

Title	Germanium- and silicon-doped indium-oxide thin films prepared by radio-frequency magnetron sputtering
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Citation	APPLIED PHYSICS LETTERS (1994), 64(11): 1395-1397
Issue Date	1994-03-14
URL	<a href="http://hdl.handle.net/2433/43527">http://hdl.handle.net/2433/43527</a>
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Type	Journal Article
Textversion	publisher; none

# Germanium- and silicon-doped indium-oxide thin films prepared by radio-frequency magnetron sputtering

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(Received 18 October 1993; accepted for publication 16 December 1993)

Indium oxide ( $\text{In}_2\text{O}_3$ ) thin films doped with either germanium or silicon were prepared by using a radio-frequency magnetron sputtering method. The target was the  $\text{In}_2\text{O}_3$  powder mixed with either Ge or Si powder. The resistivities of the films were compared with that of the film doped with tin (ITO). The Ge and Si dopings yielded lower carrier concentrations and higher Hall mobilities compared to those for Sn doping, and they gave different dependencies of resistivity on atomic ratio. The minimum resistivity of the films doped with Ge was nearly equal to that of ITO.

Indium oxide ( $\text{In}_2\text{O}_3$ ) thin films have a wide range of applications, e.g., transparent electrodes of liquid crystal and other displays, with developing preparation methods of thin films of high quality. In particular,  $\text{In}_2\text{O}_3$  films doped with tin ( $\text{In}_2\text{O}_3:\text{Sn}$ , ITO) are widely used as transparent conductive films. However, there are few reports on the use of other dopants. Out of the Ti,<sup>1,2</sup> Sb,<sup>1</sup> Zr,<sup>1</sup> Bi,<sup>2</sup> Pb,<sup>2</sup> Te,<sup>3</sup> B,<sup>4</sup> As,<sup>4</sup> S,<sup>5</sup>

and F<sup>6-9</sup> dopants, and the Te, S, and F dopants have been reported to be able to give a resistivity in the order of  $10^{-4}$   $\Omega$  cm.

This letter shows the electrical and optical properties of the  $\text{In}_2\text{O}_3$  thin films doped with group V elements, i.e., germanium and silicon compared with that doped with tin.

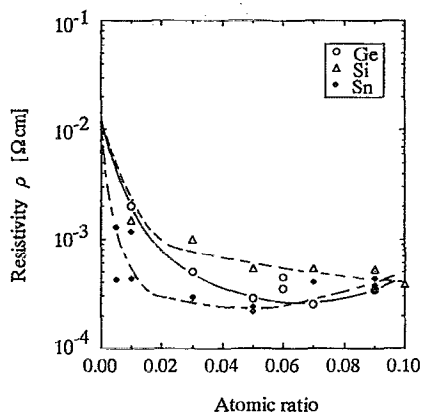


FIG. 1. Electric resistivities for  $\text{In}_2\text{O}_3:\text{Ge}$ ,  $\text{In}_2\text{O}_3:\text{Si}$ , and  $\text{In}_2\text{O}_3:\text{Sn}$  films as a function of atomic ratio of impurity to In.

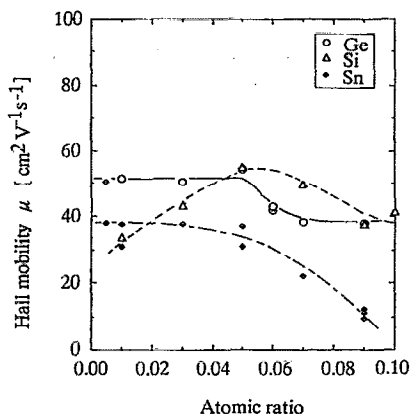


FIG. 2. Hall mobilities for  $\text{In}_2\text{O}_3:\text{Ge}$ ,  $\text{In}_2\text{O}_3:\text{Si}$ , and  $\text{In}_2\text{O}_3:\text{Sn}$  films as a function of atomic ratio of impurity to In.

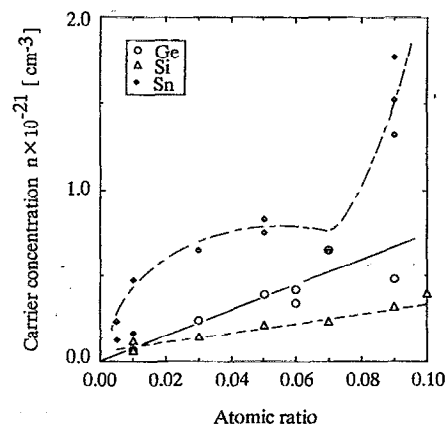


FIG. 3. Carrier concentrations for  $\text{In}_2\text{O}_3:\text{Ge}$ ,  $\text{In}_2\text{O}_3:\text{Si}$ , and  $\text{In}_2\text{O}_3:\text{Sn}$  films as a function of atomic ratio of impurity to In.

