Patterned LiNbO₃ thin film fabrication basing aqueous precursor and the study on pattern quality and film morphology

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Abstract

Patterned LiNbO₃ thin films basing aqueous precursor are fabricated in photolithography and laser-induced crystallization ways. The effects of LN gel solubility, laser scanning parameters and substrate temperature on the pattern quality of LN film are demonstrated. We emphasize the importance of the temperature gradient at the crystallization front to the pattern quality for laser-induced crystallization. Moreover, the distinct morphology features (porous and compact) of patterned LN films fabricated in the two ways are shown and explained by their difference of crystallization modes. These two fabrication ways are suggested for the integrated-optical and biomedical applications, respectively.

Keywords: optical materials; thin films; laser processing; microstructure

1. Introduction

Lithium niobate (LN) is one of the most popular materials for integrated optics, due to its remarkable ferroelectric, piezoelectric and nonlinear optical properties. In particular, LN thin films are favorable in many photonic applications: LN thin film, fabricated on semiconductor such as silicon, can be used as waveguide or frequency converter, becoming the key part of silicon-base integrated optical devices [1]. At the mean time, LN thin film is also considered as a promising material in biomedical field: the photocatalytic activity of LN thin film can be utilized in Lab-on-chip for unraveling the biological complexity in population through degradation of the cells [2]. However, for both photonic and biomedical applications, well-patterned LN thin film is particularly critical because of the requirement of compact structure in future devices.

In the past few years, few groups demonstrated the fabrication of patterned LN thin film. Hirano et al. firstly made a systematic investigation on this issue and they presented a creative method for preparing patterned LN thin film by using a ethoxides-based precursor containing UV sensitive 1-phenyl-1,3-butanedione (PBD) [3-6]. However, alkoxides---the necessary starting materials for this route are expensive and easily hydrolysable, which makes the fabrication of the patterned LN thin film inconvenient. Recently, Komatsu and his colleagues carefully studied YAG-laser-induced crystallization of LN crystals lines at the surface of a series of doped LN silicate glass in the reference [7-10], where the orientation of LN crystals lines could be obtained easily showing the incredible superiority of this method. Unfortunately, this successful method is only for glass system, and it is not valid if other substrate such as silicon is required. Definitely, an inexpensive and flexible method is necessary for the fabrication of patterned LN thin film. Recently, Xue and Liu et al. [11-13] made an overall study on the preparation of LN precursor and a couple of convenient aqueous routes were introduced

by them. Basing on aqueous precursor routes, well-patterned LN thin film is expected to be fabricated in satisfying ways.

In this paper, basing on an aqueous precursor route, two different ways were tried for the fabrication of the patterned LN thin film: photolithography and laser-induced crystallization ways. We will demonstrate the effects of several experimental parameters on the pattern quality of LN film. The importance of the temperature gradient at the crystallization front to the pattern quality will be emphasized, and the distinct morphology features of patterned LN films fabricated in two ways will be shown and explained.

2. Experimental procedures

Niobic acid, oxalic acid, citric acid, lithium hydroxide and ammonium hydroxide were used as starting materials without further purification. Niobic acid was firstly dissolved in oxalic acid aqueous solution, in the molar ratio of $[\text{Nb}^{5+}]:[\text{oxalic acid}] = 1:3$ at 80°C for 0.5h, forming a transparent solution. Aqueous solution of ammonia was dropped into the solution till the white precipitation completely separates out. The precipitation was filtered thoroughly and washed with distilled water and then dissolved in citric acid solution, in the molar ratio of $[\text{Nb}^{5+}]:[\text{citric acid}] = 1:3$. LiOH followed to be added into the mixed solution with a molar ratio of $[\text{Li}^+]:[\text{Nb}^{5+}] = 1:1$. The transparent precursor solution usually was obtained after several-hour stirring and then dried at 80°C for agitation. The as-prepared LN gel was coated on Si substrate by spin-coating and the obtained LN gel film can be pre-heated (30 min) for solubility tuning or just be kept ready for patterning.

