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## Properties of Germanium-Doped Indium Oxide Thin Films Prepared by DC Magnetron Sputtering

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Ge-doped indium oxide ( $\text{In}_2\text{O}_3$ ) thin films were prepared by dc magnetron sputtering. The electrical resistivity,  $1.6 \times 10^{-4} \Omega\cdot\text{cm}$ , of the film deposited at  $200^\circ\text{C}$  was obtained at 5.5% Ge doping. This was comparable with that of ITO (tin-doped  $\text{In}_2\text{O}_3$ ) films. Furthermore, amorphous films with Ge content higher than 5.0% were obtained when the substrate temperature was  $20^\circ\text{C}$ , while they were obtained with Ge content higher than 7.0% when the substrate temperature was  $200^\circ\text{C}$ . The electrical resistivity of 6.0% Ge-doped amorphous  $\text{In}_2\text{O}_3$  film deposited at  $20^\circ\text{C}$  is  $4.1 \times 10^{-4} \Omega\cdot\text{cm}$ . The etching rate of the film by 5% HCl is  $1400 \text{ \AA}/\text{min}$  and is nine times as high as that of ITO films.

**KEYWORDS:** indium oxide, ITO, electrical conductivity, germanium, amorphous, etching rate

### 1. Introduction

Transparent conducting thin film is used in optoelectronic devices such as transparent electrodes in liquid-crystal displays (LCDs), plasma displays or solar cells. Since tin-doped  $\text{In}_2\text{O}_3$  (ITO) has low electrical resistivity and high optical transparency, it is used as a transparent electrode in LCDs.<sup>1)</sup> Numerous studies on the ITO's properties have been reported. For example, the electrical and optical properties have been studied by measurements of the Hall effect,<sup>2,3)</sup> X-ray photoemission and the absorption coefficient.<sup>4,5)</sup> The structure has been investigated by X-ray absorption spectroscopy and Mössbauer spectrometry.<sup>6,7)</sup> From these studies, it is pointed out that the high transparency of ITO films results from the large band gap and carrier electrons originating from the Sn donor and oxygen vacancies brought about by the high electrical conductivity.<sup>2,5,8,9)</sup>

In order to improve the performance of the LCD, transparent conducting films with low electrical resistivity and good etching behavior which enables fine patterning are needed. Numerous investigations on the relationship between properties and deposition conditions have been carried out in order to obtain a low electrical resistivity film deposited by the magnetron sputtering method.<sup>10–15)</sup> The etching property of ITO has also been investigated.<sup>13,16–21)</sup> The etching rate is enhanced when the microstructure of ITO consists of grains embedded in an amorphous matrix.<sup>16)</sup> However, the amorphous ITO films were difficult to prepare by magnetron sputtering, so they were prepared by ion beam sputtering.<sup>17)</sup>

The electrical properties of  $\text{In}_2\text{O}_3$  with dopants other than tin have been studied. The effects of Te,<sup>19)</sup> Ge,<sup>22,23)</sup> Si,<sup>22)</sup> Mg,<sup>24)</sup> F,<sup>25)</sup> Ca,<sup>26)</sup> Cu,<sup>27)</sup> S and As dopants have been reported.<sup>28)</sup> In those studies, the electrical resistivity of Ge-doped indium oxide films was rather low and the resistivity of this film deposited by the rf sputtering method was reported to be  $4 \times 10^{-4} \Omega\cdot\text{cm}$ .

In this study, the properties of Ge-doped  $\text{In}_2\text{O}_3$  film deposited by dc magnetron sputtering were investigated in detail. First, the deposition condition dependence on the electrical resistivity was studied in order to obtain the minimum resistivity of the Ge-doped  $\text{In}_2\text{O}_3$  film. The carrier density and the carrier mobility were measured to evaluate the film's quality.

Second, in order to improve etching properties, amorphous Ge-doped  $\text{In}_2\text{O}_3$  was deposited by controlling the dopant con-

tent and deposition conditions. The etching rate of amorphous Ge-doped  $\text{In}_2\text{O}_3$  films etched by HCl and  $\text{HNO}_3$  was compared with that of ITO films.

### 2. Experimental Method

Ge-doped  $\text{In}_2\text{O}_3$  targets of 6-inch diameter were sintered from a mixture of  $\text{In}_2\text{O}_3$  powder and  $\text{GeO}_2$  powder. As a reference, an ITO (90 wt%  $\text{In}_2\text{O}_3$ –10 wt%  $\text{SnO}_2$ ) target was prepared. Ge-doped  $\text{In}_2\text{O}_3$  films and ITO films as references were deposited on a glass substrate (Corning No. 1737 glass) by dc magnetron sputtering. Before sputtering, the chamber was evacuated to  $5 \times 10^{-6}$  Torr. The target was presputtered for 10 min.

