Amorphous Oxide Semiconductor Adopting Back-channel-etch Type Thin-film Transistor

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Kobe Steel has developed a new amorphous oxide semiconducting material available for the back-channel-etch (BCE) type thin-film transistor (TFT) adapting mass production of flat panel displays. The material has high chemical resistivity for the conventional etchant of Mo/Al source and drain interconnection. It has been shown that good electrical characteristics and high reliability in BCE-TFT can be obtained by means of the additional annealing process to repair back-channel damage on the oxide semiconductor thin film.

Introduction

Lately, the performance of flat panel displays (FPDs), such as liquid-crystal displays (LCDs) and organic light-emitting displays (OLEDs), is being upgraded in terms of, for example, increased screen size, higher driving speed and elevated definition as seen in 4 k and 8 k displays. Hence thin-film transistors (TFTs), switching elements that drive picture elements, are required to be driven at higher speed under higher current. Accordingly, semiconductor thin film, the heart of a TFT, must be made of a semiconductor material with high electron mobility.

Amorphous oxide semiconductor materials,[1), 2)] as typified by indium gallium zinc oxide (In-Ga-Zn-O, IGZO),[3)] have electron mobility, an index showing how easily the electrons can move, more than ten times faster than those in conventional materials; and they can be deposited on substrates with large areas. Thus they are gathering attention as semiconductor material for next-generation displays. Oxide semiconductors, however, are sensitive to the external environment. This makes it important to have stable control of the TFT manufacturing process in mass production.

Against this background and to improve productivity, Kobe Steel has developed a new oxide semiconductor material, KOS-B02, which has an electrical performance equal to that of IGZO and superior chemical stability. This material was adapted for back-channel-etch TFT (BCE-TFT), which is more suitable for mass production. The production process was optimized, which resulted in favorable electrical characteristics and high reliability, as reported in this paper.

1. Issues with oxide semiconductor materials for FPD

Thin-film-transistor (TFT) elements are switching elements that switch the picture elements of LCDs and OLEDs. Each display may contain more than a million TFT elements. In the case of LCDs, each drain electrode is connected to its own picture-element electrode that supplies voltage to liquid-crystal molecules. The semiconductor thin film plays an important role in controlling the current between drains and sources.

Hydrogenated amorphous silicon (a-Si: H) has hitherto been used for the material for semiconductor thin film; however, performance improvement, such as increased screen size, higher driving speed and elevated definition, requires material with higher carrier mobility (hereinafter simply referred to as "mobility".) Hydrogenated amorphous silicon has mobility that is insufficient for next-generation 4 k/8 k displays and OLED applications. There is a need for semiconductor material with greater mobility.

Table 1 compares the features of various semiconductor materials used for displays. Low temperature polycrystalline silicon (LTPS) and amorphous oxide semiconductors, each having mobility higher than that of a-Si: H, are used for high-spec applications.[4)] Low temperature polycrystalline silicon exhibits the greatest mobility; however, there are problems in that its crystallization requires laser annealing, making it inapplicable to large areas, and its production cost is high. Oxide semiconductors, on the other hand, can easily be deposited on large areas by sputtering and are superior in productivity because the TFT production process, similar to the one based on conventional a-Si: H, can be used. Moreover, oxide semiconductors exhibit a little leak current, an advantageous feature for decreasing power

Table 1 Semiconductor materials used in flat panel display

	a-Si:H	LTPS	**Oxide**
material	Si	Si	**IGZO, ZnO, ZTO, etc.**
mobility(cm^2/Vs)	1<	50-100	**1-30**
TFT uniformity	Good	Poor	**Good**
TFT reliability	Poor	Good	**Good**
Process temperature	150-350℃	250-550℃	**RT-400℃**
Substrate	LCD	LCD OLED(small size)	**LCD, OLED, E-paper**

consumption, and are well suited for smartphone displays. As described, oxide semiconductors can achieve high performance, but their yield and productivity must be improved before they are used widely.