Two methods were tried to fabricate the patterned LN thin film: photolithography and laser-induced crystallization. In the photolithography route (see Fig. 1(b)), the positive photoresist was firstly coated covering the LN gel film. Then it underwent the selective exposure but no mask was used in this procedure: the selective exposure was realized by direct laser beam writing. The basic experimental setup for beam writing is shown in Fig. 1(a), where laser beam (405nm) was focused onto sample with the two-dimensional motorized stages controlling its movement. During development, the irradiated part of photoresist was firstly dissolved, leading to the local LN gel film (covered by this part of photoresist) exposed in the dissolving agent. In this way, LN gel film could be removed selectively, depending on LN gel solubility. Finally, we anneal the sample at 550°C (in the furnace) for 2h in order to get rid of photoresist and make the patterned LN gel film crystallized.

Fig. 1(c) shows the procedures for laser-induced crystallization method, in which no photoresist was used at all and the selective removing of the LN gel film was realized by direct laser beam writing. It should be noticed that the laser used here is high-power (Max 1.5W) laser with the wavelength of 445nm. Moreover, a substrate heater was used for changing the temperature of Si substrate, as shown in Fig. 1(a). In this method, high-power focused laser irradiation will directly induce the crystallization of the local LN gel and change the solubility there. Thus, pattern could be easily created after dissolving procedure. At last, similar annealing step was carried out for enhancing the crystallization of LN film.

The thermal properties of the LN precursor sol were studied using differential scanning calorimeter (DSC). The LN thin film was characterized by using X-ray diffraction (XRD, Philips Xpert) with 2θ range of $20-60^\circ$ and Micro-Raman microscopy with spatial resolution of 0.5 μm . Optical microscope (Olympus STM6) and scanning electron microscopy (SEM, JSM-IT300, S-4800 and NanoSEM450) were used for the morphology acquisition of the patterned LN thin film.

3. Result and Discussion

The XRD patterns of LN powders, LN thin films with thickness 175nm and 350nm are shown in Fig. 2(a). Since the LN powders were prepared through the same aqueous route as the LN film was, they can be treated as the reference sample of LN films. All the XRD peaks of LN powders can unambiguously be assigned to LiNbO_3 crystalline phase, in excellent agreement with a reference pattern of LN (JCPDS No. 20-0631). The patterns of LiNbO_3 film shown in Fig. 2(a) are apparently different from that of LN powders. Two sharp peaks exist in the pattern and their intensities increase with the increase of film thickness, indicating highly preferred orientation of the LN film. Fig. 2(b) shows Raman spectra of Si substrate, LN thin films with thickness 175nm and 350nm in the range of $100\text{-}250\text{cm}^{-1}$. The Raman peaks at 125, 152, 236 cm^{-1} , which becomes much more obvious for the thick LN film, reinforce the existence of the orientation-preferred LN film crystallization on Si substrate.

As mentioned in experimental procedures, in photolithography way the selective removing of LN gel film highly depends on its solubility. In other words, LN gel solubility, which is usually tuned by pre-heating, may have an effect on the pattern quality. Figure 3 shows the morphology of patterned LN film with different solubility tuning, for which varied temperatures were selected for pre-heating. It can be seen from Fig. 3(a), where no pre-heating was performed, that the LN gel film covered by the photoresist film is totally destroyed because of its huge solubility in agent. In Fig. 2(c), two endothermic peaks can be found below 200°C , and they are most likely due to the release of solubilizer such as water vapor and organic matter from gel. Therefore, through the pre-heating over 200°C , the solubility of LN gel film can be significantly reduced into a proper range. Fig. 3(b)-(f) shows the dependence of pattern quality on pre-heating temperature varying from 220 to 260°C . It can be seen that the pattern quality undergoes a transition from over-dissolving to under-dissolving. The optimized temperature for pre-heating is around 240°C of Fig. 3(d), where the straight and smooth pattern can be obtained through photolithography method.

