
**MAGNETISM
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Effect of the Substrate Temperature and Deposition Rate on the Initial Growth of Thin Lithium Niobate–Tantalate Films Deposited from a Thermal Plasma

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Abstract—Thin lithium niobate–tantalate ($\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$) films are studied at the initial stage of deposition from a thermal plasma. The effect of two deposition parameters (the substrate temperature and the deposition rate) on the film morphology, the film crystallinity, and the density of nuclei growing on a (0001) sapphire substrate are investigated. It is shown that the crystalline structure and roughness of a film are determined, for the most part, in the initial growth stage and therefore depend directly on both parameters. At the optimum temperatures and growth rates for obtaining good characteristics of (0006) texture, crystallinity, and surface roughness of the films, the film nuclei on the substrate have a high density and good epitaxial orientation to it. If the growth conditions are not optimum, the islands are either amorphous or have a low density on the substrate surface. The nucleation activation energy is observed to decrease as the deposition rate increases, which supports the assumption that the species that are active in film deposition are “hot” clusters forming in an oxygen–argon plasma in the immediate vicinity of the substrate.

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1. INTRODUCTION

Thin films of lithium niobate LiNb_xO_3 (LN), lithium tantalate LiTaO_3 (LT), and lithium niobate–tantalate $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ (LNT) with a high degree of crystallinity and texture are of great importance for a number of electro-optic and acoustooptical applications [1–10]. The main advantages of devices based on these films over the single-crystal-based devices currently in use consist in (i) the possibility of using a large difference in the optical indices of a film and the substrate, (ii) the possibility of monolithic integration with widely used microelectronic and optoelectronic components, and (iii) a higher resistance of the films to optical damage [3].

Over the past decade, many researchers have tried to deposit LN, LT, and LNT films onto various substrates using various techniques. They have used magnetron sputtering [11, 12], pulsed laser deposition (PLD) [5, 7, 13–15], various sol-gel techniques [6, 10, 16–19], liquid-phase epitaxy [20, 21], and metal-organic chemical vapor deposition (MOCVD) [1–3]. Researchers have succeeded in depositing films having a root-mean-square surface roughness of 0.5–1.5 nm, an optical loss of less than 2 dB/cm, and a (0006) rocking curve full width at half-maximum (FWHM) of 0.04°–0.07° [2, 3, 7, 11, 16, 18]. However, these properties need to be improved for practical application, which entails

detailed knowledge of the growth mechanisms and the possibility of controlling these mechanisms at all deposition stages.

The electro-optical properties of the materials of the LN family are anisotropic and depend substantially on the presence and character of structural defects in their films. Therefore, it is very important to grow epitaxial films with a controlled orientation and lattice perfection. Since the materials under study have the same (trigonal) structure as that of sapphire ($\alpha\text{-Al}_2\text{O}_3$) and since the latter has a lower refraction index, it is convenient to use sapphire as a substrate to grow heteroepitaxial LN, LT, and LNT films for optical and optoelectronic purposes [1, 3, 7, 9, 13–15, 17–19]. However, the difference in the crystallographic parameters is rather significant (about 8% in the (0001) plane for LN and $\alpha\text{-Al}_2\text{O}_3$ [1, 14]); therefore, it is a challenge to deposit films with a high degree of crystallinity and perfection on (0001) sapphire substrates [1, 3, 4, 22–24]. This problem requires comprehensive study of the mechanisms of film formation and growth in order to find ways to optimize and improve the deposition processes.

The initial stage of LN film formation and growth has been investigated only in a few works [3, 13, 14]. The films were mainly deposited by MOCVD [3] and PLD [13, 14] and were mainly examined by atomic-force microscopy (AFM) [3, 13] and transmission elec-

Basic parameters of film deposition onto a (0001) α - Al_2O_3 substrate

Metal ratio (Li : Nb : Ta) in the initial solution	Plasma power, kW	Pressure, Torr	Deposition rate, nm/min	Substrate temperature, °C	Deposition time, s
2 : 1 : 1	46.2	150	20–500	580–800	0.3–600

tron microscopy (TEM) [14]. In this work, we study the nucleation of thin $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (LNT) films deposited from a thermal plasma at deposition rates one to two orders of magnitude higher than those used in other techniques of depositing LN films from a gas phase [22, 23, 25, 26]. The results obtained with scanning electron microscopy (SEM) are compared with earlier x-ray diffraction data.