The metal element contents in the films were analyzed by inductively coupled plasma (ICP) emission spectroscopy. The dopant content is calculated by  $x/(x + In)$ , where  $x$  is the amount of Ge or Sn in atomic units and  $In$  is the amount of indium in atomic units. The crystallinity of the films was measured by the X-ray diffraction (XRD) method with  $\text{Cu K}\alpha$  radiation. The electrical resistivity of the film was measured by the van der Pauw method. The carrier concentration and mobility were measured by using the Hall effect. The transmittance of the films was measured using a spectrophotometer. The thickness of the films was measured by the cross-section profilemetry method.

The etching rate of the amorphous film was measured as follows. After producing a resist mask, wet etching in  $\text{HNO}_3$  or HCl was performed at room temperature. The etching profile is measured by cross-section profilemetry and etching rates were calculated.

### 3. Results

#### 3.1 Low electrical resistivity film

This section describes how conditions were studied in order to obtain low electrical resistivity films. First, Ge content dependence on the electrical resistivity was investigated. The deposition conditions for Ge-doped  $\text{In}_2\text{O}_3$  films are listed in Table I. In this study, films of about  $2200 \text{ \AA}$  thick were deposited. As a reference, ITO films were deposited. Under the conditions described in Table I, films of about  $1700 \text{ \AA}$  thick were deposited. All the films had a polycrystalline structure. In the table, the distance between target and substrate is indicated by T/S distance.

Figure 1 shows the electrical resistivity of the film as a function of dopant content. The squares indicate results for

Table I. Deposition conditions.

Film	Power (W)	Sputtering gas	T/S distance (mm)	Pressure (mTorr)	Substrate Temperature (°C)	time (s)
Ge/In <sub>2</sub> O <sub>3</sub>	800	Ar + 2.0% O <sub>2</sub>	45	2	200	30
ITO	350	Ar + 0.5% O <sub>2</sub>	75	2	200	90

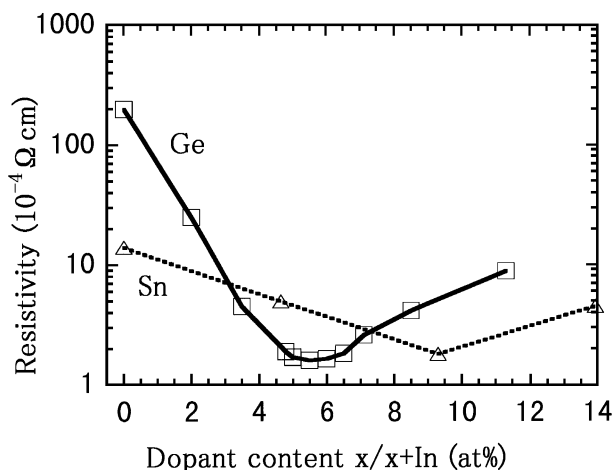


Fig. 1. Electrical resistivity of indium oxide deposited at 200°C as a function of dopant content. The dopant content is calculated by  $x/(x + In)$ , where,  $x$  is the amount of Ge or Sn in atomic units and  $In$  is the amount of indium in atomic units.

Ge-doped In<sub>2</sub>O<sub>3</sub> films and triangles indicate ITO. Because the deposition conditions for squares relevant to Ge-doped In<sub>2</sub>O<sub>3</sub> are different from those for triangles relevant to ITO, the electrical resistivities of the films without dopant differ. We found that the most suitable deposition conditions of Ge-doped In<sub>2</sub>O<sub>3</sub> for low electrical resistivity are high-power deposition and a short T/S as compared with that for In<sub>2</sub>O<sub>3</sub> or ITO.

The minimum resistivity for Ge-doped In<sub>2</sub>O<sub>3</sub> is  $1.6 \times 10^{-4} \Omega\text{-cm}$  at 5.5% Ge doping. The electrical resistivity of ITO with 9.3% Sn doping is  $1.8 \times 10^{-4} \Omega\text{-cm}$ .<sup>2)</sup> The minimum resistivity of the films doped with Ge is slightly lower than that of ITO at 200°C deposition.

Figure 2 shows carrier density and carrier mobility as a function of dopant content. The vertical axis on the left-hand side indicates carrier density and that on the right-hand side indicates carrier mobility. In the figure, circles indicate the density and squares indicate the mobility. The carrier density increases as the Ge dopant content increases and reaches a peak at 6.5%. The maximum value of the carrier density is  $11.3 \times 10^{20}/\text{cm}^3$ . The change in the carrier density is small above 6.5%. The carrier mobility has a peak at 5.5% and the maximum value is  $37.5 \text{ cm}^2/\text{Vs}$ . As a result, the minimum value of resistivity is obtained at 5.5%. The carrier density at minimum resistivity is  $10.5 \times 10^{20}/\text{cm}^3$ . The carrier density and the carrier mobility for ITO with low electrical resistivity,  $1.8 \times 10^{-4} \Omega\text{-cm}$ , are  $11.2 \times 10^{20}/\text{cm}^3$  and  $31.7 \times \text{cm}^2/\text{Vs}$ , respectively. The mobility of Ge-doped In<sub>2</sub>O<sub>3</sub> film is greater than that of ITO. The average transmittance from 378 nm to 778 nm is measured and is about 90% below 7.0% Ge content. However, it decreases above 7% Ge content. It is said that the absorption of light by impurity levels originating from the Ge

