PIEZOELECTRICITY IN GERMANIUM DOPED SILICA FILMS PRODUCED BY POLING

Takehiko UNO and Satoru NOGE

Kanagawa Institute of Technology, 1030 Shimo-Ogino, Atsugi 243-0292, Japan

Abstract

Piezoelectricity produced by a poling treatment was investigated in germanium-doped silica (germanosilicate, $Ge:SiO_2$) films. The germanosilicate films were prepared on Si substrates by RF magnetron sputtering. The films were poled by electric fields of 2 - 4 $\times 10^7$ V/m at a temperature around 350℃. Before the poling, a piezoelectric response was never observed. After the poling, a piezoelectric response caused by normal stress T_{33} on the film surface appeared. The poled film's maximum value of the piezoelectric constant, d_{33}, was more than twice that of quartz, d_{11}. Various applications of the piezoelectric $Ge:SiO_2$ film are expected to emerge.

KEY WORDS: Ge-doped silica, silica, germanosilicate, piezoelectricity, piezoelectric thin film, poling

1. INTRODUCTION

Silica glass has been widely adopted for use in optical wave-guides because of its superior optical transmission characteristics. The doping of germanium into silica glass (germanosilicate glass, $Ge:SiO_2$) is generally applied to increase its refractive index for optical wave-guide use. Many useful phenomena occur in germanosilicate glass, such as refractive index changes and increases of optical non-linearity under ultraviolet irradiation. These phenomena are applied to fabrication of optical fiber type devices such as optical fiber gratings. Furthermore, some authors have reported the presence of the Pockels effect in poled germanosilicate -Ref.1, Ref.2. An optical-fiber type electro-optic modulator and a planer light-wave circuit (PLC) type electro-optic switch that use the Pockels effect in poled germanosilicate have been developed -Ref.3, Ref.4. Because the Pockels effect exists in materials lacking point symmetry, piezoelectricity will appear as a result of poling the germanosilicate. We investigated the piezoelectricity in poled germanosilicate films deposited by a sputtering process. High piezoelectricity far larger than that of quartz was observed.

2. PREPARATION OF SAMPLES

To manufacture optical fibers and planer light wave circuits, silica glass is fabricated by melting an accumulation of fine silica particles. However, this process is not suitable for fabricating piezoelectric devices. A simpler process is desirable for fabricating piezoelectric thin films. For our study, the germanosilicate thin films were fabricated on silicon substrates by using RF magnetron sputtering. A silica plate was used as the sputtering target and germanium pellets were put on the silica plate for doping. The films were prepared for various doping conditions. However, the degree of doping in the films has not yet been analyzed. In this paper, instead of the actual degree of doping in the film, we used the percentage of the germanium pellet area to the total area of the target (germanium area ratio) as the measure of the degree of doping. The thickness of the deposited films was 4 - 10 μm. The films were poled by electric fields of 2 - 5$\times 10^7$ V/m at a temperature near 350℃.

3. OBSERVATION OF PIEZOELECTRICITY

3.1 Observation method

Figure 1 shows the observation apparatus of the piezoelectricity. A poled germanosilicate film and an x-cut quartz plate (reference plate) were positioned between metal rods. Then, dynamic stress was applied to both the sample and the reference plate by pushing and releasing the insulator rod. Piezoelectric response voltage was amplified and recorded by an x-y recorder. The piezoelectric response voltage for the film, V_{film}, is given by

$$V_{film} = R_{in} A \frac{\partial D}{\partial t} = R_{in} A \left(d_{33} \frac{\partial T}{\partial t} + \varepsilon^T \frac{\partial E}{\partial t} \right)$$

$$= R_{in} A \left(d_{33} \frac{\partial T}{\partial t} - \frac{\varepsilon^T}{h} \cdot \frac{\partial V_{film}}{\partial t} \right)$$

∴

$$V_{film} + \frac{\varepsilon^T}{h} \cdot \frac{\partial V_{film}}{\partial t} \approx V_{film} = d_{33} R_{in} A \frac{\partial T}{\partial t} \qquad (1)$$

where T is the applied stress, R_{in} is the input impedance of the amplifier, d_{33} is the piezoelectric constant of the film, A is the surface area of the metal rods, h is the film thickness, and C_0 is the

