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Effect of oxygen intercalation on properties of sputtered $CuYO_2$ for potential use as *p*-type transparent conducting films

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Abstract. Transparent films of copper yttrium oxide doped with 2% calcium have been prepared by rf magnetron sputtering. The films show a conductivity of 8 Scm^{-1} on intercalation of oxygen at high pressure, which reduced the transparency in the visible region. The Ca-doped $CuYO_2$ films before oxygen intercalation show an average transmission of about 60% which reduces to about 45% upon oxygen intercalation. The temperature dependence of the conductivity indicates semiconductor behaviour with low activation energy of 0·59 eV at room temperature. The positive sign of Seebeck coefficient (+274 μVK^{-1}) confirms the *p*-type conductivity of the films. The optical bandgap of $CuYO_2$ was found to be 3·15 eV.

Keywords. Transparent conducting oxide; RF sputtering; *p*-type TCO.

1. Introduction

Transparent conducting oxide (TCO) thin films have a wide range of applications in optoelectronic devices (Chopra *et al* 1983), because of their unique transparent and conducting properties. Most of the TCOs exhibit *n*-type electrical conductivity. Indium tin oxide (ITO) and aluminum doped ZnO which has a bandgap of > 3 eV, transmission, >80% in the visible region and conductivity of the order of 10^4 S cm^{-1} are *n*-type conductors. These *n*-type TCOs have a wide range of applications but limited use as passive components such as transparent electrodes, IR reflecting coatings etc. The development of *p*-type TCOs will open up new applications in optoelectronic devices. The theoretical prediction of the possibility of producing *p*-type conducting ZnO (Yamamoto and Yoshida 1999) by co-doping with nitrogen and gallium has aroused much interest in the field of TCOs. There are several reports in recent times on the growth of *p*-type ZnO (Minegishi *et al* 1997; Gao *et al* 2001; Joseph *et al* 2001; Ryu *et al* 2001, 2003; Look *et al* 2002; Kim *et al* 2003). However, the reproducibility of good *p*-type ZnO TCO material remains a difficult task. *p*-Type conductivity has also been reported in NiO films (Sato *et al* 1993) which has 30% transparency in the visible region. The $CuAlO_2$ thin films having a delafossite structure has shown a transparency of 80% in the visible and infrared regions with electrical conductivity, 1 S cm^{-1} (Kawazoe *et al* 1997). This has generated much interest in *p*-type conducting transparent thin films (Thomas 1997; Banerjee and Chattopadhyay 2005). *p*-Type conductivity was found in a number of delafossites compounds such as $CuYO_2$ (Jayaraj *et al* 2001), $CuScO_2$ (Duan *et al* 2000), $CuCrO_2$ (Hoffmann *et al* 2001; Nagarajan *et al* 2001a), $CuGaO_2$ (Kawazoe *et al* 2000; Tate *et al* 2002), $CuInO_2$ (Yanagi *et al* 2001) and $CuAlO_2$ (Brian *et al* 2004).

$CuYO_2$ is a *p*-type semiconductor having wide bandgap isostructural with $CuAO_2$ delafossite (where A = Fe, Co, Rh, Ga, Sc, Y or lanthanides) (Shannon *et al* 1971). Intercalation with oxygen to form $CuAO_{2+\delta}$ phases is possible for compounds with large A^{3+} cations. Cava *et al* (1993, 1994) investigated the properties of polycrystalline $CuYO_{2+\delta}$ and $CuLaO_{2+\delta}$ phases. The $CuYO_{2+\delta}$ doped with calcium show conductivity as high as 10 S cm^{-1} after oxygen intercalation. Similar observation of increase in conductivity has been reported for $CuScMgO_{2+\delta}$ films on oxygen intercalation (Yanagi *et al* 2003). But oxygen intercalation results in the reduced transmittance in these films. The cause of *p*-type conductivity shown by these types of materials is due to excess oxygen (or metal deficit) within the crystallite sites of the material i.e. the defect chemistry plays an important role. This deviation from the stoichiometric composition of the components can be induced by regulating the preparation condition of the materials. Also, intercalation of excess O^{2-} ions in the interstitial sites may trap electrons, leaving behind empty states in the valence band, which act as holes. The formula for oxygen-excess delafossite films may be written as $CuYO_{2+x}$. The value of x i.e. the percentage of excess oxygen, may be no more than 25% in $CuYO_{2+x}$ polycrystalline powder (Nagarajan *et al* 2001b).

