Development of High Mobility Oxide Semiconductors for Next-Generation Electronic Devices

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Transparent amorphous oxide semiconductors (TAOS) typified by amorphous IGZO (In-Ga-Zn-O) are promising materials for next-generation electronic devices. They can provide homogeneous and large area thin films inexpensively by using sputtering equipment for mass production. The special properties of TAOS-based devices, such as their amorphous structure, high mobility and low leak current, may have the potential to replace conventional Si-based technology. Development of new TAOS materials which have high mobility and high reliability is essential for oxide-based technology to become widespread. In this paper we describe Target H, which we developed as a high mobility oxide semiconductor sputtering target. A thin film deposited by DC (direct current) magnetron sputtering shows high Hall mobility above 25 cm^2/Vs and an amorphous structure regardless of the partial pressure of oxygen during film deposition. BCE-type TFTs (thin film transistor) using Target H and IGZO were demonstrated. The estimated mobility of Target H was 34.8 cm^2/Vs, which is 3 times greater than that of IGZO.

1. Introduction

The application of transparent amorphous oxide semiconductor (TAOS) materials in electronic devices began in 2004 with a report in *Nature*[1] by Hosono et al. of Tokyo University of Technology, which demonstrated that their thin film transistor (TFT) element using the oxide semiconductor material IGZO (In-Ga-Zn-O) for the channel layer had achieved a field-effect electron mobility of about ten times the existing industrial application technology of amorphous Si (a-Si) TFTs.

Until then, the history of electronic device technology had been the history of Si TFT technology. Through historic turning points such as the development of a-Si[2,3] low temperature poly silicon (LTPS)[4], Si TFT technology has continued to evolve, maintaining its position as a champion of semiconductor materials for around 50 years. Particularly, in the flat panel display (FPD) field, Si TFT production technology, centered on large TVs and mobile devices, has spread widely and fierce price competition has arisen, a development inspired by the concept of the active-matrix liquid crystal display (LCD) drive system proposed in 1971[5].

Against this background, manufacturers are examining how to differentiate their display products with added value, for example by offering large-scale production, higher definition, flexibility, a narrower bezel around the display panel, lower power consumption, higher frequency driving, and self-luminescence (high brightness and high contrast).

After a decades-long gap in the availability of materials that could substitute for Si, Si's dominance is now starting to face a challenge from oxide semiconductor materials in the form of new material systems that can deliver the kinds of added value required for next-generation displays. Indeed, the fact that FPD products were manufactured within a few years of publication of the first journal article proves its high potential as a material.

At ULVAC, we have been aware of the high potential of IGZO since the first reports on the material appeared. We pioneered the development of sputtering targets for large-area industrial applications, succeeded in developing the world's first 8.5-generation integrated target for industrial use, and have been continually conducting comprehensive research and development of deposition equipment, materials, and processes[6, 7].

As a result, to this day we continue to maintain the top position in the IGZO sputtering target market in the FPD industry. In addition, the industrial technology of electronic devices that use oxide semiconductors has continued to develop, and products using oxide semiconductor materials can now be found in everyday electronic devices. We forecast that the market for oxide semiconductors will grow along with the proliferation of these products and will roughly double in size by 2024. The growth of oxide semiconductors as an alternative to Si technology has just begun, and the market is expected to expand rapidly. In addition to its adoption in the FPD industry, research and development on elements using oxide semiconductors has

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been actively conducted in the fields of semiconductor memory[8] and sensor devices[9,10] in recent years, and further market expansion is expected.

2. Oxide Semiconductor Materials

2.1 TFT devices

As noted above, the FPD industry is at the forefront of industrial application technology for oxide semiconductor materials, which are used as channel layer materials for TFT devices placed on the backplane that controls the display section of the FPD. Here we briefly describe the operating principles and roles of TFT devices.

