–70 mW) and SS (10–25 mm/s). (f) LP–SS matrix showing improved geometric fidelity at reduced height. (g) Close-up of a representative pillar with dimensions closer to the design target (height $\sim 35 \mu\text{m}$, diameter $\sim 23 \mu\text{m}$).

Step 1: voxel-overlap screening (HD–SD matrix). The first optimization step focused on overlap-driven effects by printing a parameter matrix in which hatching distance (HD) and slicing distance (SD) were varied from 0.2 to 1.0 μm , while laser power and scan speed were kept constant at a previously validated condition. The resulting array (Figure 3.16) exhibits a clear morphology maximum at low HD combined with intermediate SD. In particular, $\text{HD} = 0.2 \mu\text{m}$ and $\text{SD} = 0.6 \mu\text{m}$ provided the most uniform cylinders and the most continuous sidewalls within the explored overlap range. This condition was fixed for the subsequent dose-refinement step.

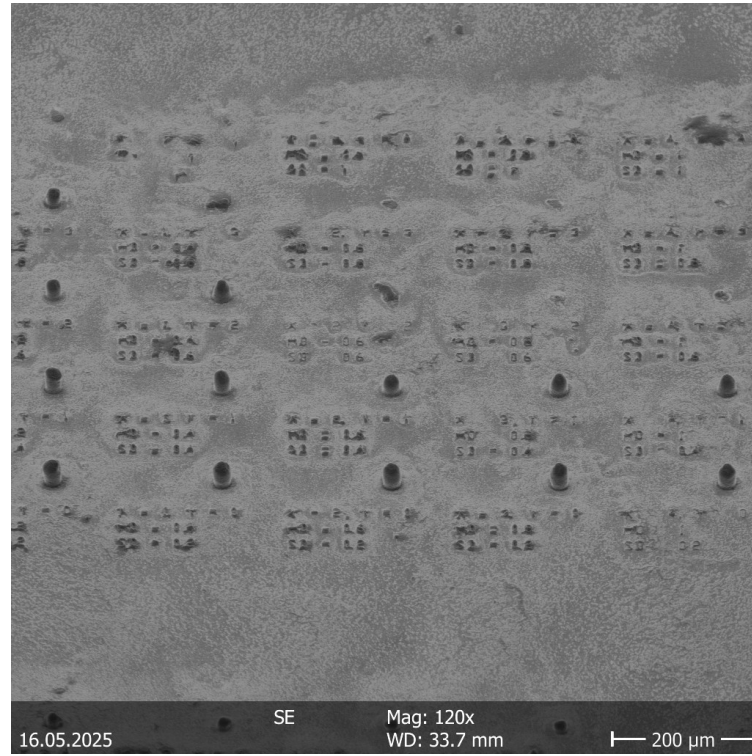


Figure 3.16: HD-SD screening matrix for $15 \times 30 \mu\text{m}$ pillars printed at fixed laser power and scan speed. Hatching distance (HD) and slicing distance (SD) were varied from 0.2 to $1.0 \mu\text{m}$. The most uniform morphology was obtained at $\text{HD} = 0.2 \mu\text{m}$ and $\text{SD} = 0.6 \mu\text{m}$.

Step 2: dose refinement and stability check (LP-SS matrices). After fixing $\text{HD} = 0.2 \mu\text{m}$ and $\text{SD} = 0.6 \mu\text{m}$, the process window was refined by printing multiple LP-SS matrices (Figure 3.17). Repeating the mapping was necessary because, at this scale, reproducibility becomes more challenging and the “best” region must be confirmed across separate matrices. Across the explored conditions, the most consistent pillars—near-cylindrical shape, sufficient polymerization, limited taper, and absence of obvious overexposure artifacts—were repeatedly observed around $\text{LP} \approx 70 \text{ mW}$ and $\text{SS} \approx 10 \text{ mm/s}$.

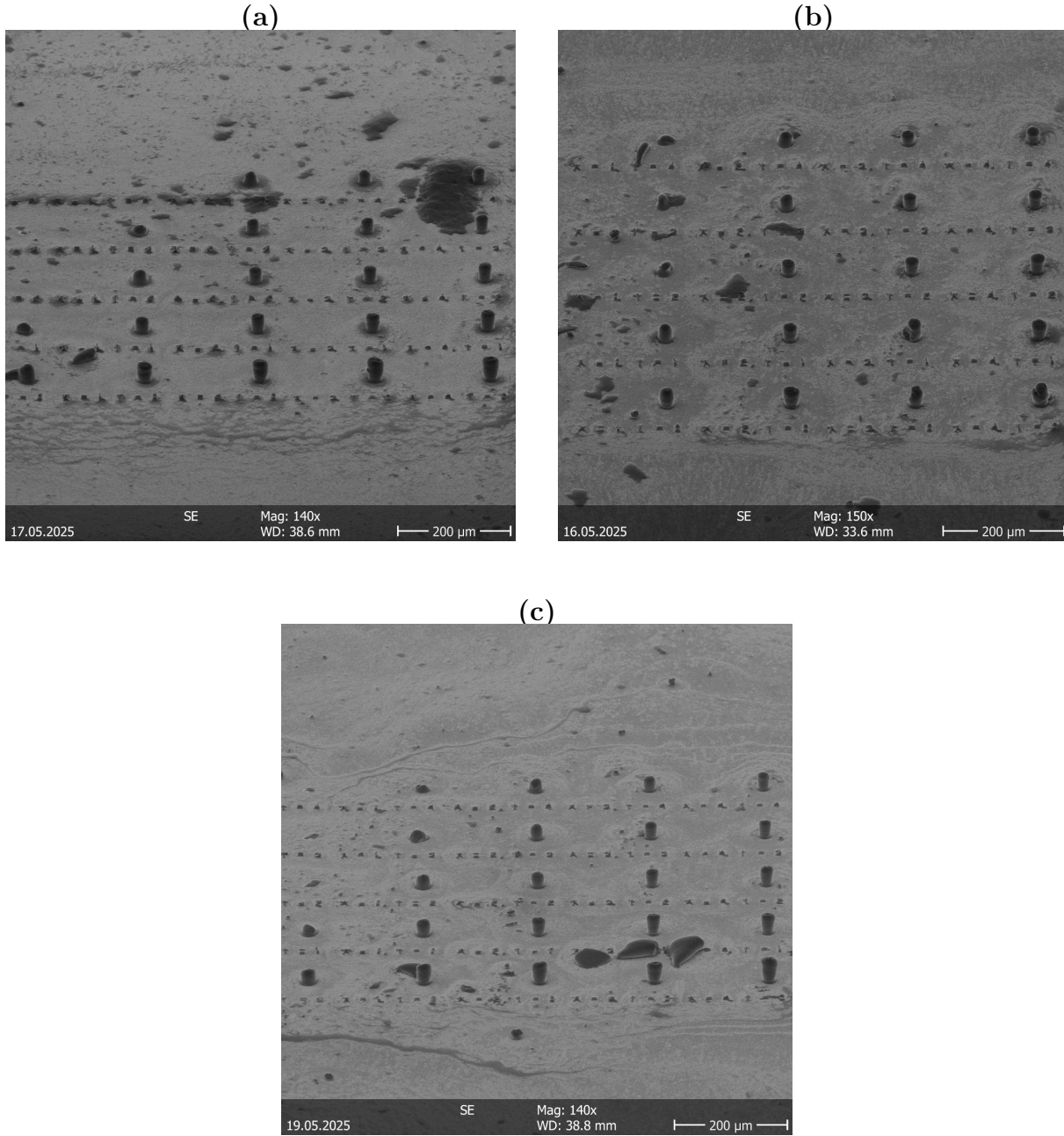


Figure 3.17: Repeated LP-SS matrices for 15x30 μm pillars printed at fixed HD = 0.2 μm and SD = 0.6 μm. Laser power was varied from 30 to 70 mW and scan speed from 5 to 25 mm/s. Across repetitions, the most stable morphology was consistently observed around LP ≈ 70 mW and SS ≈ 10 mm/s.

Step 3: intra-sample reproducibility (10x10 array). The optimized parameter set (LP ≈ 70 mW, SS ≈ 10 mm/s, HD = 0.2 μm, SD = 0.6 μm) was then used to fabricate a dense 10x10 array (100 pillars) on the same substrate (Figure 3.18). This configuration probes intra-sample reproducibility and isolates residual pillar-to-pillar

scatter that persists even when process parameters are held constant.

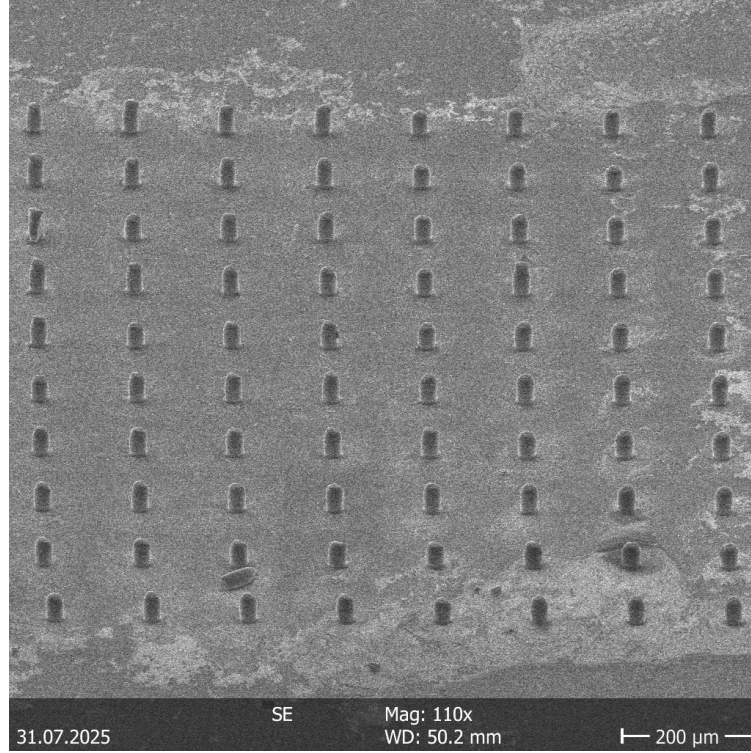


Figure 3.18: 10×10 array (100 pillars) printed with identical nominal geometry (15×30 μm) using the optimized parameter set (LP $\approx$ 70 mW, SS $\approx$ 10 mm/s, HD = 0.2 μm , SD = 0.6 μm). The array was used to assess intra-sample reproducibility under fixed conditions.

Residual geometric variability and implications for mechanical testing. Even within the 10×10 array, measurable differences in pillar geometry remained. Four representative pillars were selected to quantify residual variability in effective height, mean diameter, and top diameter (Figure 3.19), and the measured values are summarized in Table 3.1.

Table 3.1: Measured geometry of representative pillars selected from the 10×10 array (Figure 3.19). Reported values are the effective height H , mean diameter D_{mean} , and top diameter D_{top} , extracted from SEM images.

Pillar	H (μm)	D_{mean} (μm)	D_{top} (μm)
(d)	40.4	27.2	16.5
(e)	34.4	28.5	21.4
(f)	42.3	27.4	20.1
(g)	33.5	26.1	17.6

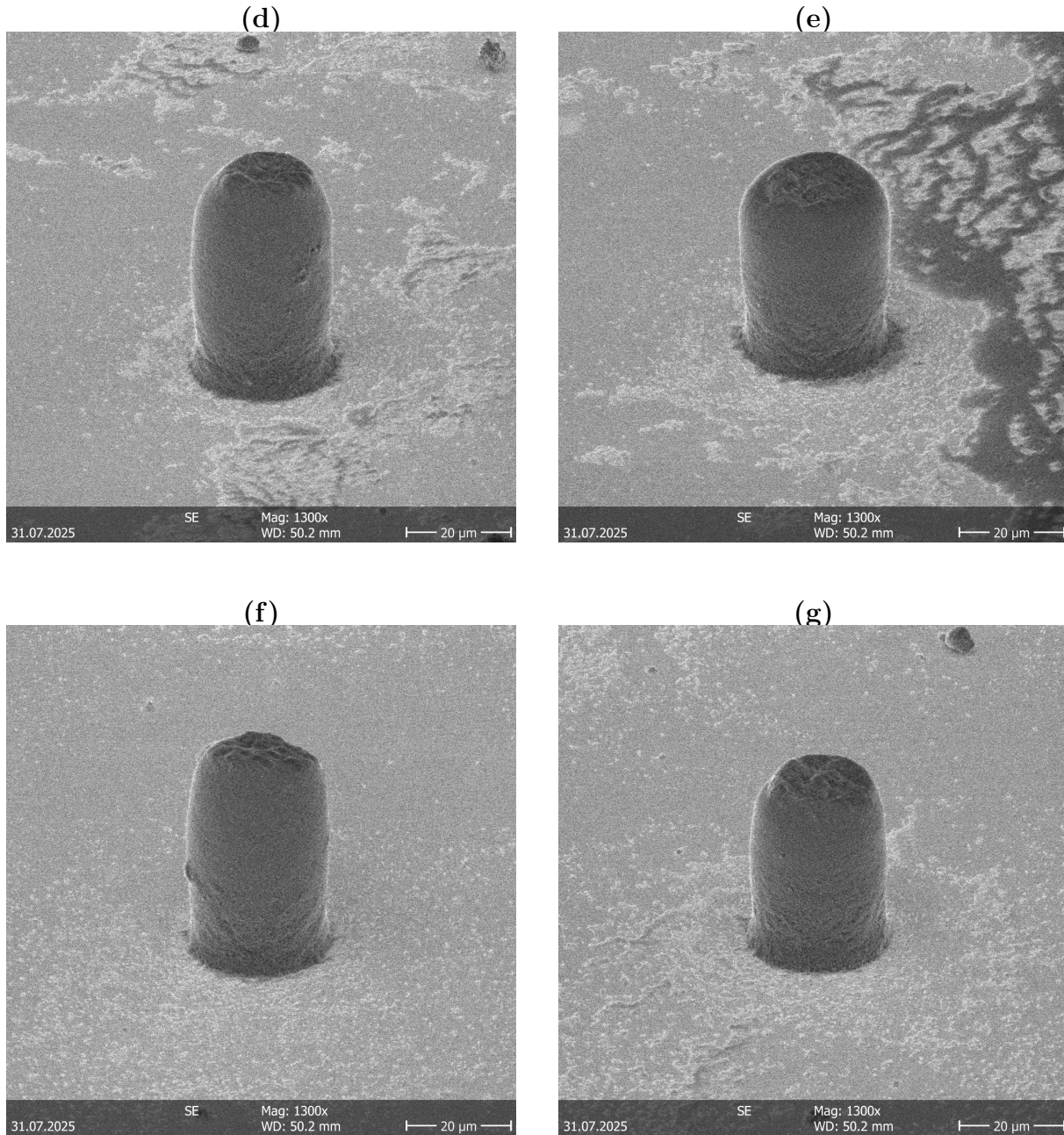


Figure 3.19: Representative pillars selected from the 10×10 array to highlight residual geometric variability under fixed optimized parameters. Differences in effective diameter, height, taper, and top morphology are visible even for nominally identical prints, and these deviations are expected to contribute to scatter in microscale mechanical response.

These measurements confirm that, under nominally identical printing conditions, residual scatter is non-negligible and is dominated by variations in height and taper rather than by mean diameter. The height spans from 33.5 to 42.3 μm , while D_{mean} varies more weakly between 26.1 and 28.5 μm . In contrast, the top diameter D_{top} shows the largest

relative dispersion, indicating that dominant variability manifests as differences in taper and top-shape definition rather than as uniform lateral scaling.

From a mechanical perspective, this variability is strategically important: (i) the effective aspect ratio H/D_{mean} varies substantially across pillars, affecting the propensity for barreling, splitting initiation, and post-peak instability; and (ii) variations in D_{top} imply that local contact and stress concentration conditions near the top region are not constant across specimens. Therefore, mechanical scatter should be interpreted as the coupled outcome of intrinsic fused-silica behavior and fabrication-limited geometric repeatability at the 15 μm scale.

Take-home message. At the 15 μm scale, fabrication becomes reproducibility-limited rather than failure-limited. Even under optimized parameters, height fluctuations and top-diameter dispersion impose a lower bound on the achievable scatter of stress-strain curves and on the repeatability of the observed failure mode.

3.3. Influence of Environmental Conditions: Time and Relative Humidity

When printing GP-Silica close to the lower feature-size limit ($15 \times 30 \mu\text{m}$), additional sources of variability emerged that could not be explained by printing parameters alone. In this regime, the effective process window becomes sufficiently narrow that modest changes in boundary conditions translate into visible morphology drift. Two factors were found to be particularly relevant: (i) elapsed time within a session and (ii) cleanroom relative humidity (RH).

Key message (environmental boundary conditions). At $15 \times 30 \mu\text{m}$, process robustness is not controlled only by LP/SS/HD/SD. Even with unchanged parameters, (i) time drift within a session and (ii) high RH reduce stability, increasing taper, top roughness, and parasitic polymerized artifacts.

Figure 3.20: Summary of why time and RH must be treated as first-order boundary conditions when printing GP-Silica near the lower-size limit.

3.3.1. Temporal Stability of the Printing Process

Observation. For 15×30 μm pillars, print quality progressively deteriorated with elapsed time within the same printing session, despite unchanged printing parameters. The degradation manifested as increased scatter in height, rougher and less planar top surfaces, loss of cylindricity (taper/shape distortion), and a higher fraction of defective pillars within the same array. Importantly, the change was not a simple “shift” of the process window (e.g., all pillars becoming uniformly smaller or larger), but rather an increase in variability: some pillars remained acceptable while others showed clear defects, indicating that the process became less repeatable as the session progressed.