2. TFT structure and production process

To decrease the production cost, TFTs must have simplified structures so as to reduce the number of process steps. **Fig. 1** shows the structures of two typical types of TFT elements, each having a gate electrode on its substrate. The etch-stop (ES) type, shown in Fig. 1(a), has its semiconductor thin-film surface protected by an etch-stop layer (ESL) and achieves excellent reliability. The back-channel-etch (BCE) type, shown in Fig. 1(b), has no etch-stop layer, which requires fewer photo-patterning steps than the ES type; a feature more advantageous as regards the production cost.[5] In addition, it allows the use of the conventional process of a-Si: H-TFTs. Hence there are many manufacturers adopting the BCE type. In addition to the cost reduction, the BCE type can adopt a shorter channel length (L in the figure), which makes the downsizing of TFTs easier and has the advantage of permitting the parasitic capacitance, a cause of signal delay, to be made smaller.

The BCE type, on the other hand, is more susceptible to defects and contamination on the surface of the semiconductor thin film (back-channel) and requires highly sophisticated process control. Furthermore, during the patterning of the source and drain electrodes, the semiconductor thin film is exposed to the etchant, such as acid, which may reduce the thickness of the semiconductor thin film, thus posing a problem. Such etching damage may cause problems of deteriorated TFT characteristics and decreased reliability, often rendering the TFT elements impossible to make.[6), 7)]

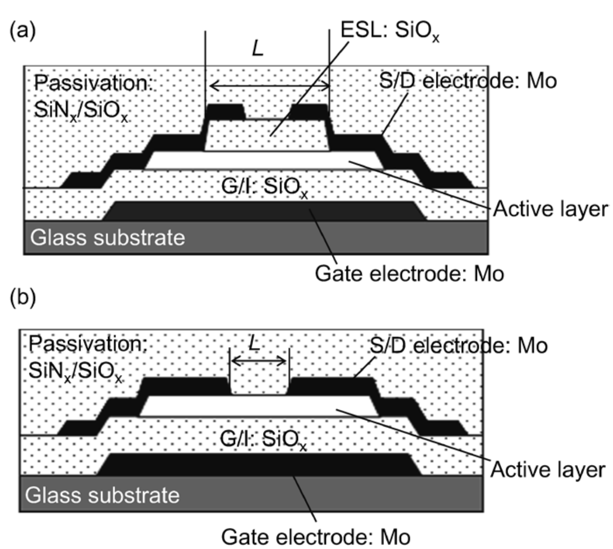

Fig. 1 Schematic of (a) ES-type, and (b) BCE-type TFTs

3. New oxide semiconductor material compatible with BCE type TFT

Oxide semiconductor thin films must have increased resistance against acid etchant to be compatible with the manufacturing process of BCE type TFTs, the process with a low production cost. Hence Kobe Steel revised the compositions of oxide semiconductors and has developed a material having both electrical characteristics comparable to those of IGZO and excellent acid resistance.

Among the constituents of IGZO, In is considered to improve conductivity, Ga decreases oxygen deficiency, and Zn stabilizes the amorphous structure.[8] In addition to these constituents, an addition of new elements was devised to achieve both the desired electrical characteristics and acid resistance.

In general, impurity elements in a semiconductor cause the carrier to be scattered, decreasing electron mobility. **Fig. 2** shows the results of a study on the field effect mobility of TFTs based on IGZO with addition of various elements. Most elements decrease the mobility to a greater or lesser extent. The results show that tin (Sn), even added in the amount of approximately 10 at%, exhibits no decrease in the mobility, implying no degradation in the electrical characteristics of IGZO thin film. This is attributable to the fact that, as is the case of In, Sn has a large ion radius and forms conductive oxide with less electron scattering. Moreover, SnO_2 is acid-insoluble with high chemical resistance and is effective in improving acid resistance.