Fig. 1 shows a schematic diagram of the elements of a typical back channel etch (BCE)-type TFT device. The TFT element consists of source and drain electrodes placed on either side of the channel layer, which is the path of electric current, a gate insulator (dielectric) in contact with the channel layer, and a gate electrode directly under the insulator.

Normally, there is no carrier to flow in the channel part, and even if a voltage is applied between the source and drain, no current flows in the OFF state. By applying a voltage to the gate electrode, an ON state is obtained in which an electric charge is collected at the interface between the channel and the gate insulator and a current can flow. The TFT element can acquire switching functionality by controlling the ON state and the OFF state, or acquire current control functionality by controlling the current flow process. In this way, it is able to serve as, for example, a selector switch or brightness control in the display portion of an electronic device.

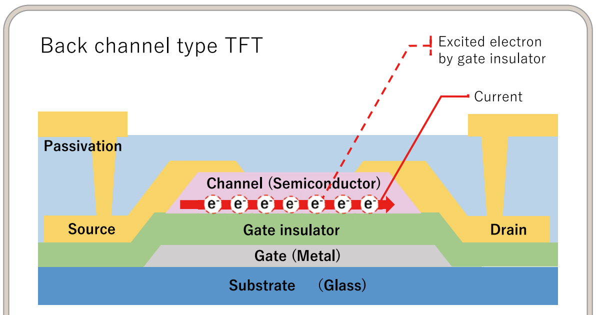

Fig. 1 Schematic view of BCE-type TFT structure

Here, the electron mobility of the channel material is a material-specific parameter that determines the current that can flow through the element. It is an important indicator that directly determines a product's specifications.

2.2 Characteristics of oxide semiconductors

Table 1 compares the properties of existing silicon technologies (a-Si and LTPS) with oxide semiconductor materials[11,12]. The greatest feature of oxide semiconductors is their high adaptability in industrial technology. Specifically, the features of a larger sputtering surface area, lower deposition and process temperatures, and amorphous crystallinity make it possible to boost the size of the display and accommodate changes in the shape of next-generation displays, for example towards flexible and foldable devices.

LTPS, which is distinguished by its mobility and reliability, has advantages and disadvantages. Its crystalline structure makes the material inflexible, and the laser and high-temperature processes required for uniform crystallization make it difficult to achieve increases in size and cost-effectiveness, which has limited the application of LTPS to mobile handsets and other small devices.

The table also shows that a-Si, which is widely used in industry for large surface area applications, has inferior electrical properties compared to oxide semiconductors.

Another physical property specific to oxide semiconductors is the high resistance when the TFT element is turned off. These properties are highly advantageous for low power consumption and sensor applications.

Low power consumption in particular is a very useful way to add value in today's world where mobile devices are becoming smaller and lighter.

As mentioned above, oxide semiconductor materials have the same high versatility as a-Si with superior electrical

Table 1 Semiconductor materials for flat panel display

	LTPS	a-Si	Oxide
Crystalline	Poly-crystalline	Amorphous	Amorphous
Film deposition	CVD＋Laser anneal	CVD	PVD
Large size sub.	Average	Good	Good
Cost	High	Low	Low
Flexible sub.	Average	Good	Good
Film flexibility	Poor	Good	Good
Process temp.	450〜550℃	150〜350℃	RT~400℃
Mobility	50-100	0.5〜1	〜30
Reliability	Very Good	Poor	Good
Leak current (TFT)	~10^{-13} A/μm	~10^{-12} A/μm	~10^{-16} A/μm

properties (although inferior to LTPS). If electrical properties comparable to LTPS can be obtained through future material development and device technology development, oxide semiconductors will emerge as a new material option that surpasses existing technologies.

3. High Mobility Material

This section introduces the applications and required characteristics of high mobility oxide semiconductor materials, based on examples of applications in the display industry.

3.1 Pixel circuits

Fig. 2 shows the pixel circuits of simplified LCD and active-matrix organic light emitting diode (AMOLED) displays. Since the LCD is voltage-driven, it is represented by a 1T1C circuit having one switching TFT that acts as a switch and one capacitor for each pixel. It functions as a pixel circuit by writing the signal voltage to the capacitor with the TFT device as the switch.