2. EXPERIMENTAL

The thin LNT films studied at different deposition stages were deposited from a thermal plasma (see [4, 22, 23, 25, 26] for details). An advantage of this technique is the high deposition rate. The initial products were solutions of lithium–niobium and lithium–tantalum alkoxides in trimethylbutylacetate (Kojundo, Japan) [22, 23, 25, 26]. The metal concentration in these two initial solutions was 3 wt % when recalculated for LiNbO_3 or LiTaO_3 . The solutions were mixed to form a solution with a metal ratio Li : Nb : Ta = 2 : 1 : 1. The main deposition parameters are presented in the table. The data on the gas composition of the oxygen–argon plasmas can be found in [22, 23]. For substrates, we used $10 \times 10 \times 0.5$ mm (0001)-oriented single-crystal sapphire (α - Al_2O_3) plates polished mechanochemically (Earth Chemical, Japan). The substrate surface morphology as visualized by AFM and SEM is shown in Fig. 1. Before deposition, the substrates were cleaned in acetone and ethanol (in an ultrasonic bath).

The LNT nucleation on a sapphire surface was studied with a Hitachi S-5000 scanning electron microscope. The degree of crystallinity of the films (having a thickness of 170–200 nm) was determined with an x-ray diffractometer. For comparison, the surfaces of some samples were scanned with a Nanoscope IIIa atomic-force microscope (Digital Instruments, United States). To investigate the microstructure of LNT islands and their epitaxial relation to substrates, we used a Hitachi 9000 NAR transmission electron microscope. The preparation of the samples to be examined along the direction normal to the substrate surface was described in [4].

To minimize the surface diffusion of LNT particles, the plasma in the reactor and substrate heating were switched off immediately after deposition. This issue is especially important in investigating film nucleation (over a period of time as short as a fraction of a second). The deposition time was estimated with a digital video camera having a resolution of 1/30 s.

From previous studies, it is known that, in order to obtain LNT films having the highest crystalline quality and the highest orientation on (0001) sapphire through deposition from a thermal plasma, the deposition temperature and the deposition rate should be 600–700°C and 260–420 nm/min, respectively [22, 23]. In this work, these parameters were varied over wider limits to reveal the complete picture of their effect on the nucleation and initial growth of a film.

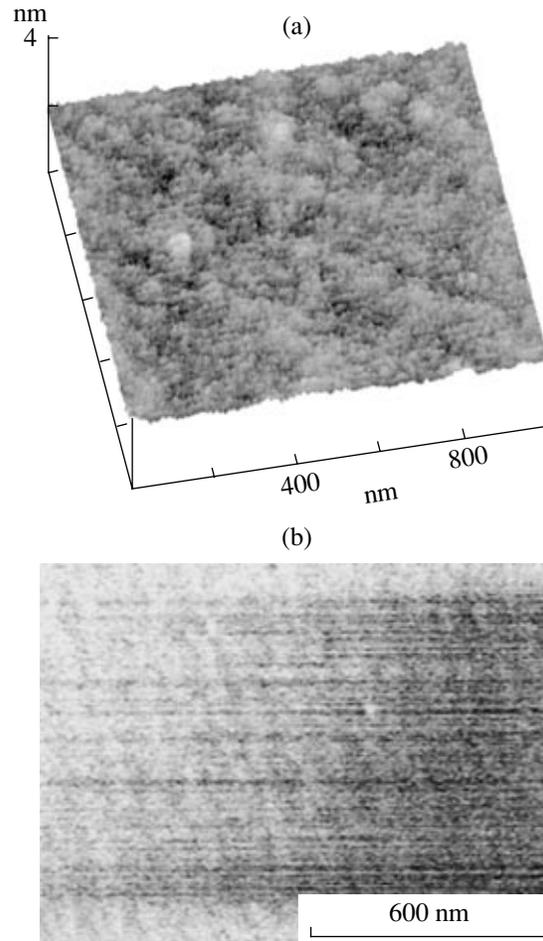


Fig. 1. Surface morphology of the (0001) sapphire used in this work: (a) AFM image and (b) SEM image.

