Impurity Evaluations of SiO₂ Films Formed on LiNbO₃ Substrates

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SiO₂ films deposited by sputtering (SP) and vacuum evaporation (VE) techniques are commonly used as buffer layers in LiNbO₃-based devices. The impurity levels in such films are measured as 10¹⁷ to 10²² atoms/cm³ for H, Li and Nb ions, which might affect the electrical properties of the devices. The major differences between the SP and VE films are in the density and the hydrogen contents, which possibly influence the I/V characteristics of the films and leads to different dc drift phenomena of LiNbO₃ optical modulators made of such layers.

KEYWORDS: SiO₂, LiNbO₃, impurities, films

1. Introduction

In LiNbO₃ optoelectronic devices, SiO₂ films are generally used as buffer layers between Ti:LiNbO₃ waveguides and metallic electrodes. Consequently, characteristics of the SiO₂ layer influence the device performance. For instance, the mechanical stresses induced by the film formation cause a refractive index fluctuation in the light waveguides, resulting in a shift of the operating point.⁴) Electrical properties of the device, such as the dc drift phenomenon, may be related to the chemical compositions of the buffer layer.⁵) In order to understand the dc drift, which is the key factor in device lifetime,⁶) the SiO₂ structure formed on LiNbO₃ must also be investigated, in addition to the defects and impurities in the LiNbO₃ wafer. It is known that the dc drift phenomena are significantly influenced by the nature of the SiO₂ layer. For instance, the SiO₂ layers formed by different deposition techniques lead to different dc drift results.⁶) Furthermore, the films generally require high-temperature annealing in an oxygen atmosphere,⁵) where diffusion of cations from the LiNbO₃ to SiO₂ is an inevitable problem, possibly leading to the formation of defects at the interface. These cation impurities themselves might be the origin of the dc drift, as well as oxygen defects.⁵) However, there have been no reports on the impurity analysis of SiO₂ films on LiNbO₃ substrates.

This article presents such data for two types of SiO₂ films deposited by sputtering (SP) and vacuum evaporation (VE) techniques. These two kinds of films were examined because different dc drift phenomena were observed for devices with SP and VE SiO₂ buffer layers. Figure 1 shows typical dc drift data for Mach-Zehnder modulators with SP and VE SiO₂ measured at 80°C and a fixed dc bias of 5 V during a 100-day period. The operating point of the SP sample drifts in the suppressing direction of the applied dc bias of 5 V within 1 day of operation. On the other hand, for the VE samples, the initial drift direction is opposite to that of the applied bias, and the drift rate is considerably slow throughout the long-term operation.

2. Experimental Results

The films were deposited on the –z face of LiNbO₃ wafers without any waveguides, and some of them were annealed at 600°C for 5 h in flowing wet O₂.⁶, ⁷) The samples for I/V measurements include the Ti indiffused waveguides. The rf-sputtering depositions (SP) were carried out using a SiO₂ target and an Ar/O₂ (=9/1) mixture at ambient temperature and 0.15 Pa. In the vacuum evaporation depositions (VE), the SiO₂ material was evaporated by electron-beam heating under 3 × 10⁻³ Pa of O₂. The purity of these SiO₂ source materials was 5 N grade.

Fig. 1. The dc drift results measured on the Mach-Zehnder optical intensity modulators consisting of the sputtered (SP) and vacuum evaporated (VE) SiO₂ buffer layers. The measurements are carried out at 80°C and fixed dc bias voltage of 5V during a 100-day period.

Fig. 2. Refractive indices of the sputtered (SP) and vacuum evaporated (VE) SiO₂ films on LiNbO₃ substrates. The broken and solid lines show the results of as-deposited and annealed films, respectively.
Figure 2 shows the refractive indices (n) of the 30-nm-thick films measured by ellipsometry. The n value of the as-deposited films (broken lines) decreased after the annealing treatment (solid lines) due to a reduction of the oxygen defects in the films.8) The smaller n of the VE-films indicate that the materials prepared by VE had a lower density than those prepared by SP. The relatively low densities of the VE-films were also detected via Si peak intensities in the Rutherford back-scattering (RBS) method.