With this in mind, Sn was selected as the fifth element to be included in IGZO. The composition of In, Ga, Zn and Sn was optimized to simultaneously achieve field effect mobility, reliability and acid

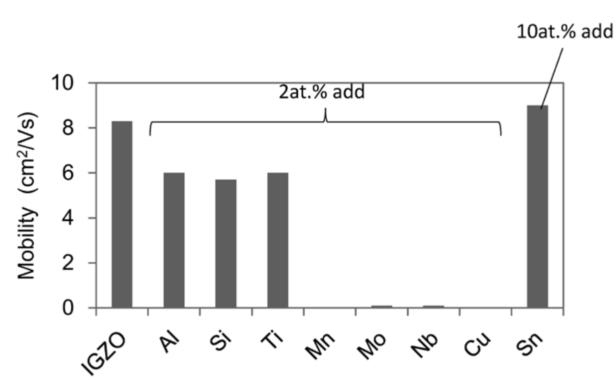

Fig. 2 Field effective mobility of IGZO-TFT with additional element

resistance. As a result, a new amorphous oxide semiconductor, KOS-B02, was developed, which is compatible with the production process of BCE type TFTs.[5), 6)] The manufacturability of a sputtering target with the proposed composition and sufficiently high density and quality was confirmed. A prototype sputtering target was prepared by Kobelco Research Institute, Inc., and the target was subjected to a trial production of TFTs and thin-film evaluation, as described in the following sections.

4. Characteristics of newly developed oxide semiconductor thin film

4.1 Comparison of basic characteristics

Table 2 compares the physical properties (carrier concentration, hole mobility, bandgap), sputtering rate and etching rate for the acid etchant of the newly developed KOS-B02 thin film with those of IGZO. The carrier concentration of $1.0\times10^{16}/cm^3$ is in the standard range of carrier concentration for oxide semiconductor, and both the hole mobility and bandgap have values similar to those of IGZO. The sputtering rate is higher than that of IGZO by almost 20%, indicating superior productivity.

The etching rate for acid etchant was measured using PAN etchant (a mixture of phosphoric acid, nitric acid and acetic acid) commonly used for the fabrication of source/drain electrodes. The etching rate of molybdenum (Mo) thin film, used for source/drain electrodes, is 83Å/s and that of a-IGZO is about a quarter of that value. In general, the thickness of semiconductor thin film used for TFT is around 40 nm, which is much thinner than that of the source/drain electrodes (300-500 nm.) Thus there is a concern that the semiconductor thin film might be significantly removed during the fabrication of source/drain electrodes in the TFT manufacturing. It is noteworthy that KOS-B02 thin film is insoluble to PAN etchant, exhibiting no reduction in film thickness during immersion. Hence, this indicates that this semiconductor thin film will exhibit almost no thickness reduction during the TFT manufacturing process and is applicable to BCE type TFTs with a low production cost.

Table 2 Comparison of IGZO and KOS-B02 thin film

	IGZO	KOS-B02
Carrier concentration ($1/cm^3$)	4.0×10^{16}	1.0×10^{16}
Hall mobility (cm^2/Vs)	11.6	15.1
Photonic band gap (eV)	3.15	3.08
deposition rate ratio (IGZO : 1)	1	1.19
Etching rate for PAN (Å / sec)	20	0

4.2 Prototype evaluation of BCE type TFT

The characteristics of display TFTs are significantly affected not only by the semiconductor thin film alone, but also by the production process of the TFTs. In an attempt to confirm the performance in a real TFT, a prototype TFT based on KOS-B02 was prepared by the process commonly used for BCE type TFTs and was evaluated.

Fig. 3 illustrates the process used in the preparation of the prototype BCE type TFTs. The TFT comprises a gate electrode of Mo thin film deposited on a glass substrate and a gate insulation layer of SiOx deposited by plasma CVD (Fig. 3(a).) A semiconductor (IGZO or KOS-B02) thin film, 40 nm thick, was deposited and patterned on top by magnetron DC sputtering, and this laminate was then heat-treated in the atmosphere at 350℃ for 1 hour to improve the film quality (Fig. 3(b).) Subsequently, source/drain electrodes (Mo thin film) were deposited, and the resulting laminate was subjected to wet etching using PAN etchant to fabricate source/drain electrodes (Fig. 3(c, d).)

