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Executive Summary of the Thesis

Functional properties of $K_{0.5}Na_{0.5}NbO_3$ based devices fabricated by Pulsed Laser Deposition and Rapid Thermal Processing

Laurea Magistrale in Physics Engineering - Ingegneria Fisica

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1. Introduction

This thesis work was carried out at PoliFAB, the micro and nanotechnology center of the Politecnico di Milano, with the help and support of STMicroelectronics. The goal of the present joint research project was to synthesize, study, and optimize the functional properties of potassium sodium niobate (KNN, with formula $K_{0.5}Na_{0.5}NbO_3$). KNN is a lead-free piezoelectric material that could be a suitable candidate to replace the more commercially available, and widely used, lead-based piezoelectrics like lead zirconate titanate (PZT, with formula $PbZr_xTi_{1-x}O_3$). The European Community has legislated on laws to eliminate toxic elements, such as lead, from electronic devices by the end of 2025. Therefore, the research, study, and implementation of lead-free materials has become crucial. In addition, as the absence of harmful elements for the human body make them interesting for bio-applications, lead-free materials give rise to the opportunity of research in new fields. Nevertheless, one major issue of KNN films with respect to PZT is its high propensity to suffer from current leakage, making it difficult to exploit the piezoelectric effect effectively. Promoted by high temperature processes, the loss of alkaline elements (K and Na), and the formation of oxygen vacancies are the main culprit of leakage increase. Thus, it is important to elucidate, reduce, and possibly eliminate the mechanisms that give rise to unacceptable leakage levels.

In this work, KNN thin films were grown by the Pulsed Laser Deposition (PLD) technique on $Pt(111)/TiO_2/SiO_2/Si$ substrates using an optimized process previously described in works of the group [1], [2]. Crystal orientation, morphology, stoichiometry, and other properties were characterized. To test for the piezoelectric performance of the KNN films, a cantilever design was modelled and simulated by finite element analysis (FEA). The design was also implemented for the fabrication of KNN cantilevers from PLD-deposited samples. Due to leakage issues, the piezoelectric performance of the cantilevers was poor. Yet, important lessons were learned for future fabrication, which can eventually lead to the application of KNN in functional MEMS devices. During another stage of this work, particular attention to electrical conduction mechanisms in Metal-Insulator-Metal (MIM) stack devices was given.

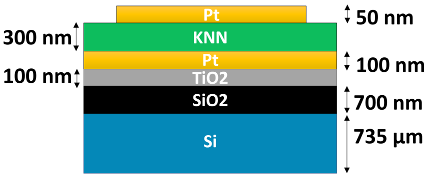
The effect of different metals (Pt, Ni, Ti, and Cr) on the electrical properties of KNN was evaluated. Pt is commonly employed as electrode in KNN systems; however, Pt is expensive and it is desired that a suitable replacement is found. In the course of this study, it was found that other metal electrodes can create oxygen vacancies that degrade the insulation properties of KNN at the interfaces, and even within the films. The formation of a Schottky diode at the bottom interface, and of an ohmic contact at the top one was demonstrated. Finally, with the aim of reducing alkaline and oxygen vacancies to decrease leakage currents, Rapid Thermal Processing (RTA) of KNN was studied. It was observed that 60 s at 650 °C is enough time and temperature to crystallize KNN from an amorphous phase to a preferentially oriented crystal. Voltage-current measurements showed that leakage is decreased due to stabilization of stoichiometry of the KNN films. All in all, this thesis is a step further towards the implementation of KNN in thin film devices for MEMS applications.