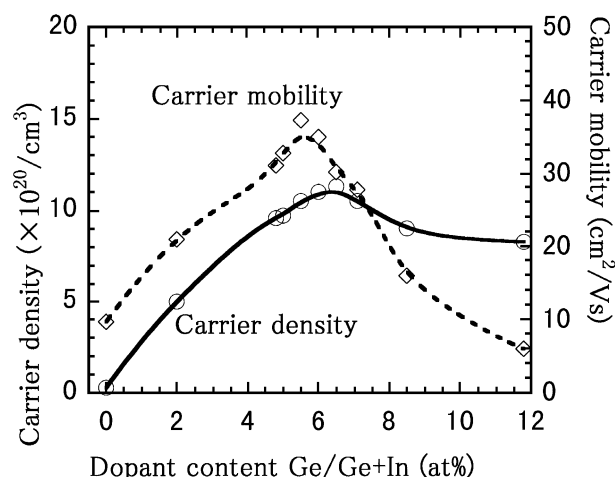


Fig. 2. Carrier density and carrier mobility of indium oxide deposited at 200°C as a function of Ge content. Circles denote carrier density and squares denote carrier mobility.

dopant becomes large above 7.0%.

The substrate temperature dependence of resistivity was measured for the film with 5.5% Ge content. The resistivity of the film deposited at 20°C is  $4.5 \times 10^{-4} \Omega\text{-cm}$ . The resistivity decreases as the temperature increases. The electrical resistivity was  $1.6 \times 10^{-4} \Omega\text{-cm}$  at 200°C and saturated at  $1.2 \times 10^{-4} \Omega\text{-cm}$  above 400°C. It may be possible to further reduce the resistivity of the film deposited at 400°C by optimizing the deposition conditions. Likewise, the resistivity of ITO is  $4.5 \times 10^{-4} \Omega\text{-cm}$  for 20°C,  $2 \times 10^{-4} \Omega\text{-cm}$  for 400°C, and  $1.1 \times 10^{-4} \Omega\text{-cm}$  for 400°C. The resistivity of Ge-doped In<sub>2</sub>O<sub>3</sub> is comparable to that of ITO.

The deposition condition dependence, i.e., oxygen content in sputtering gas, target-substrate (T/S) distance and deposition power dependence on electrical resistivity are also studied for the film deposited at 200°C with 5.5% Ge content.

Figure 3 shows the electrical resistivity as a function of oxygen content in sputtering gas. The squares indicate the electrical resistivity of Ge-doped indium oxide and triangles

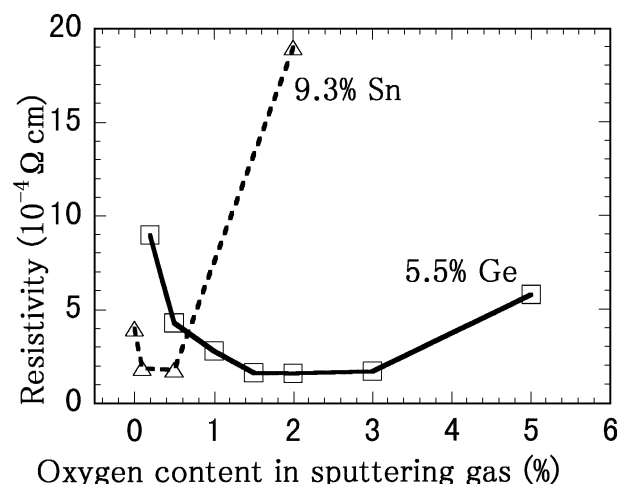


Fig. 3. Electrical resistivity of indium oxide as a function of oxygen content in sputtering gas. Squares denote the electrical resistivity of 5.5% Ge-doped indium oxide and triangles denote that of 9.3% Sn-doped indium oxide.

indicate that for ITO. The resistivity of Ge-doped  $\text{In}_2\text{O}_3$  shows a minimum at 2% oxygen and the dependence of resistivity on the oxygen content is lower than that of ITO. The carrier electrons in Ge-doped  $\text{In}_2\text{O}_3$  originate from the vacancies in  $\text{In}_2\text{O}_3$  and from the Ge dopant. The partial oxygen in the sputtering gas controls the amount of vacancies in  $\text{In}_2\text{O}_3$  and hence affects the resistivity and transparency of the films. The difference in the optimum condition for each film is related to the difference in the amount of oxygen vacancy content in  $\text{In}_2\text{O}_3$ . It is estimated that oxygen vacancies are made more easily for Ge doping than for Sn doping.

