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Control of the growth orientation and electrical properties of polycrystalline Cu₂O thin films by group-IV elements doping

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The effects of group-IV element dopants on the structural and electrical properties of Cu₂O thin films were studied. Similar dopant-induced behavior was found in the observed variations of the growth orientation and electrical properties of Si- and Ge-doped Cu₂O thin films. Ge doping was found to induce electrically active acceptors with an activation energy of 0.18 eV, comparable to the 0.19 eV value of Si-doped Cu₂O. These results suggest that locally formed silicate and germanate have the same effect on the structural and electrical properties of Cu₂O. On the other hand, Sn and Pb likely act as donors when incorporated substitutionally onto Cu-lattice sites, although further study may be required to suppress self-compensation effects in Cu₂O to achieve *n*-type conductivity. © 2004 American Institute of Physics. [DOI: 10.1063/1.1827352]

Cuprous oxide (Cu₂O), with a direct band-gap energy of 2.0 eV, is a candidate material for the fabrication of highly efficient and cost effective thin film solar cells.^{1–4} Though practical applications have not been achieved because of the difficulty in controlling its electrical properties, Cu₂O is still considered to be an attractive material since it has the advantages of a relatively high absorption coefficient in the visible region, low-cost production, is nontoxic, and is fabricated from abundantly available materials.^{5–8} It is particularly important to investigate the controllability of the electrical properties of Cu₂O for practical device applications. We have investigated the optimal deposition conditions and doping effects for Cu₂O thin films. It was found that single-phase Cu₂O thin films with the high Hall mobility of 60 cm²/V s could be obtained by controlling the growth conditions of reactive rf magnetron sputtering.⁹ It was also found that nitrogen could act as a *p*-type dopant in Cu₂O with the relatively low activation energy of 0.14 eV in comparison with that of Cu₂O native acceptors of 0.25–0.4 eV origination from Cu-vacancies.¹⁰ Furthermore, Si was verified to act as an effective *p*-type dopant with an activation energy of 0.19 eV in Cu₂O by means of forming silicates. The hole carrier density in Cu₂O thin films can be easily controlled by adjusting the doping level of Si.¹¹ In this letter, we have expanded our study of Si doping in Cu₂O to include other group-IV elements such as Ge, Sn, and Pb. Although these elements belong to the same elemental group of the periodic table, the properties of their oxides are different. The properties of the oxides of Si and Ge, that is, SiO₂ and silicates or GeO₂ and germanates, are quite similar and have been found to be dominated by the invariable tetrahedral Si- or Ge-O₄ pyramidal structure coordinated with four oxygen atoms regardless of whether in a crystalline or amorphous state.^{12–14} While the oxides of Sn and Pb crystallize in a tetragonal structure, in particular, Pb₂O forms in the cuprous structure, the same structure as Cu₂O.¹⁵ It is, therefore, expected that these group-IV elements incorporate by individually unique

mechanisms and give rise to different doping effects in polycrystalline Cu₂O. In the current work, Ge doping was focused upon and compared to the results of Si doping. The effects of Sn and Pb doping are also discussed.

Polycrystalline Cu₂O thin films were deposited by rf magnetron sputtering on Corning 7059 glass substrates at 400 °C. Cu target of 4N purity, Ar sputtering gas, and O₂ reactive gas were used for deposition. The detailed procedures have been described elsewhere.⁹ Doping of group-IV elements into Cu₂O was carried out by placing small pieces of source wafer or metal sheets on the Cu target. The doping level was controlled by varying the fraction of the target area composed of dopant source and final compositions were measured using an electron-probe microanalyzer. Typical film thickness and deposition rate were 1.8–2.0 μm and 2.7–3.0 μm/h, respectively, as determined by scanning electron microscopy. The characteristics of the chemical bond of Ge in Cu₂O were analyzed using Fourier transform infrared spectroscopy (FTIR). The structural properties were studied by x-ray diffraction (XRD) in the θ - 2θ mode using Cu *K* α radiation. The resistivity, Hall mobility, and the hole density of Cu₂O thin films were measured by the van der Pauw method.