From the RBS spectra, the major impurities in the films were clarified. Figure 3(a) exhibits the glancing-angle RBS results of the as-deposited (broken line) and an annealed (solid line) VE-films and the LiNbO3 wafer. The channel positions corresponding to O, Si and Nb are denoted by the arrows in Fig. 3(a). The SiO2 film thicknesses were determined to be about 300 nm from the RBS data and agreed with thicknesses measured by ellipsometry. It was assumed that the high-energy tails of the spectra were the result of the existence of Nb ions throughout the films. Furthermore, the hydrogen content of the annealed films was measured by the hydrogen forward scattering method, as shown in Fig. 3(b). The large peak of the SP-film (solid line) spectrum originated from surface adsorbed molecules. The number of hydrogen atoms was measured as $1.1 \times 10^{21}$ and $1.3 \times 10^{22}$ atoms/cm$^3$ for the SP- and VE-films, respectively. One of the reasons for such a large difference is that the VE-film of lower density could adsorb larger amounts of H$_2$O.

Finally, secondary ion mass spectroscopy (SIMS) was carried out to investigate Li and Nb contents in the films. Figures 4(a) and 4(b) show the impurity distributions of the SP-films, while (c) and (d) represent those of the VE-films. Results (a) and (c) are for the as-deposited films, while (b) and (d) are for the annealed films. To check the accuracy of the measurements, a SP-SiO2 film on a Si substrate was evaluated, where no Nb ($<<10^{15}$ atoms/cm$^3$) and $5 \times 10^{17}$ atoms/cm$^3$ of Li were detected. From the results, it is evident that Nb ions diffused into the film from the LiNbO$_3$ during the film deposition processes. A surprising result is that considerable amounts of Nb ions were incorporated in the VE-film, which is known to be formed via a lower energy process compared to the SP-film.9) After annealing, about $1 \times 10^{19}$ atoms/cm$^3$ of Nb ions remained in both films. The Nb concentrations of the as-deposited and annealed VE films seem to be different by one order of magnitude (Figs. 4(c) and 4(d)), although they appear to be almost the same in the RBS measurements (Fig. 3(a)). As a possible reason, an uneven concentration depending on the wafer position was considered but the results are yet to be confirmed. Concerning the Li ions, however, since $5 \times 10^{17}$ atoms/cm$^3$ of Li were detected, even in the film on the Si substrate, most of the Li incorporated in the films was transferred from the deposition source. For instance, the Li content in the VE source SiO$_2$ material was measured as 0.5 ppm. Due to the annealing, Li amounts in the films increased to the order of $10^{19}$ atoms/cm$^3$.

Figure 5 shows the SIMS depth profile through the film/LiNbO$_3$ interface of the annealed VE sample. The interface seems indistinct and Si was also detected in the LiNbO$_3$ surface. The presence of phases laterally formed at the LiNbO$_3$ surface by the interdiffusion phenomena and the concentration of OH ions (H$_2$O) may cause fluctuation of the SIMS profile at the interfaces. Furthermore, the RBS spectrum of the same sample could be fitted well to the curve assuming interdiffusion of Nb and Si rather than outdiffusion of Nb only. It is possible that SiO$_2$ film formation causes the compositional and structural fluctuations at the interface. Such fluctuations could influence the dc-drifts of the devices, as well as those introduced by the Ti indiffusion process which was previously reported by Minakata.10)

As mentioned above, the SiO$_2$ films on the LiNbO$_3$ contained H, Li and Nb impurities in the range of $10^{17}$ to $10^{22}$.

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Fig. 3. (a) RBS results of the as-deposited (broken line) and annealed (solid line) vacuum-evaporated (VE) SiO$_2$ films on LiNbO$_3$ substrates, and the LiNbO$_3$ substrate by itself is shown by the dotted line. The angle between the incident 2 MeV He$^+$ beam and the detector is $85^\circ$. (b) Result of hydrogen forward scattering of the annealed SP (solid line) and VE (broken line) films.