The AMOLED, in contrast, is a self-luminous display and is represented by a 2T1C structure. Since the light-emitting element is driven by current, a driving TFT that adjusts the current flowing to the light-emitting element is required in addition to the above-mentioned switching TFT. These examples demonstrate how the required characteristics differ depending on the target product and the role of the TFT element.

3.2 LCD displays

In the field of LCDs, where sizes of 65 inches or more are standardized and sizes are increasing, differentiation is being promoted by adding value with features such as high definition and high frequency drive. In addition, the spread of eSports and other electronic competitions is creating new demand for displays with a high response rate of 240 Hz.

In the control of the liquid crystal molecules by the active matrix, the potential required to change the liquid crystal molecular arrangement at each pixel needs to be stored in the capacitor within the time allotted for selection of the pixel. This can be a problem as the pixel selection time gets shorter due to higher drive frequencies and more scanning lines on higher definition displays. Therefore, high mobility of the TFT channel material (lower resistance in the ON state of the TFT) is required as a characteristic for a short charging time. High mobility of semiconductor materials is an important issue because the performance of TFT elements is a factor that directly determines the specifications of products.

3.3 Self-luminous displays

Self-luminous displays such as OLEDs and μLEDs are known to provide higher contrast than LCDs, which express black by blocking the light from the liquid crystal molecules. Since they are self-luminous, they can deliver a wider viewing angle and higher response speed as well as a lighter weight. OLEDs, whose light-emitting parts are coated with organic materials, offer certain advantages including an inkjet production method and support for flexible devices.

In μLEDs, the luminous layer is composed of inorganic materials. They offer the advantages of high brightness, long service life, fast response speed, and adaptability to the

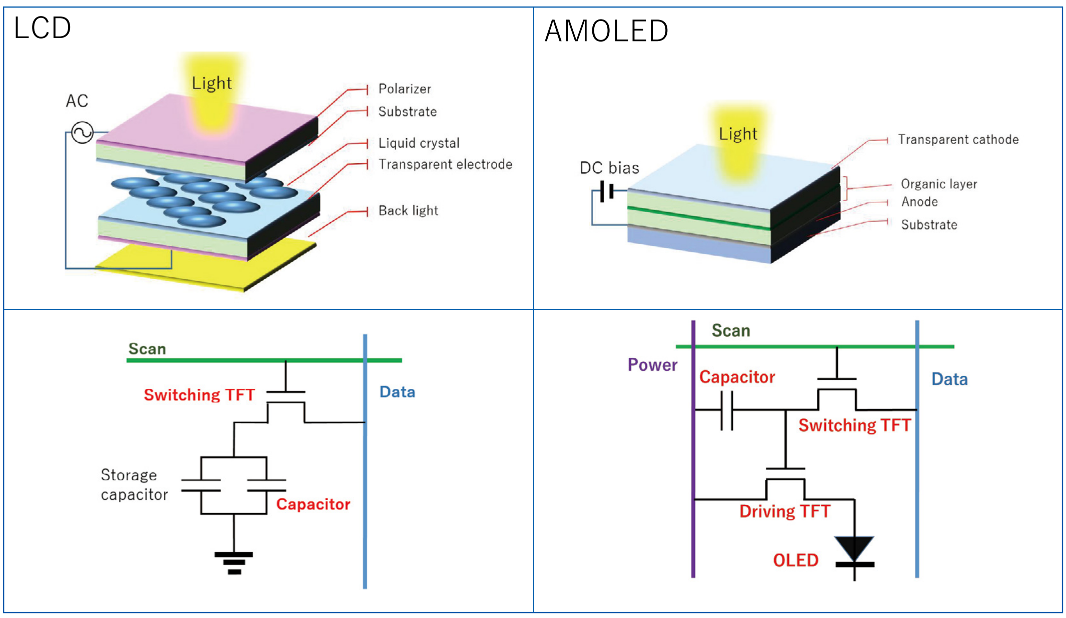

Fig. 2 Schematic view of LCD and AMOLED with simplified 1T1C circuit and 2T1C circuit, respectively

shape of the device. Although self-luminous displays have problems in terms of production cost and upsizing, they are becoming increasingly popular as an alternative to LCDs in next-generation displays, especially in smaller devices.

