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Amorphous KNbO_3 thin films with ferroelectriclike properties

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Amorphous KNbO_3 films are prepared by a low-cost sol-gel method. These films show a smooth surface morphology and have good waveguiding properties. Ferroelectriclike hysteresis loops are observed in these amorphous KNbO_3 films with a remanent polarization of about $6 \mu\text{C}/\text{cm}^2$. After corona poling, a stable effective second harmonic generation coefficient of 0.523 pm/V is achieved.

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Potassium niobate (KNbO_3) is a very promising ferroelectric material with large spontaneous polarization and excellent electro-optic and nonlinear optical (NLO) properties.^{1,2} For waveguide-based applications, such as frequency converters, modulators, and switchers for future advanced integrated optical systems, high quality KNbO_3 thin films are needed.³ Currently, reliable and reproducible processing techniques for fabrication of KNbO_3 are a subject of intense research. The growth of KNbO_3 thin films has been demonstrated by various deposition techniques: sol-gel,⁴ ion beam⁵ and radio-frequency sputtering,⁶ metalorganic chemical vapor deposition,⁷ and pulsed laser deposition.⁸ The films obtained are typically polycrystalline, with various grains and textures that greatly decrease light transmission due to grain boundary scattering. Thin film fabrication technology for this material has yet not progressed to a point where integrated optoelectronic device application is possible.

In contrast to polycrystalline thin films, an amorphous film (e.g., glass) does not have the problem of light loss by scattering from the grain boundaries and, hence, allows better light transmission. A good example is fused silica (amorphous SiO_2), which has been widely used in optical communications owing to its excellent optical clarity. However, amorphous materials possess inversion symmetry on a macroscopic scale ($\sim \lambda$) and, consequently, second-order NLO processes, such as second harmonic generation (SHG) and the linear electrooptic effect, are strictly forbidden. For a transparent amorphous solid, its optical inversion symmetry must be altered to use in NLO applications. One way to break inversion symmetry is to apply an external field to polarize (pole) the sample electrically in a preferred direction. Recently, second-order nonlinearity was obtained in poled silica glass.⁹ For NLO applications, a ferroelectric material is superior to fused silica. In 1970, Lines¹⁰ argued that molecular dipoles may still be identifiable in an amorphous ferroelectric material. Lines' suggestion was subsequently confirmed by several experiments,¹¹ and hysteresis behavior with large remanent polarization has been found in amorphous $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, BaTiO_3 , and LiNbO_3 thin films.

In this letter, we report our recent work on the study of amorphous KNbO_3 thin films prepared by the sol-gel method. The advantages of the sol-gel method for film preparation include its ability to produce large area films with good uniformity, its ease of control of chemical stoichi-

ometry, and its low production cost.¹² KNbO_3 has the additional important advantage that its precursors can be formed at room temperature (as will be seen later), and hence film preparation can be accomplished at low temperature, which is particularly attractive for future fabrication of integrated optoelectronic devices.

The complex KNbO_3 precursor solution was prepared using potassium *t*-butoxide $[(\text{CH}_3)_3\text{COK}]$, Nb(V)-ethoxide $[\text{Nb}(\text{OC}_2\text{H}_5)_5]$ precursors and anhydrous 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) as the solvent. Potassium *t*-butoxide and Nb(V)-ethoxide 2-methoxyethanol solutions (0.2 M) were made separately using a dry glovebox under a nitrogen atmosphere because the precursors are extremely sensitive to moisture. After completely dissolving them in 2-methoxyethanol, these two precursors, in an amount sufficient to coat several samples, were then mixed in a rubber-sealed glass bottle in the correct stoichiometric ratio. A few drops of 1 M water in 2-methoxyethanol solution were added to the $\text{KNb}(\text{OC}_2\text{H}_5)_x(\text{OCH}_3)_y$ solution for hydrolysis purposes. The solution was kept at 70°C for 24 h for hydrolysis and gelation. Films were prepared by repeated spin coating and drying (at 250°C for 5 min in a furnace). Both fused silica and indium-tin-oxide (ITO)-coated glass were used as substrates. The thickness of the film was determined by the number of coating layers. Finally, the film was annealed (densified) and decarbonized at 500°C for 3 h in a furnace. As will be seen, annealing temperatures higher than 550°C will result in film crystallization and create grains that scatter light.