2. Piezoelectric cantilevers at PoliFab

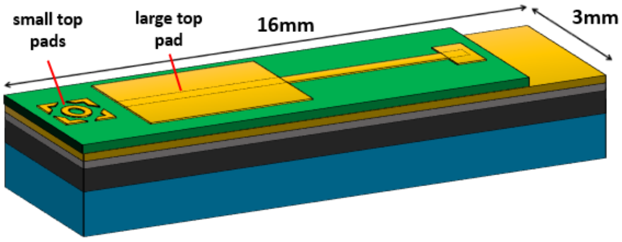
A first attempt to create piezoelectric cantilevers in PoliFab was made using a full stack design instead of a more complex suspended trampoline. Even if the latter is more able to exploit the deflection of the structure to achieve a better mechanical-to-electrical conversion, the former can still take advantage of the bending of the whole structure which is usually a multi-layered substrate where the active material is deposited all over it (fig. 1a.) By using this configuration, rather complex steps in microfabrication design, such as wet etching, are avoided. Still piezoelectric d coefficients of the piezoelectric material (such as d_{31}, d_{33}) can be calculated with this rather simple design, both using mathematical models and finite elements simulations, or by directly measuring it [3]. KNN films were grown using the methods described in previous works, and characterized in terms of morphology and current leakage [1], [2]. Piezoelectric characterization was performed by STMicroelectronics. The grown KNN films showed good morphology properties such as compactness and few defects. Still, other crystal phases arose in the sample (discussed later). Platinum has been sputtered to be the top electrode material as it has the best performances in terms of leakage [1]. Inverse photolitography has been exploited to shape the top contact pad. The obtained stack and its cross section are presented in figure 1b. Current-voltage measurements in top-top configuration using the smaller top platinum pads showed a leakage comparable to the previous works. However, top-bottom measurements, in particular the ones using the big platinum pad as top contact, showed an ohmic behavior (fig. 1c). Using a simple physical model, the estimated slope of the J-E curve is comparable to the conductivity of platinum. Thus, it is possible that the platinum pads, the top one and the bottom one, are short-circuiting the system. This can be explained by means of morphological defects as explained in section 3. The probability of covering a defect is high considering that the top platinum pad area is of 17.2 mm^2, covering 41% of the KNN film. Tests performed by STMicroelectronics showed a null polarization saturation, the device thus behaved like an ohmic resistor. This apparent problem is due to leakage. Capacitance-voltage measurements also showed unreliable data. Resonant frequency was found to be $\sim$ 8kHz and, due to ohmic behavior, it was possible to measure the displacement only around this frequency. No linearity for the displacement was measured thus confirming the resonant frequency.

3. Asymmetric leakage

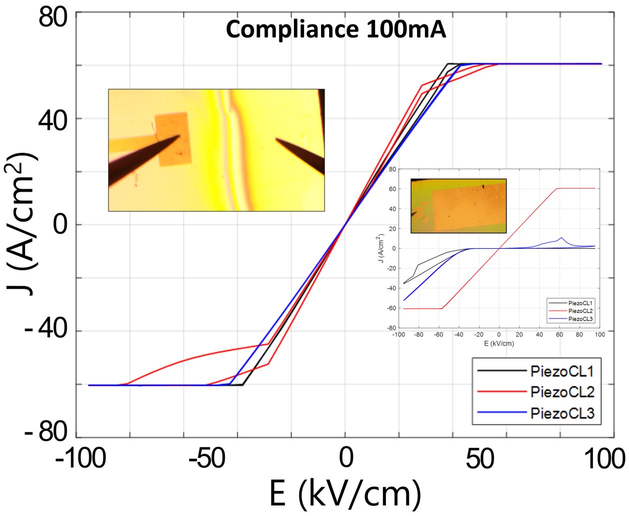
High quality, compact KNN films were electrically probed using different metals (Pt, Ni, Cr, Ti) as top electrode contacts in a top-bottom measurement configuration. The morphology of KNN films and the XRD diffractogram showed a highly texturized KNN(001), still with some defects such as crystal outgrows (fig. 2a). C-AFM (Conductive Atomic Force Microscopy) measurements showed that leakage is concentrated at the border of crystal outgrows (fig. 2c) and, by looking at the cross section of fig. 2b, it is clear that defects have a favourable access to the bottom electrode. This defectivity could also be associated to the ohmic behavior found for the current leakage and the polarization-voltage graphs seen in fabricated cantilevers. Different metal top pads, with a common Pt bottom



(a) Cantilever cross section.