The average transmittance of Ge-doped  $\text{In}_2\text{O}_3$  is dependent on the oxygen content. The transmittance of the film deposited by 100% argon gas is 10%. The transmittance becomes larger as the oxygen content in the gas increases. The transmittance is 70% when the films are deposited by 1% oxygen content and is 90% for 2% oxygen content. The transmittance is saturated above 3% and is 91%. On the other hand, the transmittance of ITO is 80% for 0% oxygen content and is 90% for 0.5% oxygen content. This is explained by the assumption that oxygen vacancies are made easily when Ge is doped in indium oxide. Therefore, in order to obtain a high-transparency film, a higher content of oxygen is necessary for Ge-doped indium oxide as compared with ITO.

The T/S distance is an important factor in obtaining low-resistivity Ge-doped  $\text{In}_2\text{O}_3$  films. The resistivity is  $3.3 \times 10^{-4} \Omega\text{-cm}$  at 75 mm. The resistivity decreases as the T/S distance decreases and is  $1.7 \times 10^{-4} \Omega\text{-cm}$  at 55 mm and  $1.6 \times 10^{-4} \Omega\text{-cm}$  at 45 mm. Due to the limits of the apparatus, the resistivity of the films deposited at a T/S distance shorter than 45 mm was not examined. However, it is expected that the resistivity is saturated at a shorter T/S distance. The transmittance is slightly decreased at a short T/S distance because the film gains many oxygen defects by taking the argon bomber when the T/S distance is short.

The deposition power is also an important factor in obtaining low-resistivity film. The resistivity is  $4.2 \times 10^{-4} \Omega\text{-cm}$  when the power is 200 W and the T/S distance is 45 mm. The resistivity decreases as the power increases. The resistivity is  $1.6 \times 10^{-4} \Omega\text{-cm}$  at 800 W and saturated above 800 W. On the bases of these results, it is noted that deposition at a high power and at a short T/S distance is desirable in order to obtain low electrical resistivity film.

In this study, the deposition conditions are investigated in detail for 200°C deposition. The resistivity of Ge-doped indium oxide is comparable to that of ITO. The Ge atom is a group IV element and functions as a donor in  $\text{In}_2\text{O}_3$ . Therefore, the electrical resistivity of Ge-doped indium oxide is smaller than that of  $\text{In}_2\text{O}_3$ . However, the resistivity depends on the impurity concentration, ionization rate and solubility or grain boundary. Investigations of these phenomena will also be necessary in the future work.

### 3.2 Amorphous film

#### 3.2.1 Electrical and optical properties of amorphous films

First, the dependence of film crystallinity on Ge content and substrate temperature was investigated. The deposition conditions are listed in Table II. Films of about 1400 Å thick were deposited.

Both the crystallinity and resistivity of Ge-doped  $\text{In}_2\text{O}_3$  films are shown in Fig. 4. The circles on the solid line indi-

Table II. Deposition conditions.

Film	Power (W)	Sputtering gas	T/S distance (mm)	Pressure (mTorr)	Substrate Temperature (°C)	time (s)
Ge/ $\text{In}_2\text{O}_3$	300	Ar + 2.0% $\text{O}_2$	75	1	200,20	90
ITO	300	Ar + 0.5% $\text{O}_2$	75	1	200,20	90

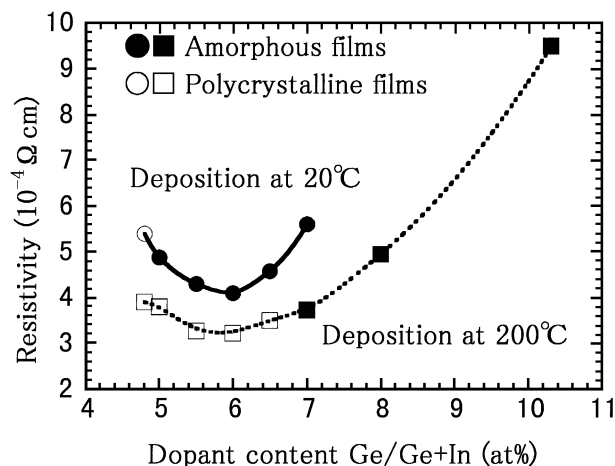


Fig. 4. Electrical resistivity and crystallinity of Ge-doped indium oxide as a function of dopant contents. Circles denote the film deposited at 20°C. Squares denote the film deposited at 200°C. The open circle and open squares denote polycrystalline film. Solid circles and solid squares denote amorphous film.

cate the electrical resistivity of films deposited at room temperature (20°C) and the squares on the hatched line indicate that for films deposited at 200°C. With respect to the crystallinity of the film, a solid circle or a solid square indicates that the film is amorphous and an open circle or open square indicates that the film is polycrystalline. In the case where the films are deposited at room temperature, they become amorphous when the Ge content is above 5.0%. In the case where the films are deposited at 200°C, the films become amorphous when the Ge content is above 7.0%.

