Forward Transfer of Thin-Film Devices to Flexible Substrates by Applying Thermal Stress

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We report the transfer of thin semiconductor films from a glass substrate to a plastic film using a germanium dioxide (GeO_2) removing layer formed between the thin semiconductor films and the glass substrate. We applied thermal stress to achieve a rapid lateral etching of the GeO_2 layer at several tens of mm/min by introducing an epoxy layer as an adhesive to attach the thin films to the plastic films. The GeO_2 layer was dissolved up to a distance of 5 mm from the edge region of the 4-in.-diameter samples when the samples were kept in an 80–100 °C hot water bath for 90 min. The subsequent cooling of the sample at room temperature caused the complete etching of the GeO_2 layer within 2 min. The rapid GeO_2 dissolution resulting from the thermal stress induced by the epoxy layer bent the thin semiconductor layer and plastic films in the edge region and introduced water into the central region of the samples. Polycrystalline silicon thin-film transistors (poly-Si TFTs) were successfully transferred onto plastic films using the present method.   [DOI: 10.1143/JJAP.46.6469]

KEYWORDS: germanium dioxide, high-rate etching, thermal stress, transfer

1.   Introduction

Low-temperature polycrystalline silicon (LTPS) thin-film transistors (TFTs) have received increasing attention since the development of active-matrix liquid crystal displays owing to the cost-effectiveness and high-performance of such devices. Recently, the fabrication of LTPS TFTs on plastic substrates has also received attention since they are light-weight, inexpensive, and robust. It is difficult to fabricate polycrystalline silicon (poly-Si) TFTs directly on plastic substrates because the fabrication includes a processing temperature of more than 300 °C. A technique of transferring thin-film devices provides a solution to this problem, since the thin-film devices can be transferred to plastic substrates after being fabricated on glass substrates. Since Sameshima proposed the laser-induced forward transfer of thin-film materials, several thin-film transfer methods have been proposed.[1–8]

The authors have also developed a new forward transfer method.[8] Thin-film devices on foreign plastic substrates can be obtained using this transfer method with the following procedure. A sample with a layered structure of plastic, adhesive, a thin-film device, a GeO_2 layer, and a glass substrate (plastic/adhesive/thin-film device/GeO_2/glass) is first prepared. The device layer can be fabricated even at processing temperatures of more than 300 °C, because it is fabricated before being attached to a plastic substrate. The sample is immersed in an etchant to dissolve the GeO_2 layer; consequently, the plastic/adhesive/device layered structure is separated from the glass substrate, as shown in Fig. 1.

One of the critical issues is that the GeO_2 removing layer, which has a thickness of ~1 μm, is etched laterally only from its narrow side edges. Thus, a technique for high-rate GeO_2 etching is indispensable. It is commonly believed that a high etching rate can be achieved by mainly considering solution temperature, concentration, and the components of the etchants used. In fact, we have reported the removal of a GeO_2 film at a high etching rate of 60 μm/min in a 25 °C hydrochloric acid solution with a pH of 0.1. In addition, we
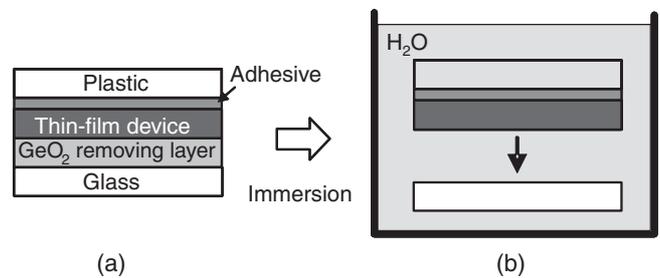
Fig. 1.   Schematic diagram of present forward transfer method. (a) shows the sample before immersion in the 80–100 °C hot water and (b) shows the image after the glass was separated from the original sample.

considered using wet etching with the help of ultrasonic vibration or stirring.[9] As another example, Takechi *et al.* reported that spray etching is also effective for obtaining a high etching rate higher than 10 μm/min.[10] However, even with an etching rate of several tens of μm/min, it still takes as long as 10 h to etch the GeO_2 layer to a distance of only 50 mm from the sample edge. For a practical transfer process, an innovative high-rate etching method should be developed.