Under the irradiation of the laser, the light energy absorbed by the sample may heat the local material, leading to the transition of the material from amorphous to crystalline state [11]. Thus, laser-induced crystallization of LN gel film was tried in our work. However, there is a poor retention of heat in the film for our case because the Si substrate with large thermal conductivity drains off heat effectively. Therefore, focused high-power visible laser is required to initiate crystallization in the LN gel film on Si substrate. In order to further reduce the heat dissipation, we introduce a substrate heater by which the temperature of Si substrate can be controlled in the range below 150°C . Note that the substrate temperature is far lower than the crystallization temperature (at least 500°C) of the LN gel and not lead to the film crystallization directly.

Many experimental factors may influence the pattern quality produced through laser-induced crystallization, but the substrate temperature (T_s), laser power (P) and scanning speed (V) are three important ones. For optimize the experimental parameter T_s , P and V , different values in the ranges of $110\text{-}140^\circ\text{C}$, $0.5\text{-}1.2\text{W}$ and $0.625\text{-}6.250\text{ }\mu\text{m/s}$ were selected respectively for them in 64 ($4*4*4$) experiments. The results show that the parameter set of $T=130^\circ\text{C}$, $P=1.2\text{W}$ and $V=0.625\mu\text{m/s}$, can yield the best pattern quality. For demonstrating individually the effects of substrate temperature (T_s), laser power (P) and scanning speed (V) on pattern quality, we show in Fig. 4(a)-(d), (e)-(h) and (i)-(l) the three cases where only one parameter is tuned but the other two fixed at the optimum value. It can be seen that lower substrate temperature may lead to the bubble-like irregular structure in the patterned LN film. But too high temperature is also adverse to the pattern quality because some dendrites are found in the edge of line pattern. For laser power, lower one cannot produce sufficient heat to crystallize the LN gel completely,

leaving some imprints of partial dissolving in the line pattern. As far as the scanning speed is concerned, both bubble-like irregularity and partial dissolving imprints were observed for too fast scanning.

For explanation the formation of bubble-like irregularity in the patterned LN film, the temperature gradient at the crystallization front has to be considered. As shown in Fig. 5(a), the light energy absorbed by Si substrate at the focus point may induce the local temperature increasing to T_f , which results in a temperature gradient G ($G=(T_f - T_s)/L=\Delta T/L$) at the crystallization front. Here the T_s is the average substrate temperature (T) controlled by substrate heater and L is the heat dissipation distance which is inversely proportional to the scanning speed V . We have known from the endothermic behavior shown in Fig. 2(c), water and organic matter may release from gel in the form of gas during the gel crystallization. The large temperature gradient G usually leads to the fast outgasing process, which could produce many bubbles inside the sticky gel. By decreasing temperature gradient G , the outgasing process can be slow down with the bubble formation completely avoided. There are two ways to lower G : one is elevating the substrate temperature T_s and another is decreasing the scanning speed. This is why the bubble-like irregularity was absent from the cases with $T_s \geq 130^\circ\text{C}$ and $V=0.625\mu\text{m/s}$.

The morphology of the patterned LN film is quite important for its applications. For example, compact patterned LN film is favorable to the fabrication of integrated optical components because of the low loss for light propagation. However, for the biomedical application of patterned LN film, porous morphology is beneficial to the enhancement of their photocatalytic activity. Fig. 6 shows SEM photographs of the patterned LN films fabricated in two ways. In Fig. 6 (a) and (b), stripe group made in photolithography way and a single stripe made through laser-induced crystallization are demonstrated in general view. The pattern quality in both cases is quite good, and in particular, straight and smooth edges can be observed at the laser-crystallized LN stripe. Fig. 6 (c) and (d) show the morphologies in both cases and significant difference can be found between them: the film prepared in photolithography way is rough and porous, but laser-induced crystallization can yield quite smooth and compact film. The assembly or dispersion states in both cases are given in high-magnification SEM pictures (Fig. 6(e) and (f)). LN agglomerates with size in micron-scale leave many sub-micron gaps in the film prepared in photolithography way. These sub-micron gaps can also be reflected by the rugged structures in the cross-sectional morphology of LN film (see the inset of Fig. 6(e)). By contrary, in laser-crystallized LN film such serious agglomeration is absent and LN particles tend to form compact film with nano-scale texture. As shown in the inset of Fig. 6(e), the porous LN film has a thickness of about 170nm. Thus under the similar LN gel preparation condition, laser-induced crystallization is expected to produce compact LN film with a much less thickness. Two sharp peaks in the XRD pattern (see Fig.2 (a)) indicate the LN film has a highly preferred orientation (104) and (006). The crystallite size can be evaluated from XRD pattern by the Scherrer equation: $d = k\lambda/(\Delta\cos\theta_0)$, where $k = 0.89$ is chosen as the crystal shape factor, λ is the wavelength, Δ is the full width at half maximum, and θ_0 is the peak position. On the orientation (104) and (006), the crystallite sizes are estimated to be 82 and 21nm for the film with the thickness of about 170 nm, respectively.

