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Piezoelectricity in Poled Silica Films with Tetravalent Metal Dopants

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Abstract. Piezoelectricity was produced in silica films with tetravalent metal dopants by poling. Poling treatment in germanium-doped silica (Ge:SiO_2) glass films raises their of optical non-linearity and produces, among other things, the Pockels effect. We generated piezoelectricity in poled Ge:SiO_2 glass thin films. Tetravalent-metal-doped SiO_2 (M^{4+}:SiO_2) films were prepared on Si substrates by RF magnetron sputtering. We used germanium, titanium, and tin as doping materials. The piezoelectricity of the films was compared with the piezoelectricity of quartz. Piezoelectricity of the same order of magnitude as that in quartz was observed in the M^{4+}:SiO_2 films. However, less than a week later, the piezoelectricity disappeared almost completely in all the samples. To prevent the piezoelectricity from disappearing, we tried to pin the doping ions. We developed a pinning technique based on the structure of a Ge:SiO_2-Ti:SiO_2-Sn:SiO_2-super-lattice. This super-lattice structure was very effective in preventing the piezoelectricity from disappearing.

Keywords: Ge-doped silica, silica, germanosilicate, piezoelectricity, piezoelectric materials, poling, super-lattice structure

1. Introduction

Silica glass has been widely used in optical waveguides because of its superior optical transmission characteristics. Germanium (Ge) is typically doped into silica glass (germanosilicate, Ge:SiO_2) to increase the refractive index of optical waveguides. Many interesting phenomena can be observed in Ge:SiO_2 glass under ultraviolet irradiation, such as refractive index changes and increases in optical non-linearity. Some researchers have reported the presence of the Pockels effect in poled Ge:SiO_2 glass [1, 2]. An optical-fiber electro-optic modulator and a planer light-wave electro-optic switch that takes advantage of the Pockels effect in poled Ge:SiO_2 glass were developed [3, 4]. Because the Pockels effect is observed in materials lacking point symmetry, there will also be piezoelectricity in poled Ge:SiO_2 glass. We previously observed piezoelectricity in poled Ge:SiO_2 glass [5]. In this paper, we obtain piezoelectricity in germanium-doped and tetravalent-metal (such as titanium (Ti) and tin (Sn))-doped silica (M^{4+}:SiO_2) glass films fabricated by RF magnetron sputtering and subjected to poling treatment. However, although piezoelectricity was clearly observed, it rapidly disappeared with time. In many samples, the piezoelectricity disappeared almost completely in a matter of days. We believe that this was because the doping ions displaced by the poling returned to their original position. From disappearing, we developed a super lattice structure that enables the pinning of doping ions.

2. Mono-Impurity-Doped Films

2.1. Sample Preparation

Tetravalent-metal-doped silica (M^{+4}:SiO_2) glass films were fabricated on silicon substrates by RF magnetron sputtering. We used germanium, titanium, and tin as doping materials. A silica plate was used as the sputtering target, and doping material Ge, Ti, and SnO_2 pellets were put on the silica plate for doping. The films were deposited in an atmosphere of 90% argon and 10% oxygen by sputtering. The thickness of the deposited films was 4–10 μm. The films were poled by electric fields of 2–4 × 10^7 V/m temperature of 350–400°C.

2.2. Piezoelectricity Measurements

Figure 1 shows the experimental apparatus for measuring [5]. A poled M^{+4}:SiO_2 (M^{+4}: Ge, Ti and Sn) film and an x-cut quartz plate (reference plate) were positioned between metal rods. Then a dynamic stress was applied to the sample and the reference plate by pushing and releasing the insulator rod. The piezoelectric response voltage was amplified and recorded by an x-y recorder. Because the stress applied to the sample and to the reference plate are equal, d_{33} can be estimated from V_{sample} and V_R. A multi-channel electrocardiograph was used to amplify the faint piezoelectric response voltage.