In this paper, we introduce a method of dissolving the GeO_2 removing layer at an ultrahigh rate of several tens of mm/min. We also discuss the removal mechanism and the factors that play important roles in the rapid GeO_2 etching. Moreover, we demonstrate the transfer of a TFT array onto a plastic substrate.

2.   Experimental Procedure

By using $4 \times 4 \, cm^2$ samples with a layered structure of plastic/adhesive/50-nm-thick amorphous silicon (a-Si)/200-nm-thick SiO_2/1-μm-thick GeO_2/quartz, the removal of the GeO_2 layer was carried out to investigate the effect of the adhesive layer on the processing time and the extent of damage of the a-Si layer. Two adhesive materials with different elastic and thermal expansion coefficients, shown in Table I, were used to prepare two samples. The two samples were fabricated using the following procedure. 1-μm-thick GeO_2, 200-nm-thick SiO_2, and 50-nm-thick a-Si

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Table I. Comparison of thermal expansion coefficient and elastic coefficient between two kinds of adhesives.

Main component	Acrylic and special polymer containing silyl group	Epoxy
Thermal expansion coefficient ($\times 10^{-5}$/°C)	21	6.5
Elastic coefficient (MPa)	1.5	413

films were sequentially formed on $4 \times 4\,cm^2$ quartz substrates using 13.56 MHz RF sputtering. A thermosetting epoxy adhesive was used to coat the Si film for one of the two samples. A soft elastic adhesive, made of acrylic and a special polymer containing a silyl group, was used to coat the Si film for the other sample. The thermosetting epoxy was cured at 120 °C for 30 min, whereas the soft elastic adhesive was cured at room temperature for 3 h. The plastic substrates were attached to the adhesive layers at room temperature using a silicone resin. The two samples were immersed in H_2O at a constant temperature of 80 °C for 30 min to dissolve the GeO_2 removing layer up to approximately 1 mm from the sample edge and then cooled in 25 °C ambient air and visually checked whether substantial change in the etching rate of the GeO_2 layer occurs.

As described later in §3 a rapid GeO_2 dissolution occurs when using the epoxy as the adhesive layer. We investigated whether the rapid GeO_2 dissolution was related to the thickness of the epoxy layer and the cooling rate during the cooling. We prepared samples with different epoxy thicknesses of 270 and 130 μm on the basis of a plastic/silicone/epoxy/50-nm-thick poly-Si/200-nm-thick SiO_2/1-μm-thick GeO_2/quartz structure with a size of 4 in. The 130- and 270-μm-epoxy-coated samples were immersed in H_2O at 80 °C for 90 min. After that, both were cooled in 25 °C ambient air and visually checked whether rapid GeO_2 dissolution had occurred. A transfer experiment was also carried out on another 270-μm-epoxy-coated sample using a cooling rate lower than that occurring in ambient air. The sample was immersed in 80 °C H_2O for 90 min. Then it was slowly cooled at 1 °C/min to 25 °C using a heater by keeping it in hot H_2O. We determined whether the complete separation of the glass substrate from the original sample finished before the temperature reached 25 °C.