Then, passivation layers of SiOx and SiNx were deposited in sequence to protect the TFT element

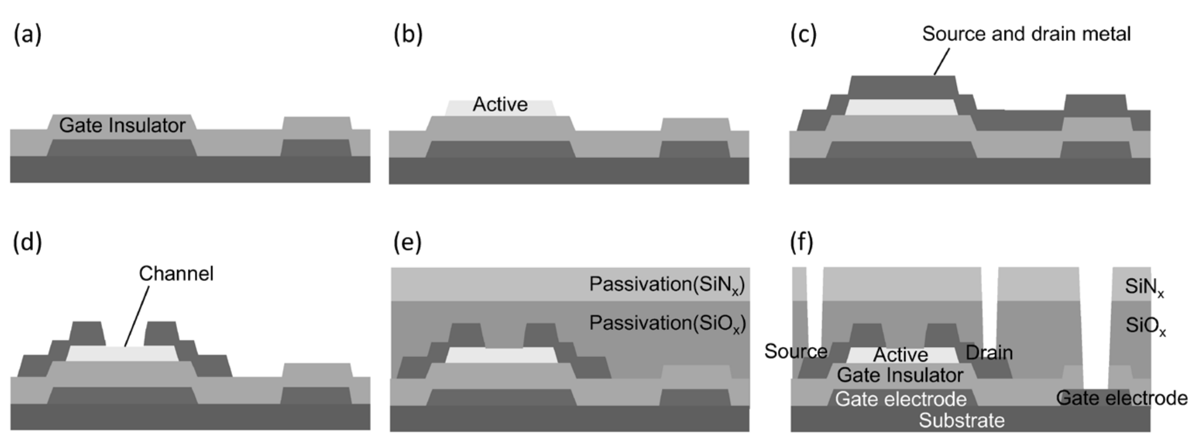

Fig. 3 Process flow of BCE-TFT

(Fig. 3(e)). Finally, annealing was applied for characteristics improvement before the completion (Fig. 3(f)).

4.3 Static characteristics of TFT

Fig. 4 includes cross-sectional photos taken at the edges of the drain electrodes of the TFT samples prepared. Fig. 4(a) shows IGZO with its thickness decreasing as the distance from the electrode increases. This thickness distribution of the semiconductor film causes distribution in the electric field, which can adversely affect the switching characteristics of TFTs. In the case of KOS-B02 (Fig. 4(b)), on the other hand, the oxide semiconductor thin film exhibits no reduction of thickness, indicating almost no removal of the semiconductor thin film by the etchant.

Fig. 5 depicts the switching characteristics (I_d-V_g characteristics) of the TFTs prepared. The drain current was measured at a drain voltage of 10 V while applying voltages of -30 to 30 V to each gate electrode. The drain current begins to increase at a voltage close to 0 V, showing switching from OFF to ON. The KOS-B02 shows favorable characteristics with a steep rise of its drain current, while IGZO exhibits a gradual rise as well as low drain current. The current-voltage characteristics (I_d-V_g characteristics) in the saturation region are given by the following:

$$I_d = \frac{\mu_{FE} W C_i}{2L}(V_g - V_{th})^2$$

W; channel width:
C_i; gate insulation film capacitance
L; channel length V_{th}; TFT threshold voltage

The field effect mobility, μ_{FE}, was calculated on the basis of the switching characteristics shown in Fig. 5, yielding 5.4 cm^2/Vs and 7.9 cm^2/Vs for IGZO and KOS-B02 respectively, with the latter showing higher mobility. Moreover, S values, representing the steepness of the rise in drain current (i.e., the minimum gate voltage required to increase the current by an order of magnitude) were 0.84 V/decade and 0.22 V/decade respectively, demonstrating the superiority of KOS-B02. The difference in the characteristics of the two materials is considered to be attributable to the etching, as described, of the semiconductor thin film during the fabrication of source/drain electrodes. Due to the reduced film thickness, the IGZO is considered to have deteriorated switching characteristics. The KOS-B02, on the other hand, exhibits excellent switching characteristics despite the damage caused by the etchant on the back-channel surface.