Evidence (Figure 3.21). Figure 3.21 compares nominally identical pillars printed at the beginning of the session and after approximately 30 and 60 minutes. With increasing elapsed time, the top surface becomes progressively rougher, the pillar departs more strongly from the intended cylindrical shape, and parasitic polymerized features appear on the substrate. In parallel, the apparent taper becomes more pronounced and the sidewalls lose their uniformity, consistent with a drift of the effective exposure conditions toward less controlled polymerization.

A practical interpretation is that, at this feature size, the fabrication outcome is governed by small changes in the “effective dose” delivered to the resin rather than by the nominal LP/SS settings alone. Any time-dependent change that alters light transmission, scattering, or local resin response can therefore bias the exposure threshold and translate into macroscopic defects at the pillar scale. This observation motivated the adoption of short, reproducible print sessions for the final datasets and the logging of boundary conditions during parameter screening.

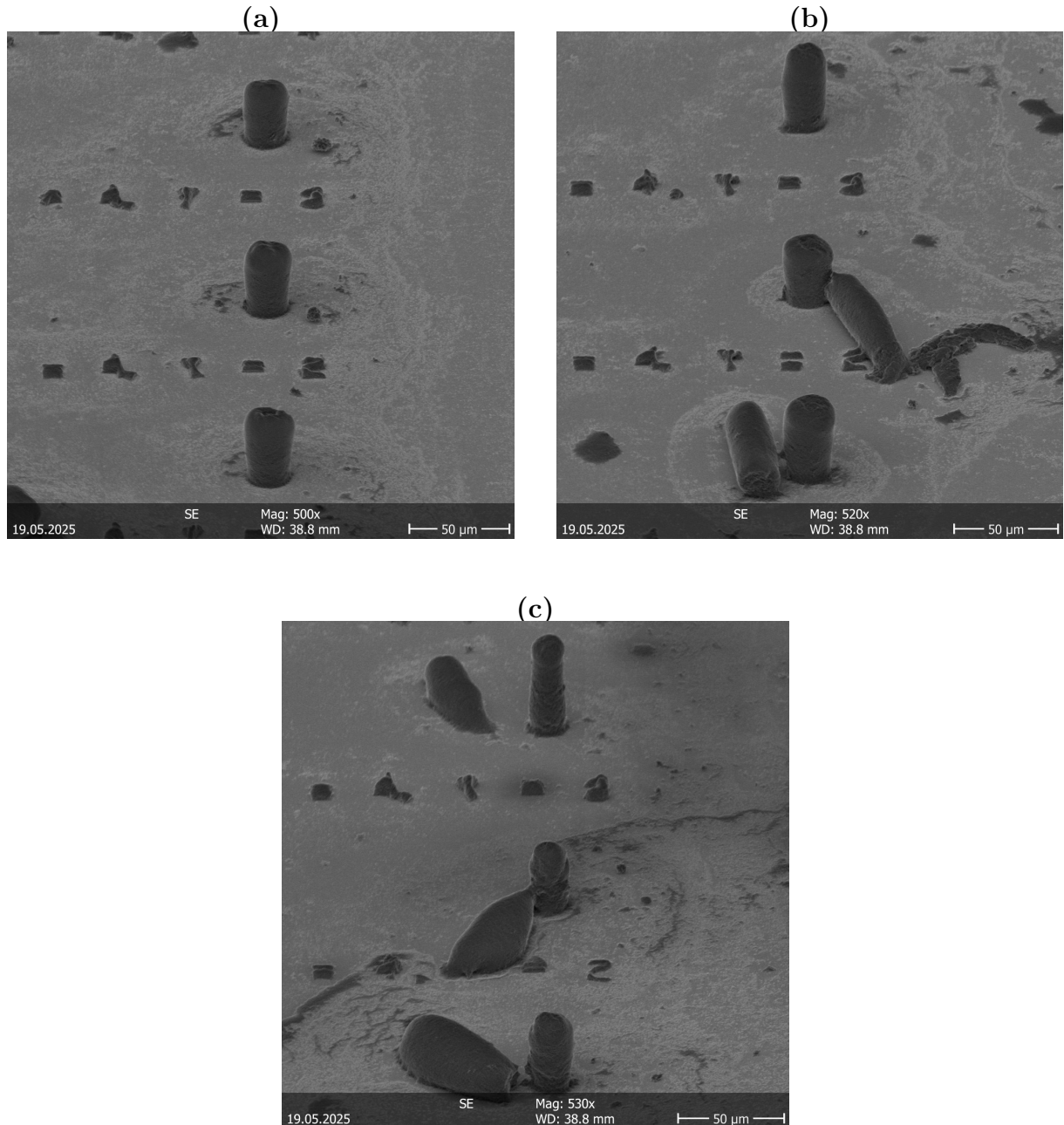


Figure 3.21: Time-dependent degradation of print quality for nominally identical 15×30 μm GP-Silica pillars printed with unchanged parameters at different times within the same session: (a) $t \approx 0$ min, (b) ≈ 30 min, and (c) ≈ 60 min. With time, top-surface roughness increases, cylindricity degrades (taper/shape distortion), and parasitic polymerized artifacts appear on the substrate.

Likely contributors (hypothesis-driven). The strong size dependence indicates that time-related effects become critical only when the stability margin is small. Several concurrent mechanisms may contribute:

- *Resin response evolution:* a gradual shift in effective polymerization threshold

during the session, so that constant nominal parameters correspond to a different effective dose over time.

- *Nanocomposite sensitivity*: small changes in rheology or dispersion state affecting local exposure conditions and radical transport in nanoparticle-filled systems.
- *Proximity-driven solidification*: increased sub-threshold polymerization around the intended voxel volume, consistent with the appearance of substrate artifacts at later times.
- *Kinetic sensitivity*: free-radical photopolymerization can be affected by oxygen availability (radical scavenging), which may amplify drift near the printability limit.

[34, 40]

Operational implication. Mechanically relevant small-feature prints were prioritized early in a session, and long uninterrupted runs were avoided to reduce morphology drift and parasitic polymerization.

3.3.2. Effect of Relative Humidity

Observation. Relative humidity correlated strongly with print quality for small GP-Silica pillars. Under otherwise fixed conditions (same geometry and parameters, elapsed time below 30 min), low-to-moderate RH produced pillars close to the intended cylindrical shape, whereas RH above $\sim 60\%$ substantially reduced robustness, leading to surface degradation and clear deviations from cylindricity. In this regime, the effect was not limited to a mild increase in scatter: high RH systematically increased the frequency of visibly defective pillars, suggesting that humidity acts as a first-order boundary condition near the process threshold.

Evidence (Figure 3.22). Representative pillars printed at RH = 22%, 33%, 55%, 65%, 74% and 92% show a monotonic loss of quality with RH. At 22–33% RH, surfaces are comparatively smooth and geometry remains stable. Around 55% RH, surface roughness increases but the overall morphology remains usable for subsequent thermal conversion and testing. Above 60% RH, geometric fidelity degrades markedly (irregular sidewalls, top-surface defects, enhanced taper/elongation), and at 92% RH reproducible fabrication becomes impractical for the present study. These trends motivated restricting the final printing campaign to a “safe” RH window to limit humidity-driven variability.

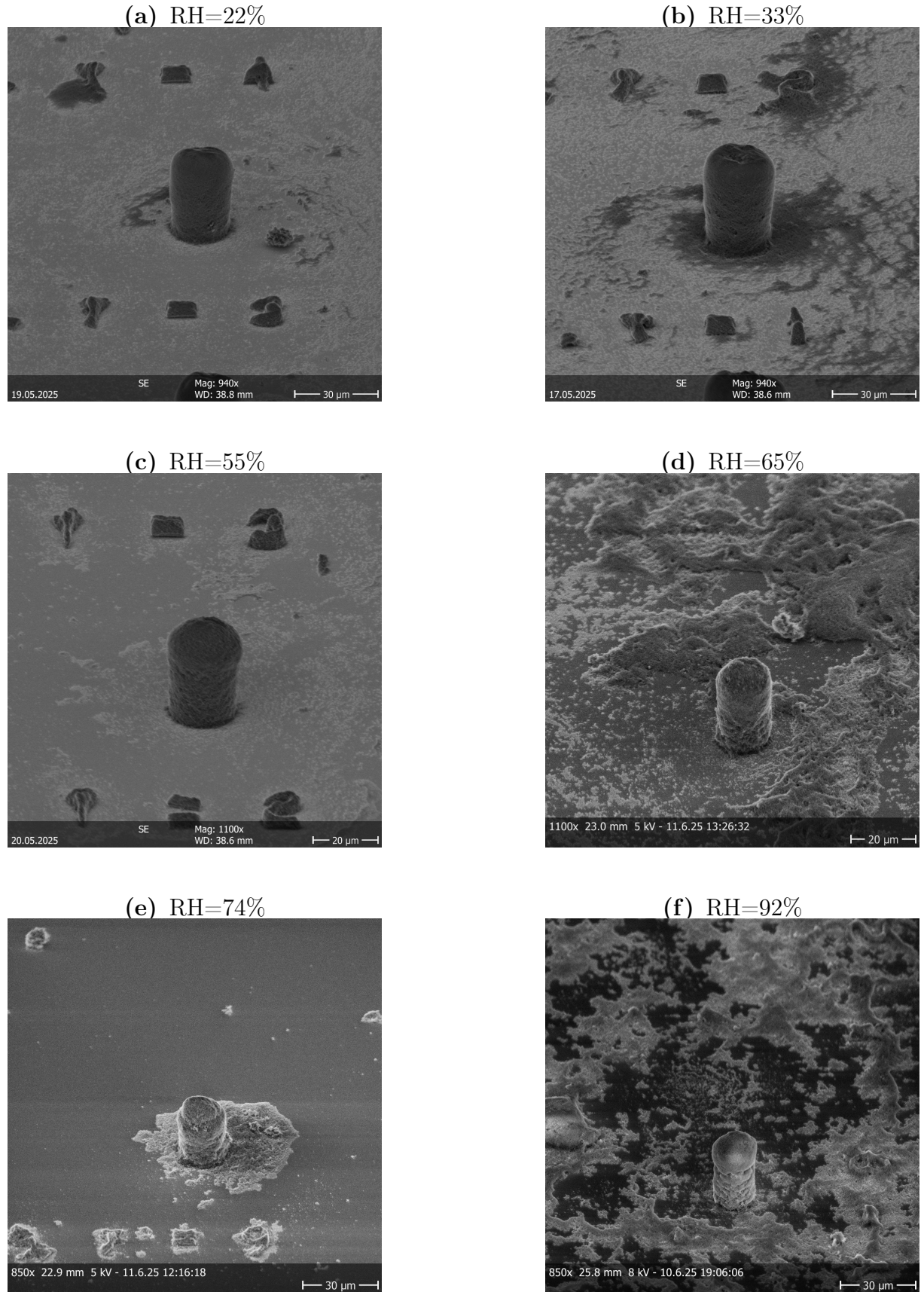


Figure 3.22: Effect of relative humidity on nominally identical GP-Silica pillars printed under short sessions (<30 min): (a) RH=22%, (b) RH=33%, (c) RH=55%, (d) RH=65%, (e) RH=74% and (f) RH=92%. Increasing RH primarily reduces robustness, leading to higher defect density and loss of geometric fidelity above ~60% RH.

Physic-chemical rationale (hypothesis-driven). High RH likely acts by reducing voxel confinement and/or altering curing kinetics in a way that becomes decisive only near the printability limit. Plausible contributors include moisture uptake affecting nanocomposite rheology/dispersion stability, changes in optical scattering and refractive-index mismatch, and indirect effects on oxygen transport and inhibition in free-radical polymerization. [25, 40]

Operational implication. A practical safe regime for $15 \times 30 \mu\text{m}$ pillars corresponded to approximately 22–55% RH, whereas RH >60% significantly compromised both surface quality and geometric reproducibility.

3.3.3. Interplay Between Environmental Conditions and Feature Size

Time and RH act as secondary variables at large feature size but become first-order boundary conditions at the $15 \mu\text{m}$ scale. The session drift (Figure 3.21) and the RH dependence under short runs (Figure 3.22) support the same practical message: as feature size decreases, the process window narrows and modest environmental variations translate into measurable morphology changes and increased defect probability.

3.3.4. Implications for Specimen Selection

To reduce geometry-driven scatter unrelated to intrinsic material behavior, only pillars fabricated (i) early in the printing session and (ii) under favorable humidity conditions were selected for thermal processing and mechanical testing. Although this filtering reduced throughput, it increased confidence that subsequent mechanical scatter reflects primarily material response and fabrication-limited geometric variability rather than uncontrolled environmental drift.

Factor	Observed signature	Decision rule for specimen selection
Elapsed time	Rougher top, taper/shape distortion, substrate artifacts	Prioritize small-feature printing early in the session; avoid long uninterrupted runs.
Relative humidity	Above $\sim 60\%$: geometry drift + higher defect density	Prefer 22–55% RH; avoid high-RH days for mechanically relevant arrays.

Table 3.2: Operational decision rules adopted to limit environmental-driven morphology drift and improve reproducibility of mechanically relevant pillars.

3.4. Thermal Post-Processing of GP-Silica Microstructures

Thermal post-processing determines the final density, geometry, and surface morphology of GP-Silica microstructures after printing. In this work, the thermal treatment was investigated by varying (i) the peak temperature and (ii) the holding time at the peak temperature, while keeping the remaining schedule parameters constant. This strategy separates temperature-activated densification (pore elimination) from time-dependent viscous shape relaxation once a dense glass network is formed.

3.4.1. Effect of Sintering Temperature

The influence of peak temperature was assessed through a qualitative screening aimed at identifying the minimum temperature required to obtain fully densified, mechanically robust fused silica pillars. Nominally identical pillars were processed at 1100 °C, 1200 °C, and 1300 °C under comparable heating-rate and holding conditions. Representative SEM images are reported in Figure 3.23.

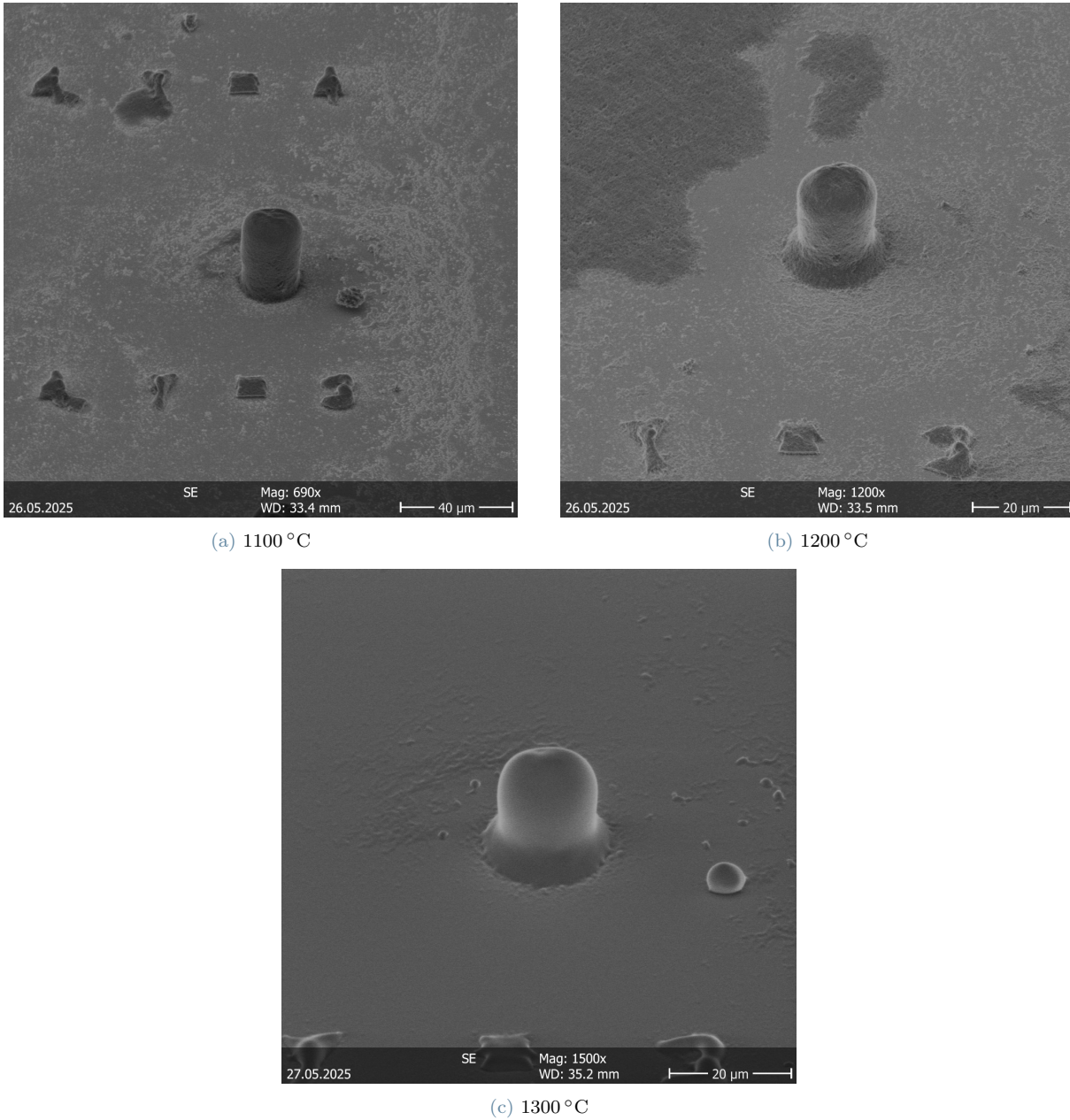


Figure 3.23: Representative SEM images of nominally identical GP-Silica micropillars after thermal treatment at different peak temperatures. The comparison highlights negligible densification at 1100 °C, partial shrinkage with persistent porosity at 1200 °C, and smooth, fully sintered pillars at 1300 °C. The images also illustrate substrate pinning: the base region remains close to the original diameter while the pillar body contracts at higher temperature.