The transfer technique was applied to a poly-Si TFT array. It was fabricated on the basis of a sample with a layered structure of 25-nm-thick a-Si/200-nm-thick SiO_2/1-μm-thick GeO_2/quartz glass substrate. Phosphorus (P) dopant atoms were implanted into the a-Si film by ion implantation. The P-doped a-Si film was irradiated with a 30-ns-pulsed XeCl excimer laser at an energy density of 250 mJ/cm² to activate the P dopants. In order to form channel regions, SF_6 etching was carried out using a metal mask. Then, an undoped 25-nm-thick a-Si layer was formed by RF sputtering. The sample was again irradiated with the 30-ns-pulsed XeCl excimer laser at an energy density of 250 mJ/cm² to crystallize all of the silicon layers. Doped-Si regions were formed because P dopants diffused up to the upper undoped Si layer during the laser irradiation. Oxygen plasma treatment was performed at 250 °C and 100 W for 10 min to reduce the number of defects in the Si films. SF_6 etching was again performed to produce silicon islands using another metal mask. Then, Al source and drain electrodes were formed on the doped regions by vacuum evaporation, and SiO_2 gate insulators were formed by RF sputtering. Finally, Al gate electrodes were formed on the gate insulators. The one-part thermosetting epoxy adhesive was coated at more than 200 μm thick on the poly-Si TFTs and cured at 120 °C for 0.5 h on a hot plate. A plastic substrate was attached to the epoxy layer using silicone resin. The sample was immersed in H_2O at 80 °C for 30 min. Then, it was cooled in 25 °C ambient air to dissolve the remaining GeO_2 layer completely. The transfer characteristics of the fabricated TFTs were measured before and after the transfer.

3. Results and Discussion

The transfer of $4 \times 4\,cm^2$, 50-nm-thick a-Si films was carried out using the two samples with the soft or epoxy adhesive and the plastic/adhesive/50-nm-thick poly-Si/200-nm-thick SiO_2/1-μm-thick GeO_2/quartz structure. By immersing the samples in 80 °C H_2O for 30 min, the GeO_2 layers of both samples were removed up to approximately 1 mm from the sample edge. Immediately after they were cooled in 25 °C ambient air, a rapid dissolution of the GeO_2 layer started for the sample with the epoxy layer, whereas there was no visible change in the GeO_2 etching rate for the sample with the soft adhesive. Consequently, the remaining GeO_2 layer on the sample with the epoxy was completely removed 40 s after the cooling. On the other hand, it took 2 h to remove the remaining GeO_2 layer on the sample with the soft adhesive by a continuous immersion in H_2O at 80 °C. Figure 2 shows the photographs of the a-Si films with the epoxy and soft adhesive that were transferred to the plastic films. Essentially, no cracking was observed in the a-Si film with the epoxy, whereas many cracks were observed in the film with the soft adhesive layer. As for the film with the epoxy, no additional cracks were observed even under an optical microscope with 50 magnifications.

(a)   (b)
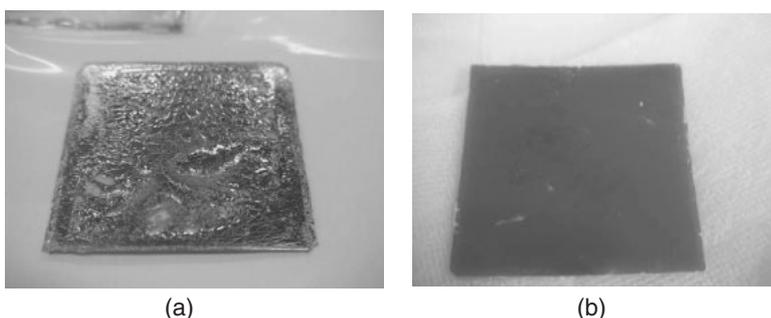
Fig. 2. Photographs of $4 \times 4\,cm^2$ a-Si films transferred to plastic substrates with two kinds of adhesives: (a) Acrylic and special polymer containing silyl group and (b) epoxy.

