Germanium Oxide Layers Used for Forward Transfer of Electrical Circuits to Foreign Plastic Substrates

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Germanium oxide (GeO_x) films were used as a removing layer in order to transfer thin-film electrical circuits to foreign plastic substrates. GeO_2 films were formed by sputtering with mixed gases of oxygen and argon at room temperature. They were rapidly removed at an etching rate of 1000 nm/s by a hydrochloric acid solution with a pH of 0.1 at room temperature and also removed at 700 nm/s by hot water at 70°C. Using GeO_2 layers, the transfer of a hydrogenated amorphous silicon layer with Al electrodes to plastic films was demonstrated. [DOI: 10.1143/JJAP.44.6421]

1. Introduction

Low-temperature process technologies allow us to use inexpensive substrates such as glass substrates for fabricating thin-film transistors (TFTs).[1–3] Laser crystallization and plasma-enhanced-chemical-vapor deposition (PECVD) processes have been developed in order to reduce the processing temperature of TFTs.[4–8] TFTs and their electrical circuits have been widely fabricated below 400°C on glass substrates using these technologies. There has been another concept of fabricating electrical circuits on substrates with a low thermal resistivity. Sameshima has proposed the laser-induced forward transfer of thin films to foreign substrates using hydrogenated amorphous silicon (a-Si:H) films with a large amount of hydrogen atoms.[9] When the a-Si:H films were rapidly heated to a high temperature by pulsed laser irradiation from the rear side of quartz substrates, hydrogen gases in the films evaporated and gas pressure rapidly increased. The rapid hydrogen evaporation removed the thin-film layers formed on the a-Si:H films and transferred them to foreign substrates placed adjacent to them. Inoue *et al.* succeeded in formation of TFT electrical circuits and demonstrated a liquid crystal display driven by the TFT circuits on plastic films using the laser-induced forward transfer with a-Si:H layers.[10]

In this paper, we propose a method of transferring thin-film electrical circuits to foreign substrates using a germanium oxide (GeO_x) removing layer. We report the structural and optical properties of GeO_x films formed by the sputtering method. We then discuss the behavior of etching GeO_x films by acid solutions. We demonstrate the transfer of amorphous silicon thin films with Al electrodes formed on the GeO_x layers to plastic films by removing the GeO_x layers.

2. Experimental

GeO_x films were formed at room temperature by 13.56-MHz plasma sputtering with a germanium target. Gases mixed with argon and oxygen were used for combining germanium atoms with oxygen atoms in the plasma region. The flow rate of argon was 40 sccm and the flow rate of oxygen gas was changed in the range from 0 to 20 sccm. Quartz and crystalline silicon substrates were used to characterize the structural and optical properties of the GeO_x films. Spectroscopic ellipsometry was also used to investigate the refractive index in the visible region. Fourier transform infrared (FTIR) spectrometry was used to investigate the optical absorption of germanium-oxide molecular vibration. Rutherford backscattering spectrometry was used to investigate the ratio of germanium and oxygen compositions in the films.

Hydrochloric acid, hydrobromic acid, nitric acid, acetic acid, oxalic acid, hydrogen peroxide and water were used to investigate the rating behaviors of the GeO_x films with these etching solutions. The optical transmissivity of the samples was measured during etching reaction. A 632-nm-He–Ne laser beam was irradiated normally onto the surface of a transparent glass box containing the etching solutions. The laser beam passed through the transparent solutions and its intensity was measured by a photodiode placed just outside of the glass box. GeO_x and 100-nm-thick amorphous silicon (a-Si) layered structure (GeO_x/100-nm-a-Si) was formed on quartz substrates. The thicknesses of GeO_x were 500 nm and 3000 nm. The a-Si layer had the role of enhancing the optical interference effect. The samples were dipped into the etching solutions to a level deep enough to have the laser beam fall incident normally to the sample surfaces. The transmissivity is governed by the optical interference effect determined by the refractive indexes of the GeO_x, a-Si and quartz and the thickness of GeO_x and a-Si films.[11] An analysis of the change in the intensity of the laser beam passing through the samples revealed the etching rate of the GeO_x films.

