POLITECNICO
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SCHOOL OF INDUSTRIAL AND INFORMATION TECHNOLOGY

EXECUTIVE SUMMARY

“CHARACTERIZATION OF ANNEALED ALUMINA THIN FILM COATINGS USING BRILLOUIN SPECTROSCOPY”

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Abstract

Few samples of alumina were deposited by laser ablation technique and annealed at different temperature and time. In the deposited state on silicon substrate, alumina coatings are essentially amorphous, and they tend to crystallize upon annealing around 950 °C. This experimental work is focused mainly to investigate the effects of annealing on the alumina coatings by estimating the variations in stiffness and elastic constant of various samples. Exploring variety of samples annealed at 500 °C, 700 °C and 950 °C using Brillouin spectroscopy. Brillouin spectroscopy is a non-destructive technique which can be used to analyze the elastic properties of thin film coatings. When laser is interacted with surface of the material, it is scattered and by evaluating its spectrum, the velocity of acoustic modes can be measured. The scanning electron microscope (SEM) has been utilized to examine the surface morphology and cross-sections of the alumina thin film coatings to have detail on the surface and thickness of the annealed films. The XRD data is helpful to detect the transition from amorphous to crystalline phase of the alumina thin film because of annealing. Data from Brillouin spectroscopy is analyzed in MATLAB to fit and measure the velocity of Rayleigh waves and longitudinal bulk waves of alumina coating. The elastic constants are calculated by using appropriate equations and data from brillouin spectra.

Keywords: Brillouin spectroscopy, acoustic modes, elastic properties, scanning electron microscopy, amorphous alumina, crystalline alumina, laser ablation technique.

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1. Introduction

Alumina (Al2O3) is most widely used as a coating for steel substrates due to their outstanding performance in applications that require hardness and resistance to wear, and phase stability at high temperatures [1]. Alumina is amorphous in general, but they are metastable material, and they can become crystalline when it's exposed to higher temperatures and it leads to brittleness, non-uniform density, surface micro-cracks and porosity, poor adhesion strength and poor mechanical compatibility with steels [2]. PLD grown alumina was already studied and their mechanical properties are good but still the properties of material at nanoscale and after annealing effects needs to be investigated. The fabrication of alumina using PLD carried out and they are annealed at different temperatures and exposure time. This experimental thesis work is focused mainly to investigate the effects of annealing on alumina. This can be evaluated by a direct and complete elastic characterization of thin films. An important technique to do elastic characterization of thin film is an acoustic microscopy called Brillouin spectroscopy- a well-established non-destructive technique that can provide a complete elastic characterization of bulk materials and thin films. Moreover, a fully optical characterization route has been recently demonstrated by combining Brillouin spectroscopy and ellipsometry. Ellipsometry is used to estimate the refractive index of a thin film coatings [1]. XRD analysis has been done to understand the crystallization of alumina coatings due to annealing.

2. Methodology

In this experimental thesis work, brillouin spectroscopy is used to characterize the elastic properties of the coatings. A laser beam of 532 nm is incident on the coating surface at an angle to the normal where the sample is positioned according to our feasibilities. The inelastic scattering takes place which is associated with the vibrational motion of the material at the microscopic level due to the thermal vibration of the atoms. As a result, acoustic waves are produced by these vibrations. These acoustic waves travel with a specific characteristic that can cause a modulated, dynamic, and periodic fluctuation in the refractive index of the material. This process is called as elasto-optical effect, and it is analogous to the Bragg's diffraction of X-rays in a crystal. Thus, acoustic waves create a diffraction grating and it is studied by brillouin scattering experiment [3]. The bragg's condition must be applied to have constructive interference between many waves if the θ is scattering angle. Because of constant displacement rate of dynamic diffraction grating, the doppler effect occurs in both absorption and re-radiation of the wave. The frequency shift of the scattered wave is as same as the elastic reflected wave. These shifts in frequencies are detected by brillouin spectroscopy to track the frequencies of acoustic waves. Under various possibilities, we will return to the classical Bragg law and provide information on the intensity and shape of the Stokes and Anti-Stokes peaks. The stokes band is the frequency downshifted one, while the anti-stokes band is the frequency upshifted one. Through the backscattering process, the inelastic scattering from the sample is collected and created as a stokes and anti-stokes band. The incident angle equals the angle of diffusion in backscattering. The frequencies and velocities of the material were determined using Brillouin spectroscopy. Rayleigh velocity from the film's surface and bulk velocity from the substrate. the relationship between the material's velocity, elastic constants, and density in below equations 2.1 and 2.2