Figure 1 shows optical micrographs of sol-gel derived KNbO_3 films that were annealed at, respectively 500°C [Fig. 1(a)] and 600°C [Fig. 1(b)]. It is obvious in Fig. 1(a) that the film shown is much clearer and smoother than that in Fig. 1(b), which shows various grains coexisting in the film. X-ray diffraction measurement has confirmed that the film shown in Fig. 1(a) is still mostly amorphous [Fig. 2(a)] and the film in Fig. 1(b) is partially crystalline [Fig. 2(b)] with each grain representing a small crystallite. Because the sizes of these crystalline grains ($20\text{--}50 \mu\text{m}$) in Fig. 1(b) are much larger than the wavelength of visible light, scattering in this polycrystalline film will greatly reduce transmission of incident light.

The light guiding property of the KNbO_3 film annealed at 500°C was characterized using a dark line prism coupling configuration with a He-Ne laser ($6328 \text{ \AA}$). Two transverse magnetic (TM) (Fig. 3) and two transverse electric (TE) (not

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FIG. 1. Optical micrographs of the sol-gel derived KNbO_3 films. (a) Annealed at 500°C ; (b) annealed at 600°C ; crystalline domains are clearly visible in the film.

shown here) modes were observed. From the measured effective refractive indices, the refractive index of the amorphous KNbO_3 film is determined to be 1.8185 and the thickness of the film is $0.45\ \mu\text{m}$, in good agreement with the thickness expected from the growth conditions. The refractive index of the amorphous film is considerably smaller than that of KNbO_3 crystal ($n_x=2.1685$, $n_y=2.2803$, $n_z=2.3299$),¹³ presumably as a result of the intrinsic nature as well as the smaller packing density of the amorphous KNbO_3 films.

One of the most important physical properties of a ferroelectric material is the hysteresis of its polarization. It is well known that, for crystalline KNbO_3 or any ferroelectric crystals, there exists a remanant polarization after removing the

FIG. 2. X-ray diffraction data of the KNbO_3 films (a) as shown in Fig. 1(a); (b) as shown in Fig. 1(b).

FIG. 3. Dark line spectrum for the KNbO_3 thin film waveguide annealed at 500°C .

electric field. For amorphous KNbO_3 , the individual dipoles are randomly oriented in the film (which is also true for polycrystalline films). Therefore, macroscopic polarization does not exist in the as-coated sample. To have a ferroelectric property, amorphous KNbO_3 films must be electrically poled to align the individual dipoles in the direction of the electric field. Figure 4 shows the electric field dependence of the polarization of the amorphous KNbO_3 films shown in Fig. 1(a). As one can see from Fig. 4, a hysteresis loop is clearly present in this sample. The maximum polarization P_s is about $20\ \mu\text{C}/\text{cm}^2$ and the remanant polarization P_r is about $6\ \mu\text{C}/\text{cm}^2$. In comparison to the value of $30\ \mu\text{C}/\text{cm}^2$ (Ref. 1) for a single KNbO_3 crystal, our sol-gel derived amorphous KNbO_3 film has achieved two-thirds of the total polarization in the crystal, which is quite impressive.

To evaluate the potential of the amorphous KNbO_3 films for second harmonic generation and electro-optical applications, the SHG from a poled amorphous KNbO_3 film was measured using an experimental setup similar to that described previously.¹⁴ Corona poling¹⁴ was used for dipole alignment. Before the poling, the sample was thermally

FIG. 4. Hysteresis loop of the KNbO_3 amorphous film shown in Fig. 1(a). The maximum polarization P_s is about $20\ \mu\text{C}/\text{cm}^2$ and the remanant polarization P_r is about $6\ \mu\text{C}/\text{cm}^2$.

FIG. 5. Time dependence of the effective SHG (d_{eff}) in the corona-poled amorphous KNbO_3 film. The d_{eff} remains constant (0.523 pm/V) after 30 h.

heated to about 300 °C to assist the rotation of the dipole in the film. Then, a high voltage of up to -2.1 kV between the grounded ITO-coated substrate and the tungsten needle was applied near the surface of the film. The magnitude of the voltage was determined by the onset of the appearance of corona. After about 30 min of heating and poling, the sample was gradually cooled to room temperature while keeping the corona poling unchanged. Then the poling field was removed and the measurement of the SHG immediately started. A cw Nd:YAG laser (Q switched and mode locked) at a wavelength of $1.064 \mu\text{m}$ was used for the measurement. The laser beam was split so that the SHG intensities from the sample (I_s) and from a quartz reference (to monitor the laser power) could be measured simultaneously. To calibrate d_{eff} , the SHG (I_q) from another Y -cut quartz placed at the KNbO_3 film position was measured. The d_{eff} was obtained in terms of the value $d_{q,11}^{(2)}$ for the quartz using the following formula:

