DIRECT-WRITE e-BEAM PERIODICALLY POLED ${\sim}400~\mathrm{nm}$ DOMAINS IN LITHUIM NIOBATE THIN FILMS GROWN BY LIQUID PHASE EPITAXY

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We demonstrate sub-micron ferroelectric domain engineering in liquid phase epitaxy (LPE) LiNbO3 thin films grown on LiNbO3 and LiTaO3 substrates using a direct-write electron beam poling method. LiNbO3 thin films of several-micron thicknesses were grown using a flux melt of 20 mol% LiNbO3—80 mol% LiVO3. To engineer domain structures in Z^- oriented LPE LiNbO3 films, a direct-write electron beam poling method was implemented. We achieved 300—400 nm wide domains spanning over 50 $\mu \rm m$ with a period of 1.1 $\mu \rm m$. It is also shown that we can engineer the domain structure of LPE LiNbO3 films by using direct e-beam poling, even though the domain orientations of the film and the substrate are of opposite polarity. By comparing the e-beam poling behavior in a congruent LiNbO3 single crystal and a LPE LiNbO3 film, it is shown that LPE LiNbO3 supports a much enhanced periodically poled structure than bulk single crystal material.

Introduction

Ferroelectric domain engineering in LiNbO₃ has been studied intensively for various applications such as quasi-phase matched optical parametric oscillators [1] and electro-optic Bragg gratings [2]. Recently, submicron domain engineering in LiNbO₃ waveguides has drawn much attention because of the possibility of implementing it in tunable Bragg grating structures [3]. To date, the electric-field poling is the most popular technique to produce periodically poled lithium niobate (PPLN). By using a backswitched poling technique and lithographically imposed stripe electrodes, domain patterns with a period down to $2.6 \mu \text{m}$ were reported [4]. However, the smallest electrode width is restricted by optical lithography, and the domain widening out of the electroded area [4] impedes the fabrication of periodically poled structures with domains down to sub-micron scales using electric-field poling. A direct-write electron beam poling technique, on the other hand, appears as a promising alternative method that does not

require optical lithography and has very high spatial resolution [5].

For a more efficient and stable functioning of PPLN devices, it is advantageous to fabricate waveguides rather than using bulk LiNbO₃. Techniques based on diffusion processes such as proton exchange [6] have been extensively studied in combination with a PPLN structure. Thin film waveguide fabrication techniques, however, provide attractive advantages such as the ability to create a step index profile by using lower index substrates or introducing dopants and the suitability for integration with other processes. Among them, LPE is a very promising technique to produce high-quality thin film waveguides of several-micron thicknesses with excellent crystallinity and surface morphology [7-10]. The PPLN structure in a LPE LiNbO₃ waveguide with an 18 μ m period by using the electric-field poling technique was reported [11]. However, to our knowledge, the sub-micron periodic poling of LPE LiNbO₃ by using a direct-write e-beam method has not been studied before.

In this paper, we report the observed advantages of combining a direct-write e-beam poling method and LPE ${\rm LiNbO_3}$ to achieve a sub-micron periodic domain structure. Periodic domains with 300—400 nm width were obtained in LPE ${\rm LiNbO_3}$ films which cannot be fabricated in a single crystal of congruent ${\rm LiNbO_3}$. The films on substrates with oppositely oriented domains were also domain engineered with an e-beam. To elucidate the underlying physical reasons, compositional effects and defect structures were studied.

1. Dynamically Switchable Filter Using PPLN

An important device using sub-micron periodic domains in LiNbO₃ waveguides is a dynamically switchable Bragg filter in DWDM. When an external DC, spatially uniform voltage is applied to the structure shown in Fig. 1, the periodic domain structure acts as a reflection grating for dropping a channel from the DWDM stream. If the applied voltage is removed, the refractive index modulation of the structure becomes close to zero and no reflection is observed. The alternating refractive index modulation due to the electro-optic effect is given by

$$\Delta n = \pm \frac{1}{2} n_e^3 r_{33} E, \tag{1}$$

where n_e is the extraordinary refractive index ($n_e \approx 2.14$ at $\lambda=1550$ nm); r_{33} is the electro-optic coefficient of LiNbO₃; and E is the applied electric field.