$$v_l = \sqrt{\frac{C_{11}}{\rho}} \qquad (2.1)$$

$$v_t = \sqrt{\frac{C_{44}}{\rho}} \qquad (2.2)$$

Where C_{11} & C_{44} are the elastic constants from longitudinal bulk waves and transverse bulk waves respectively and ρ is the mass density of alumina. The velocity of longitudinal bulk waves is independent on incident angle, and it is dependent on material's refractive index and frequency of bulk waves according to the following equation 2.3.

$$v_l = \frac{f_b \times \lambda_0}{2n_e} \qquad (2.3)$$

Where λ_0 is wavelength of incident laser beam, f_b is frequency of bulk waves and n_e is the refractive index of the amorphous alumina. The velocity of transverse bulk waves is calculated from the assumption of isotropic symmetry of crystal, and the analysis mode is given as (v_t= 5%v_r+v_r) where v_t is velocity of transverse bulk waves and v_r is velocity of surface rayleigh's waves. The velocity of surface rayleigh's waves is calculated from the frequency of surface rayleigh's waves are detected from the brillouin spectra and the equation 2.4 gives the relation between velocity and frequency of rayleigh's wave.

$$v_r = \frac{f_s \times \lambda_0}{2\, sin\theta} \qquad (2.4)$$

Where the velocity of surface rayleigh's wave is dependent on the sine of incident angle θ and f_s is the frequency of surface rayleigh waves. And the refractive index of sapphire which is crystalline alumina is 1.77 [1] and the refractive index of amorphous alumina is measured from the ellipsometry. Lorentz-Lorenz formula is used to determine the mass density of our required sample from the equation 2.5.

$$\rho_e = \rho_c \frac{n_e^2 - 1}{n_e^2 + 2} \frac{n_c^2 + 2}{n_c^2 - 1} \qquad (2.5)$$

Where ρ_e and ρ_c are the mass density of amorphous and crystalline alumina respectively, n_e and n_c are the refractive index of amorphous and crystalline alumina.

3. Materials

Alumina is more commonly known as Aluminium oxide (Al2O3), is the most widely used oxide ceramic material. The high temperature will cause crystal dimensions to change due to the anisotropy in different crystallographic directions [4,5]. Alumina (α–phase) is a thermodynamically stable phase, which can be used as a coating to keep the material surface safe from wear. The alumina phases are γ, θ, and α phase which represent the crystalline phases that are important in the alumina structure. The α–phase is stable at high temperature (i.e., melting temperature for this phase is 2051 °C) but the other phases do not always exist in the alumina. The polycrystalline alumina α–phase, is formed at the high temperature of about 1000 °C. The α–alumina has Hexagonal Close Packed (HCP) structure, and the Face Centre Cubic (FCC) oxygen lattice shows the structure for the θ–phase. The γ–alumina has two different lattices; the first lattice is comprised of aluminium ions, and it is formed from octahedral and tetrahedral interstitial locations and the oxygen lattice is formed with the face centre cubic structure [4]. The table 1 reports the details of annealed alumina coated samples.