The XRD results of the films deposited at 20°C are shown in Fig. 5. The XRD pattern shows that the film with 4.8% Ge content is polycrystalline and that with 6.0% Ge content is amorphous. The atomic radii of Ge, Sn and In are 1.22, 1.40 and 1.44 Å, respectively. The radius of the germanium atom is smaller than that of the indium atom. Therefore, it is assumed that Ge-doped  $\text{In}_2\text{O}_3$  becomes amorphous more easily than ITO does.

When the Ge content is 5.0%, the amorphous and polycrystalline are mixed in the film. The boundary of the deposition condition between amorphous and polycrystalline is ambiguous because it depends on the film thickness. Figure 6(a) shows a scanning electron microscopy (SEM) micrograph of a 5.0% Ge content film's surface and Fig. 6(b) shows a cross-sectional transmission electron microscopy (TEM) micrograph of the same film. The surface micrograph shows a grain structure, which indicates that the film is polycrystalline. However, the cross-sectional micrograph shows that about 1000 Å above the glass substrate is amorphous and polycrystals grow above the amorphous film. The structure changes from amorphous to polycrystalline during de-

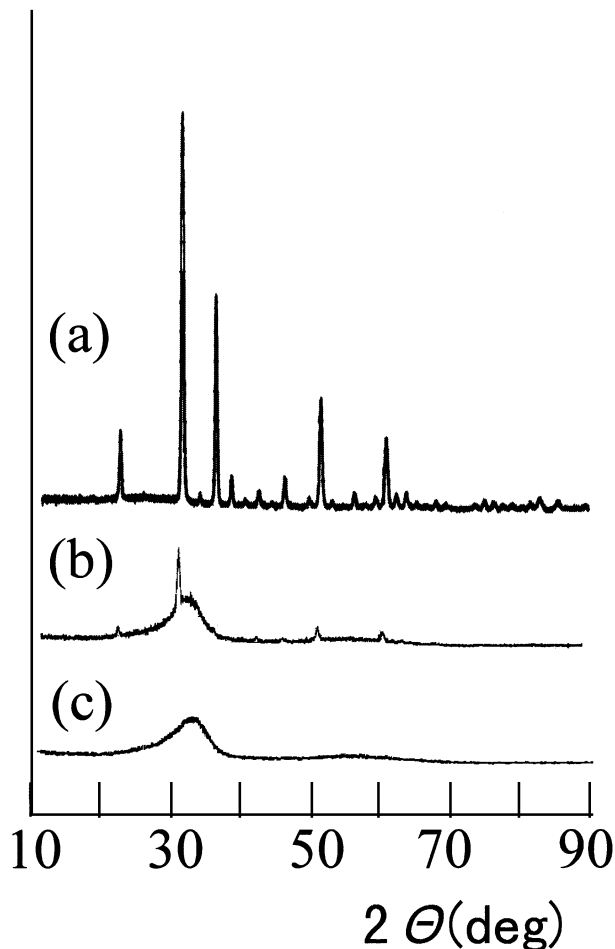


Fig. 5. (a) XRD spectra of 4.8% Ge content film deposited at 20°C. (b) 5.0% Ge content film. (c) 6.0% Ge content film.

position because the temperature increases during deposition. Figure 6(c) shows the TEM image of the film with 6.0% Ge content. When the Ge content is large, the film becomes amorphous.

The lowest electrical resistivity is obtained at 6.0% doping for both room-temperature deposition and 200°C deposition. The electrical resistivity of a film deposited at room-temperature is  $4.1 \times 10^{-4} \Omega\cdot\text{cm}$  while it is  $3.3 \times 10^{-4} \Omega\cdot\text{cm}$  for a film deposited at 200°C. However, the film deposited at 200°C is polycrystal film. The lowest resistivity of amorphous films deposited at 200°C is  $3.8 \times 10^{-4} \Omega\cdot\text{cm}$  at 7.0% doping.

As a reference, 9.3 at.% Sn-doped ITO films (10 wt%  $\text{SnO}_2\text{--In}_2\text{O}_3$ ) were deposited under the conditions listed in Table II. ITO films become polycrystalline for both room-temperature deposition and 200°C deposition. The resistivity of the film was  $8.6 \times 10^{-4} \Omega\cdot\text{cm}$  for room-temperature deposition and  $1.9 \times 10^{-4} \Omega\cdot\text{cm}$  for 200°C deposition. The resistivity of the Ge-doped  $\text{In}_2\text{O}_3$  films was lower than that of ITO for room-temperature deposition.