Since these pixel circuits are current-driven, they have a driving TFT in addition to a switching TFT. Driving TFTs need to have sufficient mobility to supply the current required for light emission, as well as reliability to adjust the brightness and improve variability. Therefore, a material with a good balance between mobility and stability is needed.

3.4 Low temperature polycrystalline oxide (LTPO)

Reducing power consumption has become an important issue as the weight and size of portable devices continues to decrease, imposing limitations on battery size. One of the factors that increase the power consumption of the device is the current leakage from the capacitor through the switching TFT. This current leak is caused by the large OFF current of the TFT element, and a process is required to restore the voltage discharged by the leak. The cycle of this process is called the refresh rate.

For oxide semiconductors, the OFF current is 1/100 to 1/10000 times smaller than for Si-based materials, which greatly reduces this refresh rate. It is especially effective in reducing power consumption in devices that continuously display a fixed screen, such as digital watches and mobile phones. Hybrid circuit LTPOs, which combine the excellent electrical properties of LTPS and the low OFF current of oxide semiconductors, are undergoing rapid development and have already been commercialized.

3.5 Gate drive circuits (gate drivers)

In addition to the pixel circuits, gate drive circuits are required for sending signals to the pixels in order to drive the display. These control all of the pixel circuits arranged on a scanning line at once. Gate driver TFTs require high mobility because of the delay caused by the increase in resistance.

P-type LTPS TFTs can be operated as gate drivers with a mobility of about 60 Vs/cm^2, which makes them an indicator of the high mobility of oxide semiconductors. The gate drive circuit must be located at the periphery of the substrate, and is currently primarily an external component. In cases where an oxide semiconductor can replace Si, the pixel circuit and gate drive circuit can be formed with a single deposition on the glass surface. This reduces costs significantly and makes it possible to narrow the bezel around the display panel by removing the external gate drive circuit.

Currently, the general Hall mobility in atmospheric annealing of oxide semiconductor materials developed for high mobility is about 15 to 30 cm^2/Vs. Even if a material is developed that can be used stably with a mobility of 30 cm^2/Vs, it would only achieve about half of the mobility required for use in gate drivers. To solve this problem, a TFT element with a double gate structure, as shown in

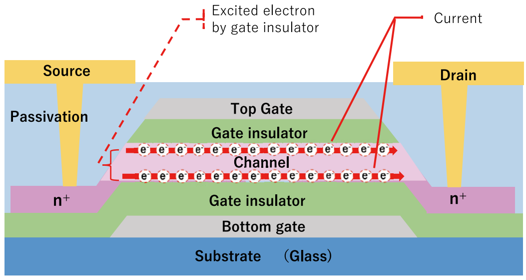

Fig. 3 Schematic view of double gate-type TFT structure

Fig. 3, has been used in recent years[13]. Whereas the channel structure of a normal TFT features one insulator and one gate, this structure features two sets each of gate insulators and gate electrodes placed above and below the channel, doubling the current path to achieve a pseudo-doubling of mobility. Research and development to replace LTPS TFTs with combinations of high-mobility materials is underway.

4. Development of Oxide Materials at ULVAC

4.1 Material development concept

In order to achieve the same superior electrical characteristics as LTPS (mobility of 60 cm^2/Vs or higher) in oxide semiconductor materials, which excel in industrial applications, ULVAC has developed a high mobility oxide semiconductor sputtering target material with a mobility of 30 cm^2/Vs or higher in TFT devices (60 cm^2/Vs in double-gate TFTs) that can be realized in an industrially stable manner.