The piezoelectric constant d_{33} of the sample is given by

$$d_{33} = \frac{V_{\text{sample}}}{V_R} d_{Q11}$$

where d_{Q11} is the d_{11} constant of quartz, and the plate normal of the substrate is defined as the z-axis. Figure 2 shows results for poled Ge:SiO_2 film. In Fig. 2(a) shows pattern of the stress applied to the film, where the negative stress corresponds to compressive stress. At time t_1, the insulator bar was pushed, and at t_3, it was released. During the stress transience from t_1 to t_2 and from t_3 to t_4, piezoelectric responses of the film and the reference plate were observed, as shown in Fig. 2(b) and (c). Figure 2(d) shows the response when the sample was positioned in the opposite direction. A reverse response voltage was observed. From these responses, we found that piezoelectricity was, in fact, produced in the poled Ge:SiO_2 film. The d_{33} value of the film was larger than the d_{11} of quartz, d_{Q11}, by 20–30%. In this case, the d_{33} value of the film was highest value of the sample for the doping amount of germanium about 12% (the germanium area ratio of the sputtering target).

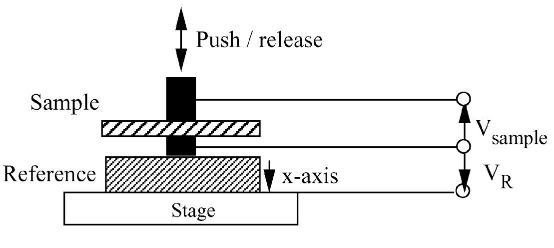


Fig. 1. Observation of the piezoelectricity.

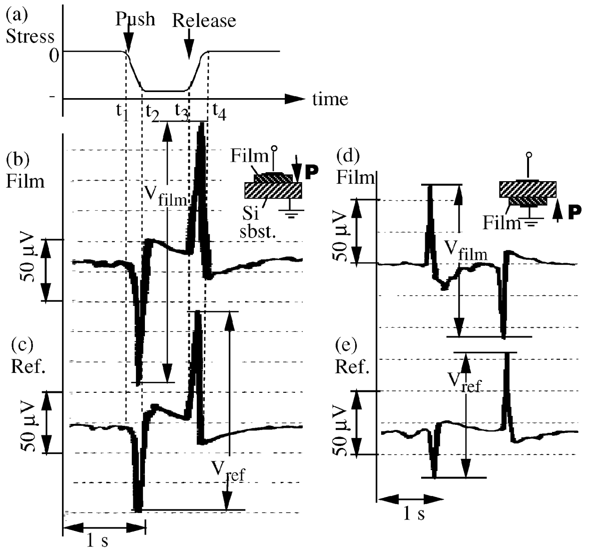


Fig. 2. Piezoelectric responses. Germanium area ratio of the target: 12%. $d_{33} = 1.2$–$1.3\, d_{Q11}$. (a) Pattern of the stress applied to the film and to the reference plate. (b) Piezoelectric responses of the film. (c) Piezoelectric responses of the reference plate. (d) The response when the sample was positioned in the opposite direction.

Figure 3 shows the dependence of the amount of the piezoelectricity on the extent of doping. The piezoelectric constant ratio is scattered because the optimum poling conditions have not yet been reached.

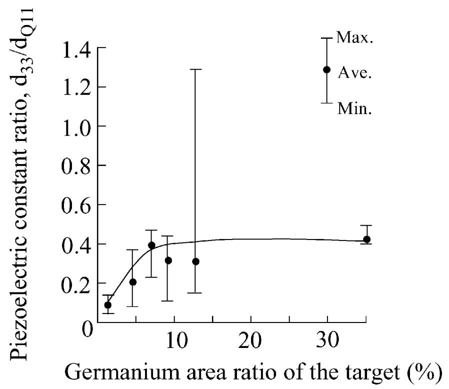
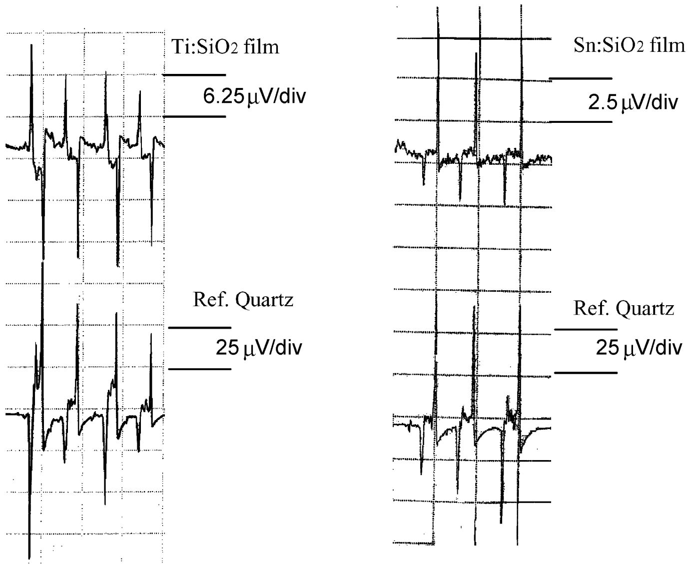