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In this paper, we report the electrical and optical properties of the Ca-doped $CuYO_2$ films. The variation in the electrical and optical properties on annealing these films under various oxygen partial pressures has also been studied. The photoluminescence (PL) emission and excitation (PLE) of $CuYO_2$ and Ca-doped $CuYO_2$ are also presented.

2. Experimental

Bulk Ca-doped $CuYO_2$ was synthesized in the laboratory from an intimate mixture of CuO, Y_2O_3 and CaO. This mixture was pelletized and heated at 1100°C for 24 h in air. The powder thus synthesized was polycrystalline $Cu_2Y_{1.96}Ca_{0.04}O_5$ ($Cu_2Y_2O_5$) (figure 1) (Shannon *et al* 1971). This powder was again heated in a flow of argon at 1050°C for 70 h producing $CuY_{0.98}Ca_{0.02}O_2$. The sputtering target was prepared by pressing the Ca-doped $CuYO_2$ powder into a 2 inch diameter pellet and heating at 1100°C for 12 h. The sputtering was carried out by on-axis geometry onto fused quartz substrates with rf power at 5 W/cm^2, with a substrate to target distance of 5 cm. The substrate temperature was kept at 100°C. The sputtering chamber was initially pumped down to a pressure of 2×10^{-5} mbar and then filled with argon gas up to 0·008 mbar. Pre-sputtering was carried out for 20 min before each deposition. The rate (2·5 Å/min) of deposition was determined by measuring thickness by the Tolansky method after deposition. The thicknesses of the deposited films were in the range of 1200 Å. The oxygen intercalation was achieved by annealing the films at various oxygen partial pressures. The annealing chamber was initially evacuated to 5×10^{-6} mbar and oxygen was fed into the chamber through a mass flow controller during annealing. The crystal structure of the films was analysed by Rigaku X-ray diffractometer in $\theta - 2\theta$ geometry using CuKα radiation. All the as deposited films were amorphous. The compositions of the target as well as the sputtered films were analysed using energy dispersive X-ray (EDX) measurements (Model 5-150 Stereoscan Cambridge (UK)). The EDX measurements show the films have the same compositions of the target with Cu/(Y + Ca) ratio equal to one. Conductivity was measured by a four-point probe in van der Pauw configuration. The transmission spectra of the films were recorded using a UV-vis-NIR spectrophotometer (Hitachi U-3410). The Ca-doped $CuYO_2$ films showed *p*-type conductivity that was confirmed by thermoelectric power measurements.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of the Ca-doped $CuYO_2$ target used for sputtering. The XRD pattern was consistent with delafossite structure belonging to *R*3*m* or *P*63/*mmc* as reported in the JCPDS files, 37-930 and 39-0224. The as deposited films were amorphous by XRD. The films were subjected to a post-deposition annealing at 700°C in air for 10 min followed by 10 min annealing in argon atmosphere at 900°C, which results in transparent Ca-doped $CuYO_2$ films. These films show an RMS surface roughness of 41·98 nm (figure 2). These films were crystalline with delafossite structure belonging to 2H or 3R polytype. Oxygen intercalation by annealing at 420°C at an oxygen pressure of one atmosphere pressure of oxygen did not result in decomposition of the delafossites into the more stable $Cu_2Y_2O_5$ phases. However, prolonged annealing at one atmospheric oxygen pressure shows considerable decrease in the intensity of the diffraction peak (figure 3). The transmission spectrum of Ca-doped $CuYO_2$ films recorded in the range of 200–900 nm is shown in figure 4. The films are transparent yellow in colour. The Ca-doped $CuYO_2$ films before oxygen intercalation is transparent in the visible range with an average transmission of about 60%. The transparency in the visible region is found to decrease with oxygen intercalation into the films. The highly transparent films are less conducting and the conductivity increases with oxygen intercalation at the expense of transparency. The oxygen intercalation into the crystalline $CuYO_2$ thin films leads to poor crystallinity on annealing in presence of oxygen and there is an increase in the amorphous peak at 20° indicating an increase of amorphous phase. Thus,