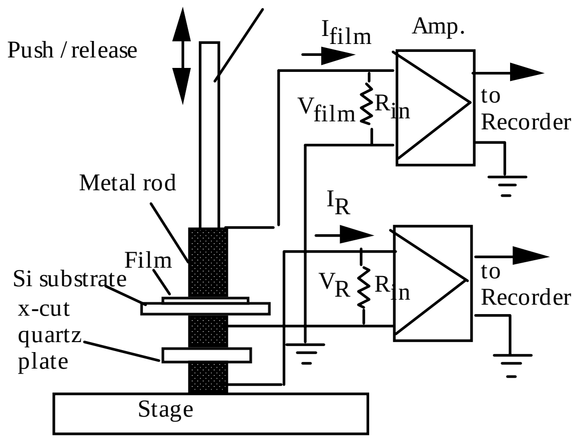

Fig. 1 Piezoelectricity observation method.

parallel capacitance, respectively. The plate normal of the film was defined as the z-axis. In this study, the second term on the left side was less than the first term by 10^{-3} even for 1 μm film thickness. Therefore, the second term of Eq. (1) can be neglected. In the same way, the piezoelectric response voltage of the reference plate, V_R, is given by

$$V_R = d_{Q11} R_{in} A \frac{\partial T}{\partial t} \qquad (2)$$

where d_{Q11} represents d_{11} of quartz, that is

$$d_{Q11} = 2.31 \times 10^{-12} \text{ C/N}$$

As the stresses applied to the sample and the reference plate are common, d_{33} can be estimated from V_{film} and V_R. A multichannel electrocardiograph was used to amplify the faint piezoelectric response voltage.

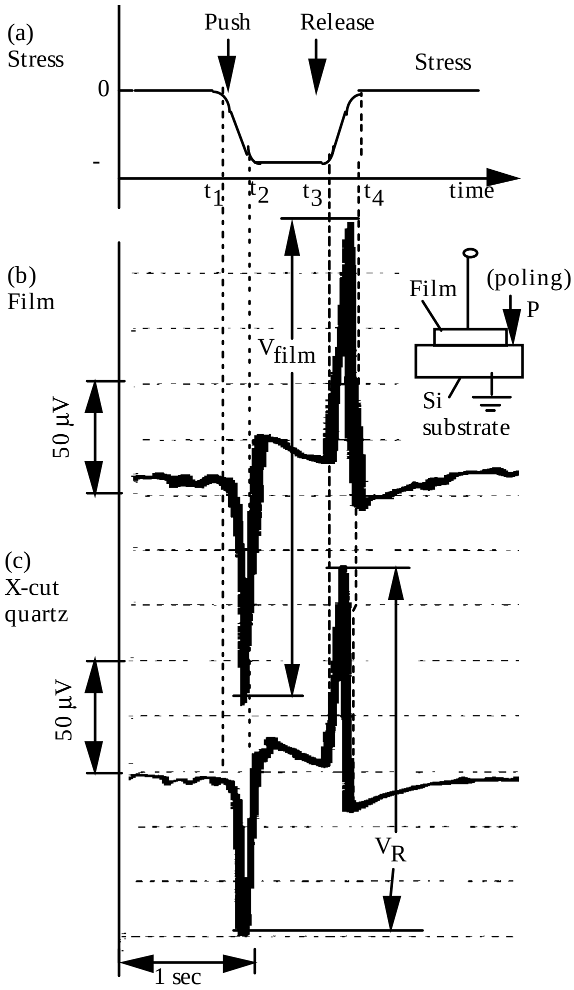

Fig. 2 Piezoelectric response (1).
Ge doping amount: about 12 %
V_{fim} = 220 μV, V_R= 170 μV,
d_{33} = 1.3 d_{Q11}

3.2 Piezoelectric response

Figure 2 shows an experimental result example. In Fig. 2, (a) is the stress pattern applied to the film, where negative stress corresponds to the compressive stress. At time t_1, the insulator bar was pushed, and at t_3, it was released. During the stress transients 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),

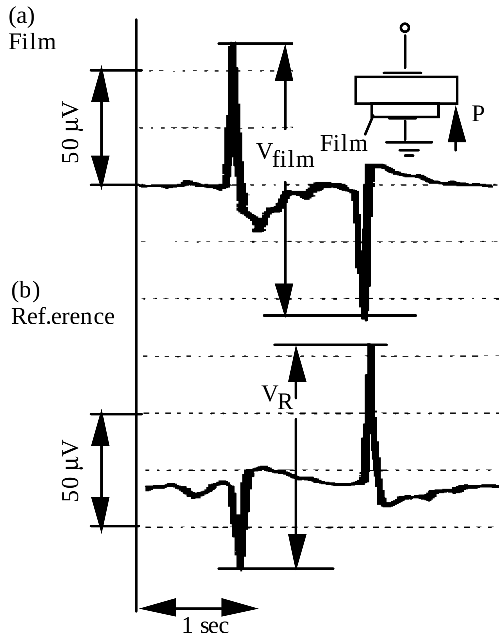

Fig.3 Piezoelectric response 2.
$d_{33} = (V_{film} / V_{ref}) d_{Q11} = 1.2\ d_{Q11}$