Fig. 3. Dependence of piezoelectric constant ratio on the germanium area ratio of the sputtering target.



(a) Ti area ratio of the target: 6.4%
$d_{33} = \fallingdotseq 0.25\ d_{Q11}$

(b) Sn area ratio of the target: 6.8%
$d_{33} = \fallingdotseq 0.12\ d_{Q11}$

Fig. 4. Piezoelectric responses. (a) Ti:SiO$_2$ film. (b) Sn:SiO$_2$ film.

However, Fig. 3 suggests that the optimum doping amount of germanium may be between 10 and 20%. In the case of Ti:SiO$_2$and Sn:SiO$_2$ samples, piezoelectricity similar to that of the Ge:SiO$_2$ film was observed. Figure 4 shows the observed piezoelectric responses. Figures 4(a) and (b) show the titanium-doped (Ti:SiO$_2$) and tin-doped (Sn:SiO$_2$) films, respectively.

There was a serious problem with the poled M^{+4}:SiO$_2$ thin films. The piezoelectricity was found to decrease with time as shown in Fig. 5. In the uniform layer, the piezoelectricity disappeared almost completely in less than five days. In all samples, the piezoelectricity continued to decrease rapidly. The origin of piezoelectricity in the poled M^{+4}:SiO$_2$ films has not been clarified yet, but a fundamental solution is needed to overcoming the disappearance phenomenon. Two methods may be effective here: (1) the construction of a super-lattice in Ge-, Ti-, and Sn-doped SiO$_2$ nanofilms, and (2) ultraviolet irradiation during the poling process. In the following section, we describe a technique to prevent the disappearance of piezoelectricity.

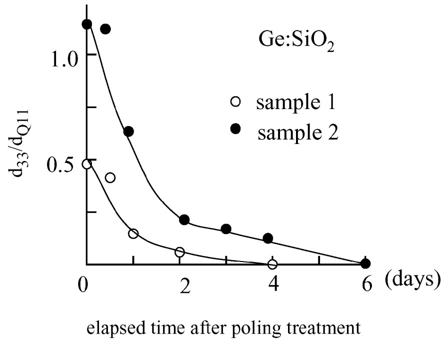


Fig. 5. Dissipation of piezoelectricity in Ge:SiO$_2$ film.

3. Super-Lattice Structure without Point Symmetry

3.1. Super Lattice of Ge-, Ti-, and Sn-Doped SiO$_2$

We constructed a super-lattice structure of Ge:SiO$_2$, Ti:SiO$_2$, and Sn:SiO$_2$ as shown in Fig. 6. In this structure, a triple layer of A (Ge:SiO$_2$), B (Ti:SiO$_2$), and C (Sn:SiO$_2$) composes the unit lattice. This structure does not have point symmetry. The ion radii of Ge^{+4}, Ti^{+4}, and Sn^{+4} are 53, 61, and 45 pm, respectively. The M^{+4} ions become displaced and scattered across the layer boundary as a result of poling.

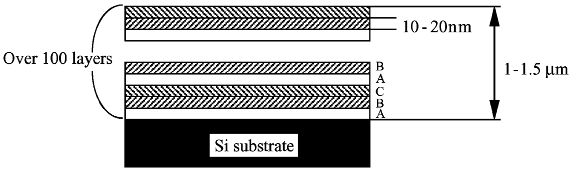


Fig. 6. Fabrication of super lattice by RF sputtering.

The M^{+4} ions penetrating into the adjacent layer will be trapped because of the ion radius difference. This structure will prevent the piezoelectricity from disappearing.