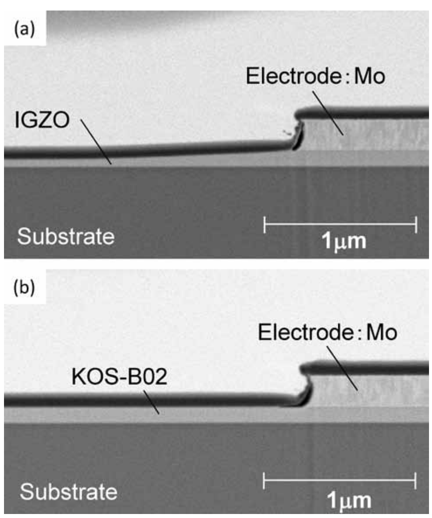

Fig. 4 Cross section SEM image of (a) Mo/IGZO and (b) Mo/KOS-B02 stacked film

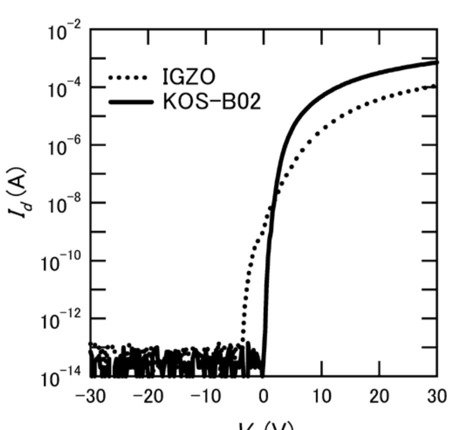

Fig. 5 I_d-V_g characteristics of BCE-TFT using IGZO and KOS-B02 thin film

4.4 Reliability of TFT

During operation, TFTs are subject to various external factors (stress). A large number of defects in semiconductor thin films and/or in interfaces cause changes in characteristics, such as a shift in TFT threshold voltages.[9] Such changes can cause uneven colors and lighting failure. Hence an accelerated test was conducted to confirm the variation in TFT characteristics.

Figs. 6(a) to 6(c) respectively show the measured characteristics of positive bias-temperature stress (PBTS), negative bias temperature instability (NBTS) and light negative bias-temperature stress (LNBTS). The measurement conditions are listed in **Table 3**. Each measurement was conducted after applying respective stress for a predetermined time period (0 s, 300 s, 1,000 s, 3,600 s, and 7,200 s.) Applying a bias to the gate electrode of a TFT causes electrons and holes to be trapped in the semiconductor thin film and interfaces, shifting the threshold voltage

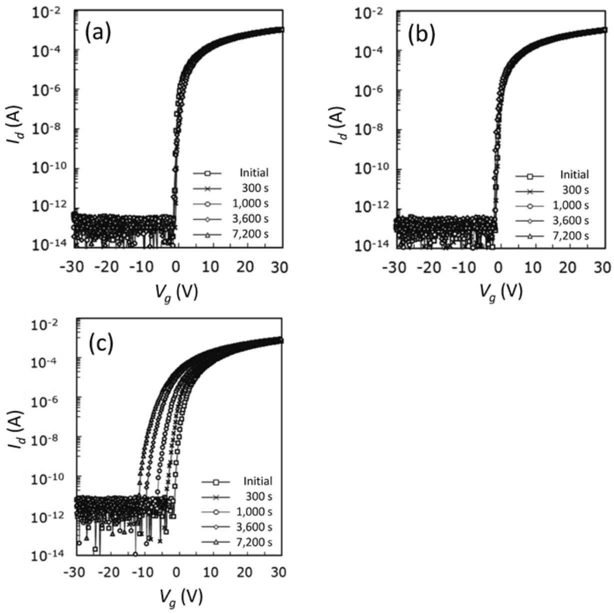

Fig. 6 Stress test results of BCE-TFT using KOS-B02 thin film (a) PBTS, (b) NBTS, (c) LNBTS

Table 3 Stress test conditions of TFT

	Vg (V)	Vs (V)	Vd (V)	T(℃)	Light	Time(s)
PBTS	20	0	0.1	60	-	0〜7,200
NBTS	-20	0	10	60	-	0〜7,200
LNBTS	-20	0	10	60	White LED 25,000 nit	0〜7,200

in the positive or negative direction. As shown in Figs. 6(a) and 6(b), the switching characteristics remain almost unchanged for the PBTS and NBTS, indicating excellent stability against these stresses.

