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LETTER TO THE EDITOR

Light emissions from $LiNbO_3/SiO_2/Si$ structures

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Abstract
$LiNbO_3$ (LN) films with a high degree of (006) texture were deposited on Si-based dense SiO_2 layers by pulsed laser deposition. After annealing, the LN/SiO_2/Si structures were revealed to have ultraviolet-, green-, and red-emitting properties related to self-trapped excitons and E′ defect pairs in the SiO_2 surface, which are induced by the photorefractive effect of the LN films. The emission wavelength can be tuned by introducing different dopants into the LN films. Waveguiding properties of the structures were demonstrated. The results obtained indicate that the LN/SiO_2/Si structures could be expected to have important applications in modern optoelectronic integration.

Enormous progress in the information and communication technologies has increased the demand for Si-based optoelectronics. This has stimulated many efforts toward realizing a large scale of integration compatible with Si-based light sources [1]. However, to further achieve fully Si-based optoelectronics in which the light source, waveguide, photomodulator, and photodetector are integrated on a Si chip, new materials and technologies need to be explored. Nonlinear optical $LiNbO_3$ (LN) films have served to provide waveguiding second-harmonic generation [2, 3] and incorporated into semiconductor integrated circuits [4]. Unfortunately, these films have no light emission properties. A possible way to realize optoelectronics is by exploring Si-based light sources on the basis of these films. In this letter, we present a novel way to achieve fundamental functions (especially providing a source of light) with fully Si-based optoelectronics by depositing the LN films on Si-based SiO_2 layers to form LN/SiO_2/Si structures.

The pulsed laser deposition (PLD) system used in this work has been described previously [5, 6]. The substrates used in the work were p-type c-Si (⟨100⟩, 5 Ω cm) wafers. Before the PLD, the substrates were first dipped in HF solution for several seconds and then repeatedly washed with de-ionized water. A laser pulse energy of 140 mJ cm^{-2} was selected to irradiate a disc-shaped LN crystal target (half of the LN target was replaced by

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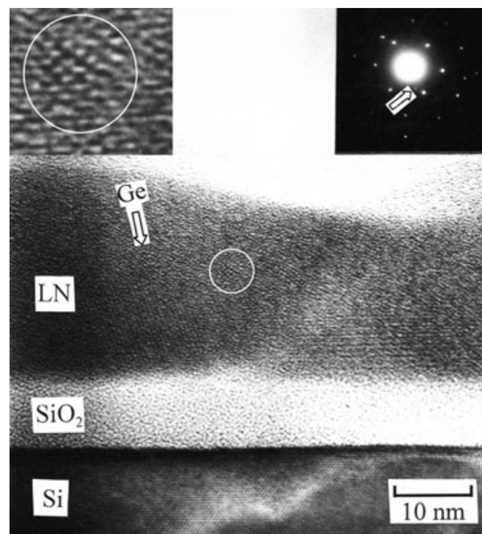

Figure 1. The HRTEM image of sample B, clearly showing a buffer layer of dense SiO_2 with thickness of ∼10 nm between the LN film and c-Si substrate and showing some Ge nanocrystals, with sizes of 2–5 nm, to be embedded in the LN lattice structure. The left corner shows the enlarged TEM image containing a Ge nanocrystal. The right corner displays the selected-area diffraction pattern that shows the diffraction spots from the Ge(111) plane (indicated by the arrow).

c-Ge for fabricating Ge-doped LN (Ge:LN) films). Introduction of Ge into the LN film was expected to give rise to new light emission. During PLD, for the LN films the substrates were put on a stage held at ∼550 °C and the deposition chamber maintained an oxygen pressure of 6.0×10^4 Pa, while for the Ge:LN films the corresponding parameters are 300 °C and 1.0×10^2 Pa. So a layer of dense SiO_2 can be expected to grow very well on c-Si surfaces to form LN/SiO_2/Si and Ge:LN/SiO_2/Si structures. Sample series with deposition times of 10, 20, and 30 min were prepared and their thicknesses were measured to be about 290, 580, and 870 nm, respectively. The deposited samples were then annealed at 800 and 1000 °C in mixed nitrogen and oxygen ambient (1:1) for 5 min for the LN films and in pure nitrogen ambient for 20 min for the Ge:LN films. The measurement systems using high-resolution transmission electron microscopy (HRTEM) [6], x-ray diffraction (XRD) [5], Fourier transform infrared (FTIR) spectroscopy [7], photoluminescence (PL) [5, 8], and optical waveguides [6] have been described. All measurements were obtained at room temperature. Some typical results from LN/SiO_2/Si (sample A) and Ge:LN/SiO_2/Si (sample B) structures with the deposition time of 20 min and the annealing temperature of 800 °C are presented in this letter.