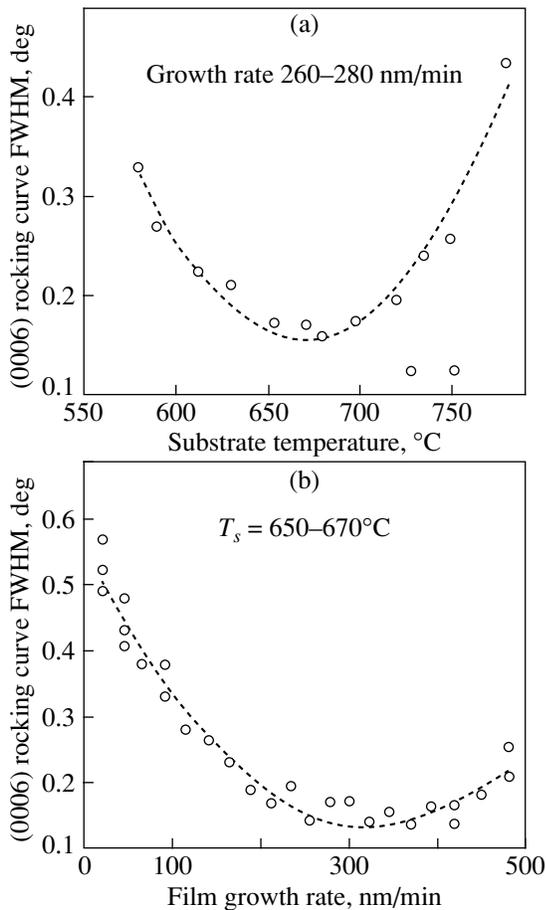


Fig. 2. Dependences of the full width at half-maximum (FWHM) of the (0006) x-ray diffraction line of LNT films on (a) the deposition temperature and (b) the growth rate. The film thickness is 170–200 nm. The dashed lines are given to guide the eye. (a) The average deposition temperature was maintained to within $\pm 10^\circ\text{C}$, and the growth rate was maintained in the range 260–280 nm/min. (b) The substrate temperature was maintained in the range 650–670°C.

3. RESULTS AND DISCUSSION

3.1. Effect of the Substrate Temperature

The (0006) rocking curve FWHM is generally accepted as a good indicator of the degree of crystallinity and perfection of LN films with a (0006) texture [1–3, 18]. This parameter can be used to estimate both the quality and misorientation of grains. The (0006) rocking curve FWHM is smaller for films having a small crystallite misorientation angle and a small amount of defects. There are LN films for which such a parameter was reported to be $\sim 0.04^\circ$ – 0.07° [3, 7, 16, 18], which is rather close to the values of this parameter for the sapphire substrates used for film deposition. The minimum value of this parameter obtained for 200-nm-thick LNT films deposited onto (0001) sapphire from a thermal plasma is $\sim 0.12^\circ$ [22], which is partly compensated by significantly higher film growth rates as compared to

the growth rates used in other growth techniques from a gas phase [22, 23].

Figure 2a shows the effect of the substrate temperature T_s on the (0006) rocking curve FWHM of LNT films deposited at a growth rate of 260–280 nm/min for ~ 42 s. The degree of crystallinity of the films is seen to be the highest at 650–700°C; the film quality decreases at lower and higher substrate temperatures. A similar effect is also observed for deposition rates varied at a fixed substrate temperature; in Fig. 2b, we can see a pronounced range of optimum film growth rates.

Figure 3 shows micrographs taken from the surfaces of samples on which films were deposited at a constant growth rate (260–280 nm/min) for 0.3 s at various substrate temperatures. Due to different electron scattering, LNT islands are visible as bright contrast regions against the background of a dark sapphire field. It is clearly visible that the number of nuclei formed at $T_s = 580^\circ\text{C}$ (Fig. 3a) is significantly larger than that in the other samples. However, the majority of nuclei in Fig. 3a are near-hemispherical islands, which consist (as indicated by TEM analysis) of an amorphous phase with extremely small LNT crystalline inclusions. According to TEM, the triangular nuclei (small in number) in Fig. 3a exhibit epitaxial relation to the substrate and still have a certain amount of an amorphous phase. As the temperature increases, the nuclei increase in size (Figs. 3b, 3c), their density decreases, and their crystallinity and the epitaxial relation to the substrate improve. However, only the sample in Fig. 3c features the absence of an amorphous phase and a high degree of island orientation. Virtually all islands in Fig. 3c are triangular pyramids whose bases are oriented along the $\langle 11\bar{2}0 \rangle$ substrate axes (as is revealed by TEM). This fact agrees well with the results from [14], where discrete LN films deposited onto (0001) sapphire using the PLD technique were observed. It is natural to assume that LNT films grown under deposition conditions similar to those for the film shown in Fig. 3c should have a good (0006) orientation and a high crystallinity, which is supported by Fig. 2a and the results from [22].