The distinct morphology features (porous and compact) of patterned LN films fabricated in the two ways can be explained by their difference of crystallization modes (see Fig. 5(b)). For photolithography method, the crystallization of LN gel happens during the last annealing step. In this situation the LN gel crystallization starts from the outside part, blocking the continuous outgasing of inside part. As a result, some gaps may form to allow the releasing of the gas, and the rough and porous surface was observed after this step. However, for the light-induced crystallization method, crystallization starts

from the inner part of LN gel film, because Si substrate absorbs the majority of light and it can be considered as the heating source. As mentioned above, if temperature gradient G is controlled in a proper range, smooth and compact morphology can be obtained easily. Fig. 7 shows the SEM photographs of the laser-crystallized LN film with bubble-like irregular structures. In this case, the improper temperature gradient leads to the fast outgasing process and the formation of the bubble-like structure. It can be seen from Fig. 7 that the film surface far from the bubble-like structure are compact and smooth. However, the fast outgasing process brings serious damage to the film surface. Near the bubble-like structure, porous morphology like LN conglomerates and sub-micron gaps could be found, which provide a good evidence for our explanation about the distinct morphology features of patterned LN films fabricated in the two ways.

4. Conclusion

Patterned LN thin films basing aqueous precursor were fabricated in photolithography and laser-induced crystallization ways. The effects of LN gel solubility, laser scanning parameters and substrate temperature on the pattern quality of LN film were studied. For photolithography way, proper gel solubility can be obtained by pre-heating around 240°C , while the parameter set of $T=130^{\circ}\text{C}$, $P=1.2\text{W}$ and $V=0.625\mu\text{m/s}$, can yield the best pattern quality for laser-induced crystallization. The temperature gradient at the crystallization front was found quite important to the pattern quality. Moreover, the distinct morphology features (porous and compact) of patterned LN films fabricated in the two ways are shown and explained by their difference of crystallization modes. These ways are suggested for the optical and biomedical applications, respectively.

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Captions of Figures

Fig. 1. (a) The basic experimental setup for beam writing and fabrication procedures for patterned LiNbO₃ film through (b) photolithography method (c) laser-induced crystallization method

Fig. 2. (a) XRD patterns of the samples: LN powder, LN thin films with thickness 175 nm and 350nm (b) Raman spectra of samples: Si substrate, LN thin films with thickness 175 nm and 350nm (c) DSC curve of LN precursor solution with heating rate 10°C/min.

Fig. 3. Microscope images of patterned LN film fabricated with different solubility tuning, for which varied temperatures from 220-260 °C were selected for pre-heating.

Fig. 4. Microscope images for the patterned LN thin film obtained by laser irradiation at different parameters (a) Si substrate temperature (b) laser power(c) scanning speed.

Fig. 5. (a) The temperature distribution around laser focus during laser-induced crystallization (b) The mechanisms of LN film crystallization in two different ways: (i) photolithography method (ii) laser-induced crystallization method.

Fig. 6. SEM photographs of patterned LN thin film. (a), (c) and (e) are corresponding to the photolithography method while (b), (d) and (f) are for the laser-induced crystallization method. (a) and (b) give the general view of patterned film, (c)-(f) show the detailed morphology of patterned film. The inset of (e) shows the cross-sectional morphology of LN film.

Fig. 7. SEM photographs of the laser-crystallized LN film with bubble-like irregular structures. (a)~(d) are corresponding to different magnifications.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7