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

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Indium oxide (In_2O_3) thin films doped with either germanium or silicon were prepared by using a radio-frequency magnetron sputtering method. The target was the In_2O_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 (In_2O_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, In_2O_3 films doped with tin (In_2O_3:Sn, ITO) are widely used as transparent conductive films. However, there are few reports on the use of other dopants. Out of the Ti,[1,2] Sb,[1] Zr,[1] Bi,[2] Pb,[2] Te,[3] B,[4] As,[4] S,[5] and F[6–9] dopants, and the Te, S, and F dopants have been reported to be able to give a resistivity in the order of 10^{-4} Ω cm.

This letter shows the electrical and optical properties of the In_2O_3 thin films doped with group V elements, i.e., germanium and silicon compared with that doped with tin.

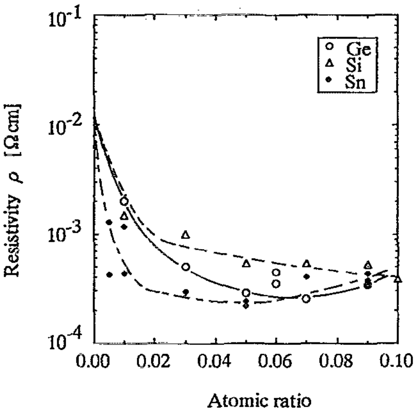


FIG. 1. Electric resistivities for In_2O_3:Ge, In_2O_3:Si, and In_2O_3:Sn films as a function of atomic ratio of impurity to In.

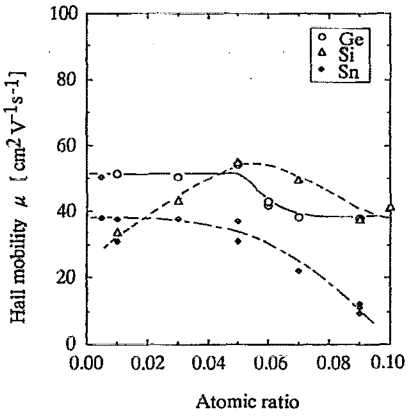


FIG. 2. Hall mobilities for In_2O_3:Ge, In_2O_3:Si, and In_2O_3:Sn films as a function of atomic ratio of impurity to In.

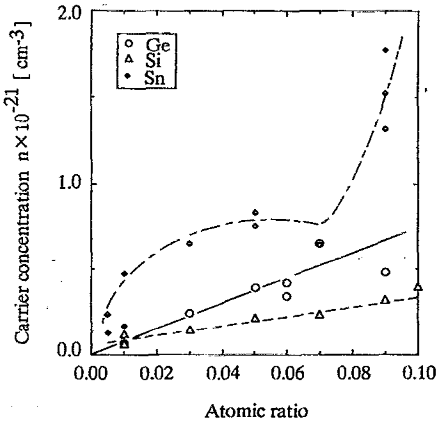


FIG. 3. Carrier concentrations for In_2O_3:Ge, In_2O_3:Si, and In_2O_3:Sn films as a function of atomic ratio of impurity to In.