The LNBTS, however, caused the threshold voltage to shift toward negative as time elapsed: a shift of 9.8 V in 2 hours. The LNBTS is the most important stress test for liquid-crystal displays. As a rough indication, a shift of less than 2 to 3 V in 2 hours is regarded as acceptable. Hence the characteristics shown in Fig. 6(c) are considered to be inapplicable to LCD drivers.

The shift of threshold voltage under LNBTS is considered to be caused by electrons and holes that are newly created by photons and are trapped in the semiconductor thin film and interfaces. Multiple defect levels in a semiconductor thin film give rise to light-induced positive holes. When trapped, these positive holes create a fixed charge, facilitating the shift in threshold voltage.[10), 11)] When used for the ES type TFT, KOS-B02 exhibits no deterioration due to LNBTS. Hence the shift found in BCE-TFT is considered to be attributable to the deterioration of, or damage to, the back-channel.

5. Improvement in the BCE type TFT production process

5.1 Surface analysis of oxide semiconductor thin films

X-ray photoelectron spectroscopy (XPS) was performed to study how the etchant alters the surface of KOS-B02 thin film.

Fig. 7 shows the depth profiles of O1s spectrum in KOS-B02 thin film. The measurement in the depth direction was conducted while sputtering the thin film surface. Fig. 7(a) depicts the profiles measured on a sample without dipping in etchant, showing the O1s peak position remaining unchanged at 531.0 eV for the outermost and interior surfaces. Meanwhile, as shown in Fig. 7(b), the sample dipped in PAN etchant exhibits a peak position at 531.0 eV for the interior surface and a peak position at 531.8 eV for the outermost surface, a peak shift toward higher energy. The O1s peak energy depends on the bonding state of oxygen and takes a value of 530.5 eV for no oxygen deficiency and 532.5 eV for oxygen deficiencies.[12)] This implies that the dip in the etchant caused the oxygen deficiencies to increase. Oxygen deficiencies are considered to be the cause of

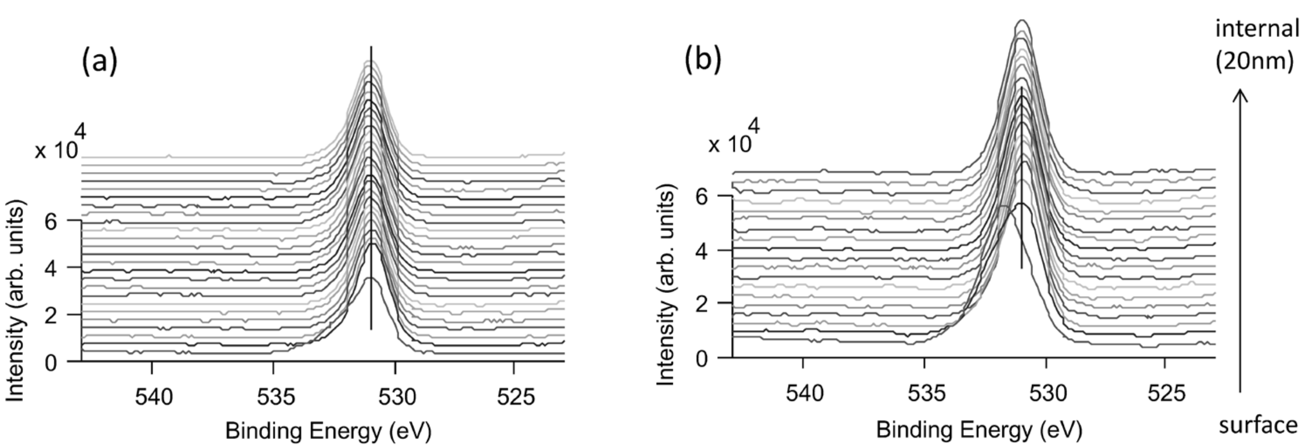

Fig. 7 Depth profile of O1s spectrum in KOS-B02 thin film; (a) without dip in etchant, (b) with dip in etchant

the deterioration due to optical-light stress.