A cross-section HRTEM view of sample B is shown in figure 1. The photograph clearly displays a buffer layer of dense SiO_2 with a thickness of ∼10 nm between the LN film and the c-Si substrate. The SiO_2 layer has sharp interfaces with both the Ge:LN layer and the c-Si substrate. It is thicker in sample A than in sample B. Figure 1 also shows some Ge nanocrystals, with sizes of 2–5 nm, to be embedded in the LN lattice structure due to segregation of Ge atoms at high temperature [9]. This can be seen further from the enlarged image containing a Ge nanocrystal (see the left corner of figure 1). The selected-area diffraction pattern shown in the right corner of figure 1 displays the diffraction spots from the Ge(111) plane (indicated by the arrow).

The XRD spectra of samples A and B are shown in figures 2(a) and (b), respectively. The two spectra are very similar, mainly showing three intense diffraction peaks at $2\theta = 33°$ (the

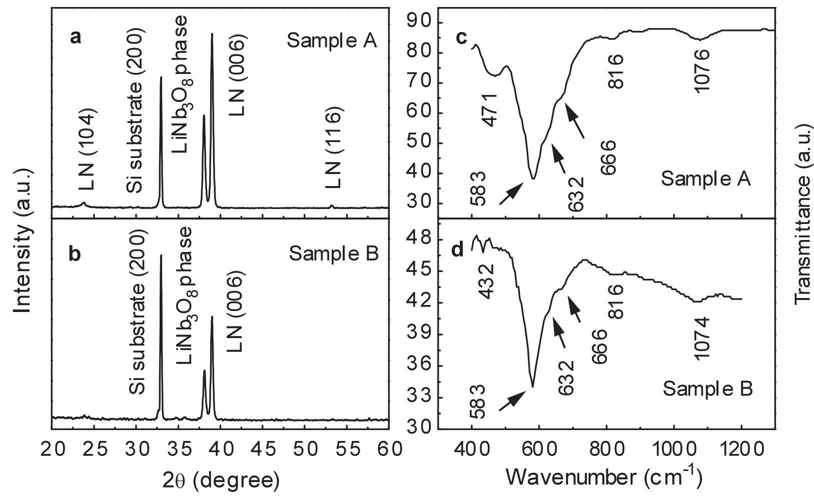

Figure 2. XRD and FTIR spectra. (a) and (b) show the XRD spectra of samples A and B, indicating that the LN(Ge:LN) films obtained are highly *c*-textured. (c) and (d) show the FTIR spectra of samples A and B, showing that the LN(Ge:LN) films obtained exhibit a strong PRE.

(200) reflection of the c-Si substrate), 38.2°, and 39° (the (006) reflection of the LN film). This result indicates that the deposited LN and Ge:LN films are highly *c*-textured. Our x-ray photoelectron spectroscopy results indicate that there exist excess Nb atoms in the two films. Thus, in sample A the 38.2° diffraction peak should be from Nb-rich lithium niobium phase ($LiNb_3O_8$) [10, 11] and in sample B it should be related to both Ge nanocrystals and the Nb-rich phase, because the diffraction peak from the (111) plane of Ge nanocrystals is at exactly the same position. This Nb-rich phase plays an important role in formation of the *c*-oriented LN films and enhancement of the photorefractive effect (PRE).

The PRE in Nb-rich LN has been reported to be due to a partial stacking-fault arrangement of Nb ions [11]. Since the PRE is connected with the space charge field (SCF) in the material, the coupling of the SCF with the spontaneous polarizing electric field $\boldsymbol{P}_s$ resulting from the disordered distribution of Nb ions will lead to change of the PRE (the situation is similar for Ge introduction). Partially excess Nb ions will directly substitute for Li ions but do not exactly occupy their ferroelectric positions. They are situated within the oxide plane [12]. The replacements of Li ions by Nb ions lead to displacements of positive charges along the z-direction and thus result in the appearance of $\boldsymbol{P}_s$ in the $-z$-direction. $\boldsymbol{P}_s$ induces the growth of LN film along the (006) orientation [13].