Observed trend. A clear evolution was observed from a dark/opaque appearance at 1100 °C toward a brighter, smoother and more uniform morphology at 1300 °C, consistent with progressive densification and pore elimination. In parallel, the final geometry changed markedly due to shrinkage and temperature-dependent viscous flow.

1100 °C: negligible densification. At 1100 °C, the pillar remained visually close to the green state, with no detectable shrinkage. Dimensional measurements were consistent with this: the base and average diameters were essentially identical (21.26 μm), indicating a largely porous structure. The apparent height measured in tilted SEM view (55°) was $\sim 27 \mu\text{m}$, corresponding to a true height of $h \approx 33.0 \mu\text{m}$ after tilt correction ($h = h_{\text{app}} / \sin \theta$).

1200 °C: onset of shrinkage, incomplete densification. At 1200 °C, the first clear signs of shrinkage were observed. The base diameter remained close to the original value (21.31 μm to 21.67 μm), indicating strong pinning at the substrate, while the pillar body contracted substantially (average diameter $\sim 15.7 \mu\text{m}$). Although the structure appeared brighter and locally smoother than at 1100 °C, it remained visibly less homogeneous, consistent with incomplete densification. The apparent height was $\sim 21 \mu\text{m}$, corresponding to $h \approx 25.6 \mu\text{m}$ after correction.

1300 °C: fully sintered, mechanically relevant morphology. At 1300 °C, pillars displayed the characteristic features of full sintering: smooth surface, sharp contours, and uniform appearance consistent with effective pore elimination. The base diameter remained approximately unchanged (21.31 μm), while the pillar body showed substantial shrinkage (average diameter $\sim 16.5 \mu\text{m}$). The apparent height was $\sim 19 \mu\text{m}$, corresponding to $h \approx 23.2 \mu\text{m}$. The slightly larger average diameter compared to the 1200 °C condition is attributed to stronger viscous shape relaxation at higher temperature (shorter, more relaxed geometry), rather than to reduced densification.

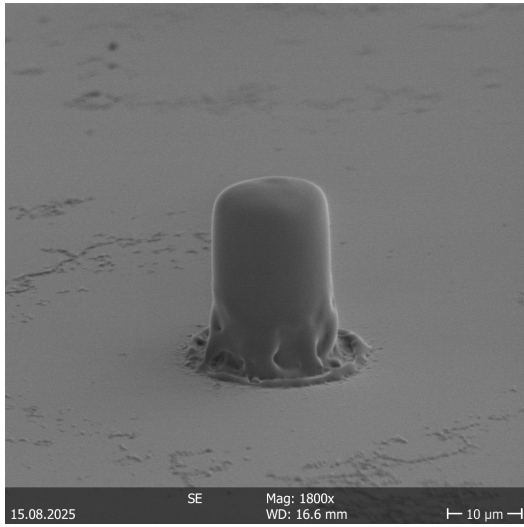
Take-home message. This screening indicates that, within the investigated thermal budget, peak temperatures below 1300 °C do not yield fully densified and mechanically robust GP-Silica microstructures. For this reason, all specimens selected for mechanical testing were processed at 1300 °C to avoid peak temperature as a confounding variable.

3.4.2. Effect of Holding Time at 1300 °C

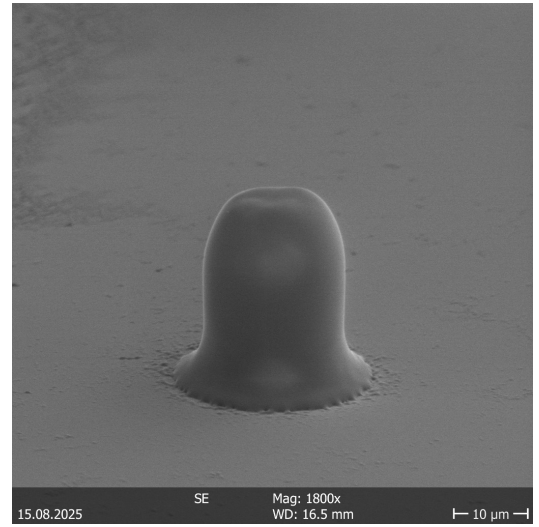
After identifying 1300 °C as the minimum peak temperature enabling full densification (Section 3.4.1), the influence of holding time was investigated by varying the isothermal dwell at constant peak temperature. Six substrates were processed at 1300 °C with dwell times of 40, 53, 72, 120, 160, and 215 minutes (i.e., 2400 s, 3180 s, 4320 s, 7200 s, 9600 s, and 12 900 s). The goal was not further densification, but to quantify time-dependent geometric relaxation once a dense glass state is reached.

Observed trend (geometry relaxation). Across the series, the mid-height diameter increased from approximately 18 μm to 19 μm at short dwells to 22 μm to 23 μm at long dwells, while the height decreased from roughly 28 μm to 30 μm to 22 μm to 24 μm . The 40–72 min conditions remained closely clustered, whereas a distinct transition emerged for dwell times ≥ 120 min, where pillars progressively lost their near-cylindrical character and developed top curvature and base-region bulging.

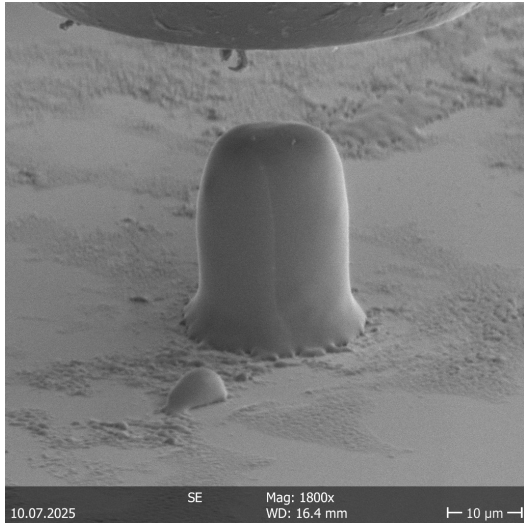
Representative SEM examples for all six dwell times are reported in Figure 3.24.



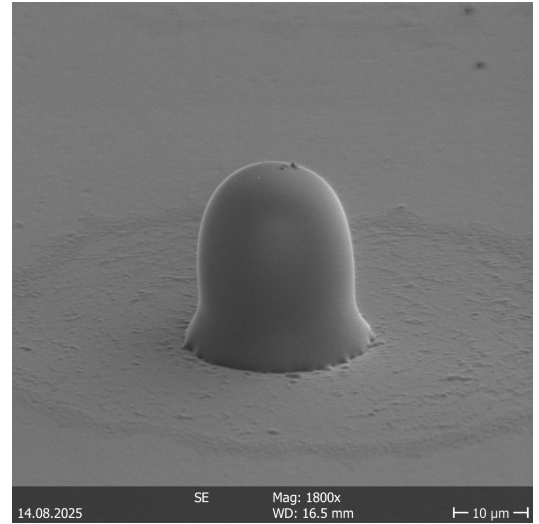
(a) Holding time: 40 min (2400 s).



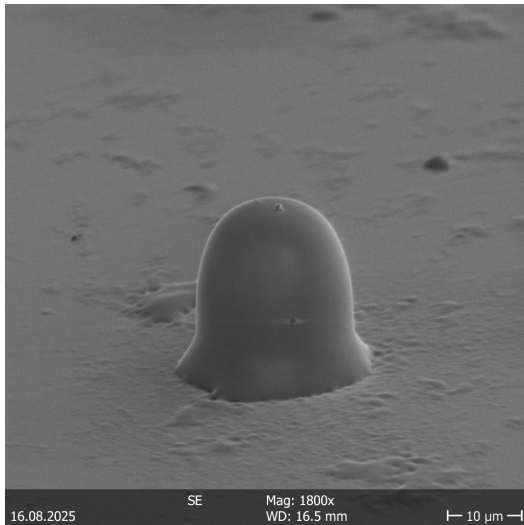
(b) Holding time: 53 min (3180 s).



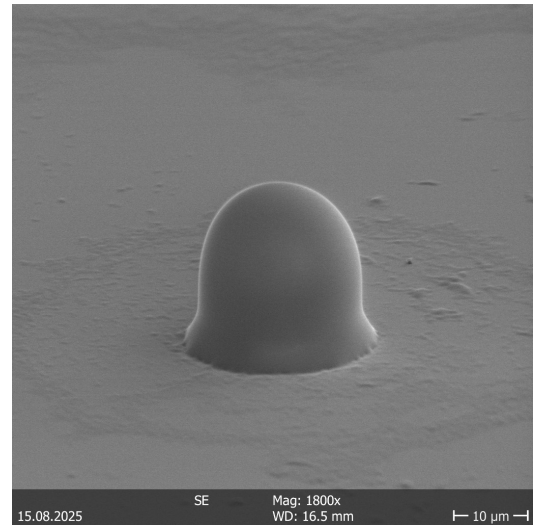
(c) Holding time: 72 min (4320 s).



(d) Holding time: 120 min (7200 s).



(e) Holding time: 160 min (9600 s).



(f) Holding time: 215 min (12 900 s).

Figure 3.24: Geometric relaxation increases with holding time at 1300 °C: pillars remain near-cylindrical for 40–72 min, but become rounded with top curvature and base bulging for 120–215 min.

Mechanistic interpretation. This behavior is consistent with the viscous nature of fused silica at 1300 °C. Once densification is complete, further shrinkage is limited, but surface-energy-driven viscous flow can continue, smoothing sharp features and promoting shape relaxation. Substrate pinning biases this relaxation, favouring anisotropic flow and base bulging rather than self-similar shrinkage. [13]

Take-home message. At fixed peak temperature, holding time acts primarily as a geometry-shaping parameter. Dwell times above ~120 minutes progressively reduce dimensional fidelity and boundary-condition definition, which is detrimental for quantitative microscale mechanics.

3.4.3. Implications for Geometry and Mechanical Response

The time series at 1300 °C highlights a practical constraint for microscale testing: even if the material state is nominally constant, the effective test geometry can drift substantially with dwell time. Rounding of the pillar top, changes in taper, and base bulging alter flat-punch contact conditions and local stress concentrations, potentially shifting apparent strength and the fracture initiation site in both microcompression and pillar splitting.

For the mechanical study, the 72-minute condition (4320 s) was selected as the reference because it provides a robust compromise between full conversion and geometric fidelity. Additional mechanical tests were also performed at other dwell times; however, long-dwell geometries depart from the near-cylindrical idealization and introduce larger uncertainty in defining representative dimensions for stress-based metrics and toughness-related quantities. For this reason, dwell-time comparisons are treated separately after establishing the baseline response for the reference condition.

Reference-state definition and decision summary

To support readability, Table 3.3 summarizes the key process decisions that define the reference mechanical state used in the following section. The table consolidates geometry, printing parameters, environmental constraints, and thermal schedule into a single overview.

Step	Selected condition	Rationale / outcome
Target geometry	15×30 μm pillars	Compatible with 2 N load cell; reduced height-dependent overgrowth; enables microcompression and splitting.
Voxel overlap	HD = 0.2 μm , SD = 0.6 μm	Best morphology in HD–SD screening; continuous sidewalls and stable cylinder definition.
Dose window	LP $\approx$ 70 mW, SS $\approx$ 10 mm/s	Most stable region across repeated LP–SS matrices at 15×30 scale.
Environment window	RH $\approx$ 22–55%, early-session printing	Minimizes time drift and high-RH artefacts; improves geometric reproducibility.
Sintering temperature	1300 $^{\circ}\text{C}$	Only condition showing fully densified/smooth morphology in screening.
Holding time (reference)	72 min (4320 s)	Compromise: dense glass + minimal geometric relaxation vs long dwells.

Table 3.3: Summary of key process decisions and the rationale used to define the reference mechanical state.

3.5. Mechanical characterization of fused silica micropillars

This section reports the mechanical characterization of fused silica micropillars fabricated by Two-Photon Polymerization (2PP) in GP-Silica and thermally converted at 1300 $^{\circ}\text{C}$ with a holding time of 72 minutes (4320 s). This condition was selected as the reference state based on the time-dependent geometry study in Section 3.4.2. Microcompression and pillar-splitting experiments were performed on pillars printed on the *same substrate* and subjected to the *same thermal history*, enabling a consistent interpretation of scatter by minimizing batch-to-batch variations in shrinkage, surface condition, and conversion state.

Matched populations and data-reduction pipeline

Mechanical results were treated as population datasets, with $n = 14$ pillars for microcompression and $n = 12$ pillars for pillar splitting. For microcompression, raw load–displacement signals were converted into engineering stress–strain curves using the measured post-sintering top diameter D_{top} and corrected pillar height H (Section 2.7.12). Before comparing specimens, the loading branches were cleaned (removal of negative/invalid points, sorting, and retention of the monotonic loading segment). A consistent strain origin was defined to mitigate initial “toe” effects (non-zero displacement with near-zero stress), which can arise from incomplete contact at the punch–pillar interface, small misalignment, and test-frame compliance. This alignment is essential to prevent systematic underestimation of the initial slope and to enable meaningful ensemble statistics.

Each microcompression curve was reduced to scalar metrics: (i) an apparent stiffness descriptor based on the incremental slope analysis ($E_k = d\sigma/d\varepsilon$) and its maximum E_{max} (Section 2.7.13), (ii) a yield stress σ_y (and ε_y) from a 0.2% offset construction (Section 2.7.14), and (iii) the peak engineering stress σ_{max} and its corresponding failure strain ε_f (defined here as the strain at σ_{max}). Population statistics are summarized through mean, standard deviation, and coefficient of variation ($\text{CV} = \sigma/\mu$).

For pillar splitting, the primary output is the critical load associated with the splitting event, extracted from the load–displacement curve as the maximum load preceding the main irreversible load drop, and used to compute an effective fracture toughness K_c through a pillar-splitting relation with a gauge factor γ (Sections 2.7.15–2.7.17). Because γ is estimated using microcompression-informed inputs, it is treated explicitly as a bridge parameter that links the splitting analysis to the same reference mechanical state.

For clarity, Table 3.4 summarizes the mechanical quantities extracted from microcompression and pillar splitting, together with the definitions adopted in this work.

Test	Primary outputs	Definition used in this work
Microcompression	$E_{\max}, \sigma_y, \varepsilon_y, \sigma_{\max}, \varepsilon_f$	$E_{\max}$ from piecewise incremental slope $E_k = d\sigma/d\varepsilon$; σ_y and ε_y from 0.2% offset; $\sigma_{\max}$ peak engineering stress; ε_f strain at $\sigma_{\max}$.
Pillar splitting	$P_{\max}, \gamma, K_c$	$P_{\max}$ from main load-drop / displacement burst; γ from microcompression-informed calibration (set-average); $K_c = \gamma P_{\max}/R^{3/2}$ with R treated as an interval for taper.

Table 3.4: Overview of mechanical metrics extracted from microcompression and pillar splitting in the reference state (1300 °C/4320 s).

Microcompression: results

Specimen geometry, representativeness, and measurement sensitivity.

Figure 3.25 shows two representative micropillars from the tested array prior to loading, illustrating the typical post-sintering geometry (top surface condition, sidewall quality, and limited taper). These images support two practical points. First, they document that the dataset corresponds to mechanically testable pillars with comparable morphology, enabling interpretation of population statistics as a meaningful ensemble rather than a collection of outliers. Second, they motivate a key experimental constraint: engineering stress is computed using the top cross-sectional area A_{top} derived from the SEM-measured D_{top} , and uncertainties in diameter propagate strongly into stress via $\sigma \propto 1/D_{\text{top}}^2$. Diameter determination is therefore a first-order contributor to apparent scatter in $\sigma_{\max}$ and σ_y , and it is widely recognized as a dominant error source when top-edge rounding and taper complicate the definition of an effective cross-section. [35]

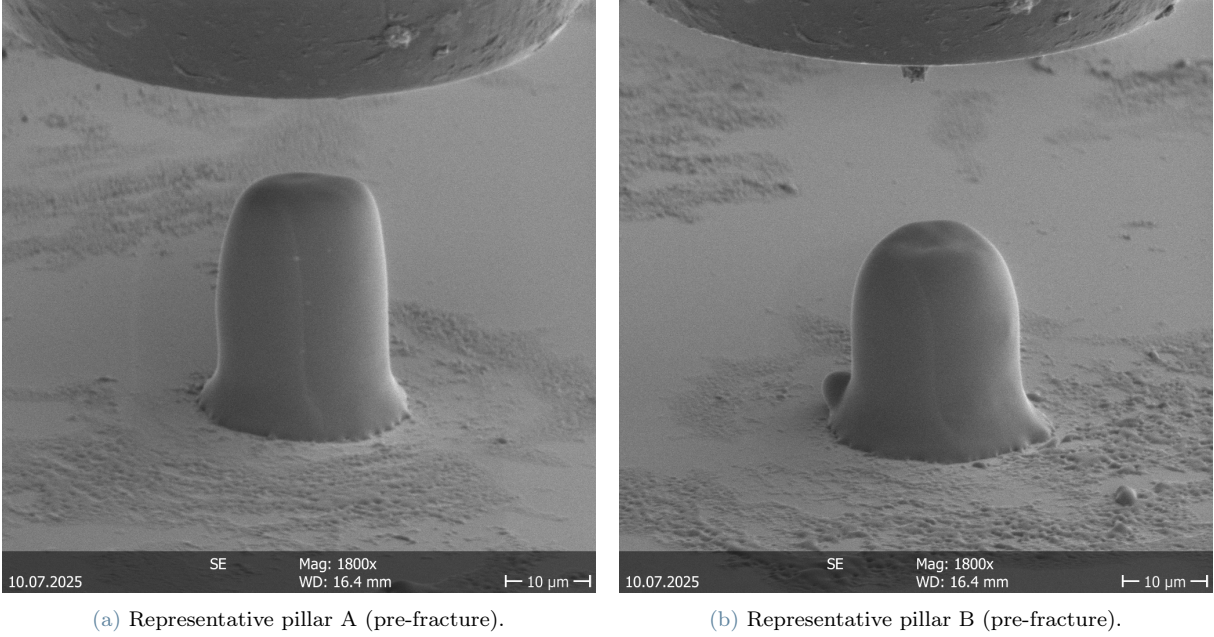


Figure 3.25: Representative fused silica micropillars (pre-fracture) selected from the microcompression array sintered at 1300 °C for 4320 s. The images illustrate the typical post-sintering geometry used for stress-strain reduction and contextualize specimen-to-specimen scatter (notably the sensitivity of engineering stress to top diameter and taper).