Annealed Alumina films	Sample thickness	Annealing temperature	Annealing time
Sample-1	1.85 µm	500 °C	105 hours
Sample-2	1.6 µm	700 °C	12 hours
Sample-3	2.2 µm	950 °C	12 hours

Table 1. Details of annealed alumina films

The brillouin experiment was carried out to detect either bulk peaks or surface peaks. If the mirror distance in the tandem interferometer is 5mm and the peaks are only surface Rayleigh waves between ±20GHz. If the mirror distance is 2mm, the peaks observed will be Bulk waves which is spotted above ±20GHz.

4. Results and Discussions

4.1. Sample-1

Referring to the details of sample 1, the brillouin experiment has been carried out and spectra is recorded. The figure 1 and 2 shows the spectra of velocity profile of surface rayleigh's waves and frequency profile of bulk waves respectively.

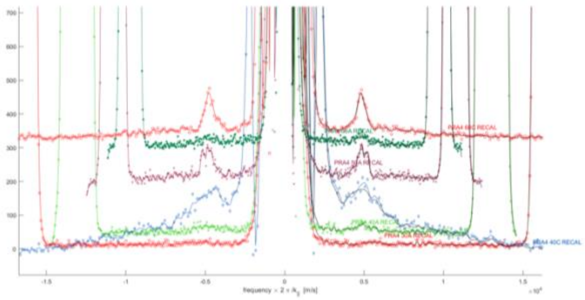

Figure 1. Spectra of surface peaks as a function of velocity for sample-1 at 30,40,50 & 60 degrees

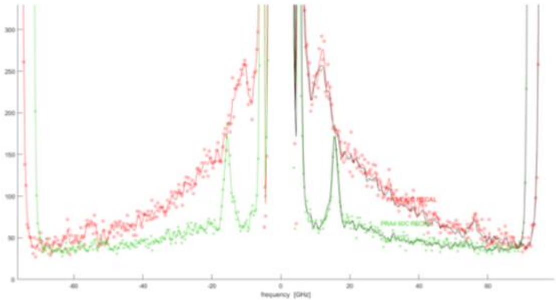

Figure 2. Spectra of bulk peaks as a function of frequency for sample-1 at 40 & 60 degrees

Angle	Mirror distance (mm)	Frequency of bulk waves (GHz)	Rayleigh velocity v_r (m/s)
40	5		4924
50	5		4892
60	5		4839
40	2	55.75	
60	2	53.88	

Table 2. Spectral data of sample-1

The table 2. gives the spectral data of sample-1 which is computed and analyzed by MATLAB. The refractive index of this sample-1 is measured using ellipsometry. The mass density of sapphire is 3970 Kg/m^3 [1] and thus, the mass density of amorphous alumina is calculated using the Lorentz-Lorenz formula from the equation 2.5. By knowing the mass density and the velocity of longitudinal bulk waves from the equation 2.3., the elastic constant C_{11} is calculated. The C_{44} is calculated from the transverse bulk waves which is taken from the rayleigh's wave of analysis mode of $v_t = 5\%v_r + v_r$

The properties of sample-1 are given below:

ρ_e=3213 Kg/m^3, C_{11}=281.38 GPa, C_{44}=76.6 GPa, C_{12}=128.2 GPa, n_c=1.77, n_e=1.547

As a function of velocity and angle, the graph compares theoretical and experimental findings in Fig 3. The red circle is experimental values and the black lines are theoretical values. The dispersion relation shows that the velocity of rayleigh waves from theoretical model is around 4800 m/s and it is flat and doesn’t change with angle. The fit between experiment and theoretical values is poor and also sezawa waves is not detected in this sample.