The periodicity of the domain grating corresponds to a specific wavelength channel, which can be either dropped $(V \neq 0)$, or passed through (V = 0). Alternatively, the grating can be used to add a channel to the DWDM stream. The required period Λ of the inverted domains can be estimated as

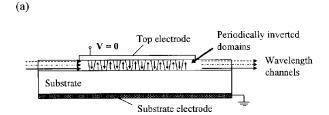
$$\Lambda = \frac{\lambda_{\text{drop}}}{2n_e},\tag{2}$$

where $\lambda_{\rm drop}$ is the specific wavelength to be dropped or added. Thus, for a $\lambda_{\rm drop}$ wavelength around 1550 nm, the periodicity of the inverted domain structure is ≈ 362 nm. This is a rather small period, which has not been obtained by using conventional electric-field poling techniques. Hence, we employed a direct-write e-beam method in combination with LPE LiNbO₃ to achieve a sub-micron domain period.

2. Experimental Procedure

LiNbO₃ epitaxial films with several-micron thicknesses were grown on LiNbO₃ and LiTaO₃ substrates with a vertical dipping technique. Optical grade Z-cut congruent LiNbO₃ (Crystal Technology, Inc.) and LiTaO₃ (Crystran Ltd.) 500 μ m in thickness were used as substrates. A flux melt of 20 mol% LiNbO₃—80 mol% LiVO₃ [7] was used for LPE film growth. The melt was homogenized at 1200 °C for 12 hours, and then cooled to a temperature 5 °C higher than the growth temperature T at a rate of 60 °C/h. The melt was held for 10 hours at this temperature and then cooled to T to achieve a supercooled state. After 30 min of holding at a fixed temperature, the substrate was dipped in the melt at T. A typical growth temperature T is 900—910 °C.

The crystallinity of resulting films was investigated by using the high resolution XRD (HRXRD) rocking curve technique. For films on LiTaO₃ substrates, (0006) peaks were measured and, for films on LiNbO₃



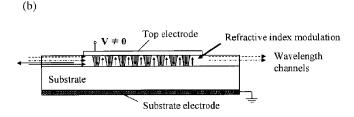
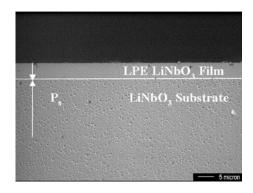


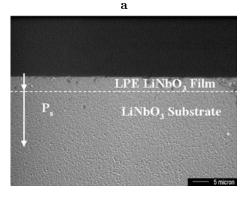
Fig. 1. Schematic diagrams of a dynamic switchable filter using PPLN. a — off state (V = 0): all the wavelength channels pass through. b — on state (V \neq 0): a selected wavelength channel (solid line) is reflected and dropped

substrates, (00012) peaks were detected. Peaks from both films on LiTaO₃ and LiNbO₃ showed similar, or even smaller FWHM values than those for substrate peaks, indicating that the crystallinity of the films is comparable to that of the substrates. The waveguide properties of films grown on LiTaO₃ substrates were studied using a prism coupler. They were planar waveguides supporting both TE and TM modes at λ =632.8 nm, and exhibited a step index profile. The refractive indices are $n_e=2.202$ and $n_o=2.287$.

To implement a direct-write electron beam poling method, the opposite surface of an e-beam exposed surface was coated with 50 nm Au for the ground electrode. Surfaces of LPE LiNbO₃ films were exposed to an e-beam with different doses ranging from 50 to 450 μ C/cm². The written patterns are composed of 3.3 μ m scanning strips separated by 3.3 μ m; 300 nm scanning strips separated by 600 nm; 300 nm scanning strips separated by 300 nm. The surface and cross sectional domain structures of these specimens were investigated after etching in a HNO₃:HF=1:1 mixture at room temperature and observed by an optical microscope and a scanning electron microscope.