$$d_{\text{eff}} = d_{q,11}^{(2)} \left[\frac{n_{\text{KNO}}^2(\omega) n_{\text{KNO}}(2\omega)}{n_q^2(\omega) n_q(2\omega) \cos^2 \theta} \left(\frac{4l_c^2}{l^2 \pi^2} \right) \left(\frac{I_s(2\omega)}{I_q(2\omega)} \right) \right]^{1/2},$$

where $n(\omega)$, $n(2\omega)$, l_c and l are, respectively, the index of refraction at frequencies ω and 2ω , the coherence length of the quartz q , and the thickness of the sample. Figure 5 shows the time dependence of the d_{eff} of our amorphous KNbO_3 film after the corona poling. As one can see, the d_{eff} quickly decreased once the electric field was removed. As time goes on, the decay slowed and eventually stayed constant after 30

h and retained the same value even after 5 days. The final d_{eff} in the amorphous KNbO_3 film is 0.523 pm/V, which is about 1.5 times as large as the $d_{q,11}$ of a quartz crystal.

In conclusion, we have prepared amorphous KNbO_3 films by a low cost sol-gel method. The films obtained show a smooth surface morphology and support guided waves. Ferroelectriclike hysteresis was observed in these amorphous KNbO_3 films and shows a remanant polarization of about $6 \mu\text{C}/\text{cm}^2$. The effective second harmonic generation coefficient after corona poling and a long (five days) waiting period was 0.523 pm/V, which is about 1.5 times as that of a quartz crystal. Our results indicate these amorphous KNbO_3 films are potentially useful for application in nonlinear optic and electrooptic devices.

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- ¹Y. Zu, *Ferroelectric Materials and Their Applications* (North-Holland, New York, 1991).
- ²V. G. Dmitriev, G. G. Gurzadyan, and D. N. Nikogosyan, *Handbook of Nonlinear Optical Crystals* (Springer, Berlin, 1991).
- ³S. L. Schwartz and V. E. Wood, *Condensed Matter News*, **1**, 4 (1992); D. Dimos *Annu. Rev. Mater. Sci.* **25**, 273 (1995)
- ⁴See for example, A. Nazeri-Eshghi, A. X. Kuang, and J. D. MacKenzie, *J. Mater. Sci.* **25**, 3333 (1990); G. J. Derderian, J. D. Barrie, K. A. Aitchison, P. M. Adams, and M. L. McCartney, *Mater. Res. Soc. Symp. Proc.* **310**, 339 (1993); G. J. Derderian, J. D. Barrie, K. A. Aitchison, and M. L. McCartney, *ibid.* **341**, 277 (1994)
- ⁵T. M. Graettinger, P. A. Morris, R. R. Woolcott, F. C. Zumsteg, A. F. Chow, and A. I. Kingon, *Mater. Res. Soc. Symp. Proc.* **310**, 301 (1993)
- ⁶S. S. Thony, *Mater. Res. Soc. Symp. Proc.* **341**, 253 (1994)
- ⁷M. J. Nystrom, B. W. Wessels, D. B. Studebaker, T. J. Marks, W. P. Lin, and G. K. Wong, *Appl. Phys. Lett.* **67**, 17 (1995)
- ⁸V. Gopalan, and R. Raj, *J. Am. Ceram. Soc.* **78**, 1825 (1995)
- ⁹R. A. Myers, N. Mukherjee, and S. R. J. Brueck, *Opt. Lett.* **16**, 1732 (1991); R. Kashyap, G. J. Veldhuis, D. C. Rogers, and P. F. McKee, *Appl. Phys. Lett.* **64**, 1332 (1994)
- ¹⁰M. E. Lines, *Phys. Rev. B* **15**, 388 (1977)
- ¹¹Y. Xu, and J. D. MacKenzie, *Int. Ferroelectrics* **1**, 17 (1992); Y. Xu, C. H. Cheng, and J. D. MacKenzie, *J. Non-Cryst. Solids* **176**, 1 (1994)
- ¹²See, for example, *Sol-gel Optics Processing and Applications*, edited by L. C. Klein (Kluwer Academic, 1994).
- ¹³In Ref. 2, p. 110.
- ¹⁴H. A. Lu, L. A. Wills, B. W. Wessels, W. P. Lin, T. G. Zhang, G. K. Wong, D. A. Neumayer, and T. J. Marks, *Appl. Phys. Lett.* **62**, 1314 (1993)