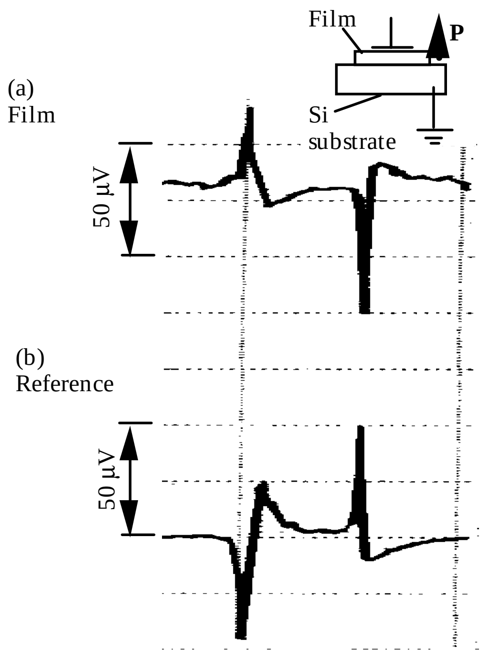

Fig. 4 Piezoelectric response (3).
d_{33} =0.95 d_{Q11}

respectively. Figure 3 shows the experimental result when the sample from Fig. 2 was positioned in the reverse direction. As compared with Fig. 2 (b), a reverse response voltage was observed in the sample. Figs. 2 and 3 show that the piezoelectric d_{33} value of the film was equal to about (1.2-1.3) x d_{Q11}.

To confirm that the piezoelectricity resulted from poling, a poling treatment for a reverse electric field was done. Figure 4 shows the piezoelectric response of a sample poled in the reverse direction. A reverse piezoelectric response was observed as compared with that in Fig. 2. These results demonstrate with certainty that that piezoelectricity was produced in a poled germanosilicate film.

The piezoelectric constant value depends on the fabrication conditions, i.e., sputtering condition, doping amount of germanium, poling condition, and others. Many investigations will necessary to clarify the optimum fabrication condition. In our experiments, we observed an interesting relationship between the film deposition method and the piezoelectricity. We did two-step deposition as shown in Fig. 5. Figure 6 shows the piezoelectric response for the poled film deposited by this two-step process. In spite of having the same poling condition as the samples in Figs. 2 - 4, very large piezoelectric response was observed in films receiving the two-step deposition. The d_{33} value was about 230% of d_{Q11}, that is

$$d_{33} \approx 5.31\times 10^{-12} \quad \text{C/N}$$

Electromechanical coupling constant, k_{33}, for the longitudinal wave was estimated as

$$k_{33} = d_{33} / \sqrt{\varepsilon^{T} s_{33}} \approx 0.256$$

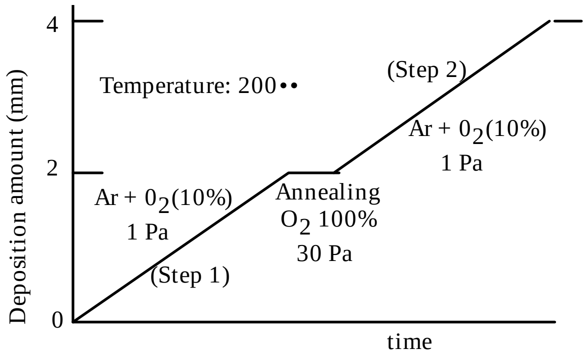

Fig. 5 Two-step deposition.