The fact that the nuclei increase in size and the nucleus crystallinity improves as the substrate temperature increases can be explained by an increase in the particle mobility on the $\alpha\text{-Al}_2\text{O}_3$ surface and agrees with the behavior of LN nuclei fabricated by metal-organic deposition [3]. However, as is seen from Fig. 3d, a further increase in the substrate temperature leads to the gradual disappearance of triangular pyramids as the dominating island shape and to intense coalescence at the early stage (within 0.3 s). The asymmetric clusters in Fig. 3d can have no (0006) texture, which is inherent in the pyramids, and the dramatically decreased island density on the substrate surface inevitably increases the film roughness. This behavior, as well as the degradation of the (0006) texture, was observed in 200-nm-thick films deposited at elevated temperatures [22].

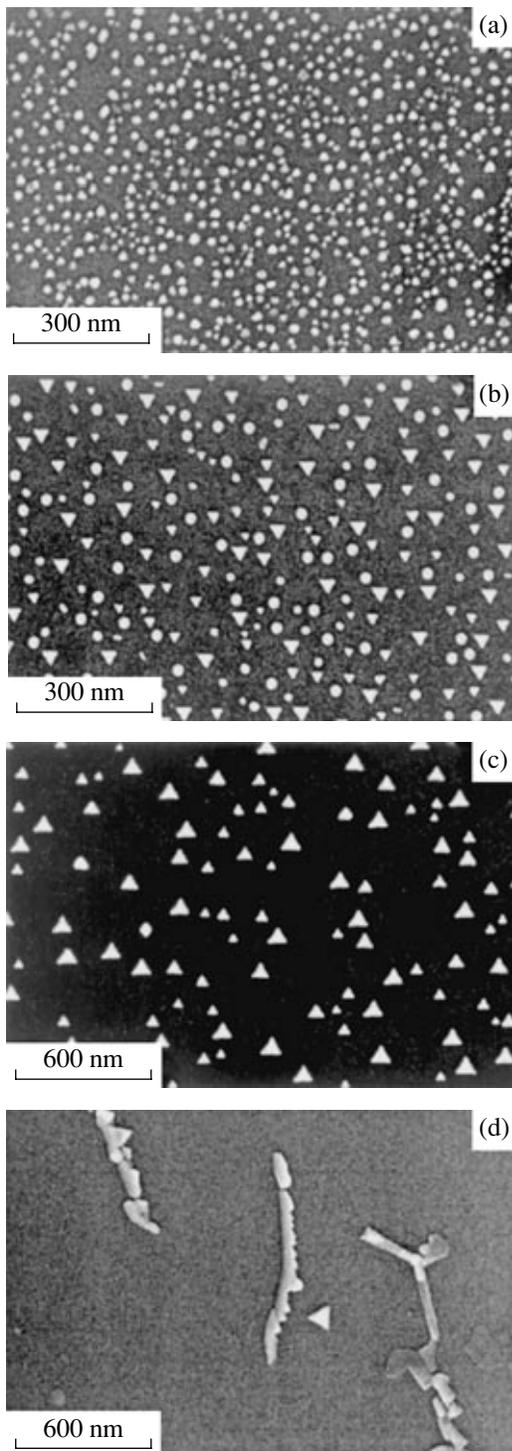


Fig. 3. Effect of the substrate temperature on the formation and growth of lithium niobate–tantalate islands at the initial stage (after deposition for 0.3 s). The nominal film growth rate is 260–280 nm/min. T_s = (a) 580, (b) 630, (c) 700, and (d) 800°C.

Figure 4 shows micrographs for the surfaces of two samples obtained under different deposition conditions. The samples are seen to correspond to the early stage of

