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Charge phenomena at the Si/$LiNbO_3$ heterointerface after thermal annealing

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ABSTRACT

Polycrystalline lithium niobate ($LiNbO_3$) films were deposited onto Si substrates by radio-frequency magnetron sputtering method in an Ar environment and an Ar + O_2 gas mixture. All as-grown films manifested ferroelectric properties with the remnant polarization of $P_r = 69 \mu C/cm^2$ and the internal field of $E_i = 2.8$ kV/cm. Thermal annealing (TA) of as-grown Si-$LiNbO_3$ heterostructures leads to decrease in the internal field of $LiNbO_3$ films grown in an Ar atmosphere and results in the change of sign of E_i for the films, grown in an Ar + O_2 gas mixture. Analysis of the capacitance-voltage and current voltage characteristics of the studied heterostructures revealed that oxygen vacancies and electron trapping on border traps with energy of about $E_t = 1.7$ eV below the conduction band are responsible for this effect. TA results in decline of conductivity of $LiNbO_3$ films, affected by the phonon scattering of electrons, making these films close to single crystal lithium niobate.

1. Introduction

Thin films of lithium niobate ($LiNbO_3$) are an elemental basis of integrated electronics and optoelectronics due to unique electro-optic, acousto-optic and ferroelectric properties of this material. Several deposition techniques are successfully used to grow $LiNbO_3$ films onto various substrates: liquid phase epitaxy (LPE) [1], chemical vapor deposition (CVD) [2,3], pulsed laser deposition (PLD) [4], sol-gel method [5]. Radio-frequency magnetron sputtering (RFMS) method is among the most effective fabrication techniques for complex oxides such as $LiNbO_3$ while preserving elemental composition [6,7]. However, RFMS is very sensitive to the technological regimes and parameters such as reactive gas pressure and composition, substrate temperature and position, magnetron power [7–9]. As a result, structure, composition and surface morphology of fabricated $LiNbO_3$ films are affected by these parameters greatly. RFMS regimes influence variations in composition, defect concentration and other critical parameters of the $LiNbO_3$ – based heterostructures and these parameters, in turns, affect their electrical properties being a crucial factor in practical application. For example, it was shown in work [10], that thin $LiNbO_3$ films, deposited in an Ar + O_2 environment, manifested lower defect concentration (oxygen vacancies) than films, grown in a pure Ar atmosphere. In the $LiNbO_3$-based heterostructures the charged defects, accumulated at the interfaces (grain boundaries and a film/substrate interface), may create local electric fields, affecting ferroelectric properties of as-grown films [11]. Furthermore, the use of $LiNbO_3$ films in memory units is limited by the presence of traps at the interfaces and associated current leakage. Thermal annealing (TA), being one of the most effective post-deposited treatments of thin films, leads to development of mechanical stress in as-grown films and it triggers their re-crystallization with declining in antisite defect concentration [12]. Nevertheless, it is suggested in [13] that TA of as-grown films in an air atmosphere can increase the trapped charge and the relaxation phenomena. Apparently, the treatment time plays a crucial role in this process. The rapid TA (RTA) which recovers local disorder, induced by the sputtering deposition, does not influence grain size of the films and does not initiate the long range diffusion. However, it is noted in work [14] that such short period of time is not enough for a total recovery and many repeating steps of RTA are recommended. Another critical point is an environment in which the heterostructures are thermally treated. It was revealed in [15], that TA in an oxygen atmosphere is more favorable in terms of reduction of oxygen deficiency. As a matter of fact, it was clearly demonstrated, that TA decreases the positive fixed charge, formed in $LiNbO_3$ films during RFMS process and most definitely, it is attributed to the positively charged oxygen vacancies [15,16]. Moreover, it is stressed in [16–18], that TA causes the formation of the $LiNb_3O_8$ phase along with $LiNbO_3$ in the annealed films. The $LiNb_3O_8$, being a nonferroelectric phase, should influence ferroelectric properties of the post-annealed films. Also, an environment in which TA is performed, affects dielectric properties of deposited films due to the