The possibility of the forward-transfer of thin-film layered structures formed on GeO_x films was investigated. 200-nm-thick hydrogenated amorphous silicon (a-Si:H) films were formed at 350°C on a layered structure of 200-nm-thick SiO_2/1000-nm-thick GeO_x/quartz-glass substrate with a size of $4 \times 4\,cm^2$ by radio-frequency plasma chemical vapor deposition using gases mixed with H_2 and SiH_4. Afterward, 100-nm-thick Al metal films were evaporated and their electrodes were defined. Silicone resin was then coated on the Al/a-Si:H layer as the adhesive layer. Plastic films were finally placed on the silicone resin layer. The samples were heated in an oven at 80°C for 10 h in order to make the silicone resin very sticky. Soft and elastic rubber balloons were pasted onto the plastic films. The samples with balloons were dipped in hot water at 70°C in order to remove the GeO_x layer and achieve the present forward transfer. The dark conductivity and photoconductivity of a-Si:H were measured. Photoconductivity was measured under the illumination of a 532-nm CW laser at $50\,mW/cm^2$.
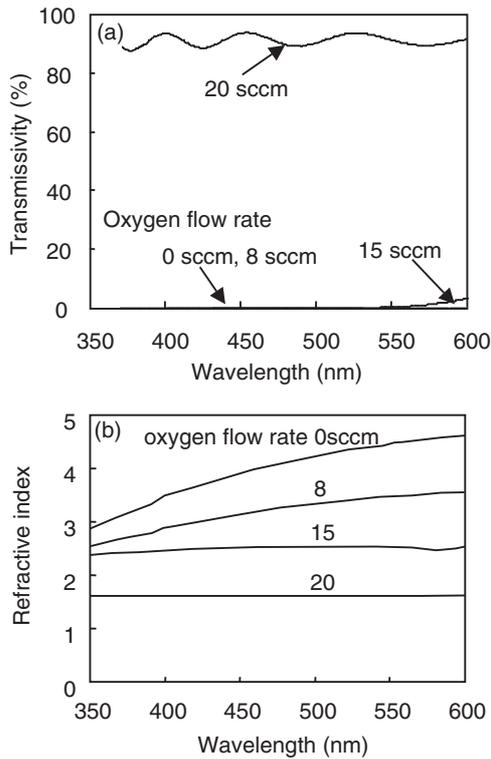
Fig. 1. Optical transmissivity spectra (a) and refractive index spectra (b) as functions of wavelength between 350 to 600 nm for 1000-nm-thick a-Ge and GeO$_x$ films formed on quartz substrates by sputtering with different oxygen flow rates in range from 0 to 20 sccm.

Fig. 2. Optical absorption spectra for GeO$_x$ films formed at different oxygen flow rates in range from 8 to 20 sccm on silicon substrates.

3.   Results and Discussion

Figure 1 shows optical transmissivity spectra (a) and refractive index spectra (b) as functions of wavelength between 350 and 600 nm for 1000-nm-thick amorphous germanium and GeO$_x$ films formed on quartz substrates by sputtering with different oxygen flow rates in the range from 0 to 20 sccm. Amorphous germanium had no optical transmission because of the high optical absorption associated with its low energy band gap. The optical transmissivity was still low for the cases of GeO$_x$ formed at oxygen flow rates of 8 and 15 sccm as shown in Fig. 1(a). On the other hand, a high optical transmissivity was observed in the case of GeO$_x$ formed at an oxygen flow rate of 20 sccm as shown in Fig. 1(a). This shows that germanium atoms were effectively combined with oxygen atoms so that the band gap increased and that the films were almost transparent. The refractive index decreased as the oxygen flow rate increased from 0 to 20 sccm as shown in Fig. 1(b). The refractive index was 1.6 at the oxygen flow rate of 20 sccm. Because the refractive index differed slightly from that of quartz substrates, there were small periodic oscillations associated with optical interference in the transmissivity spectrum as shown in Fig. 1(a). Figure 2 shows optical absorption spectra in the infrared region for the GeO$_x$ films formed at different oxygen flow rates from 8 to 20 sccm on silicon substrates. The optical absorption caused by germanium-oxide bonding was observed. The absorption intensity increased and the absorption peak wave number increased from 760 to 870 cm^{-1} as the oxygen flow rate increased from 8 to 20 sccm. Germanium-oxide bonding was effec-

tively formed by sputtering using gases mixed with oxygen and argon. The optical absorption peak of 870 cm^{-1} was lower than that of 1080 cm^{-1} for SiO$_2$.[12] The low peak wave number mainly results from the large reduced mass of Ge–O bonding compared with that of Si–O bonding. The spectral line shape of the GeO$_x$ films formed at an oxygen flow rate of 20 sccm was similar to that of stoichiometric GeO$_2$ obtained by Mei *et al.*[13] Rutherford backscattering spectrometry confirmed that films formed with a 20-sccm oxygen flow rate had 33-at. % germanium and 67-at. % oxygen. This means that our GeO$_2$ films were formed under the sputtering condition with an oxygen flow rate of 20 sccm.