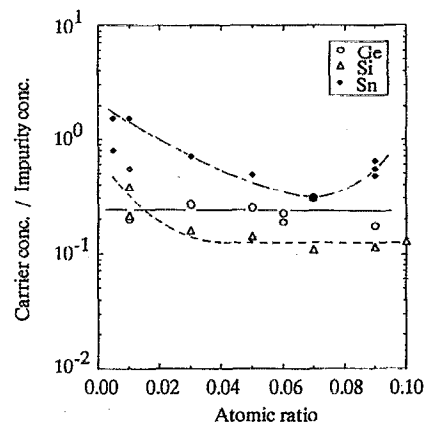
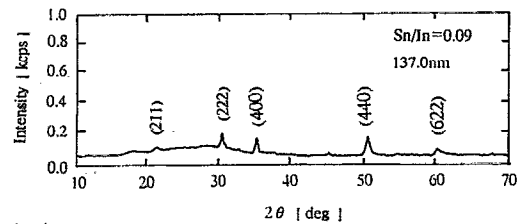
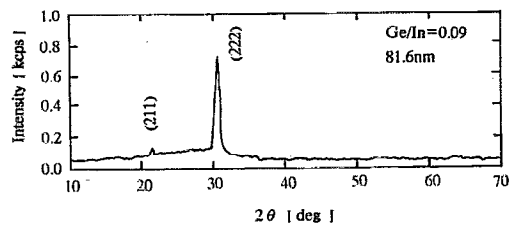
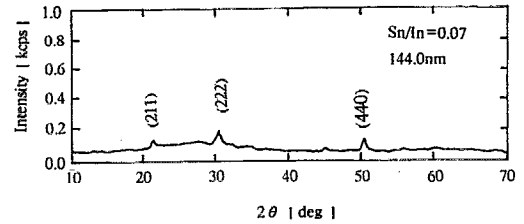
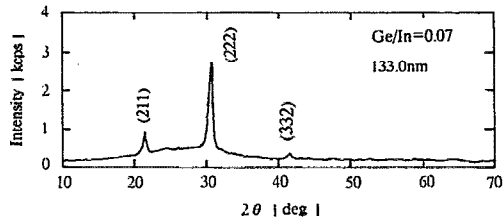
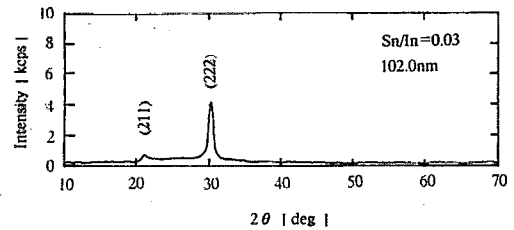
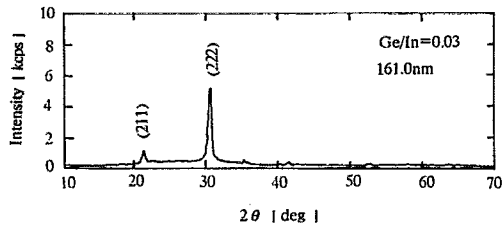
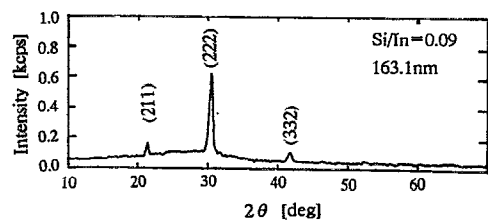
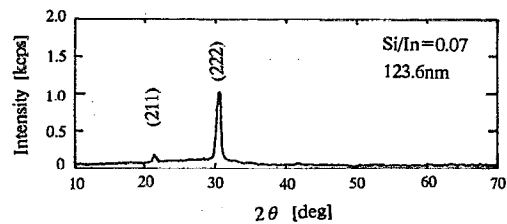
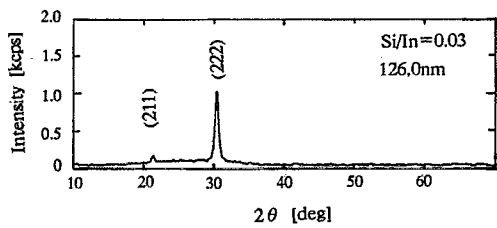


FIG. 4. Concentration ratio of carrier to impurity as a function of atomic ratio.



(a)

(c)



(b)

FIG. 5. X-ray diffraction patterns of the (a)  $\text{In}_2\text{O}_3:\text{Ge}$ , (b)  $\text{In}_2\text{O}_3:\text{Si}$ , and (c)  $\text{In}_2\text{O}_3:\text{Sn}$  films on borosilicate glass.