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difference in a charge compensation mechanism [13]. Another interesting effect is the existence of internal fields in the ferroelectric films, that can be triggered, for example, by the formation of space charge regions near electrodes [19]. The nature of charge phenomena in $LiNbO_3$ films at the substrate-$LiNbO_3$ interface is not clear yet, while they play a crucial role in the functionality of fabricated $LiNbO_3$-based heterostructures and the TA affect them greatly. The present work is focused on studying ferroelectric properties, charge transport and other phenomena at the Si-$LiNbO_3$ heterointerface after TA.

2. Material and methods

Thin films (up to 600 nm) were deposited onto Si substrates at temperature of $T = 550\,^{\circ}C$ by RFMS method at the magnetron power of 100 W. RFMS was performed in two different environments: in a pure Ar atmosphere and in an Ar(60%) + O_2(40%) gas mixture at the gas pressure of 0.15 Pa. Silicon wafers of n-type conductivity ($\rho = 4.5\,\Omega\,cm$) were cleaned by ion etching in an Ar plasma (2 min) before RFMS process. The subsequent annealing of fabricated heterostructures was conducted in an air environment at the temperature of 650 °C for 1 h. The films thickness was controlled in the following way. Along with the studied films, a controlled film was deposited onto a substrate-satellite partially shaded by the glue. After deposition, the glue was dissolved by alcohol, forming a step. The height of the formed step (equaled to the film thickness) was estimated using the atomic force microscopy (AFM; Solver 47). The mechanical properties were studied using the nanoindentation method (NanoHardnessTester; CSM Instruments). Composition of the studied heterostructures was investigated by the Rutherford-backscattering method (RBS, protons with energy of 1.1 MeV). The electrical properties of as-grown heterostructures and heterostructures after TA were studied by current-voltage (I-V) characteristics and high frequency ($f = 10^5$ Hz) capacitance-voltage (C-V) characteristics at the temperature range of 80–300 K. The measurements were carried out with the impedance analyzer "Solartron 1260". The ferroelectric properties of the studied heterostructures were investigated by the Sawyer-Tower method. The top electrical contacts ($S = 10^{-6}$ m^2) were deposited by thermal evaporation and condensation of Al in vacuum ($1{\cdot}10^{-4}$ Pa). The bottom electrical contacts were formed by spreading In/Ga eutectic alloy on the (001)Si substrate, creating the Ohmic contact. As shown in our previous papers [7,16,20,21], in the described above PFMS regimes, c-oriented single phase $LiNbO_3$ films are formed on Si substrates in both an Ar and an Ar + O_2 environment. TA leads to increase of grain size, degree of crystallinity along with formation of the non-ferroelectric $LiNb_3O_8$ phase, which should influence ferroelectric properties of the annealed films. Therefore, the present work is focused mainly on the study of electrical properties of the annealed Si-$LiNbO_3$ heterostructures.

3. Results and discussions

The results of the mechanical characterization (nanoindentation study) of the studied films are given in Fig. 1.

The films deformation demonstrates an elastic-plastic behavior. The hardness of $LiNbO_3$ films, fabricated in an Ar environment is 10.6 ± 0.7 GPa which is higher than those for the films, deposited in an Ar + O_2 gas mixture (9.6 ± 0.9 GPa). TA of the films, synthesized in an Ar environment, results in the decrease of their hardness up to magnitude of 7.2 ± 1.0 GPa. It can be explained by the appearance of tensile stresses in the studied films after TA, but this issue is beyond the scope of our work and requires further investigations. Nevertheless, some researchers have revealed very interesting dependence of nanohardness and Young's modulus on the nanoindentation load. For example, in paper [22] authors explained this dependence in nanocrystalline bismuth ferrite ceramics in terms of elastic recovery and plastic deformation energy concepts. Another research team has studied the nickel manganite powder, sintered at different temperatures and