Figure 3(a) shows the change in transmittance of the 632-nm He–Ne laser beam (solid curve) when a sample with a
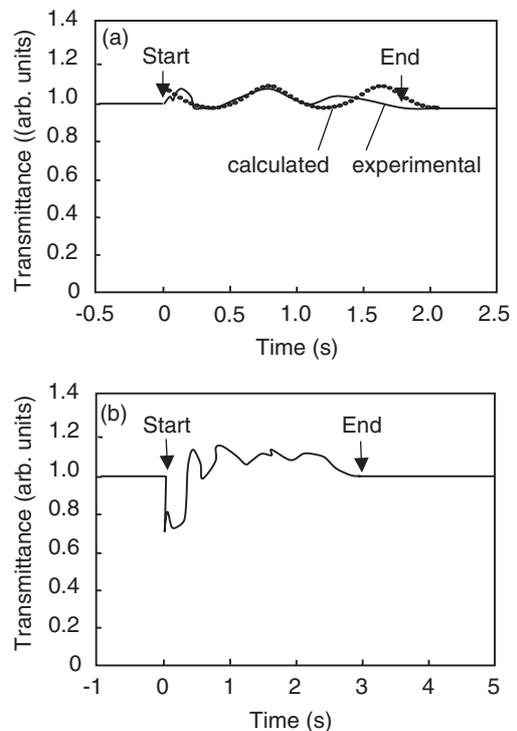
Fig. 3. Change in transmittance of 632-nm He–Ne laser beam for 500-nm thick (a) and 3000-nm thick (b) GeO$_2$ films formed on 100-nm-thick a-Si/quartz substrates. They were dipped into a hydrochloric acid solution with a pH of 0.1 at 0 s. The calculated transmittance at an etching rate of 250 nm/s is also presented in (a).

500-nm-thick GeO_2 film formed at an oxygen flow rate of 20 sccm on a quartz substrate was dipped into a hydrochloric acid solution with a pH (logarithmic value of hydrogen ion density) of 0.1 at room temperature. The transmittance had a small and periodic change for the initial 1.8 s and then leveled off. The dashed curve represents the calculated change in transmittance at 632 nm at an etching rate of 250 nm/s in the GeO_2 layer. The calculated transmittance had an oscillation caused by the optical interference effect according to the reduction in the film thickness of the GeO_2 layer. There was a good agreement in terms of oscillation between the experimental and calculated transmittances for initial 1.1 s. This means that the GeO_2 layer was removed by the hydrochloric acid solution at a rate of about 250 nm/s and it was uniformly thinned. After 1.1 s, the oscillation of the experimental transmittance changed faster than that of the calculated one. The oscillation was decreased and the experimental transmittance leveled off at 1.8 s. This indicates that the etching rate increased to about 320 nm/s after 1.0 s. On the other hand, the transmittance had a complicated change during etching in the hydrochloric acid solution with a pH of 0.1 for the 3000-nm-thick GeO_2 layer as shown in Fig. 3(b). The change in the transmittance was markedly different from the periodic change shown in Fig. 3(a). The change was completed 3 s after dipping the sample into the etching solution. These results mean that no layered etching took place but rapid etching occurred in the case of the 3000-nm-thick GeO_2 layer. The 3000-nm-thick GeO_2 film probably had a porous structure, which allowed rapid incorporation of the etching solution into the film. Therefore removal of some GeO_2 clusters probably occurred. The etching rate of GeO_x films formed at oxygen flow rates of 8 and 15 sccm were also investigated for a hydrochloric acid solution with a pH of 0.1 at room temperature. It was lower than 0.35 nm/s. This means that the formation of stoichiometric GeO_2 films is important in achieving a high etching rate.