Crystalline semiconductor materials such as LTPS, which exhibit long-range periodicity in their atomic arrangement, achieve high mobility by moving electrons through the orbital (electron path) of electrons aligned in the crystal as the current flows. In many semiconductor materials, the orbitals of electrons connecting the atoms are not spatially isotropic, resulting in a significant decrease in mobility in amorphous structures which lack long-range order in their atomic arrangement. On the other hand, oxide semiconductors such as IGZO seem to be able to demonstrate high mobility even in an amorphous structure with a disordered atomic arrangement because the main component used is In, which has an isotropic and widened spherical electron orbital (5s orbital)[1]. The content of 5s orbital materials such as In and Sn therefore have a significant effect on mobility. On the other hand, as the amount of In is increased, crystallization becomes easier, and the electrical properties of the TFT element start to become unstable. This instability is caused by oxygen dissociation (oxygen deficiency) as the oxygen bonds weaken as well as reactions with water and hydrogen in the atmosphere. In addition, Sn oxides are chemically resistant and difficult to etch.

Since the initial report of IGZO-TFT (composition ratio In-Ga-Zn 1:1:1), ULVAC has begun to develop IGZO materials with different composition ratios, and we have released our own oxide semiconductor sputtering targets for industrial use, Target D (IGZO alternative use: mobility ≈ 15 cm^2/Vs) and Target F (mobility ≈ 20 cm^2/Vs for driving TFTs). Based on these experiences, we began to focus on the bonding energy of oxides and how additives decrease mobility, and we were able to successfully develop the industrially stable oxide semiconductor material Target H, which, thanks to its combination of multiple elements, exhibits high mobility (≈ 30 cm^2/Vs) while ensuring workability and stability.

4.2 Target H

To evaluate the crystallinity of the thin films obtained by DC magnetron sputtering using Target H, we varied the oxygen partial pressure during deposition at 50 nm at a substrate temperature of 100°C. The results are shown in Fig. 4. The X-ray diffraction (XRD) measurements show no clear peaks except for a broad diffraction pattern originating from the amorphous structure of the glass, which is visible around 32° to 34°. This indicates that the material maintains its amorphous structure, which is advantageous for the workability of the material, over a wide range of oxygen partial pressure (PO_2) values (up to 60%) during deposition. Fig. 5 shows an evaluation of the etching properties of Target H and IGZO using ITO-06N (manufactured by Kanto Chemical Co., Inc.), an oxalic acid-based etching solution. Reflecting its crystalline characteristics, Target H shows high etching characteristics even when deposited under high oxygen conditions, indicating that it has workability comparable to the existing oxide semiconductor IGZO.

Next, to compare Target H and IGZO in terms of the electrical properties of the film, we measured the Hall mobility and carrier concentration estimated by Hall measurement after annealing at 400°C for 1 hour while varying the oxygen partial pressure. The results, shown in Fig. 6, indicate that Target H has a higher Hall mobility than IGZO by a factor of 2.5. This indicates that Target H has an intrinsically high mobility as a semiconductor material, even excluding the effect of higher mobility due to reduction caused by post-processing during TFT fabrication. Another advantage of this material is its distinctive ability to achieve high mobility, at or above 25 cm^2/Vs, independent of the oxygen partial pressure at the time of deposition.

A conduction model called percolation conduction [14] has been proposed for amorphous semiconductor materials. In this model, the carrier concentration tends to increase as the mobility of the material increases, and this tendency is also visible in Target H. However, under our material development concept, our guiding principle is to develop materials that can stably drive TFTs even with high mobility and high carrier concentration. From this perspective, the performance of the material can be said to be in line with its development concept.

Target H exhibited no change in crystallinity and mobility when the oxygen partial pressure was varied during deposition, which suggests that it is able to offer a wide process margin in the TFT fabrication process.

Finally, we fabricated a prototype BCE-type TFT device using Target H thin film as the channel layer. We adopted the BCE-type TFT structure for this evaluation because it is widely used in the LCD industry due to its small number of manufacturing steps and low cost.