Figure 1 shows FTIR spectra of Ge-doped Cu₂O thin films. The wavy structure observed in the region of 1000–4000 cm⁻¹ is due to interference caused by multiple scattering in the film. A prominent absorption peak was observed in Ge-doped Cu₂O at around 820 cm⁻¹ as shown in Figs. 1(b) and 1(c), whereas only a Cu–O related absorption peak at around 630 cm⁻¹ was observed in undoped Cu₂O as shown in Fig. 1(a). The absorption peak appearing near 820 cm⁻¹ can be assigned to a Ge–O–Ge asymmetric stretching vibration, which has been reported in the literature to appear at 820–860 cm⁻¹ in GeO₂ or Ge-compound oxides such as Si_{1-x}Ge_x oxides.^{16,17} As reported previously, absorption peaks, which can be assigned to stretching, bending, and rocking mode vibrations of the Si–O–Si bond in SiO₄ system, were observed in Si-doped Cu₂O thin films.¹¹ In addition to this, an extended x-ray absorption fine structure

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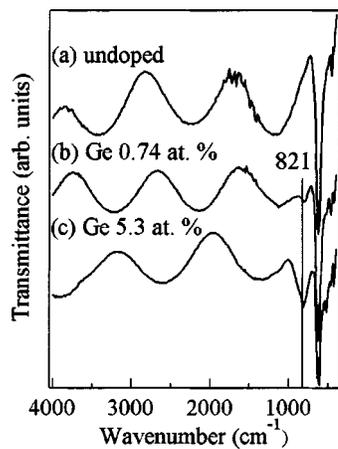


FIG. 1. FTIR spectra of undoped (a) and Ge-doped Cu₂O thin films (b), (c).

analysis revealed that the Si in polycrystalline Cu₂O forms a tetrahedrally coordinated SiO₄ pyramidal structure with four oxygen atoms surrounding each Si atom, the same as in SiO₂.¹⁸ As will be mentioned later, Ge-oxides have very analogous properties to Si-oxides. From these results, it is suggested that the Ge in Cu₂O is also coordinated by four oxygen atoms and forms a tetrahedral structure similar to that of Si in Cu₂O.

It should be noted that the growth orientation of Cu₂O dramatically changed from (200) to (111) with Ge doping as indicated in Fig. 2(a). This change has been observed for the case of Si doping as well. It is well known that silicate compounds of the form $xM_2O \cdot ySiO_2$ are easily formed with a x/y ratio of 1 or 2. Thus, it is reasonable to consider that Si-doped Cu₂O forms a mixed crystal composed of Cu₂O and silicate, which is expected to have a pseudo-hexagonal structure and results in a change in the growth orientation of Cu₂O thin films to (111).^{11,19,20} Likewise, germanium dioxide seems to be readily miscible with Cu₂O to form germanates, which have the same structures as silicates and can be generated by replacing Si with Ge.^{21,22} It is, therefore, probable that Ge in Ge-doped Cu₂O forms germanate and the growth orientation of Cu₂O is changed by the same mechanism as for Si-doped Cu₂O. As shown in Figs. 2(b) and 2(c), the full

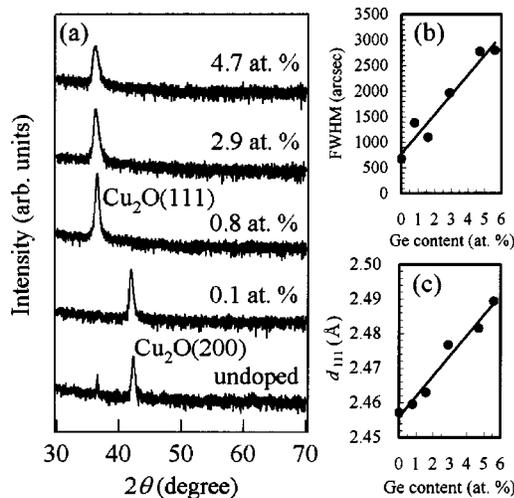


FIG. 2. XRD profiles of Ge-doped Cu₂O thin films (a), and variation in the FWHM of Cu₂O(111) (b), and the interplanar distances of (111) planes of Cu₂O (d_{111}) (c), for films with varying Ge content.