A congruent LiNbO $_3$ single crystal, a vapor transport equilibration (VTE) near-stoichiometric LiNbO $_3$ single crystal, and a V-doped LiNbO $_3$ single crystal grown in a 0.2 mol% LiVO $_3$ added melt were subjected to the





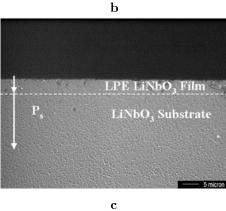


Fig. 2. Y-surface cross-section domain structures of LPE LiNbO₃ films. a — on the Z^+ surface of LiNbO₃ substrate; b — on the Z^- surface of a LiNbO₃ substrate; c — on a LiTaO₃ substrate

same e-beam scanning conditions and compared with LPE $LiNbO_3$ to study potential compositional effects. To investigate the defect structure of LPE $LiNbO_3$, transmission electron microscopy (TEM) was used.

3. Results and Discussion

3.1. Domain Structures of As-grown LPE $LiNbO_3$ Films

The domain orientations of LPE grown LiNbO₃ films were investigated by polishing and etching the cross sections of as-grown samples. The domain structures of LPE grown LiNbO₃ thin films on substrates are shown in Fig. 2. The films were single-domain, Z^- oriented on both the +/-Z surfaces of the LiNbO₃ substrates (Fig. 2, a and b), and also on the LiTaO₃ substrates regardless of the original orientation of the LiTaO₃ substrates (Fig. 2,c). Since the growth temperature of films is higher than the Curie temperature of LiTaO₃ (\sim 605 °C), the domain structure of the LiTaO₃ substrate is subject to change during the LPE process. The singledomain layer beneath a Z^- oriented LiNbO₃ film on a LiTaO₃ substrate shown in Fig. 2,c is a Z^+ oriented layer of a LiTaO₃ substrate, which appears at the surface of a LiTaO₃ crystal after heat treatment above the Curie temperature [12]. Except for the surface layer, the LiTaO₃ substrate is multi-domain.

Since the LiNbO₃ films are Z^- oriented and, in certain systems, the whole structure including the substrates is multi-layered, it is not suitable to use conventional periodic poling techniques such as electric-field poling and Ti-indiffusion, which are preferably done on the Z^+ surface of LiNbO₃. However, e-beam direct writing is performed on the Z^- surface. Hence, it is a more proper approach to engineer domains in LPE LiNbO₃ thin films.

3.2. Sub-micron Domain Engineering in LPE $LiNbO_3$ Films

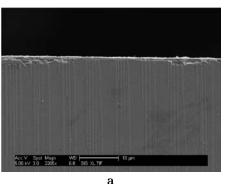
Fig. 3. shows the cross-sections of the direct-write ebeam domain engineered structures of LPE LiNbO₃ films on the substrates. Fig. 3,a is the domain structure of 3.3 μ m writing in a homoepitaxial system (a LiNbO₃ film on a LiNbO₃ substrate) with the same $Z^$ orientation of the film and the substrate. Fig. 3, b is the domain structure of 3.3 μ m writing in a heteroepitaxial system (a LiNbO₃ film on a LiTaO₃ substrate), with the domains in the film and substrate being of opposite orientation. We observe in Fig. 3, a and b that the written area has the designed period. An interesting result is that the scanned area consists of much finer domains with a width around 400 nm, and it suggests that we may obtain a much finer period domain structure by using an e-beam on LPE $LiNbO_3$. Hence, we performed 300 nm writing in LPE LiNbO $_3$ films.

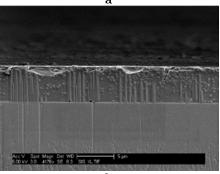
Fig. 3,c and d show 300 nm wide scanning results in the homoepitaxial system. Fig. 3,c is the cross-sectional domain structure of the same Z^- oriented film and the LiNbO₃ substrate, and Fig. 3,d is the cross sectional domain structure of the domains with an orientation in the film which is opposite to that in the LiNbO₃ substrate. As the split domains in the wider scanning experiments suggest, we obtained sub-micron domain structures consisting of ~400 nm domains with a 1 μ m period in LPE LiNbO₃ films.