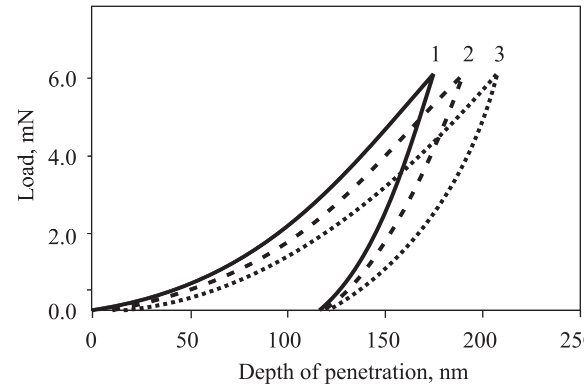

Fig. 1. Nanoindentation load-displacement diagram of the studied films. 1 – the films, synthesized in an Ar environment, 2 – the films, synthesized in an Ar + O_2 gas mixture, 3 – the films, deposited in an Ar atmosphere after TA.

atmospheres: air and oxygen [23]. Authors reported that the highest density was obtained for the sample sintered at 1200 °C in oxygen atmosphere. Furthermore, the theoretical study [24] demonstrated that the some load drops in the *P-h* curve of (0001)AlN thin films are related to the nucleation of amorphous structure, whereas the major load drop is attributed to the dislocation nucleation and expansion.

Fig. 2 shows ferroelectric hysteresis loops of as-grown Si-$LiNbO_3$ heterostructures and heterostructures after TA.

All parameters of P-E loops, derived from Fig. 1 are listed in Table 1.

As seen from Table 1, the presence of O_2 in the reactive gas environment as well as TA of as-grown heterostructures does not influence the remnant polarization of the studied films, which is very close to those for bulk $LiNbO_3$ (71 μC/cm^2) [25], despite the presence of some amount of the $LiNb_3O_8$ phase in the annealed films. The fact that P-E loops of the studied heterostructures after TA manifest a vertical shift can be attributed to the presence of a preferable grain orientation in $LiNbO_3$ films. Indeed, it was demonstrated in our work [26], that TA forms the areas with the preferable ferroelectric grain orientation ("local texture"). Another research group revealed that TA at the temperature of 700 °C (reported as optimal) leads to formation of areas with oriented ferroelectrically active grains ($LiNbO_3$ grains) with the fraction of 70% of the total number of grains ($LiNbO_3$ and $LiNb_3O_8$). Apparently, the presence of this amount of the nonferroelectric $LiNb_3O_8$ phase is not sufficient to affect the remnant polarization of the studied films. Results, given in Table 1 reveal another interesting property of the annealed films. TA of the heterostructures, fabricated by RFMS in an Ar + O_2 environment leads to decrease in the coercive field. Furthermore, TA of the heterostructures, deposited in a pure Ar atmosphere leads to decrease of the existing internal field E_i in as-grown films, whereas the annealing of heterostructures, fabricated in an Ar + O_2 gas mixture results in the change of direction of E_i (reflected in Table 1 via the negative sign). To study the nature of this phenomenon we have applied C-V and I-V analysis.

C-V characteristics of the studied heterostructures are similar to those for MIS structures and shown in Fig. 3

As follows from Fig. 3, TA leads to decline in the effective positive charge, existing in as-grown films, which is reflected as less shifted C-V curves to the left along the horizontal axis, compared to as-grown heterostructures. As it was described in our previous work [20], absence of the segment in the positive bias area of C-V curves after TA is attributed to modulation of the depletion zone in $LiNbO_3$. Apparently, TA influences the high conducting intermediate layer, presented at the Si/$LiNbO_3$ interface in heterostructures, formed in an Ar + O_2 gas mixture [20] and forms an abrupt SiO_2-film heterointerface. Also it is important to note, that C-V curves of heterostructures after TA manifest the hysteresis behavior as shown in Fig. 4.

One of the possible explanations of this hysteresis can be the