The effects of deposition pressure and oxygen content of the deposition gas on the crystallinity were also studied for 6.0% Ge content films deposited at room temperature. The deposition pressure dependence of crystallinity is large. Amorphous films can be obtained in the pressure range from  $0.5 \times 10^{-3}$  Torr to  $2.0 \times 10^{-3}$  Torr. The discharge does not occur below  $0.5 \times 10^{-3}$  Torr. When the deposition pressure

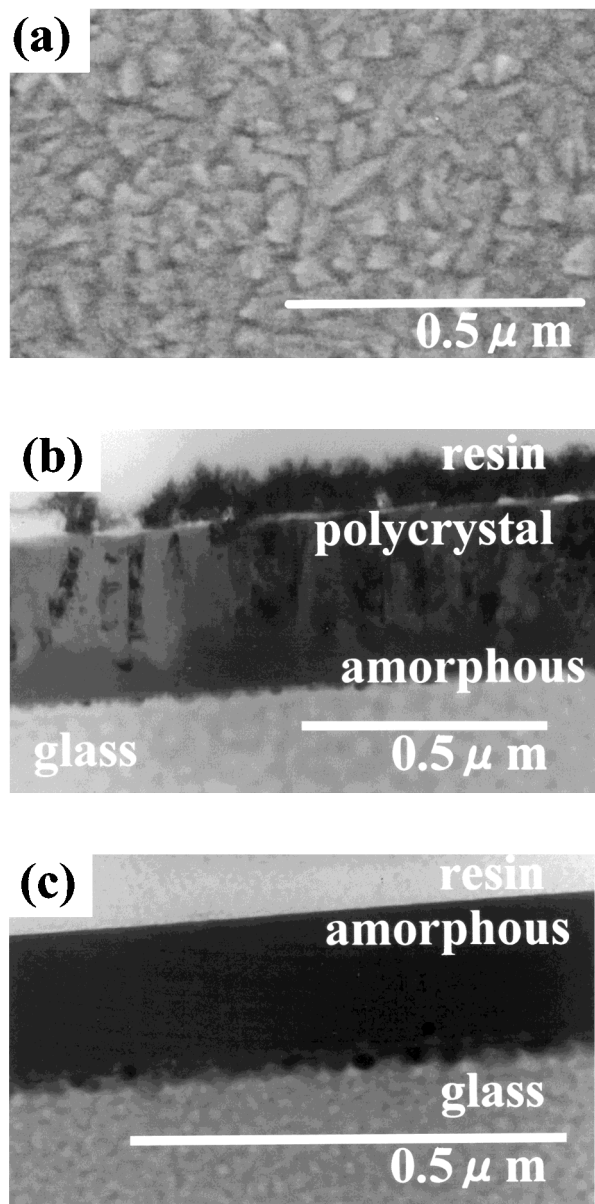


Fig. 6. (a) SEM micrograph of 5.0% Ge content film's surface deposited at 20°C. (b) Cross-sectional TEM micrograph of 5.0% Ge content film. (c) TEM micrograph of 6.0% Ge content film.

is higher than  $3.0 \times 10^{-3}$  Torr, almost all parts of the film become polycrystalline and the resistivity increases sharply beyond  $0.1 \Omega\cdot\text{cm}$ .

When the deposition pressure is high, it is assumed that the energy of the sputtered atom is decreased due to collisions with the deposition gas. Therefore, it is expected that films deposited at high pressure will become amorphous. However, films became polycrystalline at high pressure in this experiment. In the experiment, oxygen partial pressure is high when the deposition pressure is high. Therefore, the formation of amorphous film depends on the oxygen content in the sputtering gas rather than on the total pressure.

The effect of the oxygen content on the crystallinity or on the electrical resistivity was also studied. When the films were deposited under a pressure of  $1.0 \times 10^{-3}$  Torr, the structure of the film obtained in the range of 0% to 4% oxygen content was amorphous and the resistivity was between  $4.2 \times 10^{-4} \Omega\cdot\text{cm}$  and  $5.5 \times 10^{-4} \Omega\cdot\text{cm}$ . On the other hand, the

film became polycrystalline and the resistivity became higher than  $0.01 \Omega\cdot\text{cm}$  for 10% oxygen content. It is presumed that the defect originated from a decrease in oxygen vacancies and thus the film became polycrystalline.

The electrical properties, that is, the carrier density and the carrier mobility, were measured for the amorphous Ge-doped  $\text{In}_2\text{O}_3$  films. The dependence of the carrier mobility on Ge content is small and almost constant at  $30.0 \text{ cm}^2/\text{Vs}$ . The carrier density is  $3.8 \times 10^{20}/\text{cm}^3$  at 4.8% Ge content and attains a maximum of  $4.6 \times 10^{20}/\text{cm}^3$  at 6.0% Ge content, where the electrical resistivity is the lowest. The resistivity of amorphous films with 7.0% Ge deposited at  $200^\circ\text{C}$  is  $3.8 \times 10^{-4} \Omega\cdot\text{cm}$ . The carrier density is  $3.7 \times 10^{20}/\text{cm}^3$  and the mobility is  $34.0 \text{ cm}^2/\text{Vs}$  for the film.