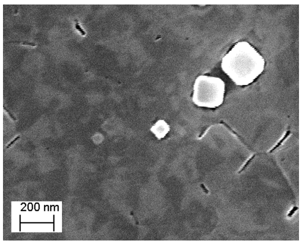


(b) Cantilever design.

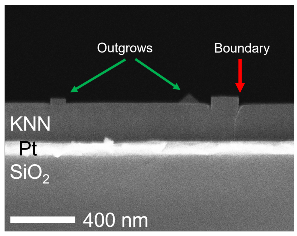


(c) Top-bottom current leakage. The top contact is the biggest one. The inset graph is instead taken using the small top pad.

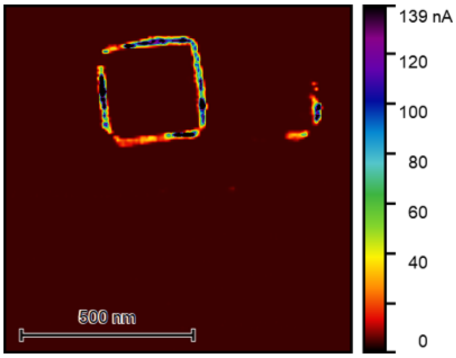
Figure 1: Piezoelectric cantilever characteristics.



(a) SEM image of KNN film. Outgrows as well as ferroelectric domains are visible [4].



(b) SEM picture of cross-section detail.



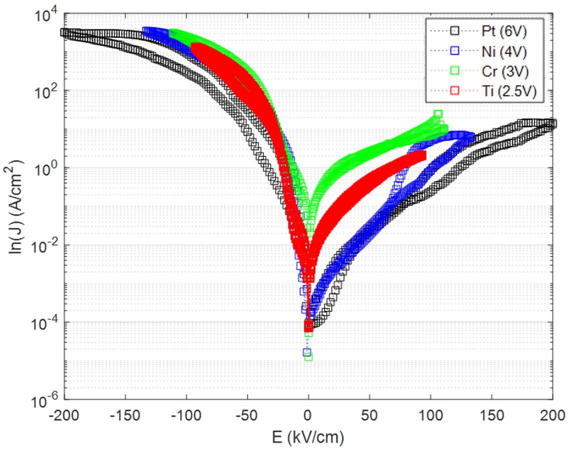
(c) C-AFM current map.

Figure 2: Characterization of the KNN film.

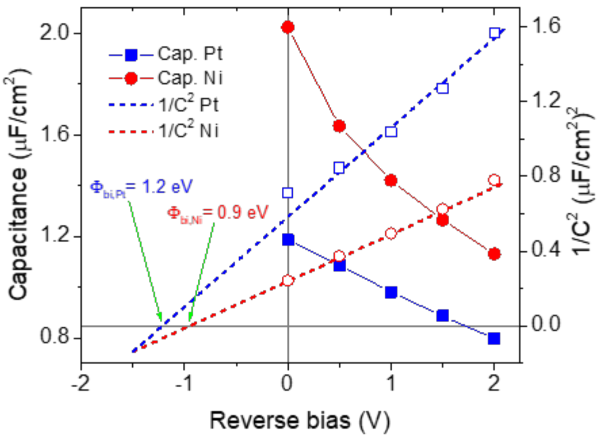
electrode, provide different current leakage and can sustain different applied voltages. In fig. 3a it is possible to observe that Pt and Ni share the best performances in term of low leakage and sustain voltage better with respect to Cr and Ti pads. However, it can also be observed that all the measurements share an asymmetry. This diode-like behaviour has been interpreted considering that at the bottom metal-KNN interface a potential barrier is formed. This has been attributed to the presence of fixed charges, possibly ionized oxygen vacancies, which spawn upon oxygen scavenging from the metals in the MIM stack or due to long processing times. The oxygen vacancies do not only create a barrier, but also are typically considered to be responsible to produce n-doping of KNN [5]. Is then clear that the bottom and the top interface behave in a very different way. Respectively, the bottom interface can be described as a rectifying Schottky junction, and the top interface behaves almost like an ohmic contact. From the Schottky conduction model, the inverse of the square capacitance ($1/C^2$) should show a linear behavior with the applied voltage. From the graph in fig. 3b, it is possible to observe a linear trend, thus confirming the presence of a Schottky junction between the bottom electrode and KNN [6]. On the contrary, for a negative bias there is no limit to current which shows ohmic behavior.