Full stress-strain set. Figure 3.26 reports the engineering stress-strain curves obtained from displacement-controlled microcompression of $n = 14$ fused silica micropillars sintered at 1300 °C for 4320 s. Force was converted to engineering stress using A_{top} , as defined in Section 2.7.12. The ensemble shows a consistent curve morphology: (i) a near-linear small-strain regime after alignment, (ii) a smooth transition into nonlinearity, and (iii) attainment of a peak stress in the multi-GPa range followed by a final loss of load-carrying capacity.

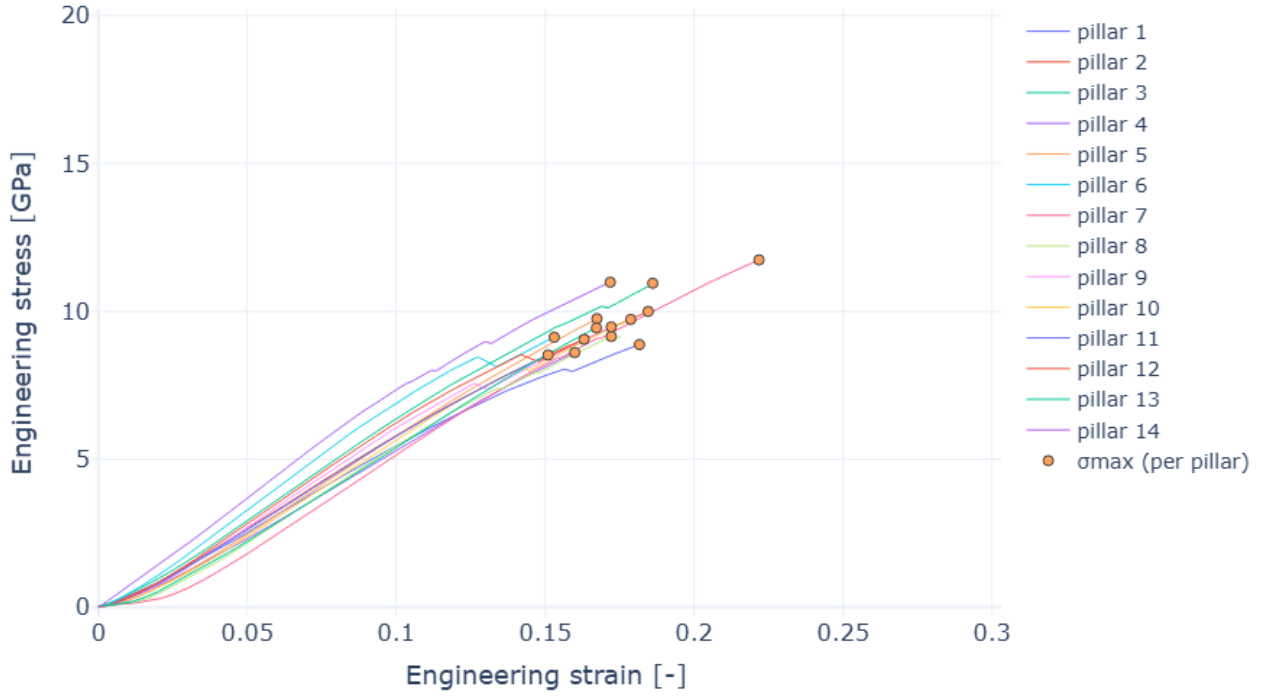


Figure 3.26: Engineering stress–strain curves obtained from displacement-controlled microcompression of fused silica micropillars sintered at 1300 °C for 4320 s ($n = 14$).

Peak stress and failure strain scatter. To compactly describe the dataset, two pillar-wise descriptors were extracted from each curve: the peak engineering stress $\sigma_{\max}$ and the strain at peak stress ε_f . Figure 3.27 shows $\sigma_{\max}$ per pillar, while Figure 3.28 reports ε_f per pillar. Across $n = 14$, $\sigma_{\max}$ spans 8.52–11.11 GPa with $\overline{\sigma_{\max}} = 9.63 \pm 0.86$ GPa ($\text{CV} \approx 8.9\%$), and ε_f spans 0.142–0.218 with $\overline{\varepsilon_f} = 0.1666 \pm 0.0187$ ($\text{CV} \approx 11.2\%$).

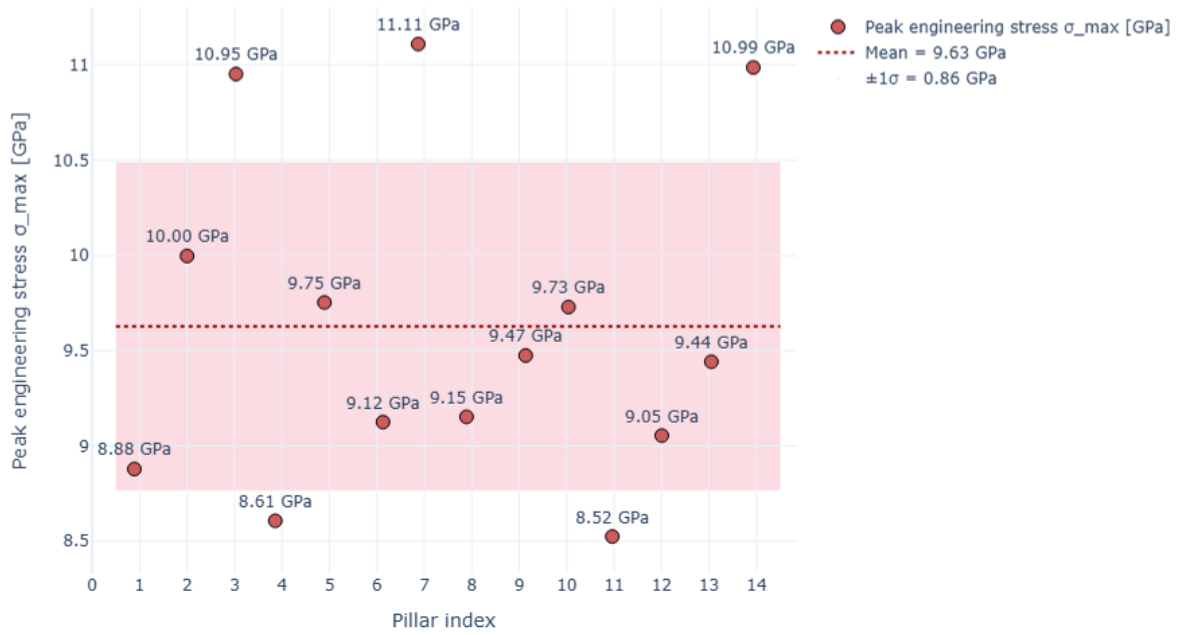


Figure 3.27: Peak engineering stress $\sigma_{\max}$ for each tested pillar ($n = 14$), including mean and $\pm 1\sigma$ band.

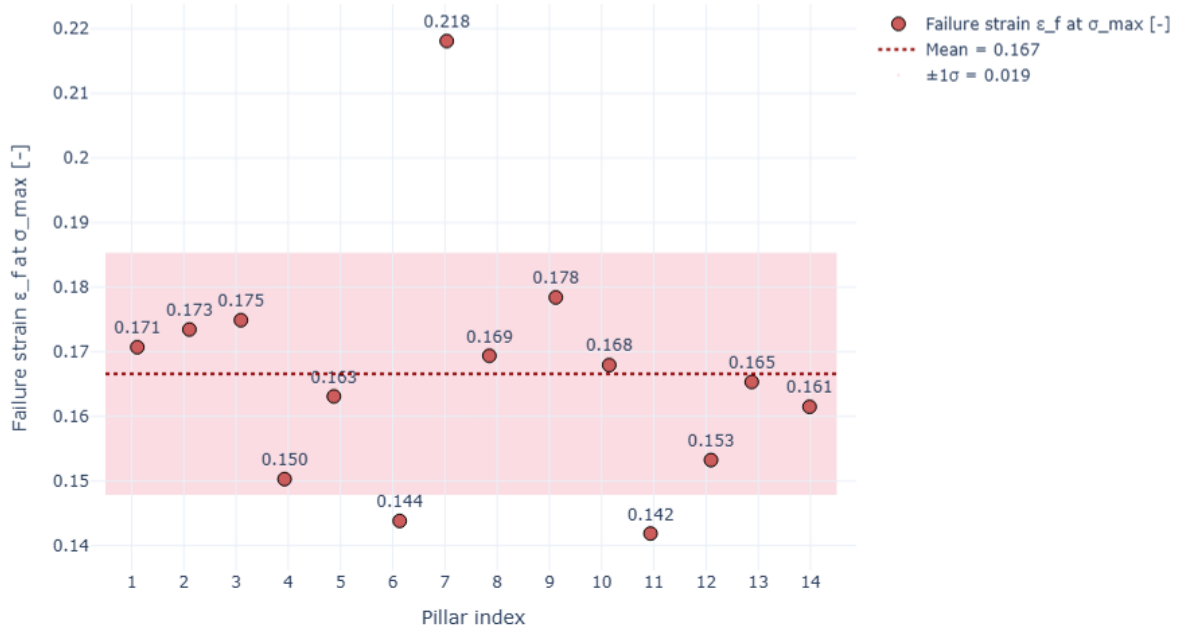


Figure 3.28: Failure strain ϵ_f (strain at $\sigma_{\max}$) for each tested pillar ($n = 14$), including mean and $\pm 1\sigma$ band.

Mean stress–strain response and dispersion. An ensemble mean stress–strain response was computed on a common strain grid and plotted together with a $\pm 1\sigma$ band (Figure 3.29) by averaging only the available values at each strain (Section 2.7.12). Dispersion is limited in the stiffness-dominated regime and increases toward $\sigma_{\max}$, consistent with defect-sensitive instability and with amplification of small differences in taper/contact conditions and diameter uncertainty as failure is approached.

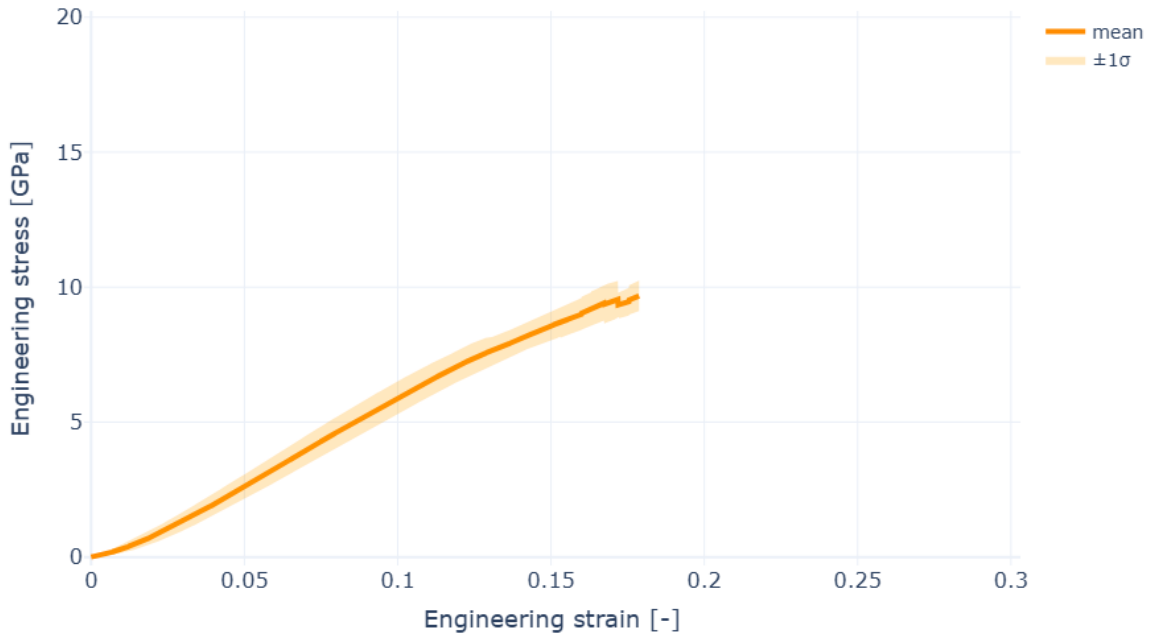


Figure 3.29: Ensemble mean engineering stress–strain response ($n = 14$) with $\pm 1\sigma$ band, computed by averaging available values on a common strain grid.

Incremental slope and stiffness benchmark. Stiffness was quantified through the piecewise incremental slope $E_k = d\sigma/d\varepsilon$ evaluated in consecutive strain windows (Section 2.7.13). Figure 3.30 reports the population-average E_k as a function of strain. A clear plateau is observed, with a maximum around ~ 72 GPa in the interval $\varepsilon \approx 0.05$ – 0.07 . This window is interpreted as the most reliable stiffness regime for the present dataset: at very low strain, toe/compliance artefacts can depress the slope, whereas at larger strain, progressive nonlinearity biases E_k downward from an elastic interpretation. The magnitude of the plateau is consistent with dense fused silica expectations, supporting effective densification at 1300 °C/4320 s. [14]

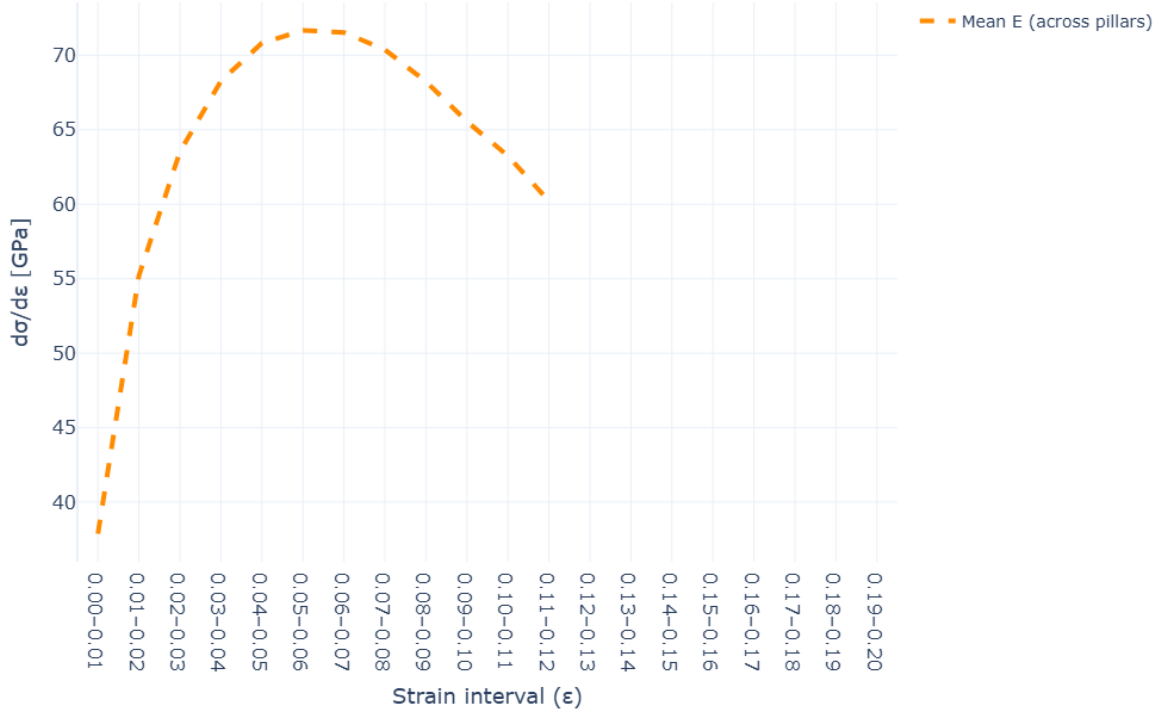


Figure 3.30: Population-average incremental slope $E_k = d\sigma/d\varepsilon$ as a function of strain, used to identify the most reliable stiffness regime and benchmark the effective stiffness of the ensemble.

Yield transition: scatter of σ_y and ε_y . Because the elastic-to-nonlinear transition is smooth in most curves, the yield stress σ_y was defined using the 0.2% offset construction (Section 2.7.14), i.e., the first intersection between $\sigma(\varepsilon)$ and a line parallel to the fitted elastic slope shifted by 0.2% strain. This approach is widely used for amorphous silica micropillars precisely because it provides an objective criterion in the absence of a sharp yield point. [14]

Figures 3.31 and 3.32 report the pillar-wise distributions of σ_y and ε_y . Across $n = 14$, σ_y spans 7.255–8.604 GPa with $\overline{\sigma_y} = 7.81 \pm 0.48$ GPa (CV $\approx 6.1\%$), while ε_y spans 0.099–0.134 with $\overline{\varepsilon_y} = 0.1195 \pm 0.0103$ (CV $\approx 8.6\%$).