Figure 4 shows the etching rates of 3000-nm-thick GeO_2 films formed at an oxygen gas flow rate of 20 sccm as functions of pH at room temperature for solutions of hydrochloric acid, hydrobromic acid, nitric acid, acetic acid, oxalic acid, hydrogen peroxide and water. The etching rates of the GeO_2 films were approximately governed by pH.
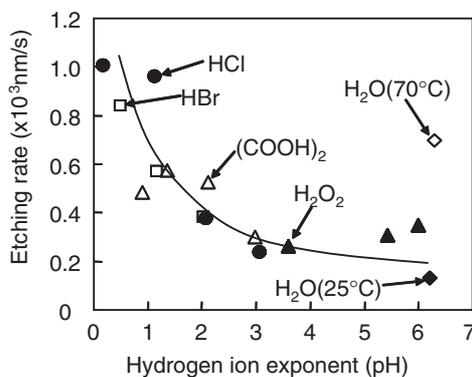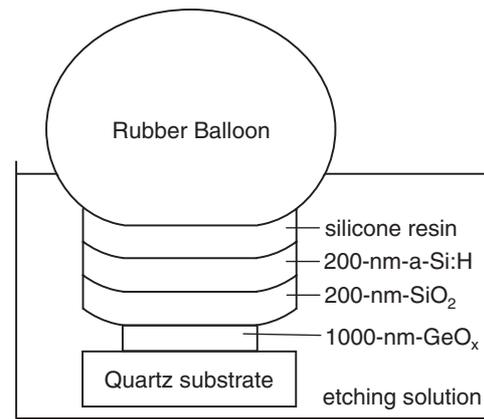
Fig. 5. Schematic image of forward transfer of a-Si:H films to plastic films by etching the GeO_2 removing layer with the help of rubber balloon.

They increased to 1000 nm/s as pH decreased to 0.1. There was no preferential solution for etching GeO_2. This result indicates that the hydrogen ion plays an important role in GeO_2 etching. Germanium oxide was effectively deoxidized by hydrogen ions and dissolved in acid solutions. The GeO_2 films were also etched by water. It is interesting that a high etching rate of 700 nm/s was achieved for hot water at 70°C, although the etching rate was 100 nm/s for water at room temperature. This indicates that the solubility of GeO_2 markedly increases with temperature as in $Alum(AlK(SO_4)_2)$.[14]

Al/a-Si:H layered structures were transferred to plastic films using a silicone resin as an intermediate adhesive layer. We used hot water at 80°C for 3 h to remove GeO_2 layers and to avoid any damage in Al because Al is susceptible to damage by acid solution or its vapor. The GeO_2 layers were successfully disolved in water and removed. The rubber balloon helped the etching of the GeO_2 layer, as shown in Fig. 5. When the GeO_2 at the sample edge region was removed, the plastic films at the edge became free and bent along the spherical surface of the balloon. This induced an easy incorporation of the etching solution to the fresh GeO_2 surface. The chain cycle of GeO_2 etching and plastic film bending resulted in an effective removal of the GeO_2 layer. Through the etching process, Al/a-Si:H structures were successfully separated from quartz glass substrates. Figure 6 shows a photograph of the Al electrodes and the underlying a-Si:H layer transferred to plastic films. The photograph was taken from the rear side of the plastic films. The Al electrodes and the a-Si:H layer were precisely transferred with no serious damage. Figure 7 shows the dark conductivity and photoconductivity of a-Si:H measured before and after the transfer process. The initial dark conductivity was 1.5×10^{-7} S/cm and the photoconductivity was 8×10^{-4} S/cm. After the transfer process, the electrical conductivity was measured by probing Al electrodes through a-Si:H layers. The dark conductivity was 1.6×10^{-7} S/cm and the photo conductivity was 1.7×10^{-3} S/cm. The reason behind the high photoconductivity after the transfer process is not yet clear. The soft silicone resin layer allowed the surface of a-Si:H to be curved owing to stress caused by the metal probes contracting the Al electrodes. The reflectivity at the wavelength of laser light might be reduced and the incident

Fig. 4. Etching rates of 3000-nm-thick GeO_2 films as functions of pH at room temperature for different solutions and water. The etching rate of the GeO_2 films for water at 70°C is also presented.
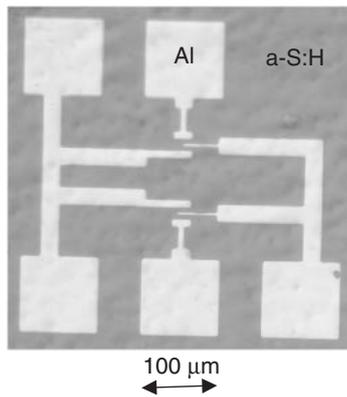
Fig. 6. Photograph of Al electrodes and underlying a-Si:H layer transferred to plastic films. The photograph was taken from the rear side of the plastic films.