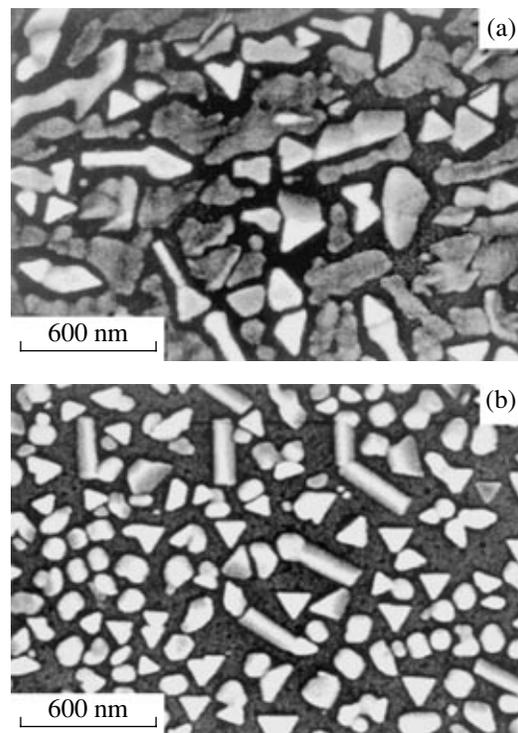


Fig. 4. Film morphology before the complete coalescence of islands. (a) The substrate temperature is 700°C, the deposition time is 2.0 s, and the nominal deposition rate is 260–280 nm/min; (b) the substrate temperature is 680°C, the deposition time is 2.5 s, and the nominal growth rate is 360–380 nm/min.

island coalescence before the entire surface is covered by a film. Both samples contain coalescing pyramidal islands, with the bases of some pyramids being oriented along the $\langle 11\bar{2}0 \rangle$ sapphire axes. In Fig. 4a, however, the triangular pyramids are smaller in number and the discrete LNT film covers a larger area of the $\alpha\text{-Al}_2\text{O}_3$ substrate. Such a film (consisting of plateaulike clusters) appears as a result of the coalescence of pyramids, as was reported for PLD-deposited LN films in [14]. Usually, such plateaus are restricted along their perimeters by inclined surfaces that do not have a well-defined crystallographic orientation [14]. During coalescence, the pyramid vertices and faces disappear and surfaces parallel to the substrate arise in their place. This process is due to surface atom migration to the sites of coalescence of pyramidal islands, which decreases the surface energy of the system [14].

Apart from triangular pyramidal islands and plateaus, Fig. 4 also contains oblong islands oriented at an angle of 120° to each other, which supports the conclusion regarding the epitaxial relation to the substrate. The authors of [3] likewise observed the formation of oblong LN islands on (0001) sapphire at a substrate temperature of 650°C despite the fact that the film growth rate during MOCVD is about 1–5 nm/min

(which is almost two orders of magnitude lower than the growth rate in our work). It was assumed in [3] that the formation of such islands was caused by stresses at the film–substrate interface. Since oblong islands have epitaxial orientation, Fig. 4b suggests that they are likely to form as a result of the joint coalescence of neighboring pyramidal islands.

Our results indicate that the temperature dependence of LNT film growth from a thermal plasma resembles, in outline, film growth during MOCVD [1, 3]. The rather large difference between the lattice parameters of LNT films and $\alpha\text{-Al}_2\text{O}_3$ induces stresses in the growing film and hinders its two-dimensional layer-by-layer growth. As a result, the film has to grow through the formation of three-dimensional islands on the substrate [3, 14] or through the formation of a thin “wetting” layer on which three-dimensional islands then grow [13]. Our results give no indication of wetting-layer formation. So, the growing island grains do not coalesce coherently, since they have many defects (including dislocations) and since the film–substrate interface is incoherent (which usually occurs when the difference between the crystallographic parameters is more than 5%). Thus, the growing islands coalesce to form grains and grain boundaries. In turn, the presence of grain boundaries causes pores and intergrain valleys to appear on the surface, which is directly related to the surface roughness [3].

At a rather low temperature (like that to which Fig. 3a corresponds), the growing isolated grains coalesce slowly, since the vertical growth rate is higher than that in the horizontal plane because of the low mobility of particles on the surface. This factor results in a high grain height-to-diameter ratio. Such grains usually have a weak epitaxial relation to the substrate due to their low freedom of rotation and low mobility of particles and give high surface roughness upon coalescence [22]. At a higher temperature, isolated grains coalesce before they become high. Moreover, the intra- and interplanar ordering of grains increases and their epitaxial relation to the substrate also increases due to a higher particle mobility on the grain surfaces and inside the grains (Figs. 3b, 3c). As a result, the crystalline quality of the films increases (Fig. 2a) and the surface roughness decreases [22].