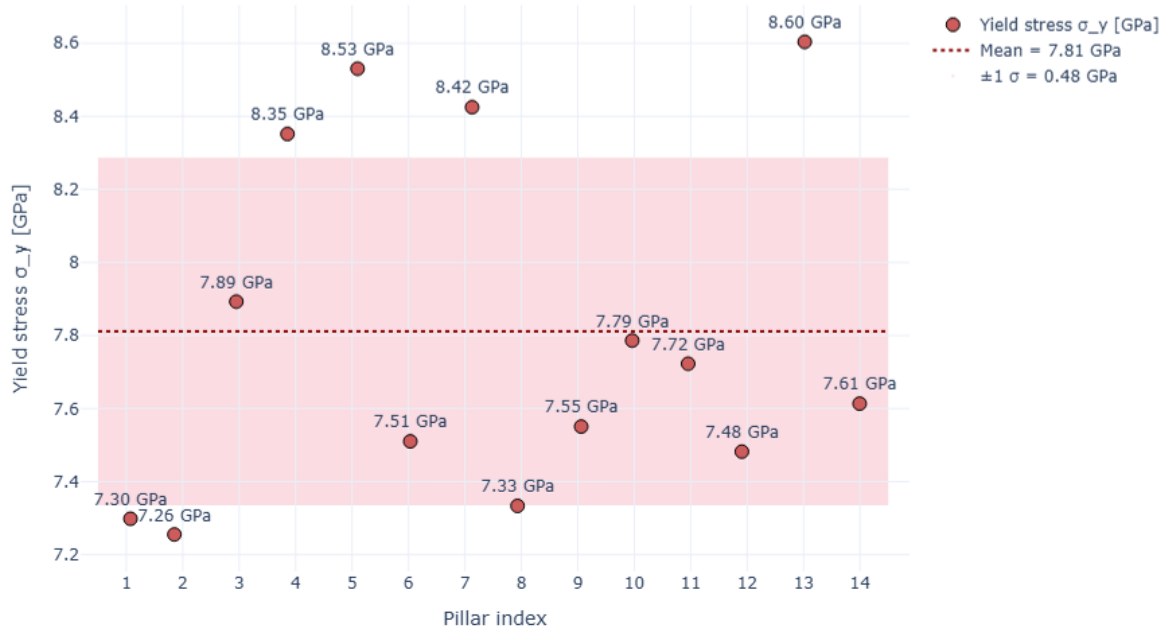


Figure 3.31: Yield stress σ_y for each tested pillar ($n = 14$), determined using the 0.2% offset method; mean value and $\pm 1\sigma$ band are shown.

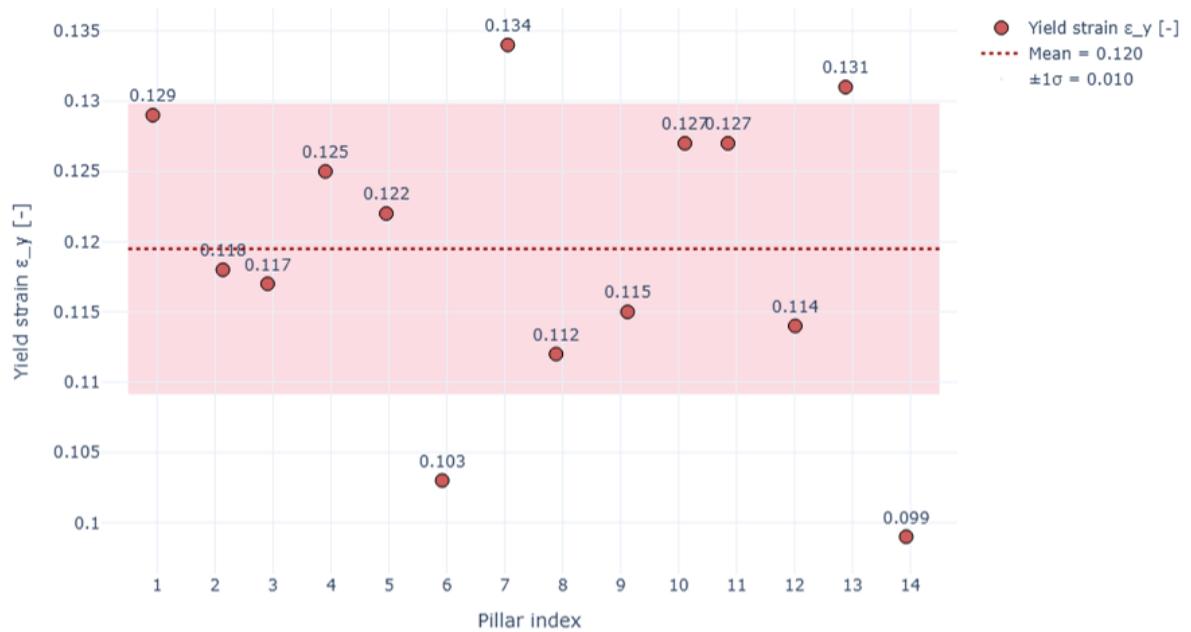


Figure 3.32: Yield strain ϵ_y corresponding to the 0.2% offset criterion for each tested pillar ($n = 14$), including mean and $\pm 1\sigma$ band.

Nonlinear interval descriptor. To quantify the extent of pre-failure nonlinearity after the 0.2% offset yield point, we define the post-yield nonlinear interval

$$\Delta\varepsilon = \varepsilon_f - \varepsilon_{0.2}, \quad (3.1)$$

where $\varepsilon_{0.2}$ is the yield strain from the 0.2% offset construction and ε_f is the strain at peak stress $\sigma_{\max}$. This descriptor is not intended as a “plastic strain” measure; it compactly captures how much nonlinear deformation develops before instability, combining confinement-driven glass deformation, damage accumulation, and contact/geometry effects. Using the population means reported above ($\overline{\varepsilon_{0.2}} = 0.1195$ and $\overline{\varepsilon_f} = 0.1666$), the corresponding mean interval is $\overline{\Delta\varepsilon} \approx 0.047$. Pillar-wise values span a finite range across the dataset, reflecting specimen-to-specimen variability in the development of pre-failure nonlinearity.

Microcompression: interpretation

The “toe” region and pre-failure drops: what is signal vs artefact. A subset of curves displays a short initial “toe” (very low apparent stress) up to $\varepsilon \approx 0.02$ – 0.03 . This behavior is commonly reported in micropillar compression and can originate from progressive seating and full-contact establishment, combined with compliance contributions in the load train. Since the toe region biases the apparent initial slope, the strain origin was aligned using the same objective procedure adopted for slope and yield extraction (Sections 2.7.13 and 2.7.14), ensuring that the stiffness regime used for property extraction is not systematically distorted.

Seven out of fourteen curves exhibit a small stress drop shortly before reaching $\sigma_{\max}$. In a brittle glass, such subtle drops are plausibly associated with precursor instabilities, including (i) local damage initiation followed by transient arrest (partial stress relaxation before final propagation), (ii) micro-slip events at the punch–pillar interface, and/or (iii) local microcracking near the pillar head under a highly confined stress state. Without in-situ imaging, these events are conservatively treated as pre-failure signatures rather than evidence of stable, homogeneous plastic flow.

Apparent large strains: size-enabled nonlinearity under confinement, not metallic ductility. The large compressive strains measured here should not be interpreted as metallic-like ductility. In micropillar compression, the apparent deformation capacity is shaped by confinement beneath the flat punch (friction-induced triaxiality that suppresses crack opening), geometry effects (taper and evolving contact area), and

progressive damage/microcracking rather than dislocation-mediated plastic flow. At the same time, the extended pre-failure deformation is also consistent with a genuine microscale shift in response: when the stressed volume is reduced, critical-flaw sampling is less likely and strength approaches near-intrinsic levels, enabling a broader nonlinear regime in compression. In amorphous silica this nonlinearity can reflect glass-specific mechanisms (e.g., shear-assisted rearrangements and/or localized densification under high confinement), while remaining fundamentally fracture-controlled. Yield is therefore reported using the standard 0.2% offset criterion to ensure comparability with the micropillar literature. [14, 35]

Scatter budget: intrinsic variability plus geometric uncertainty. The relatively modest scatter in σ_y and $\sigma_{\max}$ for a flaw-sensitive brittle material indicates that this thermal condition provides a reproducible mechanical reference state, while still retaining the expected stochasticity of microscale failure. The remaining dispersion should be interpreted as a superposition of (a) true specimen-to-specimen variability in local defect/stress concentration, and (b) geometric uncertainty (top diameter and taper definition), with the latter directly affecting stress through the $1/D_{\text{top}}^2$ dependence.

Literature bridge: where the present values sit and why. The measured yield and peak stresses fall within the range reported for fused silica micropillars tested in compression. In one study on pristine fused silica micropillars, yield strengths on the order of ~ 8 GPa and peak stresses approaching ~ 9 – 11 GPa were reported, together with bulk compressive strength values around ~ 1 GPa in supporting data, highlighting the order-of-magnitude increase commonly observed at the microscale. The same study discusses room-temperature inert–intrinsic strength values for fused silica on the order of ~ 10 – 12 GPa (with higher theoretical estimates), providing a reference range to interpret $\sigma_{\max}$ values near 9 – 11 GPa as approaching intrinsic limits when flaw populations are minimized. It also reports that improved surface condition (e.g., annealing) increases both yield and peak stresses, and identifies diameter determination as a key practical limitation for strength quantification when top-edge rounding becomes significant. [35]

In parallel, the 0.2% offset approach (often reported as $R_{p0.2}$) has been used to define yield in amorphous silica micropillar compression when the yield transition is smooth. This supports using the same criterion here and improves methodological comparability of σ_y across studies. [14]

Summary (reference mechanical state). Overall, the $1300\text{ }^\circ\text{C}/4320\text{ s}$ condition provides a mechanically consistent reference state for subsequent comparisons: $\overline{\sigma}_y =$

7.81 ± 0.48 GPa, $\overline{\sigma_{\max}} = 9.63 \pm 0.86$ GPa, $\overline{\varepsilon_y} = 0.1195 \pm 0.0103$, and $\overline{\varepsilon_f} = 0.1666 \pm 0.0187$. The combined reading of Figures 3.26–3.32 supports (i) good repeatability of the stiffness regime (plateau near ~ 72 GPa), (ii) a smooth and operationally quantifiable yield transition, and (iii) multi-GPa strength levels consistent with microscale, defect-suppressed fused silica, while emphasizing that the nonlinear interval prior to peak stress reflects confinement- and damage-assisted nonlinearity rather than classical ductile plastic flow.

Pillar splitting: results

Motivation and definition. Pillar splitting tests were performed on a population of $n = 12$ micropillars fabricated on the same substrate and subjected to the same 1300 °C/4320 s thermal cycle used for microcompression. This pairing is intentional: while microcompression probes the global compressive response (strength, nonlinearity, confinement-controlled signatures), pillar splitting enforces a crack-dominated instability under a stress concentrator, enabling a fracture-related metric within the same reference processing state.

Within the pillar-splitting framework, an effective fracture toughness is obtained from the critical load $P_{\max}$ through

$$K_c = \gamma \frac{P_{\max}}{R^{3/2}}, \quad (3.2)$$

where R is the pillar radius and γ is a geometry/material-dependent gauge factor (typically determined from cohesive-zone FE simulations and often parameterized vs. E/H). In fused silica, pillar splitting has been shown to be applicable also to anomalous glasses (densification-capable), yielding fracture toughness values consistent with literature benchmarks and commonly producing a three-fragment split morphology under ideal conditions. [32]

Load–displacement curves and critical-load scatter ($n = 12$). Figure 3.33 reports the load–displacement curves measured in the present work. Across specimens, the response typically shows: (i) an initially stiff loading segment, (ii) progressive compliance increase as damage accumulates beneath the indenter, and (iii) a splitting event marked by a sharp load drop and/or a displacement burst. The critical load $P_{\max}$ is defined as the maximum force preceding the main irreversible load drop (Section 2.7.16). The overall curve morphology is repeatable, while the critical load exhibits specimen-to-specimen variability, as expected from sensitivity to centering, local contact conditions, and near-surface defect populations.

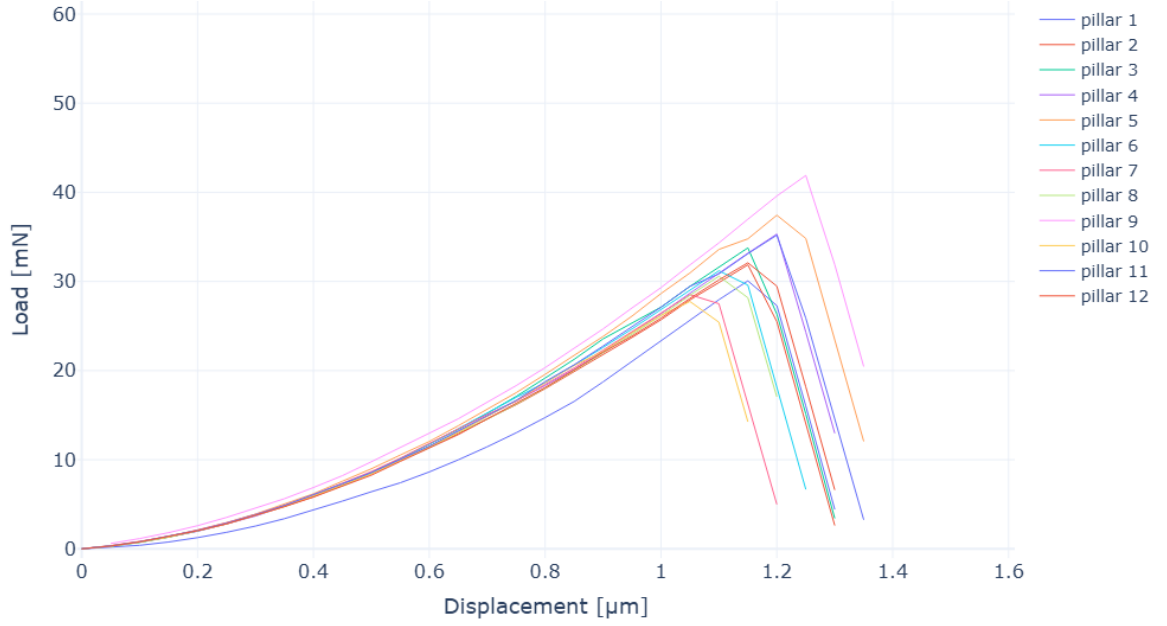


Figure 3.33: Load–displacement curves from pillar splitting experiments on fused silica micropillars fabricated on the same substrate and converted at 1300 °C for 4320 s ($n = 12$).

Figure 3.34 reports the pillar-wise scatter of $P_{\max}$ with mean and $\pm 1\sigma$ bands, while Figure 3.35 shows the ensemble mean load–displacement response (common displacement grid) with a $\pm 1\sigma$ band. Dispersion is small at low displacement (stiffness-dominated regime), and increases close to the splitting event, consistent with fracture initiation being governed by the local stress field and stochastic triggering.

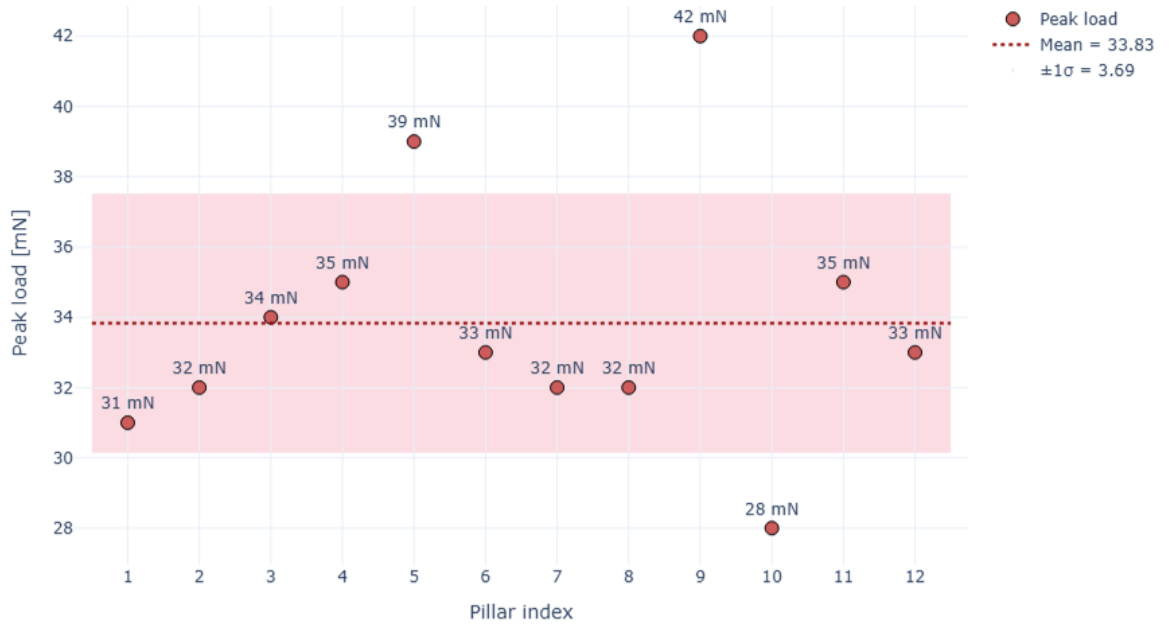


Figure 3.34: Critical load $P_{\max}$ extracted from each pillar splitting curve ($n = 12$). The dashed line indicates the population mean and the shaded region represents $\pm 1\sigma$.