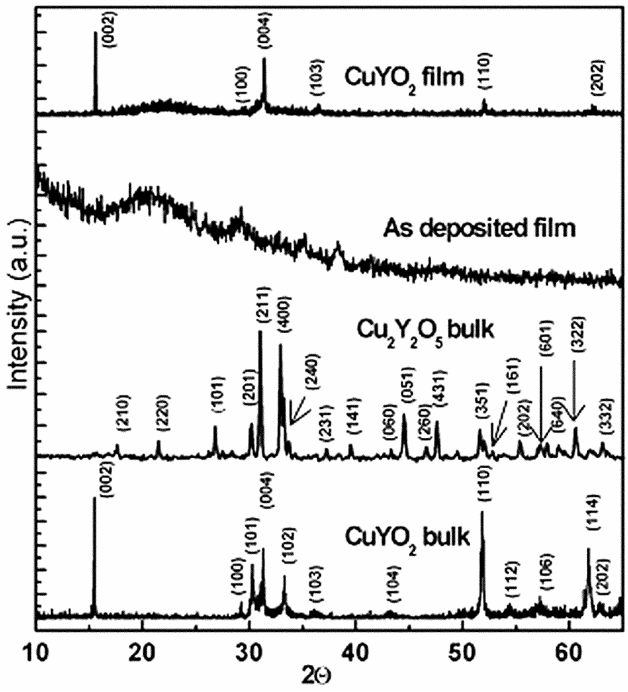

Figure 1. X-ray diffraction pattern of the Ca-doped $CuYO_2$ target, as deposited films, post annealed at 700° in air forming dimer phase followed by annealing in argon at 900°C forming the delafossite Ca-doped $CuYO_2$ thin film. The diffraction pattern of $Cu_2Y_2O_5$ phase is also shown.

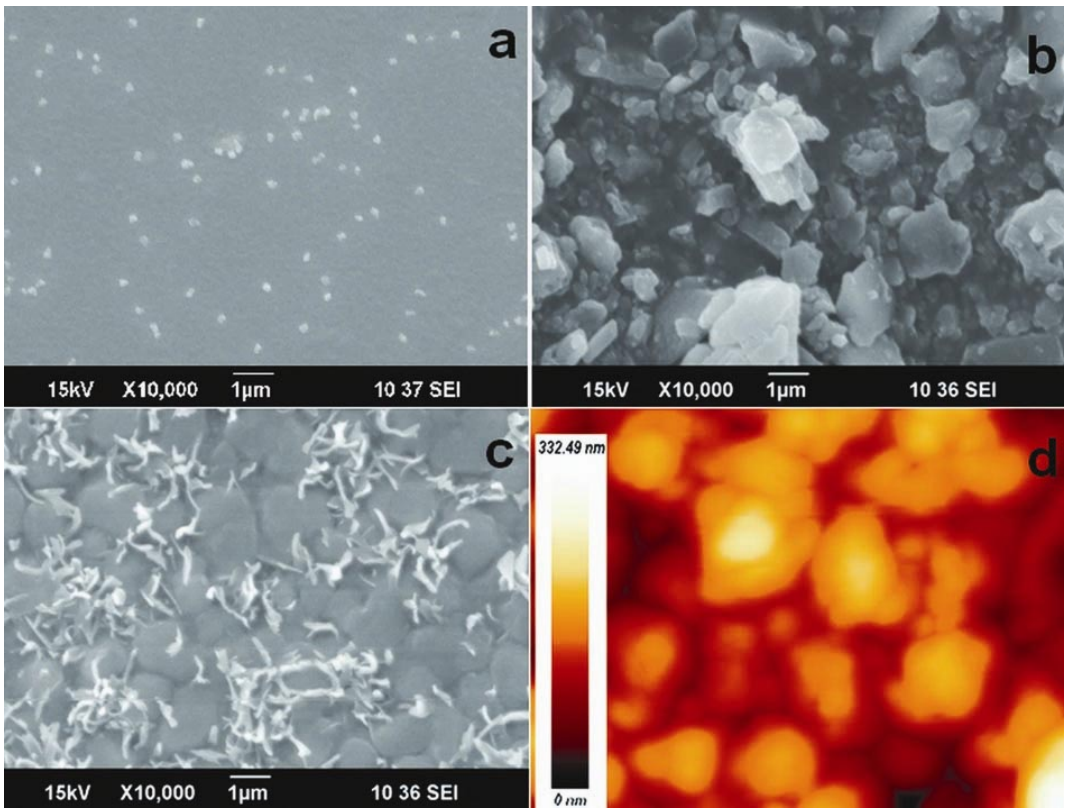

Figure 2. SEM pictures of **a**. as deposited $CuYO_2$ films, **b**. $Cu_2Y_2O_5$ phase thin film, **c**. Ca-doped $CuYO_2$ thin film and **d**. AFM image of the Ca-doped $CuYO_2$ films.