4. Rapid Thermal Processing

Free charges in KNN films are usually associated to oxygen and alkali vacancies, which originate during the deposition phase because of the high temperature of the process. By growing the film at a lower temperature it is possible to limit the formation of defects. However, the drawback is that the energy is not enough to produce the crystallization of KNN into an ordered solid. Thus, after deposition, a thermal treatment is required to promote the crystal-



(a) Mean current leakage for different metal pads.



(b) Schottky capacitance analysis.

Figure 3: Current and capacitance characterization.

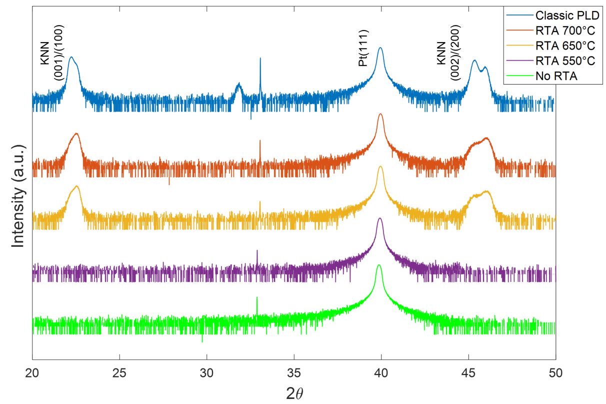
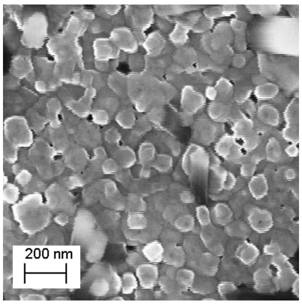


Figure 4: XRD analysis of the samples in function of the annealing temperature.

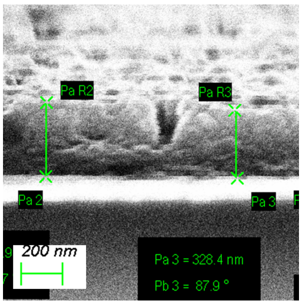
lization of the material. In this work a RTA (Rapid Thermal Annealing) process has been exploited. Temperatures in between 550-700°C were applied for 60s with a ramp of 17°C/s to PLD samples grown at 400°C. XRD measurements of PLD annealed and RTA processed samples are shown in fig. 4. The film annealed at 550°C for 60s did not show signs of crystallization. Thus, 550°C can be considered as a threshold for the crystallization process at 60s. Also, comparing with the diffraction patterns of the classic PLD process (deposition temperature $\sim$ 615°c and oxygen annealing at $\sim$ 500°C for 30min), it is clear that RTA films, rather than having a preferential orientation, show a mixture of (001) and (100) planes. The intensity ratio KNN(001)/KNN(100) was analyzed, giving back a value of 2.5 for the classic PLD approach, and a value of 0.8 for the 700°C RTA crystallized sample. In literature, (001) direction is defined as better orientation due to higher polarization in *c*-direction of pseudo-cubic phase of KNN [4]. From SEM pictures (fig. 5), it is clear that RTA processed films do not show compactness. Also, a smaller thickness of $\sim$ 200 nm was found. The former is a result of the loss of a preferential crystallographic phase and lack of time for densification, while the latter is due to a slower deposition rate due to the lower deposition temperature. The surface presents grains and some of the samples present "cracks" running along the entirety of the film. These issues arose in some samples even before the annealing and elucidation of the causes of loss of working point of PLD is still ongoing work in the group.