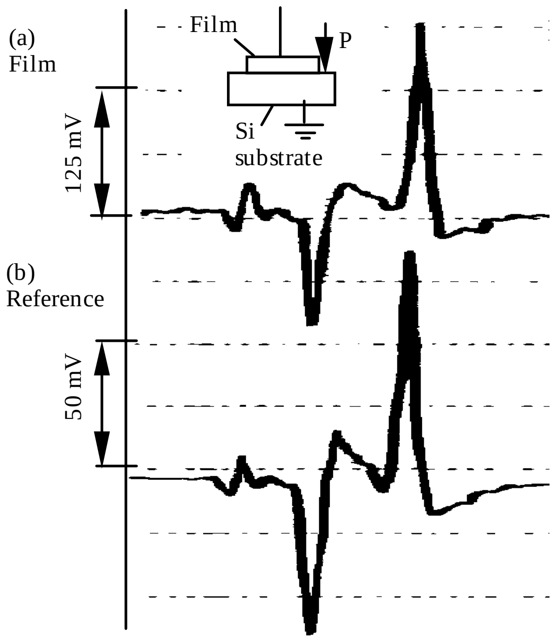

Fig. 6 Piezoelectric response of film prepared by two-step deposition.

d_{33}‡•2.3 d_{Q11}

3.3 Dependency on degree of doping

Figure 7 shows the dependence of piezoelectricity on degree of doping. Because the optimum poling condition has not been clarified yet, the resulting piezoelectric constant varies widely. Therefore, the maximum piezoelectric value for each doping condition was plotted. Fig. 7 suggests that the optimum germanium area ratio of the sputtering target may be around 10 %. The actual degree of germanium doping will not be far from this value.

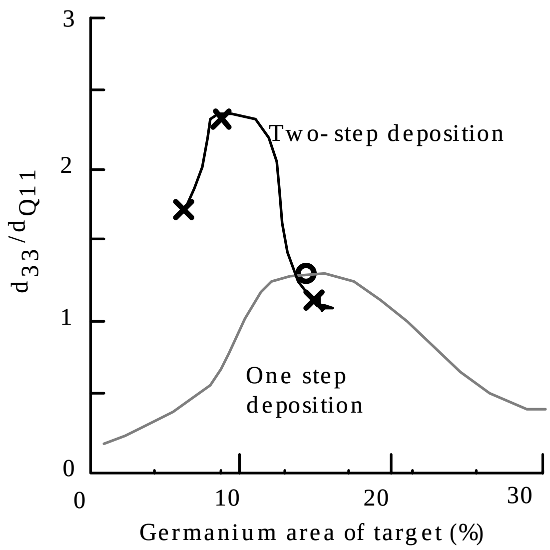

Fig. 7 Dependency on doping amount.

3.4 Reduction phenomenon

A serious problem exists in poled germanosilicate thin films at present. The piezoelectricity often decreases with time, as shown in Fig. 8 (a). Although some samples retained piezoelectricity for more than two years, the piezoelectricity rapidly decreased in many samples. We found that the piezoelectricity was easily recovered by poling at room temperature within 10 minutes. Furthermore, long term poling of more than 15 hours at room temperature slightly improved the reduction phenomenon as is shown in Fig. 8 (b).

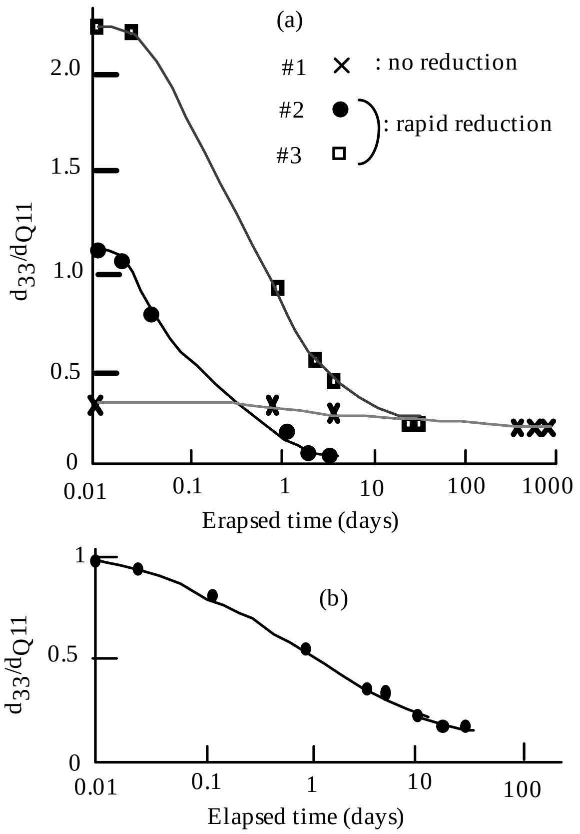

Fig. 8 Reduction of piezoelectricity.
(a) Examples of no-reduction and rapid reduction.
(b) Aging characteristic after long term poling for