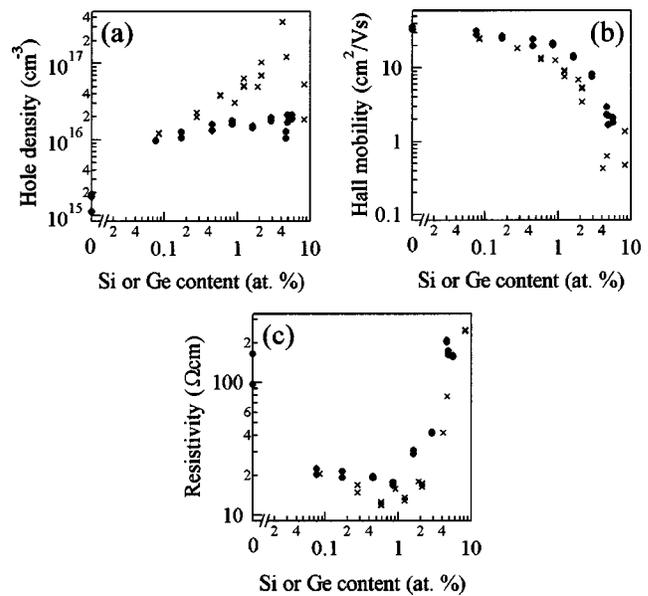


FIG. 3. Hole density (a), Hall mobility (b), and resistivity (c) measured at room temperature for Si-doped (crosses) or Ge-doped (closed circles) Cu₂O thin films.

width at half maximum (FWHM) of Cu₂O(111) and the (111) interplanar distances (d values) calculated from the XRD peak positions increased with increasing Ge content in Cu₂O. These results, which were observed for the case of Si-doped Cu₂O as well due to silicate formation, suggesting the existence of germanate in Cu₂O.¹¹

Figures 3(a)–3(c) show the variation of the hole density, resistivity, and Hall mobility at room temperature of Cu₂O thin films with various doping levels of Ge or Si. As can be seen in Fig. 3(a), the hole density increased with increasing doping level up to about 4 at. % for both Si and Ge. A linear increase in hole density was observed with Si doping, while early saturation was observed for the case of Ge doping. Although a detailed study is necessary to clarify the cause of early saturation, this may be attributed to generation of large concentrations of defects, induced by stress-induced distortion in Ge-doped Cu₂O thin films due to the larger volume of the GeO₄ over the SiO₄ unit cell since the bond length of Ge–O in GeO₂ is 1.74 Å, whereas that of Si–O in SiO₂ is 1.61 Å.^{12,13} The resistivity decreased with increasing dopant concentration and a minimum value was achieved for each dopant at around 1 at. % as shown in Fig. 3(c). Above 1 at. %, the grain size of Cu₂O was observed to decrease, as observed by atomic force microscopy. As a consequence of the reduction in grain size, the Hall mobility rapidly decreased for both Si and Ge doping as shown in Fig. 3(b).

The temperature dependence of the hole density of Ge-doped Cu₂O is shown in Fig. 4. The hole density P is given as

$$P = \frac{N_a - N_d}{2N_d} N_v \exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where N_v is the effective density of states in the valance band given by $2(2\pi m_h^* kT/h^2)^{3/2}$; and N_a , N_d , E_a , k , T , m_h^* , and h are the acceptor density, donor density, acceptor activation energy, Boltzmann constant, temperature, effective hole mass, and Planck constant, respectively.^{10,23} The activation energy of the acceptor, E_a , can be deduced from Fig. 4 using

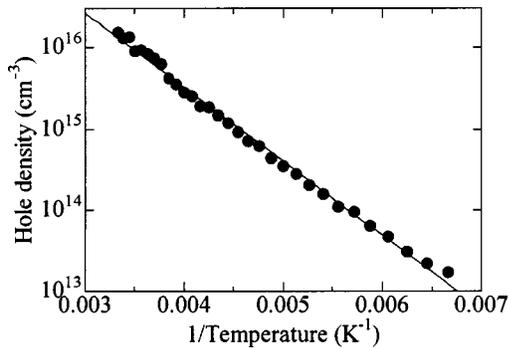


FIG. 4. Variation of the hole density with inverse temperature for a Ge-doped Cu_2O thin film with a Ge content of 0.8 at. %.