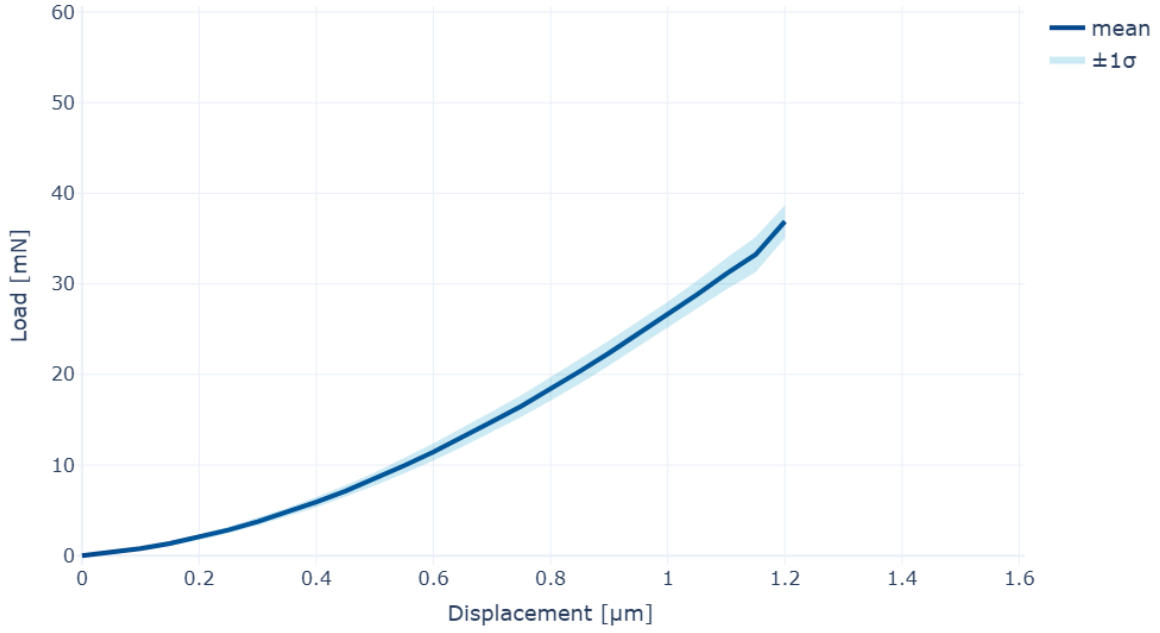
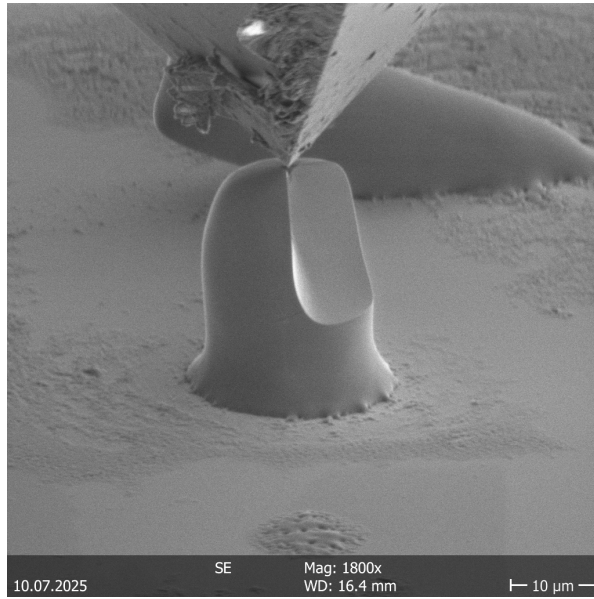
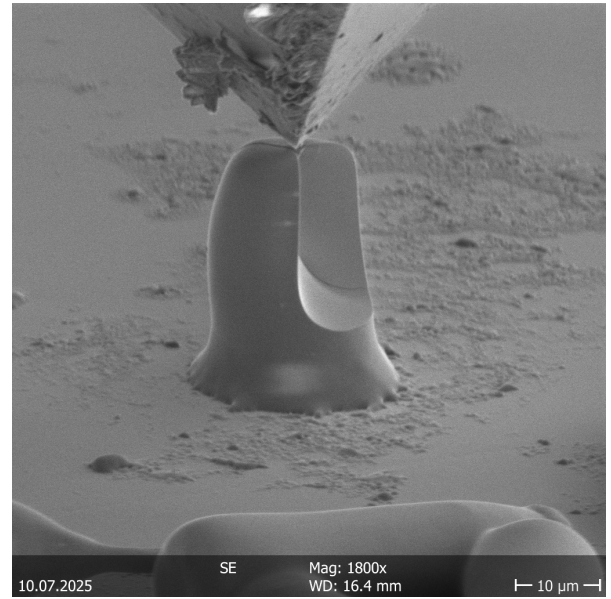


Figure 3.35: Ensemble mean load–displacement response for pillar splitting experiments ($n = 12$) computed on a common displacement grid, with $\pm 1\sigma$ band across the population. Scatter increases close to the splitting event, where cracking becomes dominant.

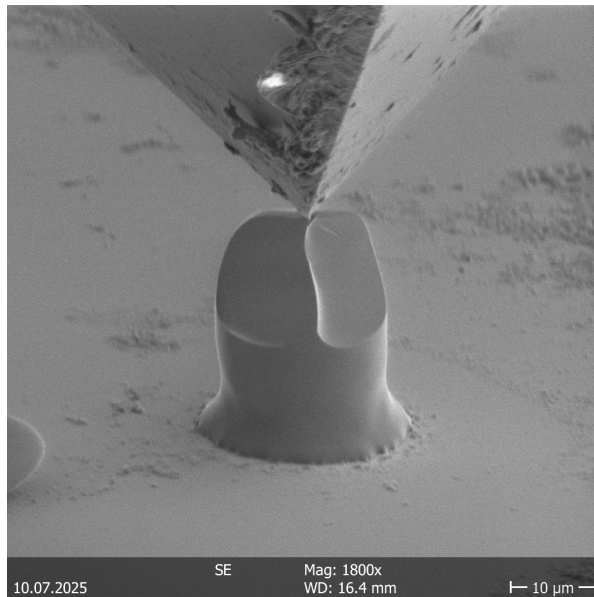
Failure morphologies: deviation from the ideal three-fragment split. A key observation is that post-mortem fracture morphologies deviate from the *idealized* three-fragment splitting pattern often reported for fused silica pillar splitting under well-centered loading, particularly for freestanding microfabricated pillars. [32] Instead, the present specimens exhibit a broader set of outcomes in which (a) only one fragment is fully detached, (b) one fragment is detached while a second branch crack is visible but remains partially attached, or (c,d) two fragments are detached but their detachment lengths vary substantially (Figure 3.36). Fracture surfaces frequently appear curved and splitting rarely propagates to the base; a remnant ligament close to the pillar/substrate junction typically remains intact.



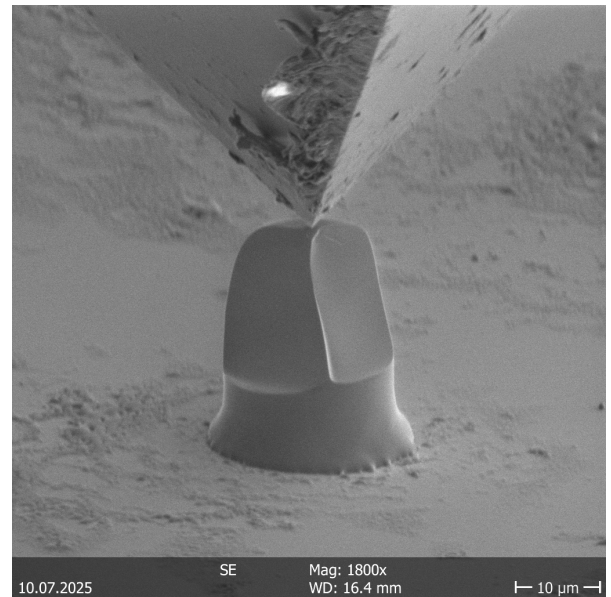
(a) Only one fragment fully detached.



(b) One fragment detached; second branch crack visible but partially attached.



(c) Two fragments detached (shorter detachment length).



(d) Two fragments detached (longer detachment length).

Figure 3.36: Representative post-mortem morphologies after pillar splitting. The observed outcomes deviate from the ideal three-fragment split often reported for fused silica pillar splitting: (a) only one fragment is fully detached, (b) one fragment is detached while a second branch crack is visible but remains partially attached, and (c–d) two fragments are detached but their detachment lengths vary substantially. These differences are attributed to boundary conditions (substrate attachment), geometric non-uniformity (taper), and small contact/alignment variations, which can promote curved fracture surfaces and crack arrest before full-height splitting.

Peak load as a proxy for crack-path extent. When morphology is considered together with the mechanical signal, a trend emerges: the critical load shows a correlation with a scalar crack-path metric extracted from post-mortem SEM (e.g., detached fragment

length or crack exit height). Figure 3.37 indicates that pillars exhibiting longer detached fragments—consistent with cracks that propagate deeper before curving outward and intersecting the sidewall—generally sustain higher peak loads, whereas pillars releasing only short fragments fail at lower $P_{\max}$.

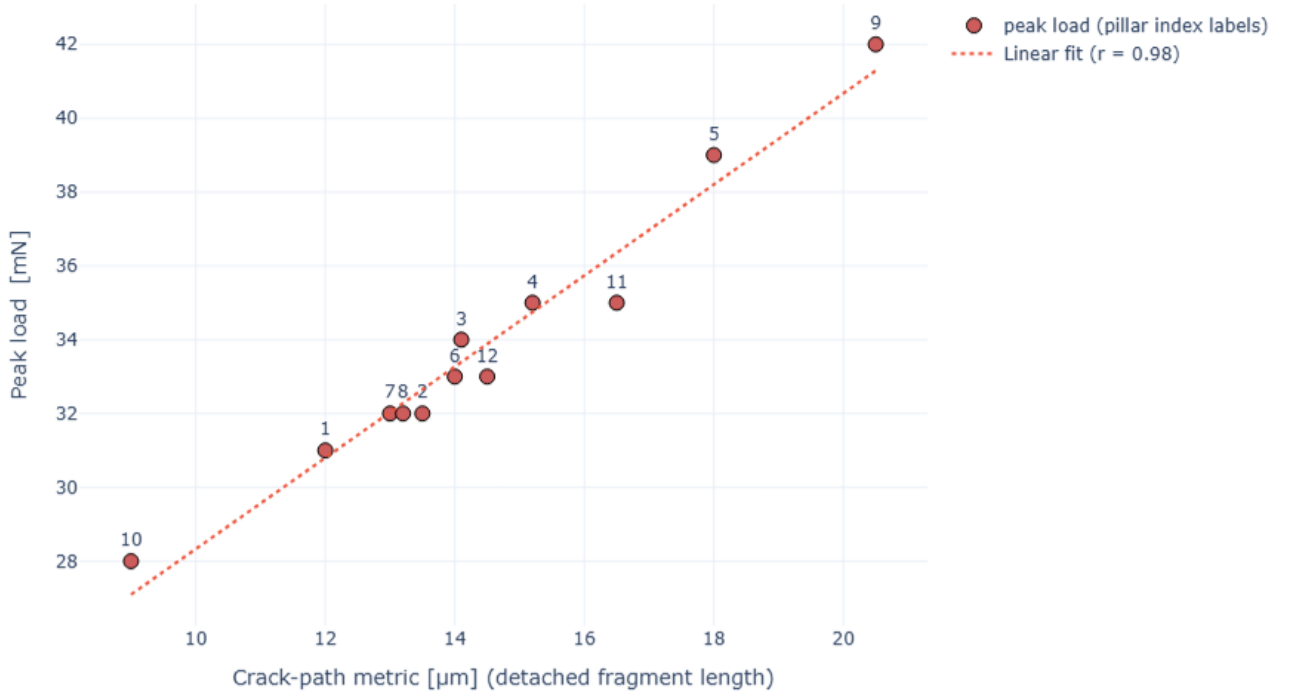


Figure 3.37: Correlation between critical load $P_{\max}$ and a crack-path metric extracted from post-mortem SEM (e.g., detached fragment length). Each marker is labelled by pillar index (1–12). The observed trend supports the interpretation that higher peak loads are associated with deeper crack propagation prior to sidewall intersection and fragment detachment.

Gauge factor γ : coupling to microcompression. In many implementations of cube-corner cracking and pillar splitting, the gauge factor γ is selected from calibrations relating γ to the ratio E/H , typically obtained from independent mechanical tests and/or from literature-calibrated FE studies. For fused silica, it is reported $\gamma \approx 0.49$ with only minor sensitivity to densification, and fracture toughness values around $\sim 0.67\text{--}0.68 \text{ MPa}\sqrt{\text{m}}$ when using a consistent calibration procedure. [32]

In the present work, γ is not an independent measurement: it is derived from microcompression-informed inputs, using $E_{\max}$ and a hardness proxy estimated from the yield stress via $H \approx 1.5 \sigma_y$ (Section 2.7.15). This coupling is stated explicitly because it makes γ a bridge parameter tying the splitting analysis to the same reference mechanical state quantified in compression. Practically, γ values are computed from pillars fractured

in microcompression, whereas K_c is extracted from a different set of pillars fractured by splitting. It is therefore not meaningful to assign pillar-specific γ values to unrelated split specimens. For this reason, a single representative value was adopted: the set-average $\bar{\gamma}$ obtained from the microcompression population.

Figure 3.38 reports the distribution of γ values computed from the $n = 14$ microcompression pillars, showing $\gamma = 0.501\text{--}0.544$ with $\bar{\gamma} = 0.522 \pm 0.013$ ($\text{CV} \approx 2.5\%$). In the subsequent pillar splitting analysis, $\bar{\gamma}$ was used for all specimens.

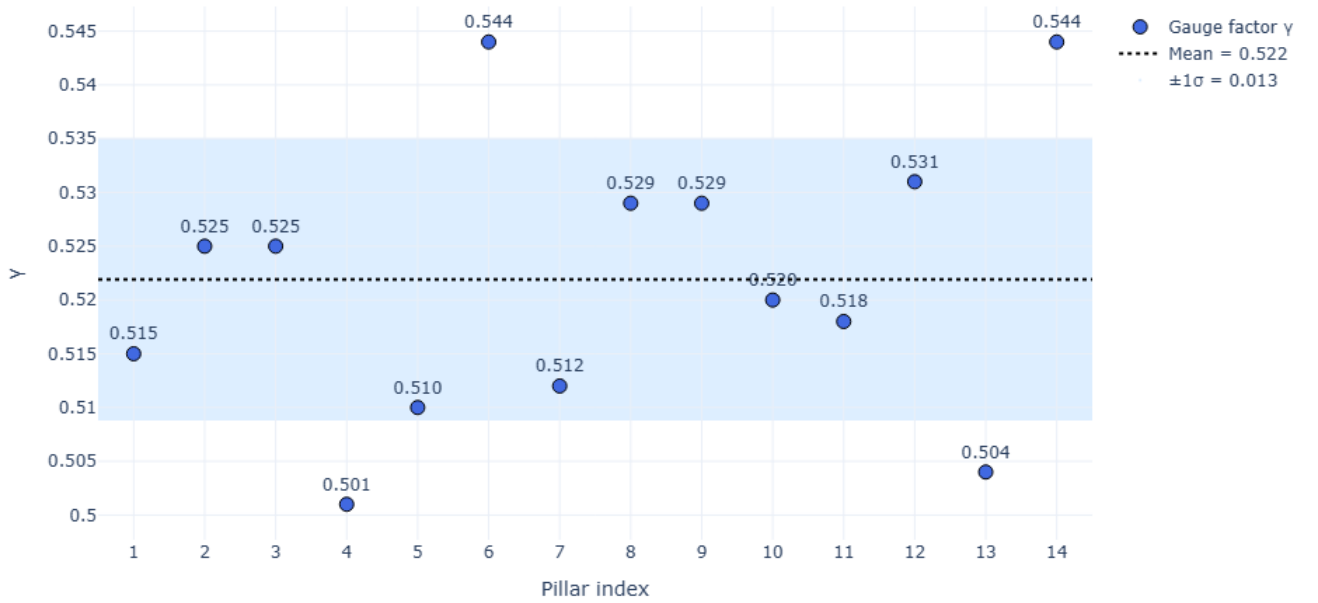


Figure 3.38: Scatter of the gauge factor γ used to compute K_c in Eq. (3.2). Here γ is derived from microcompression-informed inputs (e.g., $E_{\max}$ and a hardness proxy), and is therefore reported explicitly to document sensitivity and uncertainty propagation.

Effective fracture toughness: interval-based reporting. Because the pillar radius is not strictly constant along height, the radius used in Eq. (3.2) introduces a systematic uncertainty. In this work, R is therefore treated as an interval (e.g., using a representative range spanning a near-top radius and a near-base radius), resulting in an interval of K_c values for each pillar rather than a single point estimate. The resulting dataset is summarized in Figure 3.39 using (i) central estimates and (ii) vertical error bars representing the radius-induced interval.