4.1. Stoichiometry

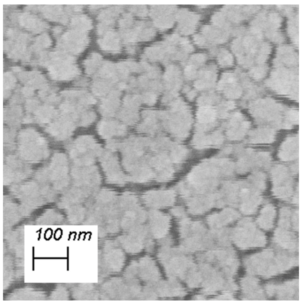
Due to their high volatility, K and Na are usually reported to be more prone to be lost during the deposition process, which is enhanced by high temperatures. As observed in fig. 7a for PLD films grown at different temperatures and with a classical annealing, the loss of alkaline elements is high. Instead, by depositing at a lower temperature the stoichiometry of the film is much more well conserved as alkalis are not lost during the process. Four different rapid annealing temperatures were tested and in all the films the stoichiometry was improved with respect to the films which followed a classic PLD growth. The proximity to the ideal 0.5/0.5 value for K and Na was closer for RTA films. In table 1, mean value of the stoichiometry ratios for films rapid



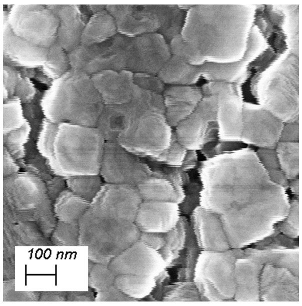
(a) RTA sample before loss of working point of PLD. RTA temperature 700°C.



(b) Crack detail of a sample grown after loss of working point of PLD. RTA temperature 700°C



(c) Pre RTA processed sample after loss of working point of PLD. Cracks are already visible.



(d) Sample RTA processed at 700°C after loss of working point of PLD.

Figure 5: SEM images of RTA processed samples.

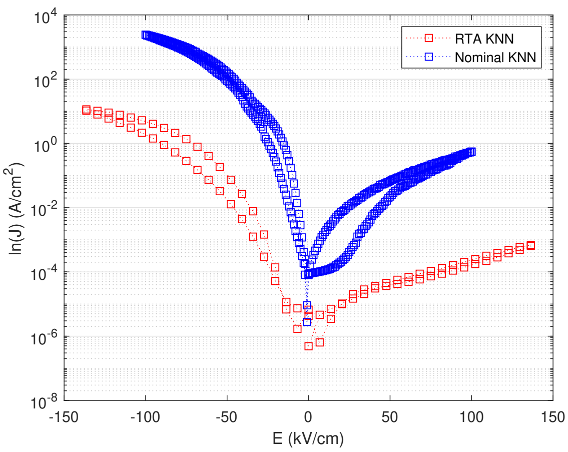


Figure 6: Current leakage comparison between the classic PLD film (blue curve) and the RTA reference sample (red curve).

thermal annealed at different temperatures are calculated. Comparison to the classic deposition process is also included [2]. Thus, RTA seems to be a promising approach to reduce the alkali loss and oxygen vacancy formation in KNN films grown by PLD.

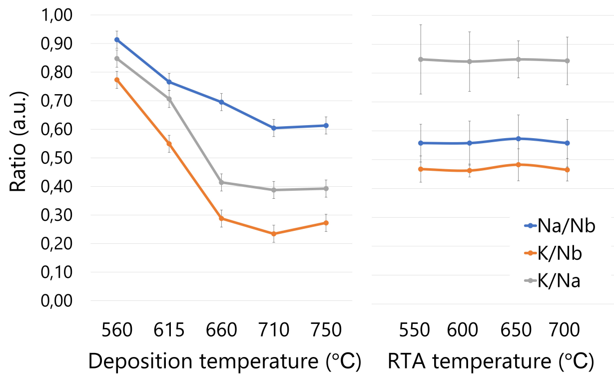


Figure 7: On the left, elemental ratios of films classicaly PLD processed using an overstoichiometric target in function of the deposition temperature and subsequent annealing in oxygen at ∼500°C for 30min. On the right, elemental ratios of films in function of the rapid thermal annealing temperature.