It was shown experimentally in [3, 22] that, as the substrate temperature increases further, the film surface roughness increases, even though the crystalline quality of the films can still improve. In any case, beginning from a certain temperature, the crystalline quality of films deposited from a gas phase deteriorates [1, 3, 22]. This phenomenon has been explained by several factors mainly dependent on the specific features of the deposition technique used [1, 3, 22]. For example, for LN films grown from a gas phase by MOCVD, the authors of [1, 3] assumed that coarse particles form when metal-organic molecules collide with each other over a substrate at a high temperature. To explain the

decreased crystalline quality of LNT films at $T_s > 700^\circ\text{C}$ (Fig. 2a), an approach was proposed in [22, 23] based on an anisotropic surface free energy. It was assumed that, at a rather high temperature, the particles on the surface of a growing film acquire a mobility that is sufficient to form grains with the minimum surface free energy [2, 22, 23, 25]. In the case of films of LN-like compounds, such grains have a $(01\bar{1}2)$ texture [2]. Since the (0006) texture is partly lost, the films also lose their crystalline order [22, 23, 25]. On the other hand, the grain size increases with temperature and inevitably causes the surface roughness to increase, since the coalescence of coarse grains causes deep intergrain valleys on the surface (as was shown by AFM) [22]. These conclusions are corroborated experimentally (Fig. 3d). It is clearly visible in Fig. 3d that, as the temperature increases, the islands are rearranged, due to the high particle mobility, into grains with an orientation other than (0006) and that the very low nucleus density inevitably causes a high surface roughness.

Thus, the high crystallinity of LNT films exists in a temperature range below which many amorphous layers and grain boundaries form as a result of slow diffusion and the low mobility of particles and above which many grains lose the (0006) orientation because the particle mobility is too high (which leads to a significant decrease in the film quality). In the initial deposition stage outside the range of optimum temperatures, we observe either amorphous islands or coarse LNT agglomerates with a very low density of growing grains on the substrate surface. As was shown in [22], the temperature dependence of the surface roughness of LNT films deposited from a thermal plasma is similar to that shown in Fig. 2a. Based on this consideration and the facts given above, we conclude that the low surface roughness of LNT films is likewise limited by the low mobility of deposited particles at a rather low substrate temperature and by a decreased nucleus density and an increased grain size at a high substrate temperature.

3.2. Effect of the Growth Rate

Figure 5 shows the micrographs of the surfaces of samples on which films were deposited at various growth rates at the same substrate temperature (670°C). The deposition time was 0.3 s. The density and morphology of island nuclei are seen to be dependent on both the temperature and the amount of the initial material supplied to the plasma. As was shown in [22], the state of the substrate surface also affects the nucleation and growth of LNT films deposited from a thermal plasma.

It should be noted that a substrate temperature of 670°C falls in the range of optimum temperatures for the deposition of high-quality LNT films ($650\text{--}700^\circ\text{C}$) [22, 23]. However, as follows from Figs. 5a and 5b, the LNT islands deposited at growth rates below the opti-

mum values have a domelike shape and are mainly amorphous (according to TEM data).

As is seen from Figs. 5a and 5b, a twofold increase in the metal concentration in the plasma causes a slight increase in the number of nuclei, the average nucleus size, and the degree of crystallinity and improves the epitaxial relation to the substrate. A further twofold increase in the film growth rate (Fig. 5c) likewise produces an increase in the island size and crystalline quality and further improves the epitaxial relation to the substrate. At a deposition rate of 360–380 nm/min (Fig. 5c), the pyramidal islands have a rather high density and a good epitaxial orientation. The films grown under these conditions have the highest crystalline quality (Fig. 2b). Note that the improvement of both the epitaxy and crystalline quality of LNT nuclei with increasing deposition rate was observed in this study for the first time, although improvement of the quality of LN and LNT films with increasing deposition rate was reported earlier in [2, 3, 22, 23].

This phenomenon can be explained assuming that the deposited species in our case are “hot” clusters forming in the immediate vicinity of the substrate because of a high temperature gradient, just as is the case with the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ films via the introduction of oxide powders into a thermal plasma [27]. As the metal concentration in the oxygen plasma increases, the average size of oxide clusters reaching the substrate surface should increase. Larger clusters have a higher kinetic energy, which results in a high mobility of such particles on the surface. Thus, at a constant substrate temperature, we can increase the particle mobility and the degree of crystallinity of deposited films by changing the amount of the initial material introduced into a plasma.

The result of the increase in the mobility of deposited particles with an increase in the film growth rate is also seen in Fig. 4. Although the amount of the material deposited onto the substrate in Fig. 4b is greater than that deposited onto the substrate in Fig. 4a, the surface of the former substrate is covered by LNT islands to a lesser extent. Thus, the mobility of deposited particles on the substrate in Fig. 4b is higher, even though the deposition temperature in the case of Fig. 4a was somewhat higher.