The strong PRE from our LN and Ge:LN films can be seen in figures 2(c) and (d), which show the FTIR spectra of samples A and B, respectively. The vibrational bands at 471, 816, and 1076 cm^{-1} obviously come from Si–O–Si bond vibrations of the SiO_2 layer [7]. The band at 583 cm^{-1} was found to only exist in the *c*-textured LN films coexisting with Nb-rich phase. We cannot attribute it to either the bending vibration of the Ge–O–Ge bond or the vibrational frequency of SiO_x ($x = 1$–2) [7], because these bands often have weak intensities in the oxide. In fact, the 583 cm^{-1} band consists of three bands at 583, 666, and 632 cm^{-1}, which exactly correspond to the vibrational frequencies of two E(TO) modes and one A_1(TO) mode of LN crystal [14], respectively. Our Raman scattering investigations also show similar results. The strong 632 cm^{-1} A_1(TO) mode is noteworthy, because it should be forbidden in this kind of backscattering geometry, which only shows E(TO) + A_1(LO) modes [15]. Further analysis

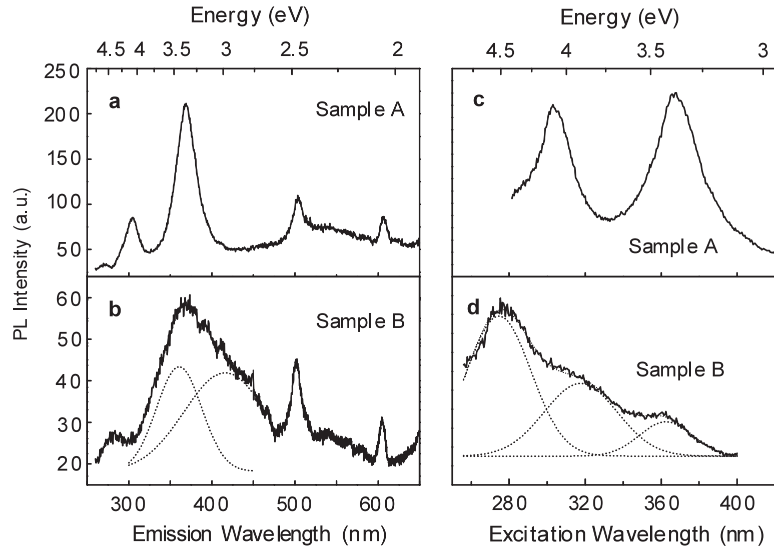

Figure 3. PL and PL excitation spectra. (a) and (b) show the PL spectra of samples A and B, displaying all-colour light-emitting properties of the LN(Ge:LN)/SiO_2/Si structures. Ge introduction leads to the appearance of a new emission peak in the blue. (c) and (d) show the PL excitation spectra of samples A and B, indicating that the onset of the PL bands occurs at ~368 nm, almost equal to the fundamental optical absorption edge position of LN crystal.

indicates that its origin is the coupling of the SCF with the polarizing electric field accompanied by extraordinary phonons. The coupling turns E(TO) + A_1(LO) into E(TO) + A(LO) + A_1(TO) and thus leads to the appearance of the 632 $cm^{-1}$$A_1$(TO) mode [12, 15]. The fact that the 632 cm^{-1} mode has larger intensity in sample A than that in sample B implies that the LN film has a stronger PRE than the Ge:LN film. This can be understood on the basis of the magnitude of $\boldsymbol{P}_s$ in the two films. Like the previous analysis [12], we find that $\boldsymbol{P}_s$ in Ge:LN is larger than that in the LN film, because Ge ions have larger displacements than Nb ions along the z-direction. Since $\boldsymbol{P}_s$ is in the $-z$-direction, the coupling of the large $\boldsymbol{P}_s$ with the SCF in the z-direction will lead to a relatively weak PRE.

Figures 3(a) and (b) show ultraviolet-to-red PL spectra of samples A and B, respectively. Four PL peaks can be observed in spectrum (a). Ge introduction leads to the appearance of a new blue PL peak (see the Gaussian profiles of spectrum (b)). This result indicates that we can tune the emitting wavelength by doping different materials into the LN film. These PL peaks have narrow linewidths (<0.25 eV) and are identical for three different excitation wavelengths: at 240, 260, and 280 nm. Their intensities exceed that of ordinary porous Si. So the designed structures have all-colour light-emitting properties. For the LN/Si structures without the SiO_2 buffer layer, no PL was observed. Similarly, for the SiO_2 layer without the LN coating, no PL was observed. This indicates that the obtained PL is closely connected with both the LN film and the SiO_2 layer. Investigations on the texture of LN films show that (006)-textured LN films have the strongest PL intensities. This provides a useful way to enhance the PL intensity. From the above results, we can infer that the photogeneration of carriers occurs in the coated films, while their radiative recombination takes place in the SiO_2 surface. To confirm this point, we examined the corresponding PL excitation spectra, as shown in figures 3(c) and (d), which were obtained by monitoring at 503 or 606 nm luminescence bands of samples A and B, respectively. We can see from the two figures that the onset of the two bands occurs at