Fig. 7 shows the process flow for fabrication of the BCE-type TFT and a photograph of the completed test element group (TEG) chip. In the TFT fabricated in this study, both the channel width and length were 6 µm. Since the size of the channel greatly affects the value of the flowing current, the same structure was adopted for the IGZO TFT used as a reference.

Fig. 8 shows the transfer curve of the Target H TFT fabricated according to the production flow in Fig. 7 and the reference IGZO TFT. As shown in the figure, the ON-state

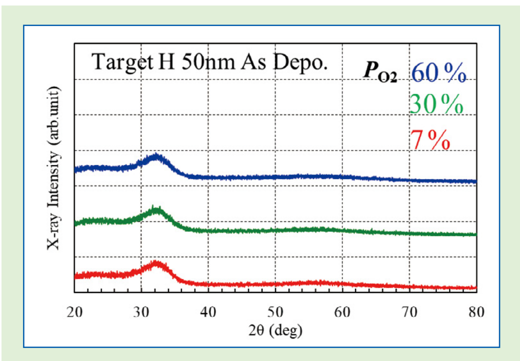

Fig. 4 X-ray diffraction patternas a function of PO_2 : Target H (blue open circle) IGZO (black solid circle)

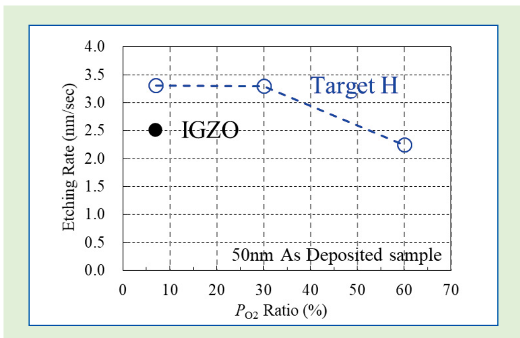

Fig. 5 Etching properties of As-deposited 50 nm sample using ITO-06N (Kanto Chem.) at 40°C: Target H (open blue circle) and IGZO (solid black circle)

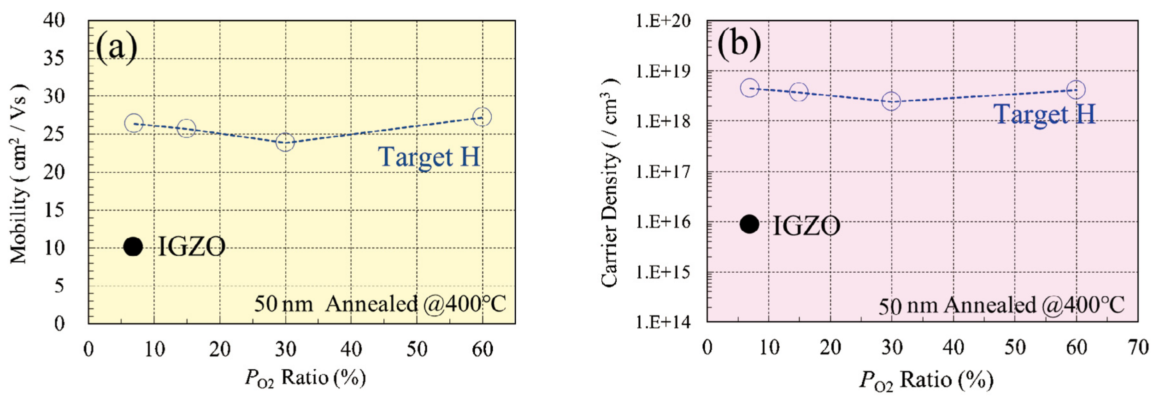

Fig. 6 Mobility (a) and carrier concentration (b) as a function of PO_2, estimated by Hall measurement: Target H (open blue circle) and IGZO (solid black circle)