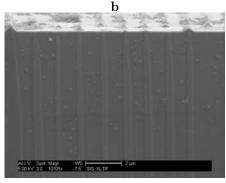
As shown in Fig 3,b and d, we can engineer the domain structure of LPE LiNbO₃ thin films by using the direct e-beam poling technique, despite the opposite domain orientations of the film and the substrate. The domain engineering in the case of an oppositely oriented film to the substrate is particularly interesting since a heteroepitaxial LiNbO₃ film on a LiTaO₃ substrate has this structure and it produces a stepindex waveguide. This multilayered waveguide structure cannot be domain-engineered by using the electricfield poling at room temperature, because the whole specimen breaks in the process of uniform repoling in the preparation for electric-field poling. On the other hand, the direct-write e-beam method can engineer the LPE LiNbO₃ films without the repoling process and the engineered domain structure is shown to be restricted to the film layer. However, problems related to the lack of complete regularity and reducing cracking along the film/substrate interface need a further study.

Based on these results, we further optimized the experimental parameters to obtain a more regular, finer period domain structure in the homoepitaxial LPE LiNbO3 film system with the same Z^- oriented films and substrates. Fig. 4. shows the surfaces of the domain engineered LiNbO3 films. The LPE films were grown at 904 °C for 10 min. Fig. 4, a and b are the surfaces after the scanning of 300 nm wide strips separated by 600 nm, Fig. 4,c is the surface after scanning 300 nm wide strips separated by 300 nm. e-beam parameters were $V=20~\rm kV$, $I=1.2~\rm nA$, and an areal dose of 300 $\mu\rm C/cm^2$ for Fig. 4,a; $V=20~\rm kV$, $I=1.4~\rm nA$, and an areal dose of 400 $\mu\rm C/cm^2$ for Fig. 4,b; $V=20~\rm kV$, $I=1.2~\rm nA$, and an areal dose of 450 $\mu\rm C/cm^2$ for Fig. 4,c.

The results shown in Fig. 4, a and b have a 1.1 μ m period spanning uniformly over $\sim 50~\mu$ m. We suspect that a slight broadening of the period results from the repulsion of e-beam scanning due to charging, which will be compensated for in future experiments. The domain sizes are ~ 300 nm for Fig. 4, a and ~ 400 nm for Fig. 4, b. The domain structure shown in Fig. 4, c consists of ~ 350 nm domains with a period of 700 nm, which is close to







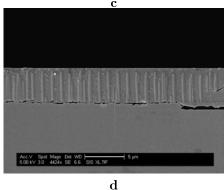


Fig. 3. Y-surface cross-section of domain engineered LPE LiNbO3 films. a-3.3 mm wide writing in Z^- LiNbO3 film/ Z^- LiNbO3 substrate; b-3.3 mm wide writing in Z^- LiNbO3 film/LiTaO3 substrate; c-300 nm wide writing in Z^- LiNbO3 film/ Z^- LiNbO3 substrate; d-300 nm wide writing in Z^- LiNbO3 film/ Z^+ LiNbO3 substrate

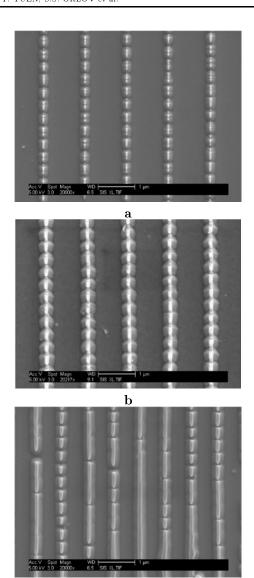


Fig. 4. Direct-write e-beam periodically poled structure on a Z-surface of a LPE LiNbO3 homoepitaxial system (Z $^-$ LiNbO3 film/Z $^-$ LiNbO3 substrate). a-300 nm domains with a 1.1 μ m period; b-400 nm domains with a 1.1 μ m period; c-350 nm domains with a 700 nm period

a 1 to 1 duty cycle. However, the areal uniformity of the structure shown in Fig. 4,c is restricted to a smaller area compared with 4,a and b. We postulate that the scanning order of strips may be responsible for the areal uniformity and the further study to improve the regularity of the domain structure is ongoing. Although a further optimization is needed,

the results shown in Fig. 4 prove the potential of the combination of the direct-write e-beam method and the LPE ${\rm LiNbO_3}$ system to produce regular sub-micron domain structures.