5.2 Treatment to repair surface damage

To achieve favorable TFT characteristics, it is important to repair the surface damage caused by etchant. So, a study was conducted on an additional annealing in oxidation atmosphere (air) so as recover surface oxygen deficiency in the production process of BCE type TFTs. When TFTs are exposed to annealing atmosphere, the electrodes may be oxidized, causing the film to peel and/or the TFT characteristics to deteriorate. Therefore, the decision was made to apply annealing in addition to the process described above, after depositing the passivation layer of SiOx.

Fig. 8 shows the relationship between the annealing temperature and resistivity of KOS-B02 thin film. The specimen was a laminate having the same structure as the TFT, and the resistivity was measured by the van der Pauw method.[13] The resistivity intrinsic to KOS-B02 thin film was approximately 10 kΩcm. In contrast, dipping in PAN etchant decreased the resistivity to about 10 Ωcm. When the additional annealing was applied after the deposition of the SiOx passivation layer, the resistivity increased up to the annealing temperature of 400℃ and decreased at higher temperatures. The resistivity became closest to that intrinsic to KOS-B02 thin film at the annealing temperature of 300℃. The film quality is considered to become most stable at this temperature. Thus the annealing temperature was set at 300℃.

5.3 Verification on the effect of recovery annealing

A sample of BCE type TFT additionally heat-treated at 300℃ after depositing SiOx passivation thin film was evaluated for reliability under LNBTS. As shown in **Fig. 9**, almost no variation of threshold voltage was observed in the period of 0 - 7,200 s during which the stress was applied, indicating that the sample had a high reliability, unlike the TFT without additional annealing shown in Fig. 6(c). Reliability against LNBTS is known to strongly depend on the oxygen deficiency in oxide semiconductor thin films. The recovery of reliability is considered to be the result of the annealing having restored the surface, damaged as described, of the oxide semiconductor thin film.

5.4 Defect-restoration mechanism of recovery annealing

The condition of the oxide semiconductor thin film before and after annealing was studied. A sample element with the same structure and substrate as the TFT element was prepared and subjected to secondary ion mass spectroscopy (SIMS) to analyze the depth profile of O^- and OH^- ions (**Figs.10**(a), (b)). Both Figs. 10(a) and 10(b) exhibit high-intensity regions around the depth of 350 nm to 400 nm in the oxide semiconductor thin film. O^- ions were compared before and after annealing, and found to remain almost unchanged by the annealing, while OH^- ions exhibit a difference in the profile inside the semiconductor thin film. The annealing increased OH^- on the surface side, making OH^- ions more uniformly distributed. It is believed that OH^- ions terminate the generation of oxygen deficiencies around metal elements,[14] which implies that the semiconductor thin-film surface, having many defects, is oxidized by the annealing, while being protected by OH^- ions. The additional annealing thus serves to repair defects created in the backchannel during the making of BCE type TFTs,

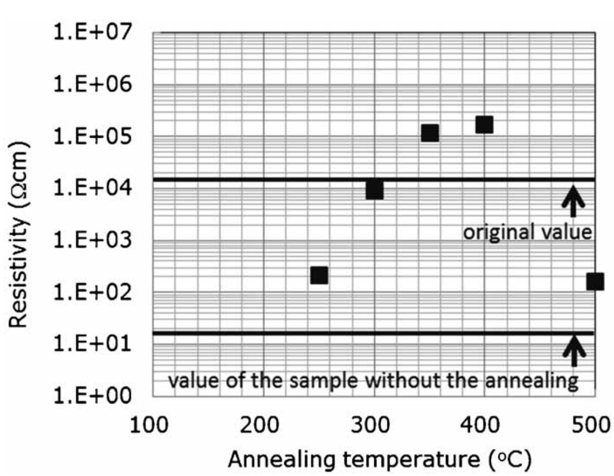

Fig. 8 Relationship between annealing temperature and electric resistivity of KOS-B02 thin film