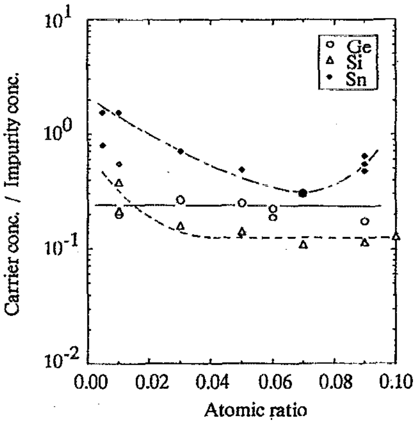
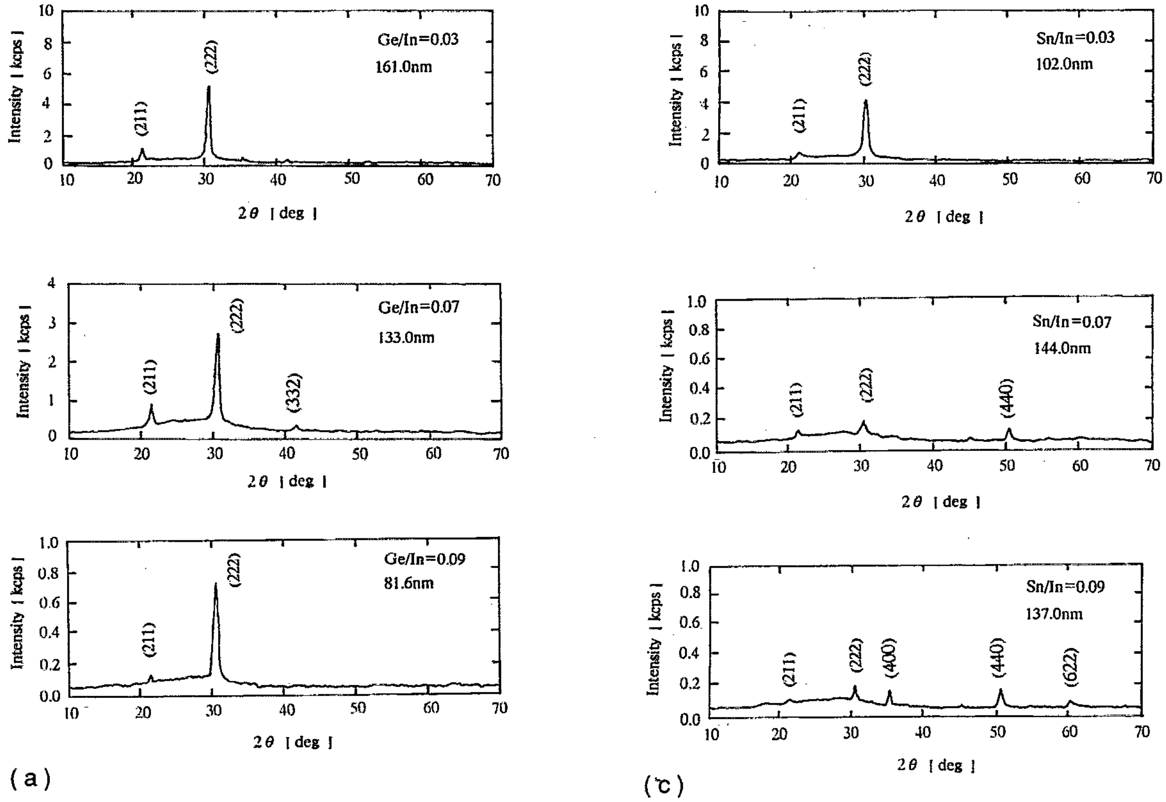


FIG. 4. Concentration ratio of carrier to impurity as a function of atomic ratio.



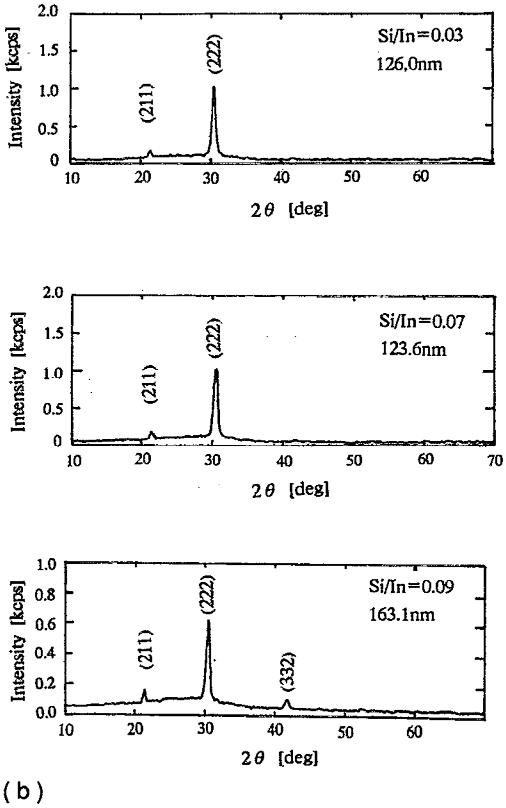


FIG. 5. X-ray diffraction patterns of the (a) In_2O_3:Ge, (b) In_2O_3:Si, and (b) In_2O_3:Sn films on borosilicate glass.

In preparing In_2O_3 films, radio frequency (rf) magnetron sputtering equipment (Osaka Vacuum Co. Ltd.) was used with a In_2O_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 5×10^{-6} Torr. The target was presputtered for 10 min. During sputtering, the substrate was water cooled, and the chamber pressure was kept at 1.5×10^{-3} Torr. The sputtering time was about 10 min. A 76×26 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 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 In_2O_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 $Sn/In\geq0.05$.

The carrier concentration of In_2O_3 films doped with an impurity is attributed to the contribution of doped ions to substitutional sites of In^{+3} ions and/or of interstitial atoms in the In_2O_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 In_2O_3 film, i.e., 2.921×10^{19} 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 (≤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 lies 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 $cm^2\,V^{-1}\,s^{-1}$) 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 $cm^2\,V^{-1}\,s^{-1}$) which agrees well with that (21.1 $cm^2\,V^{-1}\,s^{-1}$) for the nondoped In_2O_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 In_2O_3:Ge and In_2O_3:Si films are superior in crystallinity to the In_2O_3: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 In_2O_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.

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