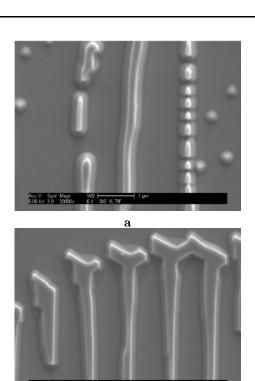
3.3 Comparison between LPE $LiNbO_3$ and Single $Crystal\ LiNbO_3$

To investigate if the sub-micron domain engineering results in LPE LiNbO₃ films by using the direct-write e-beam method are due to certain properties of LPE LiNbO₃ or are caused by the choice of the e-beam scanning parameters, the same e-beam scanning parameters were applied to a congruent LiNbO₃ single crystal. Fig. 5,a shows the etched surface of a single crystal of congruent LiNbO₃ scanned under the same e-beam conditions as in Fig. 4,a. It is clearly shown that, under the same e-beam scanning conditions, a regular domain structure cannot be obtained in a single crystal and the width of the domain is wider than that in the LPE LiNbO₃ system. Therefore, the sub-micron domain structures shown in Fig. 4 are most likely caused by the favorable properties of the LPE film.

There are two main possibilities which may explain the difference in poling behavior of a LPE LiNbO₃ film. The first possibility is that a slight difference of the composition of LPE LiNbO₃ may cause the poling behavior difference by changing materials properties such as the coercive field. From the HRXRD results, even for the homoepitaxial LPE LiNbO₃ film/LiNbO₃ substrate, there is a peak shift between a LPE film and a substrate. The XRD peak shift is postulated to be caused by the compositional difference in LPE LiNbO₃ by other researchers [10]. Based on the peak position, the LPE film has near-stoichiometric composition.

To investigate how the composition can affect ebeam poling behavior, a near-stoichiometric $LiNbO_3$ crystal produced by vapor transport equilibration (VTE) was used for experiments with the same ebeam parameters. Furthermore, to study the effect of vanadium incorporation, a V-doped $LiNbO_3$ crystal grown in 0.2 mol % $LiVO_3$ added melt was also experimented. The e-beam scanning parameters were set to be the same as in the experiments shown in Figs. 4, a and a, a.

Figs. 5,b and c show the surface of the VTE LiNbO₃ and the V-doped LiNbO₃ single crystal after irradiating with an e-beam and etching, respectively. Compared with congruent LiNbO₃ shown in Fig. 5,a, VTE LiNbO₃ and V-doped LiNbO₃ show slightly enhanced domain structures, however, these structures are still much



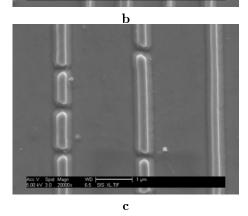
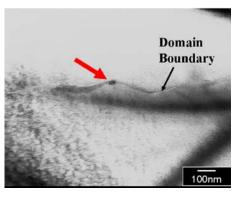


Fig. 5. A 300 nm e-beam scanned Z-surfaces of single crystals. a — a congruent LiNbO₃ single crystal; b — a near-stoichiometric VTE LiNbO₃ single crystal; c — a V-doped LiNbO₃ single crystal

worse than the domain structure of LPE LiNbO₃ shown in Fig. 4,a. Thus, compositional effects may contribute to the enhancement of the domain poling behavior of the LPE LiNbO₃ system, but cannot explain the improvement completely.