Ratio	Classic PLD growth [2]	RTA	Δ%
Na/Nb	0.45	0.56	+23%
K/Nb	0.41	0.44	+8%
K/Na	0.92	0.84	−9%

Table 1: Stoichiometry ratios comparison between the previous works (classic PLD deposition) and RTA

4.2. Electrical characterization

Ni pads were used as top contacts and top-bottom measurements were performed. Mean leakage values were calculated. The results showed that leakage can be effectively lowered with RTA (fig. 6a). After some initially successful samples some technical problems with the PLD machine arose and cracks on the films were found. Although cracks appeared in subsequent films, they were not a product of the RTA processing. Attempts were made to solve the issues, but it was determined that the PLD system needed an upgrade. Still, the initial experiments pointed out to a leak reduction and a crystallization of KNN in (001) and (100) orientation.

5. Conclusions and future outlook

$K_{0.5}Na_{0.5}NbO_3$ films were grown by pulsed laser deposition technique and different aspects of this piezoelectric material such as crystal structure, morphology, stoichiometry and current leakage were studied. It has been successfully demonstrated that a process to fabricate MEMS structures such as a cantilever by using KNN as an active layer, is feasible in PoliFab. This has been done by exploiting different microelectronic fabrication techniques such as photolithographic processes and metal sputtering. The obtained trampoline structures showed a good morphology, but lacked of proper insulating properties. This, however, seems to be material-dependent only. A further deposition and processing improvement is necessary. Nonetheless, because of this, the processed device was not capable of deforming in an appreciable way due to the high current leakage. However, numerical and simple finite elements simulations performed in this thesis support this stack device design as it can be used as a starting point to characterize and optimize piezoelectric cantilevers that exploit KNN as the active element.

Another part of this thesis was the evaluation of different metals used as top electrodes on KNN/Pt devices. Thanks to a deep electrical characterization, the observed asymmetric behavior can be interpreted by means of the oxygen vacancies created in between the piezoelectric layer and the metals, in particular in the proximity of the metal-KNN interfaces. It was found that oxygen are responsible for a rectifying behavior of the device. Their presence has been linked to the scavenging of the oxygen by the metals, showing varying degrees of oxidation. This is also responsible for free carrier doping. Due to the oxygen vacancies, the KNN is stated to be n-type doped. Thus a barrier is formed at the bottom pad, and it can in fact be depicted as a diode that, when working on reverse bias condition, is limiting the amount of charges moving through the system. On the contrary, the forward bias produces no limit in the leakage current due to ohmic contact. Considering the materials used for the top-contacts, it is evident that Pt has the best performances, but it is rather expensive. Ni pads can then be considered to be a valid substitute since Ni is cheaper and have a similiar behavior to Pt. Future improvement must consider to correct for vacancies as it is crucial to decrease the current leakage properties of the material [7].

Another part of the thesis was aimed at reducing the alkali loss in the KNN films, which has been associated to the increase of free carriers inside the film leading to an increment of the current leakage. The volatility of lightweight elements such as potassium and sodium is enhanced by the high temperature of the PLD process, in particular during the deposition of the material. To improve this aspect, lower temperature deposition has been exploited. To recover the crystal phase a rapid thermal annealing process was employed and was found to be a proper method to allow the KNN become crystalline at a shorter annealing time. A threshold temperature of 550°C for crystalization was found demonstrating that, at least for the considered exposure time, a certain energy is required to create an ordered array of atoms in KNN. The compositional characterization of the films reflected a substantial reduction of alkali loss. Coherently, the current density leaks in RTA films was in fact found to be less than the film deposited with the classic PLD process. Moreover, this new process promoted a mixed (001) and (100) crystal orientation. To research how to improve the film quality of the deposited KNN (even employing different techniques) is a crucial step to be done before attempting application in MEMS. Only after, this possibility to take advantage of this promising lead free piezoelectric can be considered.

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