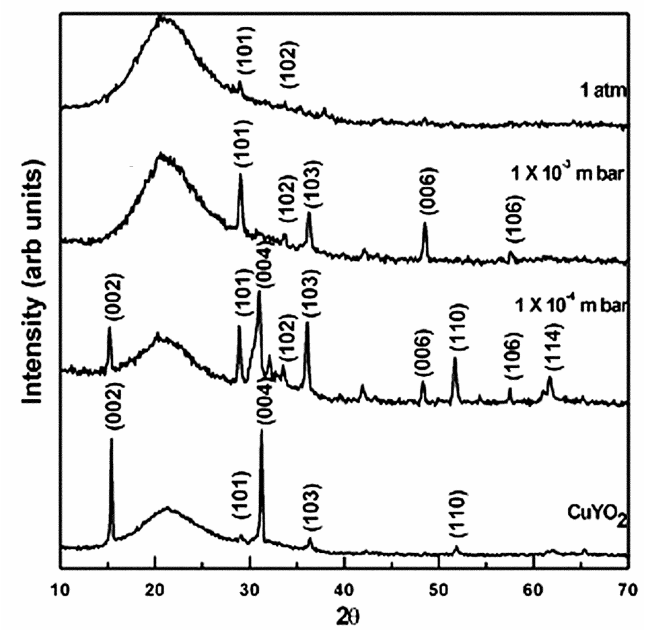

Figure 3. The X-ray diffraction patterns of Ca-doped $CuYO_2$ films annealed in oxygen at 420°C at various oxygen pressures.

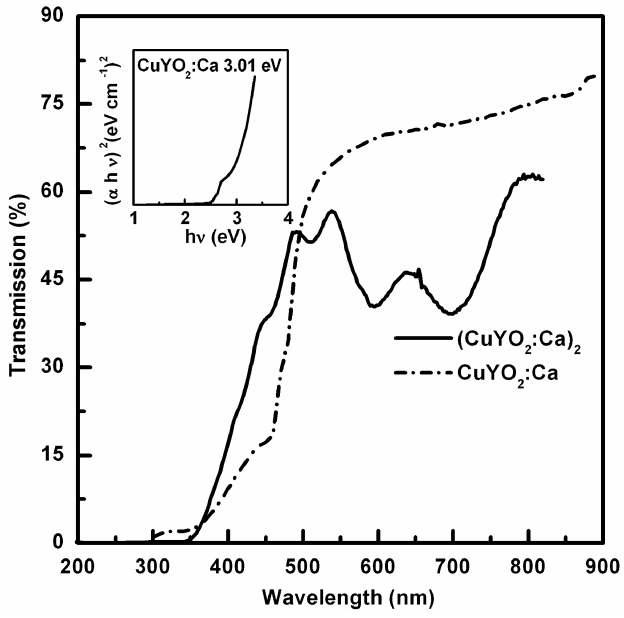

Figure 4. The transmission spectra of $Cu_2Y_2O_5$ and Ca-doped $CuYO_2$ thin films. Inset shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ for the thin films of Ca-doped $CuYO_2$ (3·1 eV).

the oxygen intercalation results in the formation of tail states in the bandgap. This is the reason for reduction in transmission on oxygen intercalation. The bandgap of the Ca-doped $CuYO_2$ films was calculated from the transmi-

ssion spectra by assuming a parabolic band structure for the material. The absorption coefficient and bandgap can be related by the expression,

$$\alpha h\nu = A(h\nu - E_g)^{1/N},$$

where E_g is the bandgap energy and α the absorption coefficient corresponding to frequency, ν (Yu *et al* 1996). The constant, N, depends on the nature of electronic transition. In the case of Ca-doped $CuYO_2$ films, N is equal to 2, for direct allowed transition. The bandgap of the films were determined from the plot of $(\alpha h\nu)^2$ vs $h\nu$ by extrapolating the linear portion of the curve to $h\nu = 0$. In the present study, the bandgap of Ca-doped $CuYO_2$, obtained after annealing the as deposited films in oxygen atmosphere at 700°C and argon atmosphere at 900°C for 10 min each, was found to be 3·1 eV (inset of figure 4).