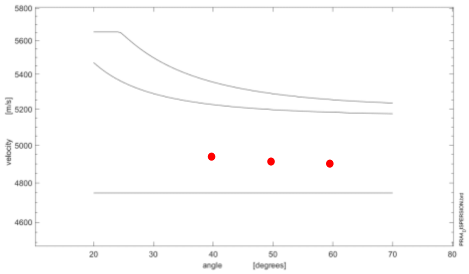

Figure 3. Dispersion relationship of sample-1

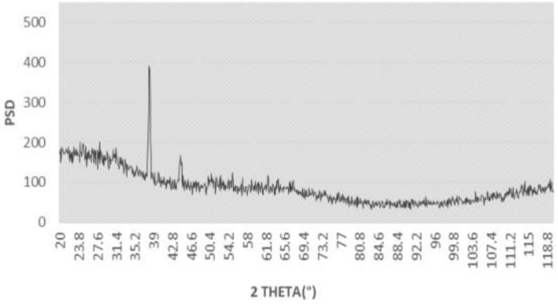

Figure 4. XRD data of sample-1

The XRD data from figure 4 says that there are no crystal phases found in the alumina film of thickness 1.85 µm. The sample-1 is amorphous and not become crystalline due to annealing conditions

4.2. Sample-2

The acoustic waves from the sample-2 are now being investigated using Brillouin spectroscopy. Brillouin measurements were taken at 5mm mirror distances for 30, 50 & 60 degrees and at 2 mm mirror distances for 50 & 60 degrees. The figure 5 and 6 shows the spectra of velocity profile of surface rayleigh’s waves and frequency profile of bulk waves respectively.

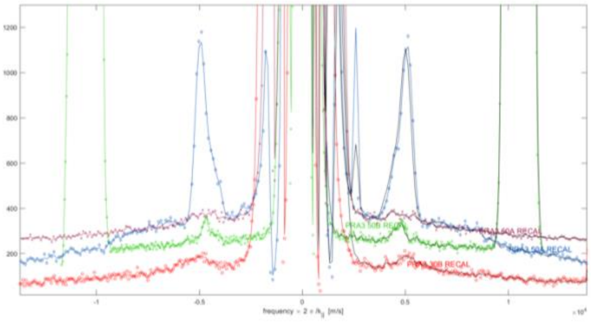

Figure 5. Spectra of surface peaks as a function of velocity for sample-2 at 30,50 & 60 degrees

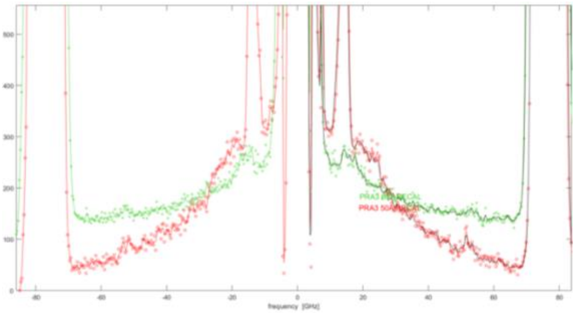

Figure 6. Spectra of bulk peaks as a function of frequency for sample-2 at 50 & 60 degrees

Angle	Mirror distance (mm)	Frequency of bulk waves (GHz)	Rayleigh velocity v_r (m/s)
30	5		5178
50	5		4721
60	5		4530
40	2	52	
60	2	53	

Table 3. Spectral data of sample-2

The properties of sample-2 are calculated as done for sample-1 and it is shown below:

ρ_e=3451 Kg/m^3, C_{11}=249.95 GPa, C_{44}=80 GPa, C_{12}=89.95 GPa, n_c=1.77, n_e=1.642