We consider the following mechanism for explaining the rapid GeO_2 dissolution for the sample with the epoxy. The quartz substrate was $500\,\mu m$ in thickness and the epoxy layer was considered to be a few hundred μm in thickness. Both materials are relatively hard. Thus, the intensity of thermal stress produced in the sample is considered to be predominated by the epoxy layer and quartz substrate. According to studies on bonded joints of two dissimilar materials, internal thermal stress intensity is mainly predominated by the difference in the thermal strain and elastic coefficient ratio of the two dissimilar materials.[11] Both the epoxy and soft adhesive have thermal expansion coefficients that are more than 100-fold larger than that of quartz. On the other hand, the elastic coefficient of the epoxy, $413\,MPa$, is 2 orders of magnitude larger than that of the soft adhesive, $1.8\,MPa$. Such a large difference in the elastic coefficient results in the rapid GeO_2 dissolution in the sample with the epoxy adhesive. (Note that this soft adhesive was originally developed to reduce the stress resulting from the bonding of two different materials.) The epoxy-coated sample for the transfer was found to be slightly bent inward. This was due to fact that the sample was cooled to room temperature ($25\,°C$) after the epoxy was cured on the Si layer at $120\,°C$. According to ref. 11, when bonded joints of dissimilar materials have a certain thermal residual stress, normal stress is present around the interface edge, whereas shear stress is present along the interface, except at its edge. It would not matter if we apply this tendency of stress distribution to our epoxy-coated sample. Figure 3 shows the predicted stress distribution of our epoxy-coated sample, which is based on ref. 11. The normal stress around the interface edge is
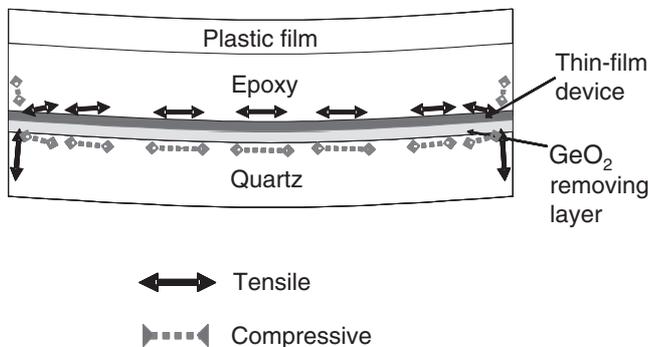
supposedly not sufficiently large to peel prior to immersion in H_2O [Fig. 4(a)]. When the sample was immersed in H_2O at a constant temperature of $80\,°C$ for 30 min, the GeO_2 layer was dissolved up to approximately 1 mm from the sample edge at an etching rate of several tens of $\mu m/min$. There is almost no doubt that the thermal stress in the sample was low during the immersion in H_2O [Fig. 4(b)]. The sample showed a shallow cave in the GeO_2-removed region between the quartz and epoxy layers. When the sample was cooled in ambient air, the thermal stress must have increased to a value as large as that present before the immersion in the hot H_2O. In addition, there was a possibility that the GeO_2 layer had become fragile during the immersion in the hot H_2O [Fig. 4(c)]. In this case, the normal stress around the remaining GeO_2 edge was sufficient to separate the quartz substrate from the original sample. This phenomenon promoted water penetration in the inner region of the remaining GeO_2 layer by capillary action. The GeO_2 in the edge region was further dissolved by the water. Consequently, the stress continued to peel the plastic/epoxy/device layered structure from the quartz substrate.

To verify the above predicted mechanism, it is useful to investigate the thermal residual stress at the bonded joint of the epoxy-coated glass substrate. It is well known that Raman spectroscopy is an effective method of examining the stress of crystalline Si. As described in ref. 12, the following relationship for peak wave number exists between a stress-free single-crystal bulk Si layer, ω_0, and a stress-induced crystalline layer, ω.

$$\omega = \omega_0 + 5.2 \times 10^{-9} \times P, \tag{1}$$

where P (Pa) is the stress intensity of the stress-induced Si. Thus, Raman scattering measurements were carried out using an epoxy/50-nm-thick poly-Si/nonalkali glass structure. In order to investigate the effect of epoxy thickness on stress intensity, $4 \times 4\,cm^2$ samples with three epoxy thicknesses of 180, 130, and $60\,\mu m$ were prepared. 50-nm-thick poly-Si films were obtained by crystallizing a-Si films, formed by low-pressure chemical vapor deposition at $300\,°C$, with a 308 nm 30-ns-pulsed XeCl eximer laser at an energy density of $280\,mJ/cm^2$. Prior to the Raman scattering measurements, the bending curvature of the glass was investigated for each sample by tracing the glass surface. All three samples showed bending and the epoxy surface was bent inward. The curvature radii were $2.5\,m$ for the 180-μm-epoxy-coated sample, $4.3\,m$ for the 130-μm-epoxy-coated sample and $11\,m$ for the 60-μm-epoxy-coated