Fig. 7. Dark conductivity and photoconductivity of a-Si:H measured before and after transfer process. Photoconductivity was measured under the illumination of a 532-nm CW laser at $50\,\mathrm{mW/cm^2}$.

light intensity would be increased by the change in the optical interference effect of the layered structure due to the surface curving. Similar dark conductivities and photoconductivities before and after the transfer process suggest that the electrical properties of a-Si:H films were retained well during the transfer process because no serious damage was inflicted during the process. The present experimental results show that the GeO_2 removing layer can transfer electrical circuits with no serious damage to foreign plastic substrates.

4. Summary

We investigated a method of transferring thin-film electrical circuits to foreign substrates using a Germanium oxide (GeO_x) removing layer. GeO_x films were formed at room temperature by plasma sputtering in mixed gases of argon (40 sccm) and oxygen with a germanium target. GeO_x films formed at an oxygen flow rate of 20 sccm had a refractive index of 1.6 in the visible region. RBS analysis clarified that the composition ratio of Ge : O at an oxygen flow rate of 20 sccm was 1 : 2. The GeO_2 films were removed at an etching rate of 1000 nm/s by hydrochloric acid solutions with a pH of 0.1 at room temperature. They were also removed at 700 nm in hot water at 70°C. 200-nm-thick a-Si:H films with Al electrodes with an area of $4 \times 4\,\mathrm{cm^2}$ were transferred to plastic films by etching the GeO_2 layers underlying the a-Si:H layers in hot water at 80°C for 3 h. Rubber balloons were used in order to enhance GeO_2 etching in the lateral direction. a-Si:H films had a dark conductivity of $10^{-7}\,\mathrm{S/cm}$ and a photoconductivity of $10^{-3}\,\mathrm{S/cm}$. They were not affected by the transfer process. These results show that the present method inflicted no

serious damage on the films to be transferred to the plastic films.

1) S. Uchikoga and N. Ibaraki: Thin Solid Films **383** (2001) 19.
2) S. Inoue, K. Sadao, T. Ozawa, Y. Kobashi, H. Kwai, T. Kitagawa and T. Shimoda: Tech. Dig. IEDM, 2000, p. 197.
3) K. Shibata and H. Takahashi: Proc. Int. Workshop Active Matrix Liquid Crystal Displays'01, 2001, p. 219.
4) T. Sameshima, S. Usui and M. Sekiya: IEEE Electron Device Lett. **7** (1986) 276.
5) K. Sera, F. Okumura, H. Uchida, S. Itoh, S. Kaneko and K. Hotta: IEEE Trans. Electron Devices **36** (1989) 2868.
6) T. Serikawa, S. Shirai, A. Okamoto and S. Suyama: Jpn. J. Appl. Phys. **28** (1989) L1871.
7) A. Kohno, T. Sameshima, N. Sano, M. Sekiya and M. Hara: IEEE Trans. Electron Devices **42** (1995) 251.
8) Z. Chen, S. K. Pang, K. Yasukake and A. Rohatigi: J. Appl. Phys. **74** (1993) 2856.
9) T. Sameshima: Appl. Surf. Sci. **96–98** (1996) 352.
10) S. Inoue, S. Utsunomiya, T. Saeki and T. Shimoda: IEEE Trans. Electron Devices **49** (2002) 1353.
11) M. Born and E. Wolf: *Principles of Optics* (Pergamon, New York, 1974) Chaps. 1 and 13.
12) T. Sameshima, K. Sakamoto and K. Asada: Appl. Phys. A **69** (1999) 221.
13) Y. F. Mei, G. G. Siua, X. H. Huang, K. W. Cheah, Z. G. Dong, L. Fang, M. R. Sheng, X. L. Wu and X. M. Bao: Phys. Lett. A **331** (2004) 248.
14) *Chronological Scientific Tables*, ed. National Astronomical Observatory (Maruzen, Tokyo, 1995) p. 452.