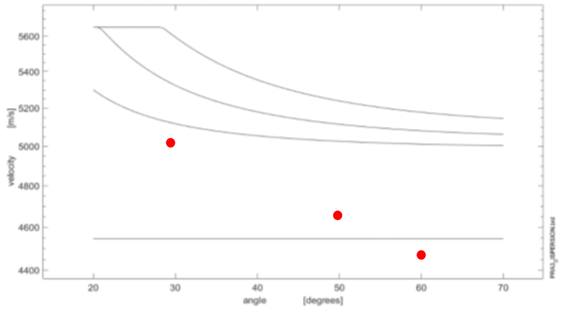

Figure 7. Dispersion relationship of sample-1

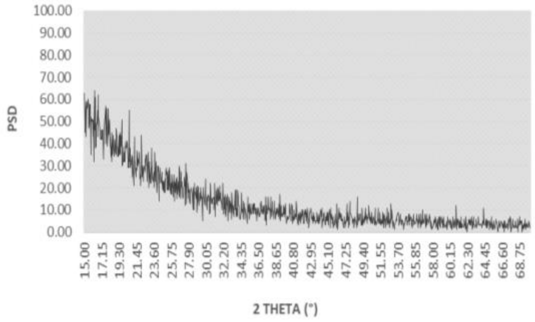

Figure 8. XRD data of sample-2

Figure 7 shows the dispersion relation computed by a theoretical model. The red circles represent the outcomes of the experimental tests. For this sample, the actual and theoretical findings are not similar since there is poor fit between them. The rayleigh velocities decrease significantly as the angle increases in the experimental findings, but the theoretical expectation is that velocity of Rayleigh waves are constant with angle. Like sample-1, Sezawa waves are not detected. The sample-2 is also amorphous and not become crystalline due to annealing at 700 °C for 12 hours. The XRD data from fig 8 says that there are no crystal phases found in the alumina film of thickness 1.6 µm.

4.3. Sample-3

Figure 9 & 10 shows the spectra of surface waves and bulk waves of sample-3 respectively which is measured by Brillouin spectroscopy.

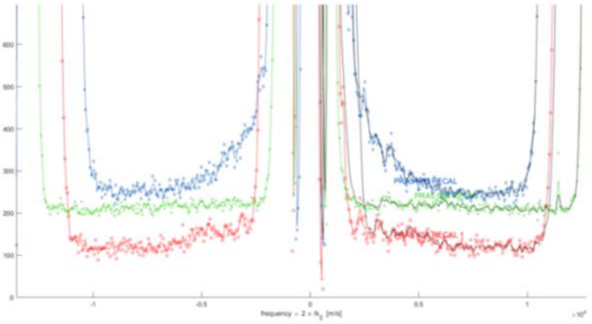

Figure 9. Spectra of surface peaks as a function of velocity for sample-3 at 40,50 & 60 degrees

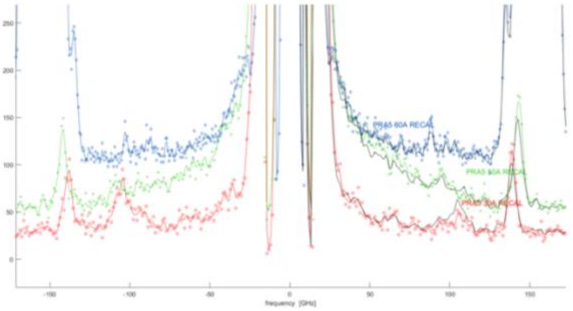

Figure 10. Spectra of bulk peaks as a function of frequency for sample-3 at 30,50 & 60 degrees

From the surface peaks spectra (figure 9), the velocity increased with increasing angle which seems to be absurd.. We know that the velocity of waves in amorphous Al2O3 is lower than velocity of waves in Silicon substrate. But this sample-3 is crystallized; the crystalline alumina is significantly stiffer than silicon and since it's not very heavy, this crystallized alumina can be acoustically faster than silicon. Figure 10 also tells us that the frequencies of bulk peaks are decreasing with increasing angle and the velocity of bulk waves are increasing with increasing angle which is not feasible since the bulk modes are usually constant with any angles measured. So, this might also have occurred due to anisotropy of the sample due to annealing and formation of crystals which is not uniform. The peaks are also not symmetric for stokes and anti-stokes. Since there are very less information on this sample, the elastic constants cannot be calculated since it needs to be further studied under various spectra in Brillouin spectroscopy.