The ensemble mean falls around $\sim 0.65 \text{ MPa}\sqrt{\text{m}}$, consistent with dense fused silica benchmarks and with pillar splitting results reported for fused silica when using cube corner splitting and an appropriate γ calibration. [32] This agreement supports the

interpretation that the 1300 °C/4320 s thermal cycle produces a glass network close to fully densified fused silica, in line with the stiffness benchmark from microcompression (plateau near ~ 72 GPa). [14]

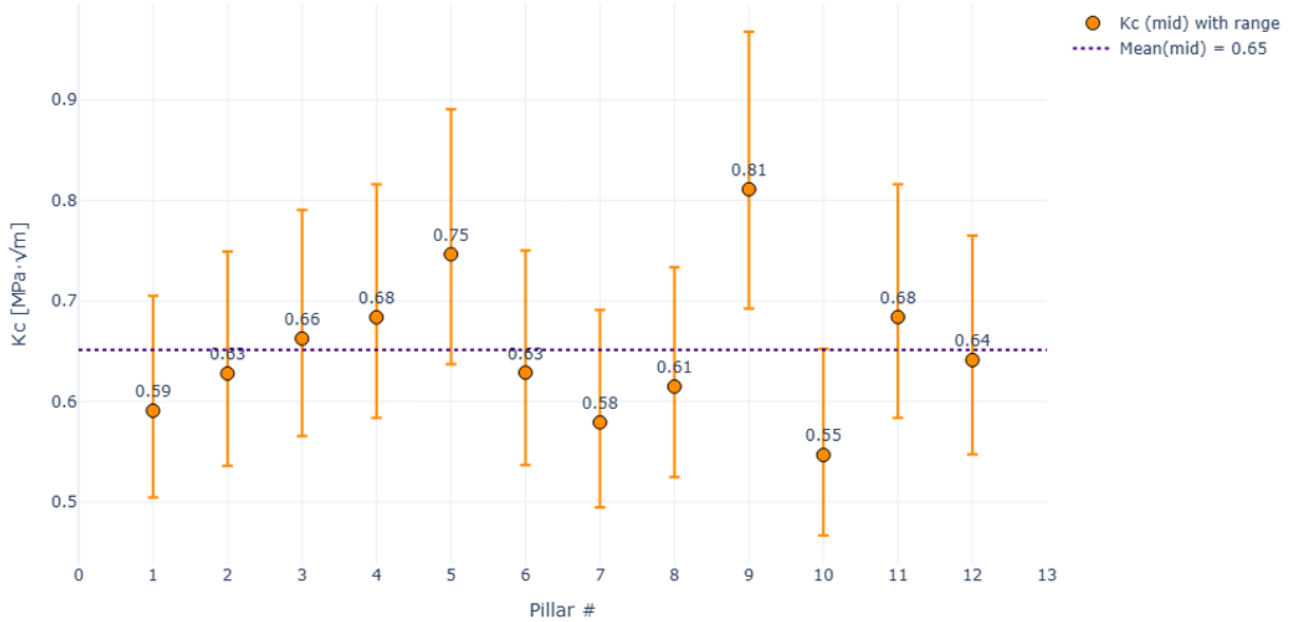


Figure 3.39: Effective fracture toughness values extracted from pillar splitting using Eq. (3.2). For each pillar, the vertical interval reflects the uncertainty associated with the choice of radius R for tapered/non-uniform specimens. The population mean is close to dense fused silica benchmarks reported for pillar splitting and related microscale fracture methods. [32]

Pillar splitting: interpretation

Curved fracture surfaces and incomplete splitting as boundary-condition signatures. The diversity of fragment patterns in Figure 3.36 is mechanistically informative: it indicates that crack initiation and propagation do not occur under perfectly symmetric boundary conditions. The common presence of a remnant ligament near the pillar/substrate junction suggests that the driving force for further propagation decreases as the crack approaches the constrained base region. As a result, the system releases strain energy by detaching one or two fragments while leaving a residual portion anchored to the substrate. The observation that fracture surfaces often appear curved is consistent with crack-path deflection rather than a fully symmetric, through-height split.

Why the crack may not reach the base: four contributing factors. The deviation from complete three-fragment splitting can be rationalized by differences

between the present pillars and the idealized reference configurations. At least four non-exclusive factors likely contribute:

- **Substrate attachment and constraint.** The pillar base is bonded to the substrate, producing a constrained stress state compared to freestanding pillars. This constraint can reduce the local crack driving force near the base and promote arrest, leaving a remnant ligament even if splitting initiates at the top.
- **Taper and radius ambiguity along height.** Because the radius is not constant, the stress field and local propensity for crack extension vary with depth. A larger effective radius towards the base reduces the normalized driving force for a given load and can bias the system toward incomplete propagation and earlier sidewall exit (shorter fragments).
- **Contact conditions and centering.** Small eccentricities or local contact asymmetries break the three-fold symmetry and can favor a dominant branch (single detached fragment) or partial development of a second branch (incipient fragment that remains attached).
- **Local damage and process-zone effects.** If local crushing/densification and microcracking develop beneath the indenter, instability may occur before a clean, symmetric crack system fully develops, resulting in mixed outcomes (chipping, partial detachment, curved fracture surfaces).

Interpretive bridge to the $P_{\max}$ –morphology trend. The correlation in Figure 3.37 is consistent with this picture: deeper crack propagation (longer detached fragments) requires sustaining higher loads before sidewall exit and fragment release, whereas earlier deflection and shorter fragments correspond to lower critical loads. This directly supports the interpretation that the splitting threshold is not governed solely by a geometry-independent material constant, but is strongly influenced by boundary conditions and crack-path steering in substrate-attached, slightly tapered pillars.

Cross-consistency and takeaway for the reference state

Interpreting pillar splitting together with microcompression is particularly useful for the present material system because it separates (i) global compressive response signatures from (ii) controlled crack-dominated instability, while keeping the thermal history fixed. Two consistent messages emerge:

- **A dense-glass benchmark is recovered by two independent probes.** The

microcompression stiffness plateau near ~ 72 GPa and the pillar splitting K_c around $\sim 0.65 \text{ MPa}\sqrt{\text{m}}$ both align with dense fused silica expectations, supporting effective conversion/densification at $1300^\circ\text{C}/4320 \text{ s}$. [14, 32]

- **Failure is strongly geometry- and boundary-condition-sensitive at the microscale.** The diversity of splitting morphologies and the incomplete propagation to the base highlight that small geometric variations (taper, radius ambiguity) and boundary conditions (substrate constraint, centering) have a first-order influence on crack paths and on whether splitting develops into the ideal three-fragment pattern.

4 | Conclusions

This thesis aimed to make a brittle material behave as a measurable engineering system at the micrometer scale. Although fused silica is intrinsically strong and chemically stable, its macroscopic strength is rarely intrinsic because fracture is governed by the largest critical flaw sampled by the stressed volume. When characteristic dimensions shrink to the micrometer range, the probability of sampling large defects decreases and the apparent strength can move closer to intrinsic limits. At the same time, the measurement becomes highly sensitive to geometrical fidelity, surface state, and handling- or process-induced imperfections. For this reason, microscale mechanics on brittle glass is only interpretable when fabrication and post-processing are treated as part of the mechanical experiment.

Within this framework, the thesis developed and validated an end-to-end workflow for producing fused silica micropillars via Two-Photon Polymerization (2PP) using the silica-loaded GP-Silica resin, followed by thermal conversion through debinding and sintering, and mechanical testing by microcompression and pillar splitting. The work was structured to stabilize the complete process chain - from design and printing to development/handling, thermal schedule selection, and geometry verification - with mechanical characterization as the final target. Rather than optimizing each step in isolation, the focus was to reach a level of reproducibility that enables meaningful discussion and comparison.

The contribution of the thesis is twofold. First, it delivers mechanically consistent datasets for thermally converted 2PP fused silica micropillars, combining microcompression results (elastic-to-nonlinear response and peak strength in the multi-GPa range for the tested geometries) with pillar-splitting measurements that provide fracture-toughness-relevant metrics for the same material state. Second, it establishes a practical and repeatable process chain that allows those datasets to be generated with sufficient consistency across batches and processing conditions.

A key outcome is that the measured curves should not be read as ideal “textbook” compression of a perfectly cylindrical, perfectly aligned brittle column. Instead, small deviations in shape and surface state leave clear signatures in the load-displacement and

stress-strain response, including progressive nonlinearity prior to catastrophic events, changes in apparent stiffness associated with contact evolution, and scatter in peak strength. In this respect, pillar splitting complements microcompression by promoting crack initiation and propagation under a tensile opening stress field generated by the splitting contact, making it more directly sensitive to fracture resistance. Using both methods on correlated specimen sets strengthens the interpretation: the response is consistent with brittle fracture of dense glass at the microscale, while remaining strongly influenced by the manufacturing signature.

The initial motivation of the thesis, namely to contribute to the “smaller is stronger” narrative for fused silica at the micrometer scale, can therefore be addressed in a nuanced way. The results support the idea that microscale pillars can reach strengths far above macroscopic engineering glass, consistent with the reduced probability of sampling a large critical flaw. However, the thesis also shows why this trend should not be treated as deterministic: at the micrometer scale, small variations in geometry, surface condition, and local defect state can dominate fracture, so scatter remains an intrinsic feature even within nominally identical batches. Consequently, size effects become convincing only when they are supported by statistically meaningful populations produced under a stable and well-documented process chain, rather than inferred from a limited number of successful specimens.

From a methodological standpoint, the thesis demonstrates that a manufacturing-aware workflow is the enabling technology for quantitative microscale testing of brittle additively manufactured glass. Even with improved control, test-specific factors such as alignment, friction, and contact quality cannot be eliminated entirely, and their interaction with local flaws can strongly affect the apparent strength. For this reason, the most robust outcomes are the trends observed within controlled batches and the explicit link between thermal history, final morphology, and fracture behavior, rather than any single “absolute” strength value. Where literature benchmarks are used for context (e.g., elastic modulus and fracture toughness ranges typically reported for dense fused silica), the measured responses are broadly consistent with the expected order of magnitude, supporting the conclusion that the thermally converted material behaves as a dense silica glass while still reflecting process-dependent variability.

An important practical boundary condition of this work is the use of a $10\times$ objective during printing, which imposes a limited resolution and constrains achievable surface quality and geometric fidelity compared to higher-magnification optics. This choice was coherent with the objective of producing mechanically testable pillars with acceptable throughput and stability, but it also means that pushing toward complex

micro-architected silica structures will likely require a dedicated reassessment of the optical configuration (objective selection, writing strategy, and associated process window), because architectural complexity amplifies the mechanical consequences of local defects and small geometric deviations.

Looking forward, the work opens a clear set of next steps that are technically realistic and scientifically valuable. A first direction is to make size scaling explicit by fabricating statistically meaningful populations with systematically varied diameters at fixed aspect ratio and consistent surface state, so that strength trends can be discussed with stronger statistical support. Coupling this with fracture-mechanics-informed analysis (effective flaw size estimates and probabilistic strength descriptions) would connect the results more directly to the glass strength literature while acknowledging the specificities of additively manufactured micro-glass. A second direction is to strengthen morphology-property correlations by quantifying taper angle, top curvature, base fillet geometry, and surface roughness, and using these descriptors to rationalize scatter and failure modes. A third direction is process robustness: humidity and time sensitivity suggest that environmental control and standardized resin-handling should be treated as first-class parameters when moving from pillars to micro-architected lattices or functional devices. Temperature-related factors (cleanroom temperature and thermal history) also deserve explicit control, because at smaller feature sizes small drifts can strongly affect fidelity and defect formation. Further scaling will likely require re-optimizing the thermal conversion, including debinding and sintering schedules, to balance densification with shape preservation. In this scenario, the route established in this thesis should be seen as a baseline that must be stabilized before increasing architectural complexity.

Overall, the objectives stated in the motivation and scope were fulfilled. A reproducible end-to-end route was built and demonstrated, and the mechanical response of thermally converted 2PP fused silica micropillars was measured and discussed in direct connection with the process chain that generated it. The broader takeaway is that at the micrometer scale, “materials” and “manufacturing” cannot be separated: fabrication is part of the mechanical experiment. Once that is accepted and controlled, fused silica microstructures produced by 2PP and thermal conversion become not only manufacturable, but also mechanically interpretable, which is the essential step required to turn microscale glass mechanics from isolated curves into a reusable engineering methodology.

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A | Appendix

A.1. Worked example of the data-reduction pipeline

To document the data-reduction workflow in a reproducible and transparent way, the Appendix provides a concise method demonstration on representative datasets. The figures are ordered to mirror the analysis pipeline from raw signals to derived metrics. The selected example corresponds to the same specimen set later discussed in the Results and Discussion chapter.

1. **Raw mechanical signals (microcompression, overview).** An overview plot showing the complete set of microcompression load–displacement curves $F(u)$ for the specimen set, including the mean response and the $\pm 1\sigma$ scatter band. This figure provides the raw experimental basis prior to stress–strain conversion.

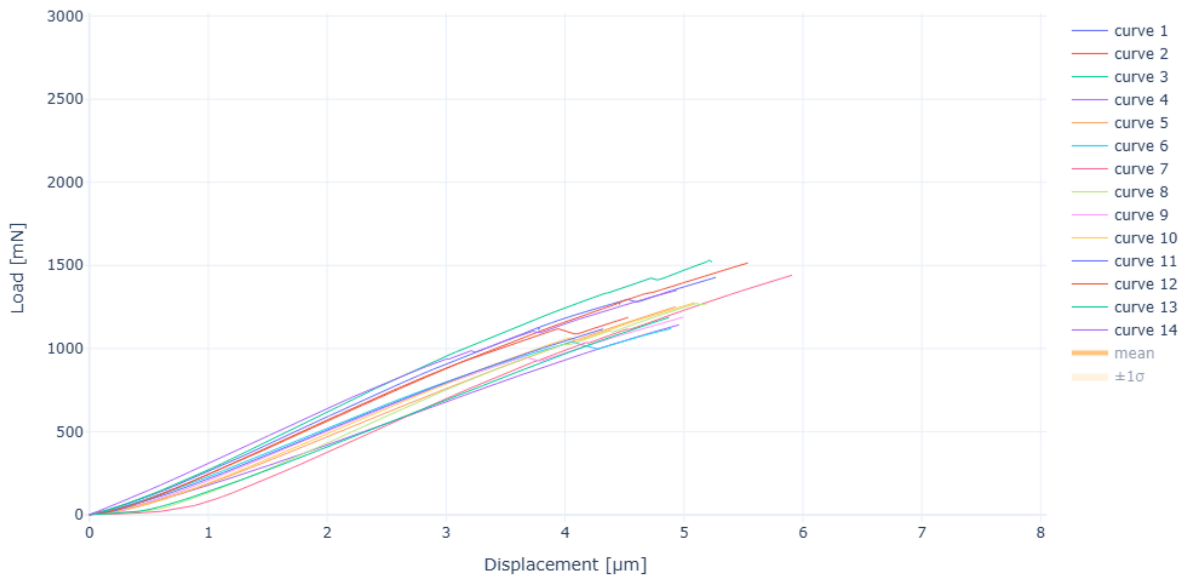


Figure A.1: Overview of microcompression load–displacement curves $F(u)$ for the selected specimen set (matched sample condition), including mean and $\pm 1\sigma$ scatter band. This plot documents the raw signals used as input for the stress–strain conversion.

2. **Stress–strain conversion (overview).** An overview plot showing all microcompression engineering stress–strain curves $\sigma(\varepsilon)$ for the same specimen set, including mean and $\pm 1\sigma$ scatter band. This figure documents the spread of responses before single-curve property extraction.

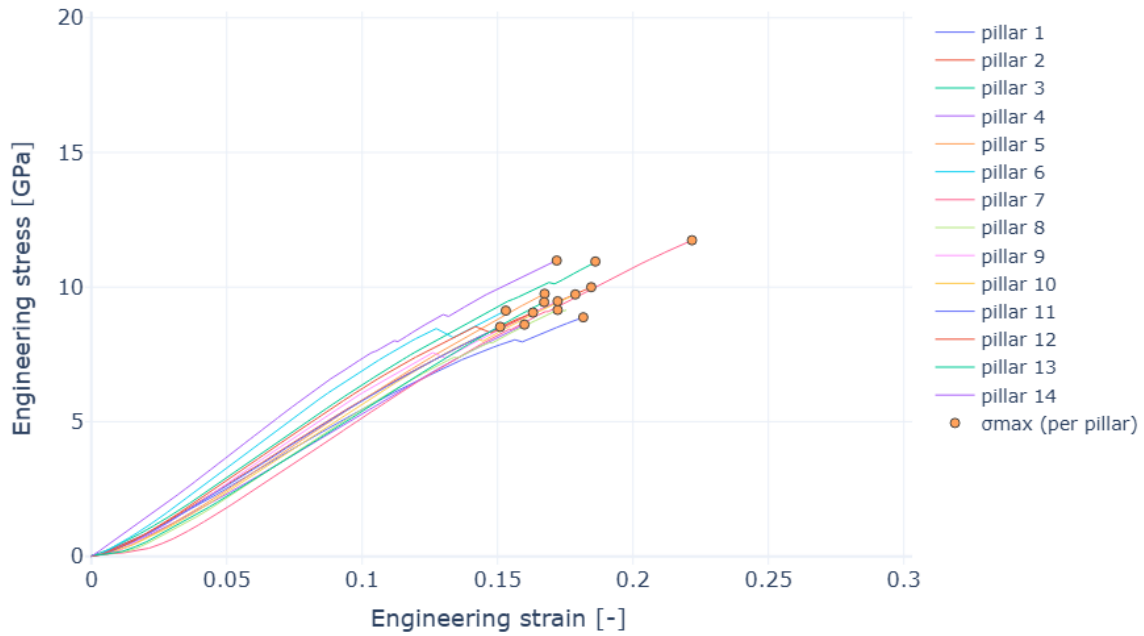


Figure A.2: Engineering stress–strain curves $\sigma(\varepsilon)$ obtained from microcompression after geometric metrology (height and top diameter) and signal correction, shown for all tested pillars in the specimen set. Mean response and $\pm 1\sigma$ scatter band are reported to visualize reproducibility before single-curve property extraction.

3. **Worked example on a single pillar (pillar #5: stress–strain).** Pillar #5 is selected as the worked example to illustrate the full analysis workflow applied to *every* tested pillar. The figure reports the corresponding engineering stress–strain curve $\sigma(\varepsilon)$ used as input for the modulus and yield constructions.