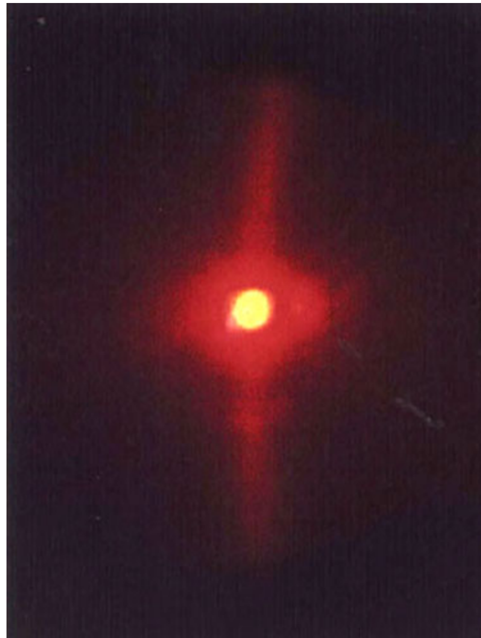

Figure 4. The observed m-lines of the waveguiding modes of sample A. The m-line is clear, indicating that the LN(Ge:LN)/SiO_2/Si structures have good waveguiding properties.

(This figure is in colour only in the electronic version)

$\sim$368 nm (3.37 eV), which is nearly equal to the fundamental optical absorption edge position of LN crystal [16]. This result supports our assignment to the observed PL bands [17].

Similar PL peaks have been observed for the crystalline and amorphous SiO_2 irradiated with ionizing radiation or with photons above the band-gap energy [17–21]. In our present samples, a strong SCF in the LN film can induce large lattice distortion in the SiO_2 surface. The photoexcited carriers in the LN films could be trapped by the distorted lattices of the SiO_2 surface to form self-trapped excitons and E′ defect pairs[2]. Since the self-trapped excitons are annihilated near to room temperature [21], the enhanced PL should be closely related to optical transitions in the intrinsic E′ defect pairs caused by the strong PRE of the coated films. They are neither pre-existing [22] nor produced by ultraviolet irradiation [20, 23–25], because the former should vanish under annealing over 800 °C and the latter should be annihilated at room temperature. Since the lattice distortions induced by the PRE may cause complicated local structure in the SiO_2 surface, slightly different emission energies can be expected in different samples. For the blue PL, the intensity decreases in the samples annealed in an oxygen atmosphere. Therefore, it could be attributed to optical transitions in the Ge-related oxygen deficiency centres [8].

Through the above investigations, we have achieved the key function of the LN(Ge:LN)/SiO_2/Si structures: serving as a light source in optoelectronics. However, when we apply the designed structures in optoelectronic integration, an important problem must be examined: do the LN films possess original optical properties? To clarify this point and meantime demonstrate optical waveguiding properties of the structures, we performed m-

[2] The self-trapped exciton is a pair of an oxygen vacancy and interstitial oxygen, which also forms a peroxy linkage with lattice oxygen (with two holes). The E′defect pair has the same composition with the self-trapped exciton.

line measurements of the transverse magnetic and electric multimodes of the waveguiding properties for our samples. A typical result for sample A is shown in figure 4. The observed line is clear, indicating that the LN/SiO_2/Si structures have good waveguiding properties and that the PRE has less influence on optical properties of the coated films. For sample B, a similar result is obtained except for a slight increase in the optical propagation losses. Therefore, this kind of LN(Ge:LN)/SiO_2/Si structure can also be expected to be applicable in photomodulators and photodetectors.

In conclusion, optoelectronic integration has been a dream for a long time. Our study shows that designed LN(Ge:LN)/SiO_2/Si structures can be expected to realize the fundamental functions (as light sources, optical waveguides, photomodulators, and photodetectors) of fully Si-based optoelectronics, which will stimulate substantial further development in information and communication technologies.

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