The second possibility is that the defect structure of the LPE LiNbO₃ may prevent domain broadening, thus producing a much narrower domain than that in a single crystal. If we assume that the peak shift is induced by the lattice mismatch between a film and a substrate, there may exist misfit defects such as dislocations at the



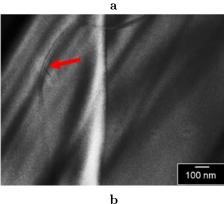


Fig. 6. TEM micrographs of the defects observed in the LPE LiNbO₃ system. a — a defect lying on the film and the substrate interface. b — a defect lying on the e-beam engineered domain wall

interface. These defects can work as a pinning center for domain walls and assist in producing a narrower and more regular domain structure in a LPE LiNbO $_3$ film. We performed cross sectional TEM at the interface of the homoepitaxial system and observed defects lying on the domain boundary. The defects observed are shown in Fig. 6.

Fig. 6,a shows a defect lying on the interface between a Z^- LiNbO $_3$ film and a Z^+ LiNbO $_3$ substrate. The interface in this system is also a domain boundary. Fig. 6,b shows other kind of defects which are lying on the wall of the e-beam engineered domain. We think defects shown in Fig. 6 can pin the domain wall and thus help in preventing the domain widening and producing finer domains. However, existing defects are sparse and we could not observe a regular array of the misfit dislocations, so it is difficult to conclude that the defect structure is solely responsible for the poling behavior of LPE LiNbO $_3$. We postulate that the synergetic combination of the compositional effect and

the defect structure, as well as the relation between the film and substrate may be responsible for the positive poling results in the LPE LiNbO₃ system. The further research into this explanation is ongoing.

Conclusion

We report the successful sub-micron domain engineering in LPE grown LiNbO3 films by using direct-write ebeams. Z^- oriented LPE films are domain engineered with 300–4400 nm wide domains even in films with domains oppositely oriented to those in substrates. We obtained a 1.1 μ m period spanning $\sim 50 \ \mu$ m in homoepitaxial LPE LiNbO₃ films. This structure cannot be obtained in a single crystal of congruent LiNbO₃ under the same e-beam scanning conditions hence the sub-micron periodic domain structure obtained in LPE LiNbO₃ is believed to be caused by the materials properties of LPE LiNbO₃. Defect structures, compositional differences and a film/substrate relation are thought to be possible reasons for the unique poling behavior of LPE LiNbO₃ films. We postulate that the narrower domains obtained in LPE LiNbO₃ films may facilitate better switchable Bragg gratings than using LiNbO₃ single crystals.

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БЕЗПОСЕРЕДНІЙ ЗАПИС ЕЛЕКТРОННИМ ПРОМЕНЕМ ДОМЕННИХ СТРУКТУР РОЗМІРАМИ 400 нм В ТОНКИХ ПЛІВКАХ НІОБАТУ ЛІТІЮ, ВИРОЩЕНИХ МЕТОДОМ ЕПІТАКСІЇ З РІДКОЇ ФАЗИ

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Резюме

Описано спосіб побудови субмікронних фероелектричних доменів в тонких плівках LiNbO3 вирощених методом епітаксії з рідкої фази (ЕРФ) на підкдадках LiNbO3 та LiTaO3, з використанням методу поляризації безпосередньо записуючим електронним пучком. Тонкі плівки LiNbO₃ завтовшки в декілька мікрон були вирощені з розплаву, який складався з 20 моль% LiNbO₃ і 80 моль% LiVO₃. Для того щоб створити доменні структури в Z^- -орієнтованих ${\rm EP}\Phi$ -плівках ${\rm LiNbO}_3$, був застосований метод поляризації безпосередньо записуючим електронним пучком. Ми отримали структуру з доменів розмірами 300-400 нм, протяжністю понад 50 мкм і періодичністю 1,1 мкм. Також було показано, що можна будувати доменну структуру ЕРФ-плівок LiNbO3 за допомогою методу поляризації безпосередньо записуючим електронним пучком, навіть у випадку протилежної орієнтації доменів плівки та підкладки. З порівняння дії поляризуючого електронного пучка у відповідному монокристалі LiNbO3 та ЕРФ-плівці LiNbO3 видно, що в ЕРФ-плівці LiNbO₃ утворюється набагато протяжніша періодично поляризована структура, ніж в об'ємі монокристалічного матеріалу.