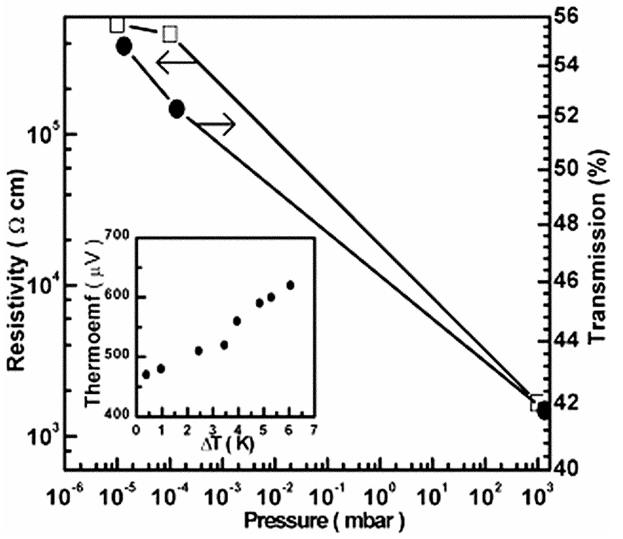

Figure 5. The variation of resistivity and transmission at 550 nm of the thin films as a function of oxygen pressure during annealing. Inset shows the plot of the thermopower of Ca-doped $CuYO_2$ film annealed in oxygen at atmospheric pressure.

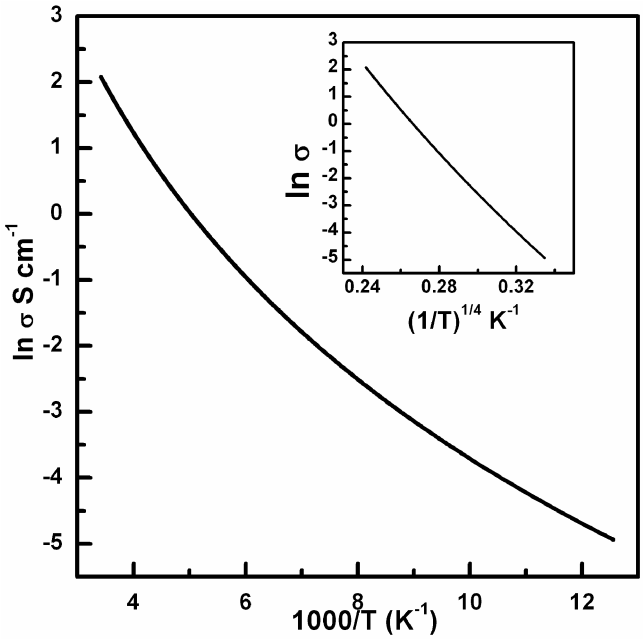

Figure 6. The variation of $\ln\sigma$ vs $10^3/T$ of Ca-doped $CuYO_2$ films. The inset shows the plot of $\ln\sigma$ vs $T^{-1/4}$.

The electrical properties of the films show a dependence on the oxygen partial pressure during annealing. The films before oxygen intercalation showed high resistivity. The resistivities as well as the transmission of the Cu_2YO_2 films are found to decrease with the oxygen partial pressure during annealing (figure 5). The highest conductivity at room temperature, 8 S cm^{-1}, was observed for films annealed at one atmospheric pressure. The temperature dependence of the conductivity of oxygen intercalated Ca-doped $CuYO_2$ films is shown in figure 6. The activated behaviour is typical of $CuAO_2$ *p*-type oxides (Duan *et al* 2000; Jayaraj *et al* 2001; Nagarajan *et al* 2001a). The activation energies obtained from the plot of $\ln\sigma$ vs $10^3/T$ are 0·59 eV and 0·19 eV at high and low temperatures, respectively. The $\ln\sigma$ vs $10^3/T$ plot is not well fit by a straight line. However, $\ln\sigma$ vs $T^{-1/4}$ plot is close to a straight line suggesting a variable range hopping model for the conduction (Mott 1974). All the films were of *p*-type as confirmed by the measurement of Seebeck coefficient. The highest value of Seebeck coefficient (+274 μV K^{-1}) was obtained for films annealed in oxygen at an atmospheric pressure of 420°C for 20 min (inset of figure 5).

4. Conclusions

The Ca-doped $CuYO_2$ thin films prepared by rf magnetron sputtering show *p*-type conductivity (8 S cm^{-1}) after oxygen intercalation. The conductivity can be increased by oxygen intercalation but at the expense of transmission. The Seebeck coefficient of +274 μV K^{-1} confirms the *p*-type conduction in these materials. The temperature dependence of the conductivity indicates a predominant hopping conduction mechanism. The films become amorphous on annealing at one atmospheric oxygen pressure.

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