As is seen from Fig. 5d, a further increase in the deposition rate to 450–500 nm/min not only increases the average nucleus size but also favors the appearance of a larger number of amorphous islands (as compared to Fig. 5c). As follows from Fig. 2b, the crystalline quality of the films grown at such high deposition rates deteriorates. It is still unclear what causes the appearance of a large number of amorphous nuclei at deposition rates of 450–500 nm/min. One possible relevant factor could be somewhat worse plasma control when such a large amount of the initial metal-organic material is introduced into a plasma.

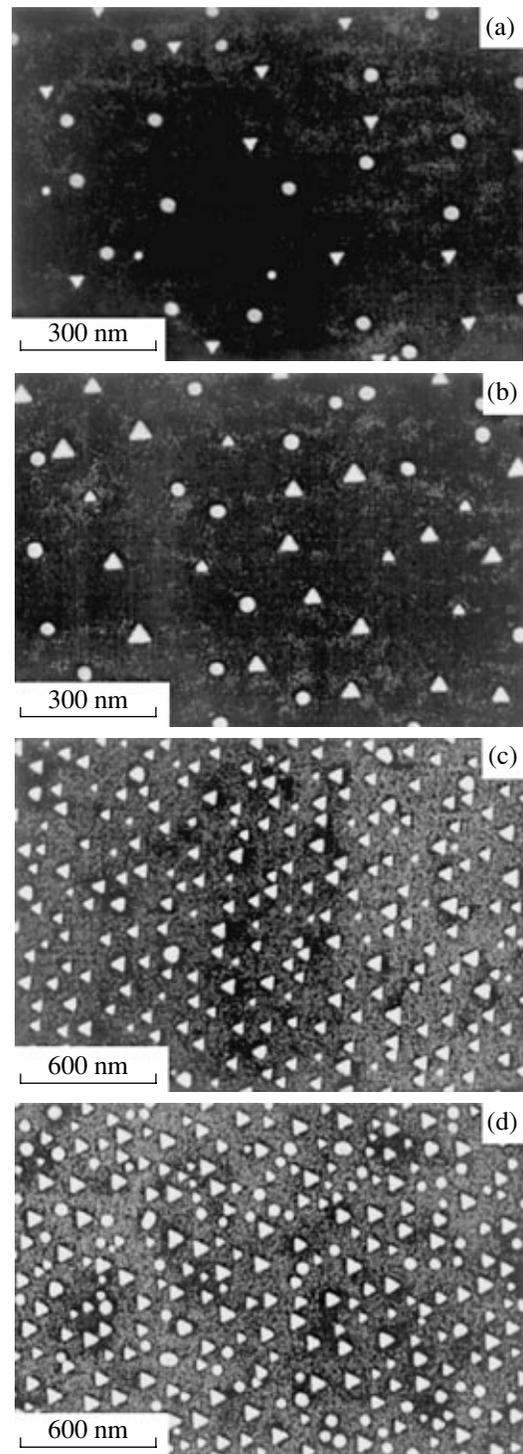


Fig. 5. Effect of the film growth rate on the nucleation of lithium niobate–tantalate films on (0001) sapphire. The micrographs were taken from samples deposited at 670°C for 0.3 s. The nominal film growth rate is (a) 90–100, (b) 180–190, (c) 360–380, and (d) 450–500 nm/min.

Thus, our results indicate that a high grain nucleus density, high crystalline quality of grains, and good epitaxial relation of the grains to the substrate are factors

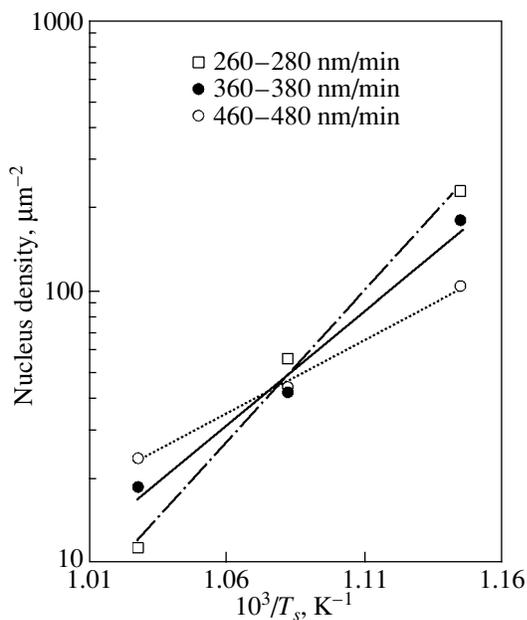


Fig. 6. Dependence of the nucleus density on the reciprocal substrate temperature (plotted on a semilogarithmic scale) at different LNT film deposition rates. The slopes of the curves give the nucleation activation energies.

that are necessary for growing films with high crystallinity, well-defined (0006) texture, and a low surface roughness. These properties are largely determined at the very initial stage of film deposition, namely, at the stage of growth-center formation on a substrate.