Fig. 3. Schematic diagrams of predicted stress distribution at room temperature in plastic/epoxy/thin-film device/$1\,\mu m$ GeO_2/glass structure sample. The epoxy was cured at $120\,°C$.
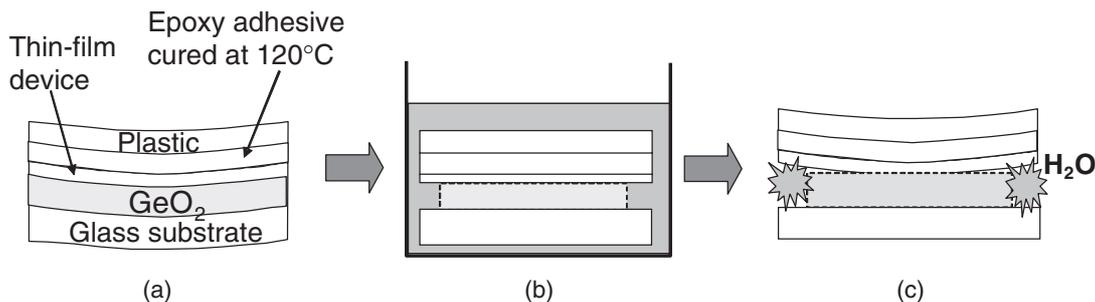
Fig. 4. Schematic diagrams explaining the predicted principle of ultrahigh-rate GeO_2 etching: (a) As-fabricated. (b) Immersed in 80–$100\,°C$ H_2O. (c) Cooled in $25\,°C$ ambient air.

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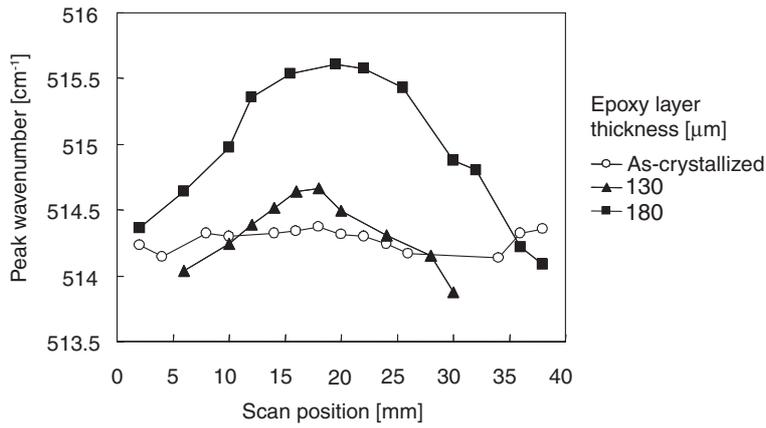
Fig. 5. One-dimensional distribution maps of transverse optical phonon peak wavenumbers obtained from Raman scattering measurements on 4×4 cm^2 epoxy/50 nm poly-Si/glass structure samples with epoxy thicknesses of 130 and 180 µm.

Fig. 6. Photographs of poly-Si films transferred to 4 in. plastic substrates by (a) rapid and (b) gradual coolings. The original samples had the same layer structure of plastic/silicone/epoxy/50 nm poly-Si/200 nm SiO$_2$/1 µm GeO$_2$/quartz.