(a) Process flow

- Gate deposition
- Gate patterning
- G.I. deposition
- Channel deposition
- Channel patterning
- Channel anneal
- S/D deposition
- S/D patterning
- N_2O plasma
- Passivation deposition
- Passivation anneal
- Passivation patterning
- Measurement (Vd 5 V, Linear region)

(b) (c)

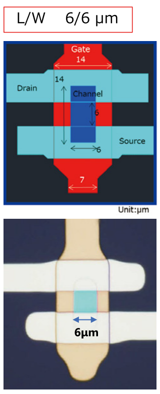

Fig. 7 Fabrication of BCE-type TFT: (a) Process flow of BCE-type TFT (b) Schematic view of BCE-type TFT (c) Photo image of fabricated TFT device

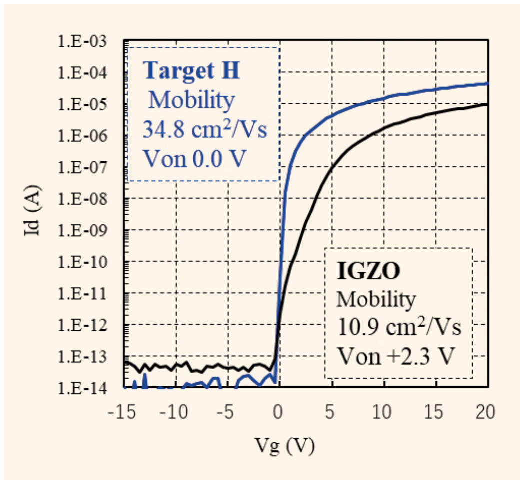

Fig. 8 I-V characteristics of BCE-type TFT: IGZO (black line) and Target H (blue line)

current value of the TFT using the Target H thin film was greater than that of the IGZO TFT.

In TFT elements with the same structure, the magnitude of the ON current value directly reflects the magnitude of the mobility. The actual field-induced mobility values estimated from the fabricated elements were 34.8 cm^2/Vs for Target H compared to 10.9 cm^2/Vs for IGZO. High mobility reflecting the inherent mobility of the material estimated in the film evaluation (Hall measurement) was also confirmed in the device characteristics. The figure also shows that the turn-on voltage Von (the gate voltage when the current value between source and drain exceeds 10^{-9}A), which is an important parameter in controlling actual products, resulted in high mobility without a large negative shift compared to the IGZO TFT. Table 2 shows the results of the reliability evaluations positive bias temperature stress (PBTS) and negative bias temperature stress (NBTS), which indicate the amount of shift from the initial value of the transfer characteristic when ±30V stress was applied to the gate electrode at the element temperature of 60°C for 0 to 60 minutes. Although high-mobility oxide materials tend to be less reliable as their mobility increases (carrier concentration increases), both PBTS and NBTS clearly showed bias stress resistance equivalent to that of IGZO. This indicates that Target H is a material that will exhibit high mobility and high reliability in device applications.

These results confirm that we have successfully developed a new material with good reliability and processability while achieving a target mobility of 30 cm^2/Vs.

Table 2　BCE-type TFT characteristics of Target H and IGZO

Target	BCE-type TFT characteristics		
	Mobility	PBTS (Δvon)	NBTS (Δvon)
IGZO (111)	10.9 (cm^2/Vs)	+3.1 V	-0.4 V
Target H	34.8 (cm^2/Vs)	+0.7 V	-0.5 V

5. Summary

We have been developing oxide semiconductor materials aimed at high mobility since the very earliest stages of their development. By leveraging this experience and the properties of a variety of elements, we were able to successfully develop Target H, an industrial sputtering target made of high-performance oxide semiconductor material. Oxide semiconductors are still new as a material, and there is still room for further development in their industrial technology. In the future, oxides have the potential to replace silicon technology not only in FPDs but also in a wide variety of other fields such as semiconductor memory and sensors. As improvements are made to their properties beyond higher mobility, we expect that oxide semiconductors will become more widespread as next-generation materials.

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