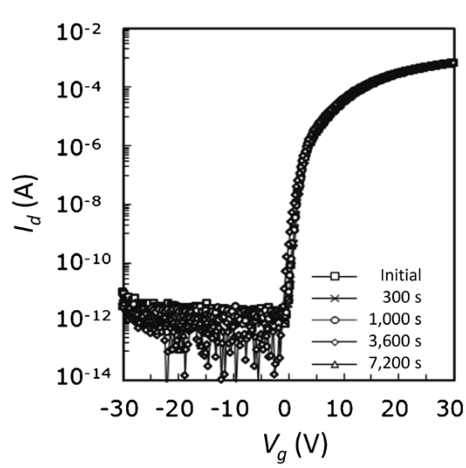

Fig. 9 Results of LNBTS for BCE-TFT using additional annealing

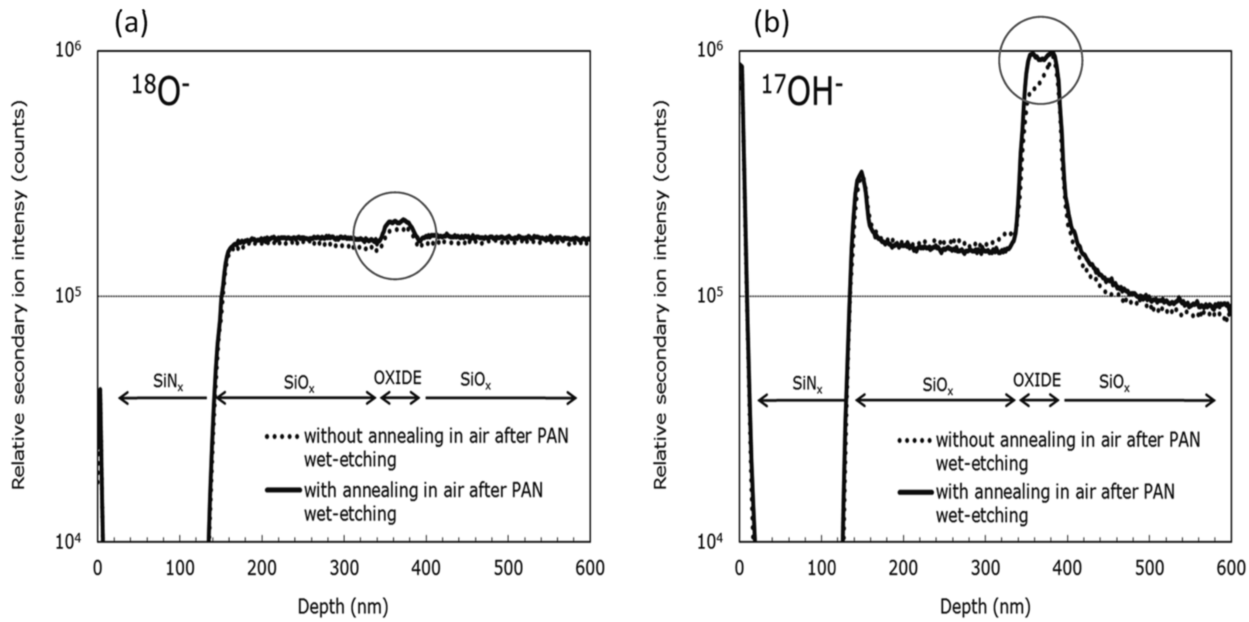

Fig.10 Ten-Depth profile of (a) O ion and (b) OH ion of BCE-TFT

by oxidation and OH termination, which realizes TFTs with high reliability. As described, KOS-B02 has been proved to be applicable to BCE type TFTs, whose production cost can more easily be reduced, and this enables the production of TFTs with excellent electrical characteristics and reliability.

Conclusions

An oxide semiconductor material, KOS-B02, which can realize both high productivity and mobility, has been developed for FPDs. The following characteristics have been confirmed:

1) The material composition of IGZO was revised in order to develop an oxide semiconductor material having high chemical stability, being almost insoluble to the PAN etchant commonly used in the fabrication of source/drain electrodes. The newly developed material is applicable to BCE type TFTs, which are low in manufacturing cost and more suited to volume production. This is expected to reduce the manufacturing cost of FPDs.
2) Regarding the use of the KOS-B02 in BCE type TFTs, adapting an annealing process that recovers back-channel damage allows the achievement of both excellent electrical characteristics and reliability.

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