sample. This shows that the curvature radius decreases with increasing thickness of the epoxy layer. Each sample, before coating with the epoxy, bent outward with a radius of more than 300 m. In order to verify whether the pattern of stress distribution in the samples follows that shown in Fig. 3, a one-dimensional mapping of the transverse optical (TO) phonon peak wavenumber from the poly-Si film was carried out for several positions from the edge of one side to the opposing edge through the Raman scattering measurement. The Raman scattering measurement was performed by irradiating a 532 nm frequency-doubled YAG laser beam from the epoxy surface to the poly-Si films. Figure 5 shows the variation in the TO phonon peak wavenumber from the poly-Si film with respect to the scan position for the samples. The average peak wavenumbers were 514.3 cm^{-1} for the as-fabricated poly-Si films on the glass substrate, 514.9 cm^{-1} for the 180-µm-epoxy-coated sample, and 514.3 cm^{-1} for the 130-µm-epoxy-coated sample. The peak wavenumbers for the 180- and 130-µm-epoxy-coated samples were largest around their middle positions and became smaller as the scan position approached the sample edge. We predicted that the normal stress, produced around the interface edge between the epoxy and glass layers, did not contribute to the stress in the poly-Si films.

The transfer of poly-Si films was carried out using the 4-in.-sized samples with epoxy thicknesses of 130 and 270 µm. Both of the samples were immersed in H$_2$O at 80 °C for 90 min and then left to cool in 25 °C ambient air. Both of the GeO$_2$ layers were dissolved up to approximately 5 mm from their sample edge. As for the 270-µm-epoxy-coated sample, the remaining GeO$_2$ layer was completely removed 2 min after the sample was removed from the 80 °C H$_2$O. In this case, the average lateral etching rate was 55 µm/min before the cooling and 2.25 cm/min after the immersion. As for the

130-µm-epoxy-coated sample, the remaining GeO$_2$ layer was dissolved up to only 3–5 mm 2 min after the start of cooling in 25 °C ambient air and the lateral etching made almost no progress for 5 min thereafter. This suggests that a thin epoxy layer has insufficient normal stress around the interface edge for a rapid GeO$_2$ dissolution. On the contrary, a substantially thick epoxy layer causes quartz cracking owing to strong thermal stress. For another 4-in.-sized sample with a 270-µm-thick epoxy layer, transfer demonstration was also carried out by immersion in 80 °C H$_2$O for 90 min followed by cooling at 1 °C/min to 25 °C using hot H$_2$O. Figure 6 shows photographs of transferred poly-Si films with the same 270-µm-thick epoxy layer. There were a few large cracks in the poly-Si film in the air-cooling case, whereas no cracks were found in the water-cooling case. In the air-cooling case, extra thermal stress may have been produced owing to the quick change in temperature, whereas in the water-cooling case the sample temperature probably decreased gradually and uniformly. These results show that the rapid dissolution of the GeO$_2$ layer was caused by thermal stress resulting from the difference in the thermal expansion coefficients between the quartz and the epoxy.