Eq. (1). The value obtained for E_a for Ge-doped Cu_2O is 0.18 eV, which is nearly identical to that for Si-doped Cu_2O (0.19 eV). This value is lower than the 0.25–0.4 eV activation energy of native acceptors in Cu_2O . This result can be seen as additional evidence that Ge acts as an effective acceptor in Cu_2O by the same mechanism as Si doping, which has been well modeled based on the formation of silicate as described elsewhere.¹¹ The compensation ratio, N_d/N_a , in Ge (0.8 at. %) -doped Cu_2O was calculated to be 0.28, while it was 0.09 in Si-doped Cu_2O . The large value of the N_d/N_a in Ge-doped Cu_2O may be due to an increase in defect concentration, which acts as carrier traps or recombination centers whose formation is induced with increasing Ge content due to the presence of internal stress.

The effects of Sn and Pb doping of Cu_2O were also examined. Figure 5 shows the variation in the electrical properties of Cu_2O thin films as a function of Pb content.

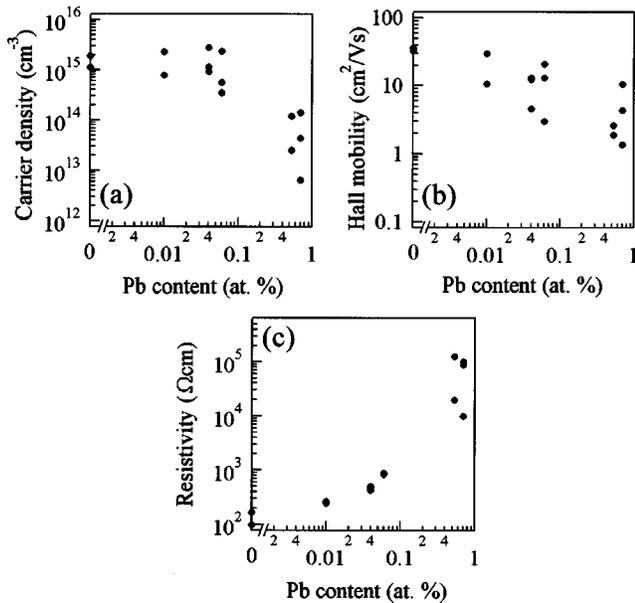


FIG. 5. Variations of the hole density (a), Hall mobility (b), and resistivity (c) of Cu_2O thin films for varying Pb content measured at room temperature.

The hole density and Hall mobility decreased, whereas resistivity increased with increasing Pb concentration, which implies Cu_2O gradually became semi-insulating. Similar results were observed for Sn doping, in contrast to the results of Si and Ge doping. Although it remains to be investigated whether Sn and Pb act as substitutional or interstitial impurities, assuming that Sn and Pb are substitutionally incorporated onto Cu lattice sites in Cu_2O , they can be expected to act as triple donors. However, it is difficult to obtain n -type conductivity from Cu_2O because electron carriers in Cu_2O tend to be self-compensated by native acceptors originating from Cu-vacancies, which are easily generated in Cu_2O due to their low formation energy. Therefore, to achieve reproducible and stable n -type Cu_2O going beyond a semi-insulating state, techniques to suppress self-compensation in Cu_2O may be required.

To summarize, the effects of group-IV elements doping in Cu_2O were studied. It was found that these dopant elements play different roles and have different effects in polycrystalline Cu_2O . In particular, Si and Ge were found to be very useful to control the crystalline and electrical properties of Cu_2O . It is speculated here that the technique of controlling material properties using silicate or germanate formation can be applied for other oxide semiconductors as well.

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