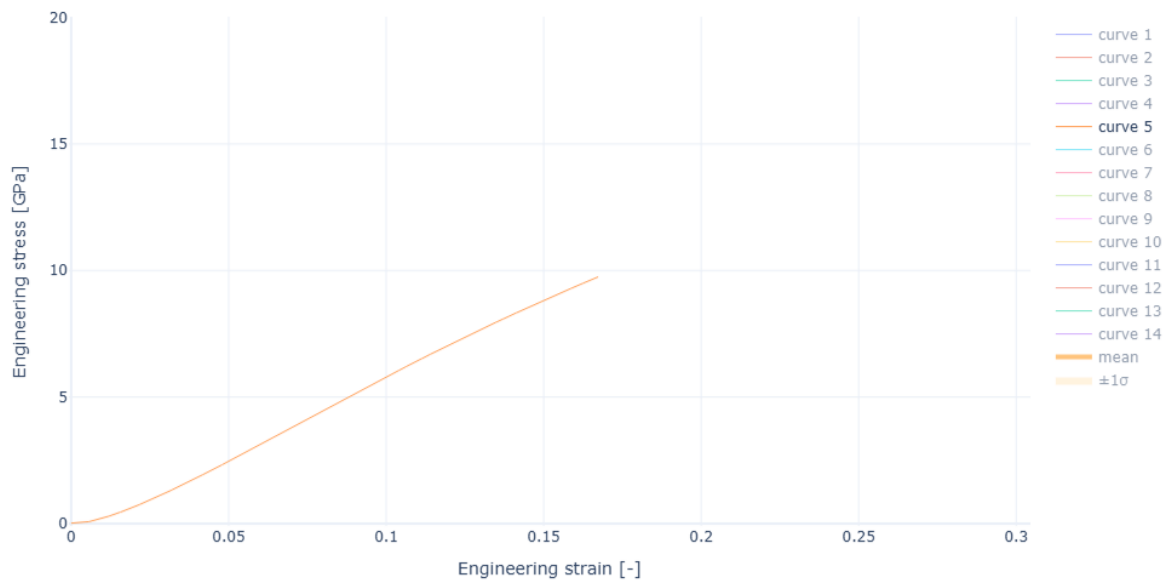


Figure A.3: Representative single-pillar stress–strain curve for pillar #5, used as a worked example to demonstrate the data-reduction workflow. The same procedure is applied consistently to all pillars in the microcompression dataset.

4. Worked example (pillar #5: piecewise modulus and window selection).

The apparent modulus evolution $E(\varepsilon)$ extracted via piecewise regression is reported for pillar #5. In this curve, the maximum modulus is observed clearly within the strain interval $\varepsilon \in [0.06, 0.07]$. The subsequent interval, in which $E(\varepsilon)$ decreases, is selected as the practical window to perform the linear fit used for the 0.2% offset yield construction shown in the next figure.

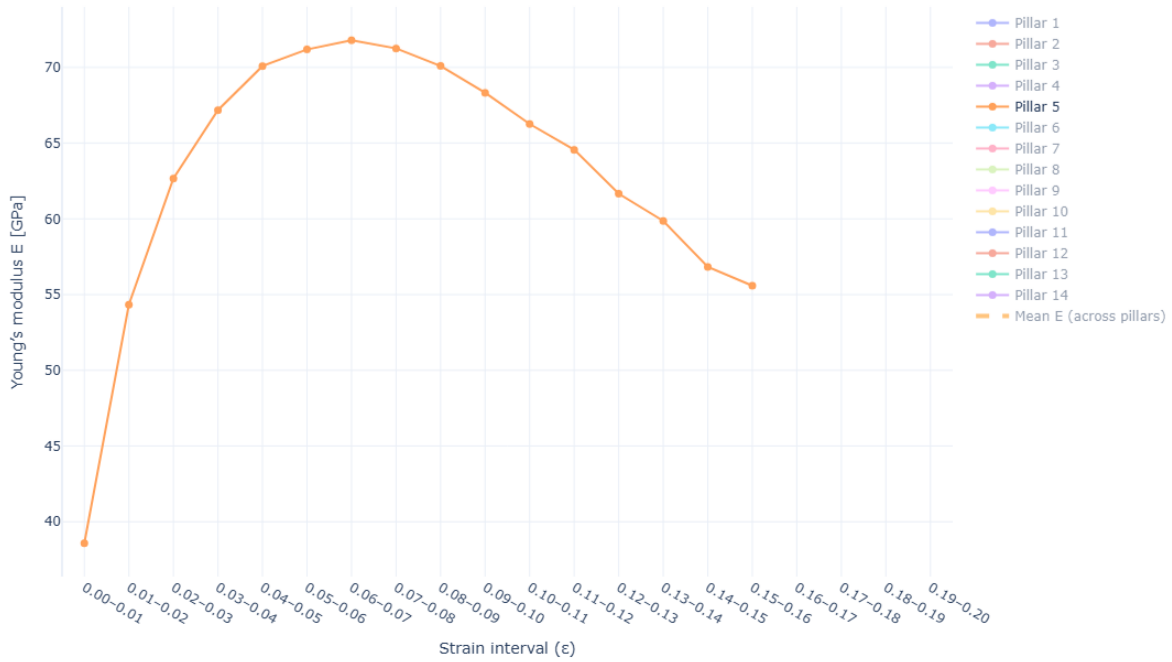


Figure A.4: Piecewise modulus $E(\varepsilon)$ extracted for pillar #5 by linear regression over small strain windows. The maximum modulus occurs in the interval $\varepsilon \in [0.06, 0.07]$. The following window, where the modulus decreases, is selected for the linear fit used in the 0.2% offset yield construction (Figure A.5).

5. **Worked example (pillar #5: 0.2% offset yield construction).** The 0.2% offset method is illustrated on the same stress–strain curve (pillar #5). The *grey line* represents the linear fit performed over the selected decreasing-modulus interval identified from $E(\varepsilon)$. The *red line* represents the same fit translated by an offset strain of $\varepsilon_0 = 0.002$. The *red cross* marks the intersection between the experimental curve and the offset line, defining the yield point and the corresponding σ_y and ε_y .

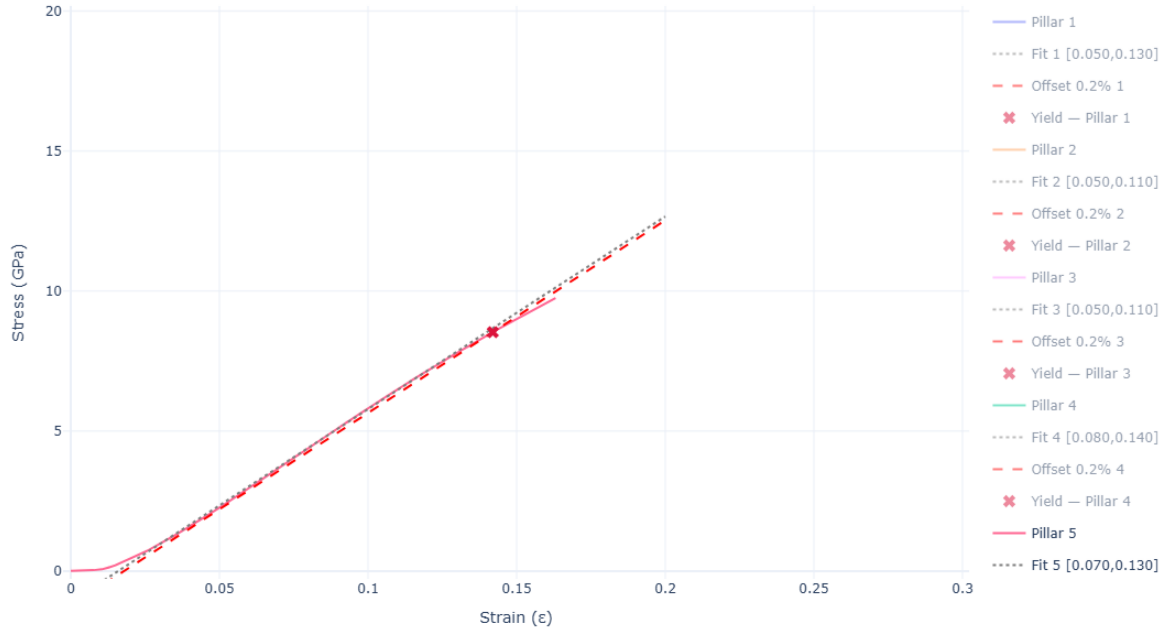


Figure A.5: 0.2% offset yield construction for pillar #5. The grey line is the linear fit performed over the selected strain interval (identified from the decreasing-modulus window in Figure A.4); the red line is the same fit translated by $\varepsilon_0 = 0.002$. The red cross indicates the yield point (intersection), from which σ_y and ε_y are extracted.

6. **Gauge factor calibration for pillar splitting.** The correlation used to estimate the dimensionless gauge factor γ as a function of E/H is shown. Pillar #5 is used as a concrete worked example: H is estimated from its yield stress (e.g., $H \approx 1.5 \sigma_y$) and a corresponding γ_5 is obtained from the linear relation. In the full analysis, the same calculation is repeated for every microcompression curve, yielding a set of values $\{\gamma_i\}$, and the set-average $\bar{\gamma}$ is adopted for the matched pillar-splitting dataset on the same substrate/sample condition.

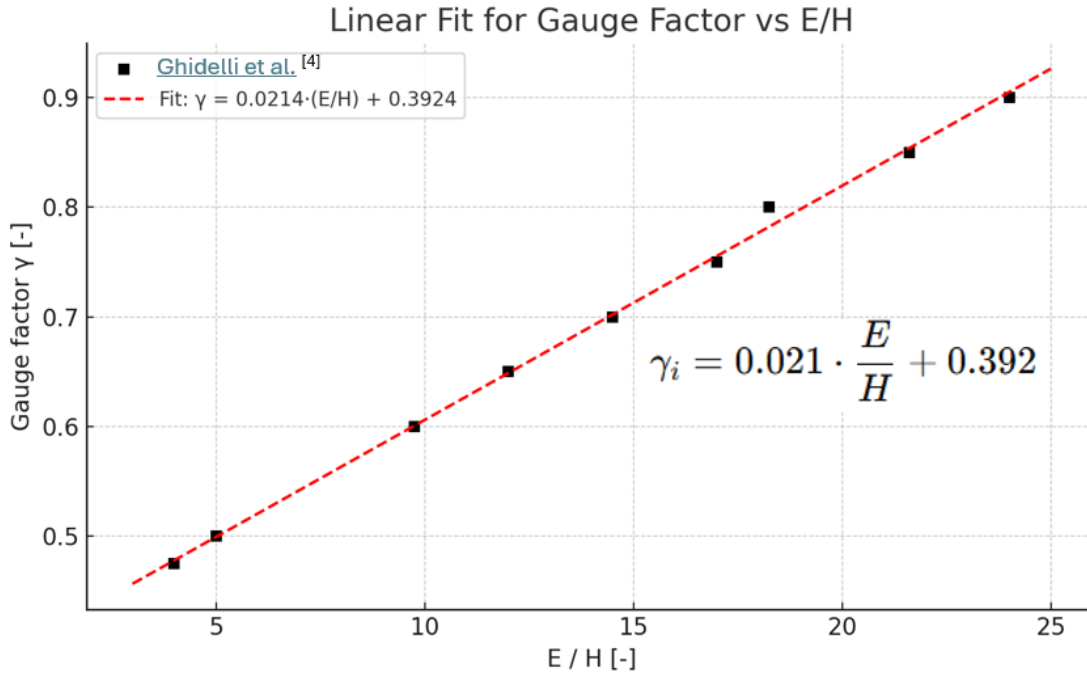


Figure A.6: Gauge factor γ estimation based on the correlation with E/H . Pillar #5 is shown as a worked example (yielding γ_5 from its E and estimated hardness H from σ_y). The same calculation is repeated for all microcompression curves to obtain $\{\gamma_i\}$, and the set-average $\bar{\gamma}$ is used for fracture-toughness extraction from the matched pillar-splitting dataset.

7. **Pillar splitting (overview) and fracture-toughness extraction output.** An overview plot showing the complete set of pillar-splitting load–displacement curves $F(u)$ for the matched specimen set, including mean response and the $\pm 1\sigma$ band. Each splitting curve provides one critical load $P_{\max}$ (maximum load preceding the main irreversible drop) and therefore one fracture-toughness value K_c computed using the set-averaged $\bar{\gamma}$ obtained above. A compact summary plot of the resulting K_c values is included to close the method demonstration; full comparisons are deferred to the Results and Discussion chapter.

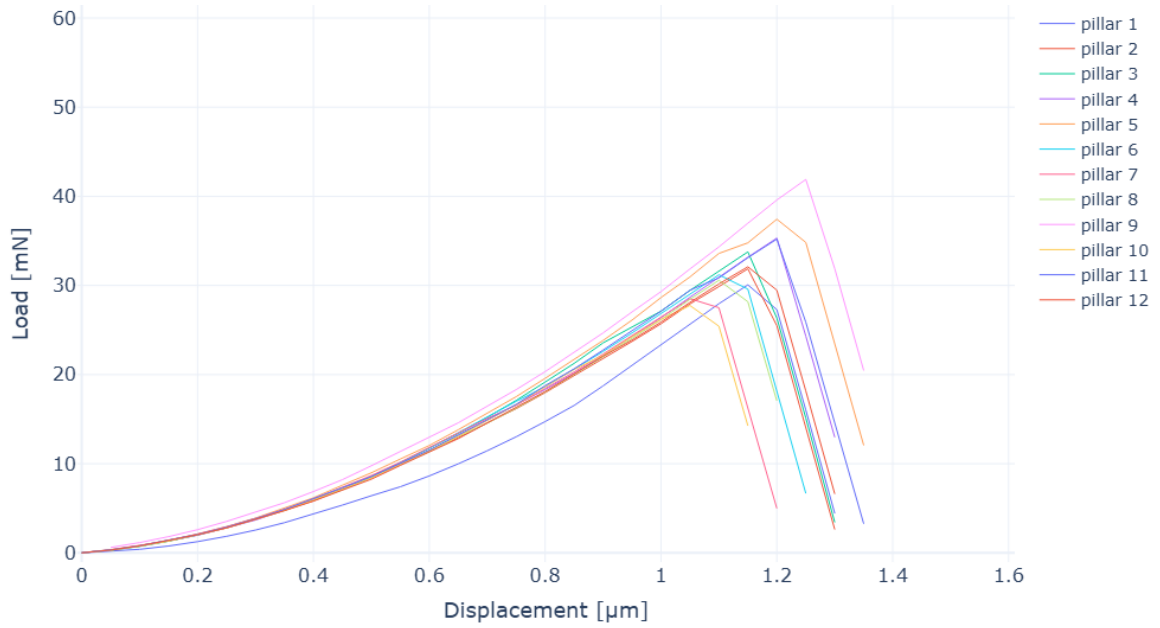


Figure A.7: Overview of pillar-splitting load-displacement curves $F(u)$ for the selected specimen set, including the mean response and the $\pm 1\sigma$ scatter band. The critical load $P_{\max}$ is defined as the maximum load preceding the main irreversible drop associated with splitting.

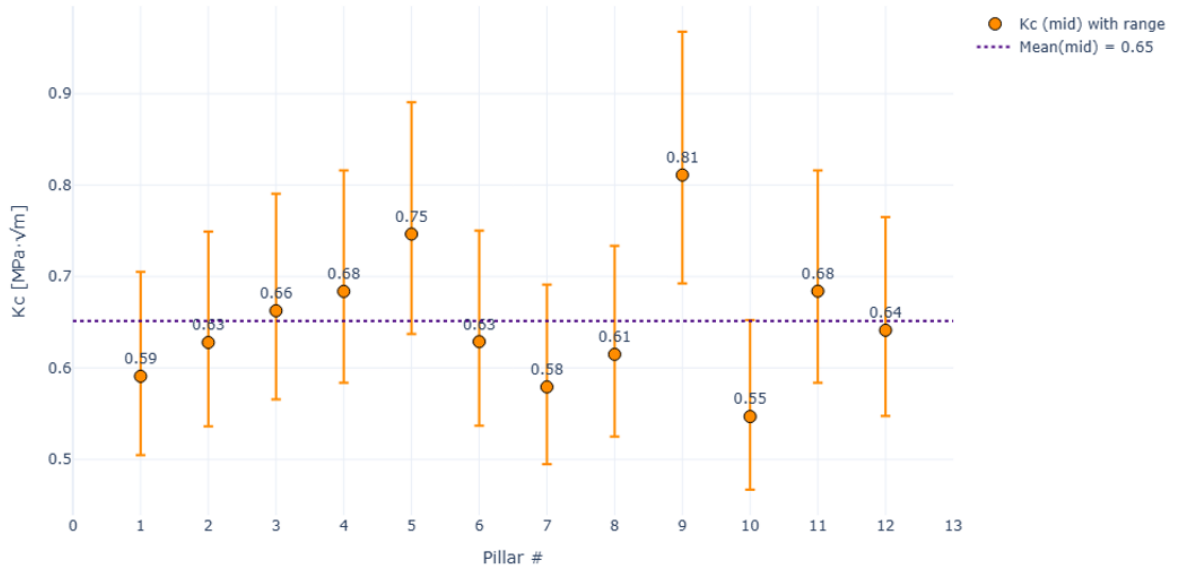


Figure A.8: Summary of the fracture toughness values K_c obtained from pillar splitting using the set-averaged $\bar{\gamma}$ (computed from the microcompression dataset following the procedure illustrated for pillar #5 in Figures A.3–A.6) and the critical load definition reported in Figure A.7. When pillar taper is considered, values are reported as bounded ranges based on the measured top and base radii. Full comparison across processing conditions is presented in the Results and Discussion chapter.