The carrier mobility of polycrystal film with 4.8% Ge content and that of amorphous film with 7.0% Ge content has almost the same value. ITO film exhibits a domain structure and the domain consists of numerous grains. The mobility decreases as domain size decreases and the domain boundary affects electron conduction more than micrograin boundaries do.<sup>12,13)</sup> The effect of domain/grain structure on the mobility was not investigated for Ge-doped film. More detailed studies are necessary. The transmittance of the films deposited at room temperature is almost constant at about 90% in the range of Ge doping below 7.0%. The transmittance decreases steadily as the Ge content increases beyond 7.0% for the film deposited at  $200^\circ\text{C}$ .

### 3.2.2 Etching property

In this section, the etching properties of Ge-doped  $\text{In}_2\text{O}_3$  film are investigated. Since the very little is known about the etching properties of Ge-doped  $\text{In}_2\text{O}_3$ , the optimum solution for etching is not known for Ge-doped  $\text{In}_2\text{O}_3$  films. However, a variety of solutions has been proposed for ITO, for example,  $\text{HI}$ ,<sup>18,20)</sup>  $\text{HF}$ ,<sup>20)</sup>  $\text{HCl}$ ,<sup>16,19)</sup>  $\text{HCl}+\text{FeCl}_3$ ,<sup>21)</sup>  $\text{HCl}+\text{HNO}_3$ ,<sup>12)</sup>  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ .<sup>16,19)</sup> In this study, a dilute solution of hydrochloric acid and nitric acid was used since it is a well-known solution.

The Ge content dependence of the etching rate is shown in Fig. 7 for Ge-doped  $\text{In}_2\text{O}_3$  films together with data for ITO as a reference. Solid circles denote the etching rate of amorphous films deposited at  $20^\circ\text{C}$  and the open circle denotes that of polycrystal film. The etching rate of the film with a 4.8% Ge dopant, which is a polycrystal film, is lower than  $50 \text{ \AA}/\text{min}$ . The etching rate abruptly increases as the Ge-doped film changes to amorphous from crystalline and then gradually increases as the Ge content becomes higher. The solid squares denote the results for amorphous films deposited at  $200^\circ\text{C}$ . The etching rate is large because the film is amorphous. The open triangle denotes the etching rate of polycrystal ITO deposited at  $20^\circ\text{C}$  as reference data. Ge-doped amorphous  $\text{In}_2\text{O}_3$  films have a high etching rate. This is because dangling bonds in the amorphous film are chemically active.

The HCl concentration dependence of the etching rate of amorphous Ge-doped  $\text{In}_2\text{O}_3$  film and that of ITO are shown in Fig. 8. Solid circles in the figure indicate the etching rates of the amorphous films with 6.0% Ge deposited at  $20^\circ\text{C}$ . Solid squares indicate the etching rates of the amorphous films with 7.0% Ge deposited at  $200^\circ\text{C}$ . As a reference, open triangles indicate the etching rate of ITO deposited at  $20^\circ\text{C}$ . Since the structure of ITO film deposited at room temperature is poly-

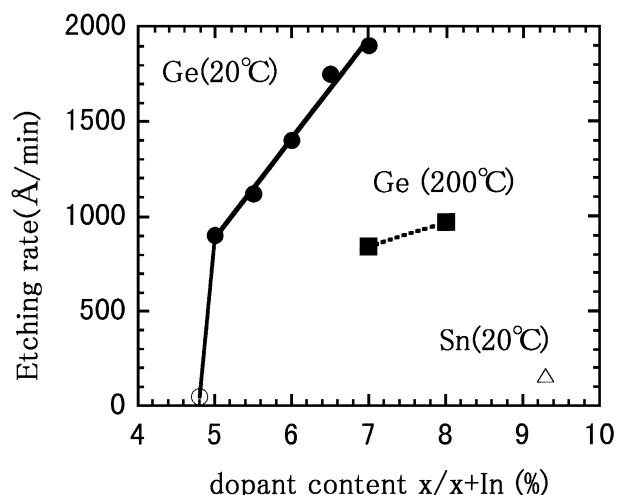


Fig. 7. Etching rate of indium oxide film as a function of dopant content. Circles denote Ge-doped indium oxide deposited at  $20^\circ\text{C}$ . Squares denote Ge-doped film deposited at  $200^\circ\text{C}$ . The triangle denotes Sn-doped indium oxide deposited at  $20^\circ\text{C}$ . The open circle denotes polycrystalline film. Solid circles and solid squares denote amorphous film.