These conclusions agree well with the results of our previous work [22], in which LNT films were grown on annealed (0001) sapphire substrates having atomically smooth surfaces. Since such surfaces contain a small amount of defects (which are the most probable nucleation centers for LNT nuclei deposited from a plasma), the crystalline quality and orientation of the films grown on these substrates are much lower (as was shown in [22]).

3.3. Activation Energy

The processes of thin-film nucleation and growth have been extensively studied and mathematically described only for physical vapor deposition (PVD) of metals [28, 29]. The models used describe individual atoms that are adsorbed by a substrate from a gas phase and then migrate along the surface to form nucleation centers. In the case of chemical vapor deposition (CVD) from a thermal plasma, LNT nuclei form from clusters of various sizes, which migrate along the surface, are bombarded by ions and other clusters, and evaporate. Thus, the nucleation and growth kinetics depend not only on surface atom migration but also on chemical processes in the plasma, especially on the chemical processes occurring in the immediate vicinity of the substrate. However, as is seen from Fig. 6, the

formation of LNT nuclei from a thermal plasma can generally be described by the classical equation of nucleation from a gas phase.

Figure 6 shows the dependence of the LNT island density on the reciprocal substrate temperature ($1000/T_s$) at three film growth rates. It is seen that, as the substrate temperature increases, the nucleus density on the sapphire surface decreases exponentially. This tendency can be described well by the equation $N^* = N_0 \exp\{E_a/kT_s\}$, where N^* is the nucleus density, N_0 is the maximum density, E_a is the nucleation activation energy, and k is the Boltzmann constant. Using the slopes of the straight lines in Fig. 6, we can determine the nucleation energy. For the straight lines in Fig. 6, which correspond to deposition rates of 260–280, 360–380, and 450–500 nm/min, we obtain $E_a = 3.57 \times 10^{-19}$, 2.68×10^{-19} , and 1.74×10^{-19} J, respectively. It is interesting that the activation energy of the LN films grown by metal-organic CVD in [3] is equal to 2.57×10^{-19} J, which is very close to our value calculated for a deposition rate of 360–380 nm/min. Thus, the mechanisms of film growth on sapphire have many features that are common for MOCVD and thermal-plasma deposition despite many technical differences in these techniques and the large difference (of almost two orders of magnitude) in the deposition rates [1, 3, 22, 23].

The decrease in the activation energy for nucleation from a thermal plasma as the film growth rate increases can also be explained by cluster deposition. As follows from the values of E_a , an increase in the growth rate is accompanied by a change in the properties of deposited particles. It is obvious that, as the metal atomic concentration in a plasma increases, the cluster size increases. It is expected that larger clusters have a higher energy and, thus, need a lower energy to form stable nuclei on a sapphire surface.

4. CONCLUSIONS

Lithium niobate–tantalate films deposited from a thermal plasma onto (0001) sapphire have been shown to obey a three-dimensional growth model, just as films deposited from a gas phase using other techniques. A study of the early stage of $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ nucleation (prior to the coalescence of island nuclei) has allowed us to reveal the two main factors determining the crystalline quality and orientation of the films.

At low substrate temperatures and low deposition rates, LNT domelike amorphous islands form. The films deposited under these conditions have a low degree of crystallinity due to a high fraction of the amorphous phase. As the substrate temperature and/or the deposition rate increases, islands grow in the form of triangular pyramids having $\{11\bar{2}0\}$ faces, which resemble earlier described islands forming under pulsed laser deposition. Then (at the coalescence stage), the surface migration of deposited particles

leads to the disappearance of the pyramidal faces and the formation of plateaus. At a temperature above the optimum value, the nucleus density on a substrate decreases significantly, which results in degradation of both the film texture and crystalline quality.

The effect of an increase in the deposition rate on the nucleation and characteristics of a film has been shown to be in many respects similar to that of an increase in the substrate temperature. This effect has been assumed to be related to an increase in the size of the clusters deposited from a plasma.

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