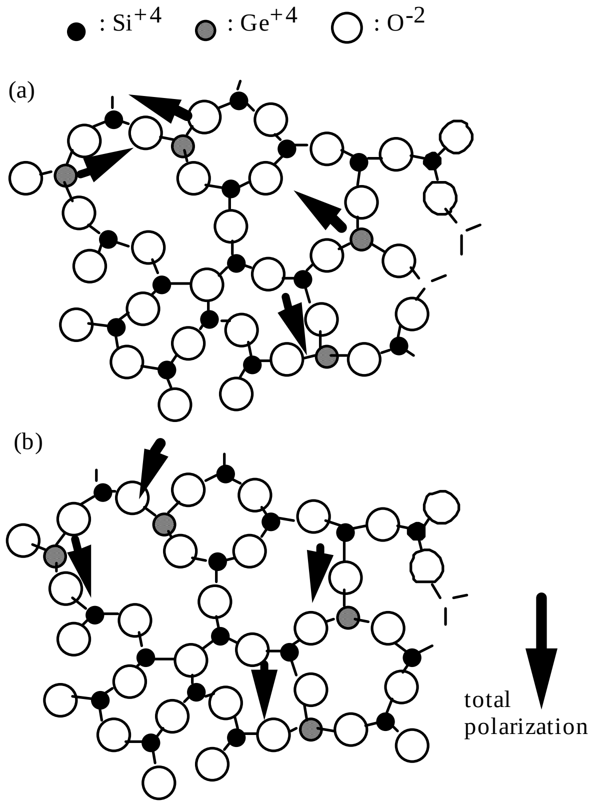

Fig. 9 Network structure of $Si\text{-}O_4$ and $Ge\text{-}O_4$ tetrahedra.
The fourth oxigen ion of each tetrahedora is not drawn in the figure.

4. MECHANISM OF THE PIEZOELECTRICITY

Although the origin of the piezoelectricity in the poled germanosilicate is not obvious yet, the network structure of $Si\text{-}O_4$ and $Ge\text{-}O_4$ tetrahedra may participate in it. Because the radius of a Ge^{+4} ion is larger than that of a Si^{+4} ion by 30 – 40%, the size of a $Ge\text{-}0_4$ tetrahedra is larger than of a $Si\text{-}O_4$ tetrahedra. Therefore, local stress exists around the $Ge\text{-}O_4$ tetrahedra and an electric dipole is produced. In non-poled germanosilicate, the dipole moments located around the $Ge\text{-}O_4$ tetrahedra cancel each other as shown in Fig. 9 (a), and piezoelectricity does not appear. During the poling process at a high temperature, the applied electric field causes ordering of the dipole moments as shown in Fig. 9 (b). Therefore, piezoelectricity appears. However, the ordering of the dipole moments gradually randomize and piezoelectricity decreases with time. To obtain permanent piezoelectricity, changes of chemical bonding around the $Ge\text{-}O_4$ tetrahedron will be necessary. Ultraviolet irradiation during the poling treatment may be effective for obtaining stable piezoelectricity.

5. CONCLUSION

We investigated piezoelectricity of poled germanosilicate thin films. In spite of the amorphous character of the film, the poling treatment produced a piezoelectric response in it. The maximum piezoelectric constant, d_{33}, obtained to date was more than 230% that of quartz d_{11}. We expect that further increases of the piezoelectric constant can be achieved by investigating the piezoelectricity mechanism and improving the fabrication process. We observed the phenomenon of a reduction in the piezoelectricity over time. Ultraviolet irradiation during poling may be effective both to increase the piezoelectricity and to solve the reduction phenomenon. Because germanosilicate is a superior material for use in constructing an optical wave-guide, new types of acousto-optical monolithic integrated circuits can be developed. We are planning to apply poled geramanosilicate films to BAW and SAW devices and new acousto-optical devices.

REFERENCES

1. X.C.Long, R.A.Myers and S.R.J.Brueck: Elentron. Lett. **30** (1994) 2162
2. P.G.Kazansky, P.St.jRussel, LDong and C.N.Pannell: Electron.Lett..**31** (1995) 62
3. T.Fujiwara D.Wong Y.Zhao, S.Fleming, S.Poole and M.Sceats: Electron. Lett. **31** (1995) 573
4. M.Abe, T.Kitagawa, K.Hattori, A.Himeno and Y.Ohmori: Electron. Lett. **32** (1996) 893