3.2. Experimental Results and Discussion

M^{+4}:SiO_2 thin films with a super-lattice structure were fabricated on silicon substrates by RF magnetron sputtering. Table 1 shows the specifications of the unit lattice. The films were prepared under various doping conditions. The thickness of each layer was about 10–20 nm, and the deposition time was 2–4 minutes. The number of layers was over 100, and the overall film thickness was about 1.5 μm. The films were poled by electric fields of about 2×10^7 V/m at a temperature of 350–400°C.

Figure 7 shows results for the poled M^{+4}:SiO_2 thin films a super-lattice structure. Clear piezoelectric responses were observed. The d_{33} value of the films was 70–100% the d_{11} of quartz.

Figure 8 shows how the piezoelectricity changed with time. In contrast to that of the uniform layer (Fig. 5), the piezoelectricity of the films with a super-lattice structure was constant for over two weeks. This suggests that the super-lattice structure is very effective as a means of piezoelectric M^{+4}:SiO_2 thin films. Further research on the super-lattice structure, doping amount, and poling condition will reveal the optimal conditions for the development of piezoelectric films.

Table 1. Structure of the unit lattice.

Layer	Material	Doping amount (%)	Thickness (nm)
A	Ge:SiO_2	7	10–20
B	Ti:SiO_2	10	10–20
C	Sn:SiO_2	5	10–20

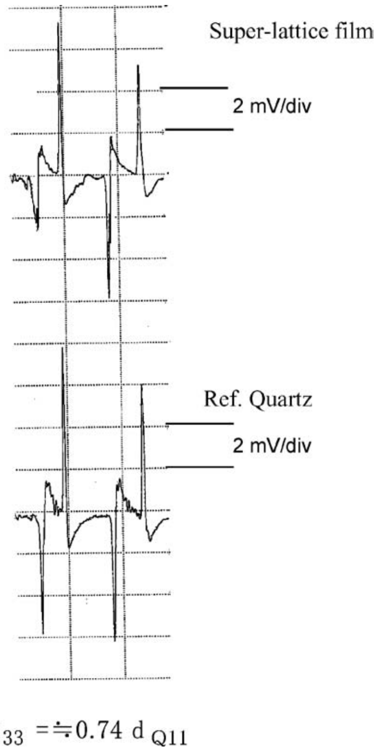


Fig. 7. Piezoelectric responses of the film with a super lattice.

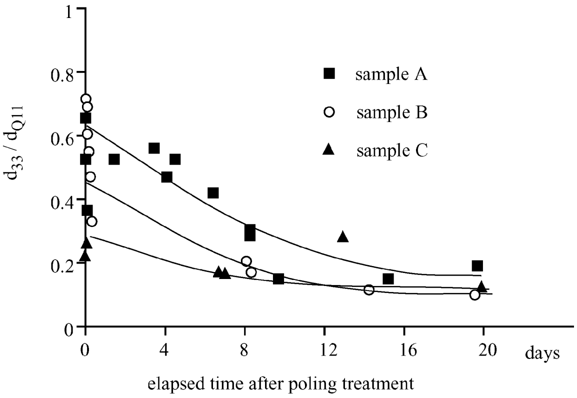


Fig. 8. Dissipation of piezoelectricity in the films with a super lattice structure film.

4. Conclusions

Piezoelectricity of SiO_2 thin films with tetravalent-metal impurities was investigated. In spite of the amorphous character of the films, poling treatment produced piezoelectricity in these films. The maximum piezoelectric constant, d_{33}, was of the same order to of magnitude as that of quartz (d_{11}). This is the highest value that has ever been obtained for Ge:SiO_2 film. We believe that it can be further to increased through investigation of the mechanism of piezoelectricity generation and improvements to the film fabrication process. The observed piezoelectricity disappeared with time. To prevent it from disappearing, we developed a super-lattice structure with three different M^{+4}:SiO_2 layers. The experimental results suggest that the super-lattice structure is an effective means of obtaining permanent piezoelectricity. Ultraviolet irradiation during poling may also be effective.

Further research is needed on the M^{+4}:SiO_2 super-lattice to produce piezoelectric films for practical use. Because SiO_2 has excellent optical properties, the fabrication piezoelectric SiO_2 films will pave the way for the development of many new acousto-optic devices.

Acknowledgment

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