The SEM surface morphology has huge crack due to crystallization effects from annealing and it is shown in below figure 11. It is clear that the crack size is huge and the measured crack length at different spots are 1.695 µm and 684.5 nm.

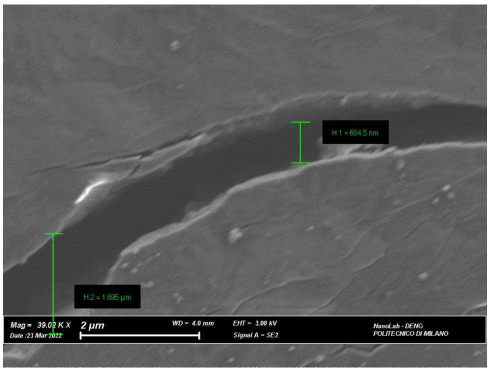

Figure 11. sample-3 crack sizes

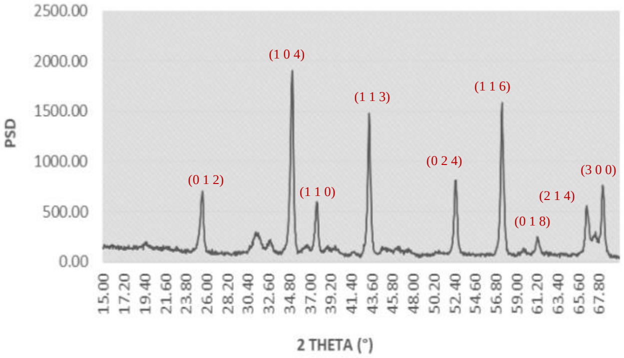

Figure 12. XRD data of sample-3

Angle	Mirror distance (mm)	Frequency of bulk waves (GHz)	Rayleigh velocity v_r (m/s)
40	5		3757
60	5		4520
30	2	91	
50	2	97	
60	2	110	

Table 4. Spectral data of sample-3

The table 4. shows the data of sample 3 and the elastic constants are not calculated since it needs further studies. The sample-3 has become crystalline due to annealing at 950 °C for 12 hours. So, the annealing at 950 °C had significant negative effects on the alumina film which was amorphous in deposited state. The XRD data from fig 12 says that there are lots of crystal phases found in the alumina film of thickness 2.2 µm annealed at 950 °C. The phases generated due to annealing are α-Al2O3. The exhibited peaks correspond to the (012), (104), (110), (113), (024), (1 1 6), (0 1 8), (2 1 4) and (3 0 0) of a HCP structure of α-Al2O3 which is identified using the standard data from the reference paper [6] and it is reported in the figure 12.

5. Conclusion

The main aim of this experimental thesis is to characterize the elastic properties of alumina film coated on the silicon substrate and to understand the crystallization effects due to annealing on alumina film deposited by PLD. Brillouin spectroscopy is a non-destructive testing for characterization of such films. In this thesis, two analyses has been done by brillouin spectroscopy, one is the detection of surface modes-Rayleigh and other is detection of bulk modes and elastic constants are measured from the velocities of

Rayleigh and bulk modes. According to the theoretical model, the experimental values are compared and explained for the obtained results which seems to be poor fit. The sample 1 (annealed @ 500 °C) and sample 2 (annealed @ 700 °C) are amorphous and sample 3 (annealed @ 950 °C) has become crystalline whose phase is α-Al2O3 as per XRD data. Sezawa waves are not detected in these three samples by brillouin spectroscopy. The elastic constants C11, C44 and C12 have been calculated for sample 1 and 2 whereas sample 3 needs to be studied further. They are being measured on the assumption of isotropic films and in this study, the anisotropic films are ignored because amorphous structures can be well studied under isotropic films but for crystalline films, anisotropic films approach must be used. Brillouin spectroscopy is one of the best method to characterize the elastic properties of thin film coatings and hence they have been adopted to study the effects on annealing on alumina thin film

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