The poly-Si TFTs were transferred to the plastic films with the epoxy resin as an intermediate layer by immersing the samples in H$_2$O at 80 °C for 30 min and then exposing them to ambient air for 1 min. Figure 7 shows entire views and microphotographs of the as-fabricated and transferred poly-Si TFTs. Every TFT has a 0.5 mm channel length and a 1 mm channel width. Although some of the TFTs showed cracks after the transfer, most of them were transferred without cracks or any other damage that could reduce TFT performance, as seen by comparing both photographs. Figure 8 shows the transfer curve for one of the fabricated
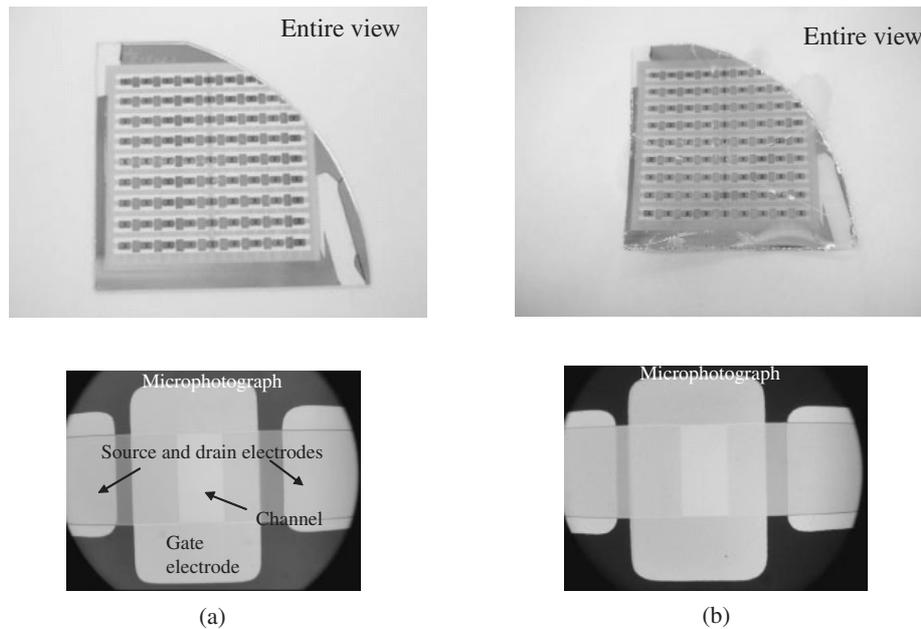
Fig. 7.   Photographs of TFTs and microphotographs of single TFT (a) before and (b) after transfer.
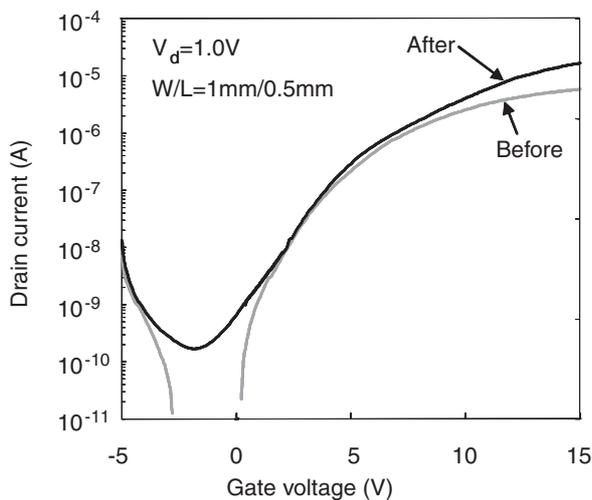
Fig. 8.   Transfer curve for poly-Si TFT before and after transfer.

elastic coefficients. It was found that the thickness of the epoxy layer is associated with a rapid GeO_2 dissolution. 50 nm-thick poly-Si films were transferred to 4-in. plastic substrates by rapid and gradual coolings after immersion in H_2O at 80 °C for 90 min. As a result, the poly-Si films were transferred regardless of the cooling rate. We also carried out the transfer of TFTs to plastic substrates. The TFTs were transferred to the plastic substrates by exposing the samples in air at 25 °C for 1 min after immersion in H_2O at 80 °C for 30 min. We examined the electrical properties of the TFTs before and after the transfer. Although there was a difference in the drain current between before and after the transfer, the transfer curve shows that the TFT was operational on the plastic substrate. These results suggest that the rapid transfer method has the potential for forming high-performance thin-film devices on plastic substrates.

TFTs before and after the transfer. Although there is a difference in drain current of the TFTs before and after the transfer, the transfer curve shows that the TFTs are operational on the plastic substrate. At this time, we do not yet have sufficient data to discuss the effect of the transfer process on TFT performance, which will be investigated in the near future.

4.   Conclusions

We introduced and discussed a high-rate GeO_2 etching method for thin-film-device transfer. The GeO_2 removing layer was rapidly dissolved at an ultrahigh rate of several cm/min when a plastic/silicone/epoxy/Si/SiO$_2$/GeO$_2$/quartz structure sample was cooled to ambient temperature after dissolving the GeO_2 layer up to a few mm from the sample edge in hot water. We predicted that this rapid GeO_2 dissolution was due to thermal stress mainly associated with the difference in thermal expansion coefficient between the epoxy and the quartz, and the difference between their

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