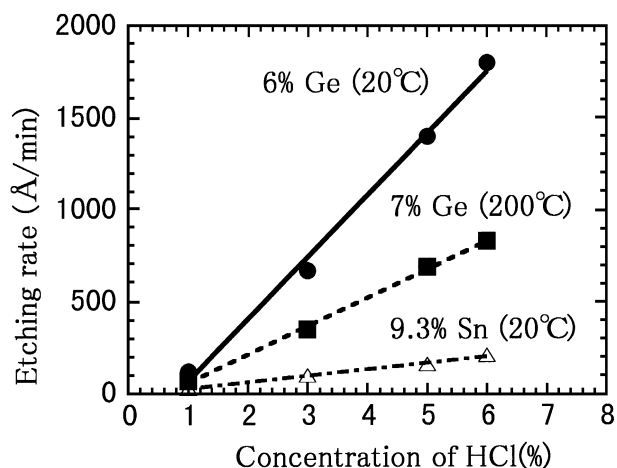


Fig. 8. Etching rate of Ge- or Sn-doped indium oxide film as a function of HCl concentration. Circles denote 6.0% Ge-doped amorphous film deposited at  $20^\circ\text{C}$ . Squares denote 7.0% Ge-doped amorphous film deposited at  $200^\circ\text{C}$ . Triangles denote 9.3% Sn-doped polycrystalline film deposited at  $20^\circ\text{C}$ .

crystalline, the etching rate is low. The etching rate of the Ge-doped  $\text{In}_2\text{O}_3$  film increases as the concentration of HCl becomes higher. The rates of the films etched by 5% HCl are  $1400 \text{ \AA}/\text{min}$ ,  $690 \text{ \AA}/\text{min}$  and  $160 \text{ \AA}/\text{min}$  for the Ge-doped film deposited at room temperature, the film deposited at  $200^\circ\text{C}$  and the reference ITO film, respectively.

The etching rate of amorphous films by 60%  $\text{HNO}_3$  deposited at room temperature is also greater than that of ITO. The tendency is the same as that for HCl etching. The rates of the films etched by 60%  $\text{HNO}_3$  are  $720 \text{ \AA}/\text{min}$ ,  $300 \text{ \AA}/\text{min}$  and  $120 \text{ \AA}/\text{min}$ , for the film obtained by room-temperature deposition, the film obtained by  $200^\circ\text{C}$  deposition and the reference ITO film, respectively. The etching rate of amorphous Ge-doped  $\text{In}_2\text{O}_3$  is larger than that of ITO.

The amorphous ITO film was obtained when the deposition power was decreased to 20 W. Under this condition, the deposition rate of ITO is decreased to  $1.3 \text{ \AA}/\text{s}$ . The deposition rate is low compared with the rate of  $16 \text{ \AA}/\text{s}$  in the normal de-

position method. The electrical resistivity is  $1.4 \times 10^{-3} \Omega\cdot\text{cm}$  and the 60%  $\text{HNO}_3$  etching rate is 1400 Å/min.

The electrical resistivity of Ge-doped amorphous  $\text{In}_2\text{O}_3$  film deposited at room temperature is smaller than that of ITO deposited at room temperature. Furthermore, the average transmittance of the film with 1400 Å thickness is higher than 90%. Therefore, Ge-doped  $\text{In}_2\text{O}_3$  films are suitable for transparent electrodes that require fine patterning.

#### 4. Conclusion

The properties of Ge-doped  $\text{In}_2\text{O}_3$  film deposited by the dc magnetron sputtering method were studied.

First, polycrystal film with low resistivity was studied. The electrical resistivity is  $1.6 \times 10^{-4} \Omega\cdot\text{cm}$  for 200°C deposition and is  $4.7 \times 10^{-4} \Omega\cdot\text{cm}$  for room-temperature deposition. The minimum electrical resistivity is  $1.2 \times 10^{-4} \Omega\cdot\text{cm}$  at 400°C deposition. This resistivity is comparable with that of ITO. Ge is a group IV element and functions as a donor for  $\text{In}_2\text{O}_3$ . Hence, the resistivity of  $\text{In}_2\text{O}_3$  becomes low when Ge is doped. It is the same as the case of Sn doping in ITO.

Films with low electrical resistivity can be obtained at a high deposition power with a short T/S distance. Therefore, a high deposition rate of about 75 Å/s can be attained. The dependence of the resistivity on the partial oxygen in sputtering gas is lower than that of ITO. These features are advantageous for the efficient deposition of transparent film on a mass-production scale in industry.

Second, a high deposition rate of 15 Å/s was achieved to deposit amorphous films in contrast with the deposition of amorphous ITO films where the deposition rate should be reduced to as low as 1.3 Å/s. That is, amorphous films can be obtained when the Ge content is higher than 5.0% for room-temperature deposition or when it is higher than 7.0% for 200°C deposition.

The optical and electrical properties of amorphous films are comparable with those of ITO deposited at room temperature. The etching rate of amorphous film by dilute HCl is from four times to nine times higher than that of ITO films. In other words, it is said that a dilute solution can be used when the Ge-doped amorphous  $\text{In}_2\text{O}_3$  films are used as transparent electrodes in optoelectronic devices. This is an important

point, because less damage to the other components in the device can be expected during the patterning of transparent film by a mild solution such as dilute HCl.

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