In preparing  $\text{In}_2\text{O}_3$  films, radio frequency (rf) magnetron sputtering equipment (Osaka Vacuum Co. Ltd.) was used with a  $\text{In}_2\text{O}_3$  powder (purity of 99.99%, Sumitomo Metal Mining Co., Ltd.) mixed with either Si, Ge, or Sn powder (purity of 99.999%) as the target. The rf power was 200 W, the sputtering gas was an argon, and its flow rate was 28 sccm. Before sputtering, the chamber was evacuated to  $5 \times 10^{-6}$  Torr. The target was presputtered for 10 min. During sputtering, the substrate was water cooled, and the chamber pressure was kept at  $1.5 \times 10^{-3}$  Torr. The sputtering time was about 10 min. A  $76 \times 26 \text{ mm}^2$  borosilicate glass plate and quartz glass plate were used as the substrate.

The composition of the film was measured by x-ray photoelectron spectroscopy. The crystallinity of the film was analyzed by the x-ray diffraction method with  $\text{Cu } K\alpha$  radiation. The electric 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 optical transmittance of the film was obtained by means of a multipurpose recording spectrophotometer. A blank glass substrate was inserted into the reference beam path of the spectrophotometer.

Figure 1 shows the resistivity of the film as a function of the atomic ratio of impurity to indium. The ratio was calculated from the content of metal power added to the  $\text{In}_2\text{O}_3$  powder target. The resistivity for each dopant shows a different dependence on atomic ratio. The minimum resistivity for Ge dopant is nearly equal to that of Sn dopant.

Figures 2 and 3 show the Hall mobilities and carrier concentrations as a function of the atomic ratio of impurity to indium. The results for Ge and Si dopants show higher Hall mobilities and lower carrier concentrations than those for Sn dopant. The Hall mobilities for Ge and Si dopants do not appreciably decrease with increasing carrier concentration, i.e., they are not affected by the ionized impurity scattering mechanism, which seems to affect the mobility for Sn dopant at  $\text{Sn}/\text{In} \geq 0.05$ .

The carrier concentration of  $\text{In}_2\text{O}_3$  films doped with an impurity is attributed to the contribution of doped ions to substitutional sites of  $\text{In}^{+3}$  ions and/or of interstitial atoms in the  $\text{In}_2\text{O}_3$  lattice, as well as of oxygen vacancies and/or interstitial In atoms. The contribution of doped ions can be assumed to be a linear function of the atomic ratio of impurity to indium. In fact, the carrier concentrations for both Ge and Si dopants increase linearly with the atomic ratio, although the carrier concentration for Sn dopant largely deviates from the linearity. The intercept to the ordinate for Si dopant shows a finite value which is nearly equal to the carrier concentration for the nondoped  $\text{In}_2\text{O}_3$  film, i.e.,  $2.921 \times 10^{19} \text{ cm}^{-3}$ . This is attributable to the oxygen vacancies or interstitial In atoms.

In order to clearly depict the linearity, the carrier concentration was divided by impurity concentration, and the results were shown in Fig. 4 as a function of the atomic ratio of impurity to indium. The results for Si dopant show an asymptotic constant value at a large value ( $>0.04$ ) of the atomic ratio. A deviation from the linearity at a small value ( $\leq 0.04$ ) of the atomic ratio can be attributed to the contribution of the oxygen vacancies or interstitial In atoms. In the meantime, the results for the Ge dopant take a different constant value. The differences in the asymptotic values between Ge and Si dopants are attributable to the difference in ionization energy. It is noted that the results for Ge dopant does not show any deviation even at the lowest value of the atomic ratio. This fact suggests that the occurrence of oxygen vacancies or interstitial In atoms were suppressed by sputtering the target mixed with Ge powder. In fact, the Hall mobility in Fig. 3 show a higher value ( $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) for Ge dopant at the lowest value (0.05) of the atomic ratio, while the extrapolation of the Hall mobility for Si dopant to the ordinate show a lower value ( $22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) which agrees well with that ( $21.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) for the nondoped  $\text{In}_2\text{O}_3$  film.

Figures 5(a)–5(c) show typical examples of the x-ray diffraction patterns of the films on a borosilicate glass. The patterns show the (222) plane texturing. Apparently, the  $\text{In}_2\text{O}_3:\text{Ge}$  and  $\text{In}_2\text{O}_3:\text{Si}$  films are superior in crystallinity to the  $\text{In}_2\text{O}_3:\text{Sn}$  film at the atomic ratios 0.07 and 0.09. This is attributable to the lower concentration of carrier, as shown in Fig. 2. The better crystallinity reflects each higher Hall mobility in Fig. 2.

In conclusion, the  $\text{In}_2\text{O}_3$  thin films doped with either germanium or silicon shows higher Hall mobilities and lower carrier concentrations compared to those doped with Sn, and they show different dependences of resistivity on atomic ratio. The minimum resistivity of the films doped with Ge is nearly equal to that of ITO.

This work was supported by the Yazaki Science and Technology Foundation, Nippon Sheet Glass Foundation, and Ookura Foundation. The authors thank K. Nakanishi and T. Yamaoka of Nippon Sheet Glass Co., Ltd. for the Hall coefficient measurements.

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*Published without author corrections*