Fig. 4. SIMS results of the as-deposited (a) and annealed (b) SP-films and the as-deposited (c) and annealed (d) VE-films on LiNbO$_3$ substrates. The incident beam is O$_2^+$ at 6 kV.
These impurities influenced the electrical characteristics of the films. For instance, H\(^+\) and Li\(^+\) ions were ionic carriers themselves, and when Nb\(^{5+}\) ions occupied the Si sites of SiO\(_2\) networks, they doped electrons into the SiO\(_2\). In order to estimate the electrical conductance of such films, \(I/V\) characteristics between surface electrodes on the Ti:LiNbO\(_3\) optical modulators, including 1 µm-thick-annealed SP- or VE-film, were measured between ±100 V at 29\(^\circ\)C and 50% RH using a HP-4140B pA meter. The dimensions of the electrode pair on the SiO\(_2\)/LiNbO\(_3\) were 25 µm gap and 40 mm length perpendicular to the gap. The samples were placed in a shielded box during the measurement. Because the relaxation times of current \(I\) were on the order of seconds, depending on the sample, the \(I\) values 2 min after the application of \(V\) were recorded. The relaxation times at \(V = -5\) V, for instance, were 3.5, 11 and 6.2 s for the SP-SiO\(_2\)/LiNbO\(_3\), VE-SiO\(_2\)/LiNbO\(_3\) and LiNbO\(_3\) samples, respectively. These time-dependent changes in \(I\) were reversible and after turning off the \(V\), the \(I\) value recovered to the initial (noise) level of \(0.5 \times 10^{-12}\) A. Figure 6 shows the Poole-Frenkel plots for the results of the modulators with SP (circles) and VE-SiO\(_2\) (triangles) layers. The \(I/V\) characteristics of the Ti:LiNbO\(_3\) without the SiO\(_2\) (black marks) showed Ohmic behavior with the resistance of 6.1 × 10\(^{11}\) Ω. In the samples, including the SiO\(_2\) layers, the Poole-Frenkel behavior was dominant beyond ±20 V, suggesting that the electrons doped by the impurities were the main carriers at these voltages. The carrier density calculated simply from the results at 100 V, with the assumption of 1 µm field penetration and typical mobility of 0.1 cm\(^2\)/Vs for doped glasses,\(^{11}\) was on the order of 10\(^7\) to 10\(^8\)/cm\(^3\) which is significantly lower than the impurity densities measured by SIMS, even considering their possible inhomogeneous distribution in the wafer. Such low densities are possibly due to carrier recombinations.

3. Discussion and Conclusions

As a source of the dc drift of the LiNbO\(_3\) devices, the required material parameters for LiNbO\(_3\) crystal itself were recently clarified by Minakata\(^{10}\). In addition to the LiNbO\(_3\), the electrical characteristics of the SiO\(_2\) buffer layer, due to its structure and compositions, will also affect the dc drift phenomena. The direction of the dc drift was reported to depend on the difference in relaxation times between LiNbO\(_3\) and the SiO\(_2\) layer.\(^{12}\) The present results for SiO\(_2\) layers were partly affected by the LiNbO\(_3\) substrate. However, the signs of the relaxation time differences were found to be negative for VE-SiO\(_2\) (3.5–6.2 s) and positive for SP-SiO\(_2\) (11–6.2 s). These signs corresponded to their dc drift behavior, where the device with...
VE-SiO₂ drifted first in the opposite direction to the applied dc bias, while the drift direction of the SP-SiO₂ was the same as the applied dc bias (see Fig. 1). Therefore, the electron conductance in the buffer layers, mentioned here, is believed to affect the early short-term dc drift of LiNbO₃ modulators greatly. The possible origins of such a difference in the relaxation times, leading to the different early drift directions, in the VE and SP films are their density and hydrogen (OH) contents, as observed here.

For the long-term drift, however, other factors should be considered. In the VE-SiO₂ samples, for instance, the activation energies of the drift differed between the early stage toward the negative direction (0.5 eV), and the following positive one (0.9 eV, see Fig. 7(a)). The activation energy of the positive drifts observed in the SP-SiO₂ modulators was 1 eV (see Fig. 7(b)) and close to that of the positive drifts in the VE-SiO₂ ones, although their drift rates were somewhat different, as shown in the vertical axes of Figs. 7(a) and 7(b). Furthermore, both the SP-SiO₂ and VE-SiO₂ modulators with reduced hydrogen were observed to retain a small drift. These results suggest that rather than the hydrogen content of the SiO₂ layer, that in the LiNbO₃ substrate influences the long-term dc drifts. The influence of the fluctuation of Li, Nb and Si contents at the film/substrate interface on the drift is not clear yet because a specific difference could not be observed for the VE and SP SiO₂ films.

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