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Ceramics International 38 (2012) 6693–6697

CERAMICS INTERNATIONAL

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Optical band gap modulation by Mg-doping in $In_2O_3(ZnO)_3$ ceramics

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Received 17 April 2012; received in revised form 18 May 2012; accepted 18 May 2012
Available online 30 May 2012

Abstract

In this study, different amounts of Mg were doped in $In_2O_3(Zn_{1-x}Mg_xO)_3$ and their thin films were grown by using the RF magnetron sputtering method. The optical and electrical characteristics of the films revealed that the lattice constant decreased while the optical band gap increased as the Mg content increased, showing an inverse proportional relationship with each other. Therefore, it was found that Mg doping in indium zinc oxide (IZO) is also effective for band gap modulation as it was reported in a Mg-doped ZnO system. When IZO thin films were grown in a more reducing ambient, the carrier concentration increased which resulted in the increase of band gap energy. This was explained due to the Burstein–Moss effect.

Keywords: Transparent conducting oxide; Indium zinc oxide; Band gap; Doping

1. Introduction

Wide band gap semiconductors such as Sn-doped In_2O_3 (ITO), Sb-doped SnO_2 (ATO) and Al-doped ZnO (AZO) have attracted attention because of their great potential for applications regarding transparent conducting electrodes in a variety of optoelectronic devices such as displays, solar cells, electrochromic devices and light emitting diodes [1–3]. Particularly, the band gap engineering of wide band gap semiconducting materials has become an essential technology to make the various kinds of optoelectronic devices work properly with high efficiency and functionality.

One good example of band gap modulation could be found in light emitting diode (LED) materials. In the case of the heteroepitaxial layers between the III–V group compounds of InAs and GaAs, the lattice constant of the materials was found to have a close correlation with their band gap energy, i.e., band gaps are inversely proportional to the lattice constant. So, the decrease in In/Ga ratios (as the value of x decreases in $In_xGa_{1-x}As$) permits the band gap to be increased from 0.36 eV to 1.43 eV whereas their lattice constant decreases from 6.06 Å to 5.64 Å [4].

In the exploitation and tailoring of wide band gap semiconductors, doping could be one of the most promising methods, and it can lead to increased carrier concentration, improved electrical characteristics, and modified band gap energy. In the context of band gap modulation of ZnO, research has shown that the band gap of ZnO can be adjusted with a doping of Mg, Al or Cd [5–8]. When Mg is doped in ZnO, however, its lattice constant is only slightly different (around 1%) from that of ZnO [9].

On the other hand, it has been reported that the band gap depends on carrier concentration. In the compound of the ZnO–In_2O_3 system, Naghavi et al. [10] and Moriga et al. [11] reported that the carrier concentration decreased together with band gap energy as the Zn content increased ([Zn]/([In]+[Zn])). This type of band gap modulation was explained by the Burstein–Moss effect [12,13] and showed that the filling of states in the conduction band causes an increase of the direct optical band gap in the degenerated semiconductors with curved bands.

Recently, the In_2O_3–ZnO (IZO) system has emerged as one of the most promising transparent conducting oxides due to its high transparency and electrical conductivity.

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.05.058

Among the various homologous compounds of $In_2O_3(ZnO)_k$ ($k=3$–9, 11, 13, 15), $In_2O_3(ZnO)_{k=3}$ (IZO, $k=3$), which has layered structure with an InO_2^{-1} layer of cubic bixbyte and a $4In_{1/4}Zn_{3/4}O^{1/4+}$ layer of the Würzite structure stack repeatedly along the *c*-axis, shows the best electrical conductive properties [14,15]. It is also known that the In–O layer has a coordination number of 6 while, depending on the circumstances, the In–Zn–O layer has a CN of 4 or 5. When Mg is doped in IZO, it is thought that Mg might replace the Zn that is located on the $4In_{1/4}Zn_{3/4}O^{1/4+}$ layers in the IZO ($k=3$) when the charge valence and ionic radius are considered. On the other hand, recently, Kim et al. reported that the transfer characteristics of thin film transistors (TFT) by using Mg incorporated IZO semiconductor channels [16]. They found that the turn-on-voltage of the TFT increased and the off-current decreased as the Mg content was increased. This was explained as being due to the reduction in the oxygen vacancy which resulted in decreased carrier concentration in the Mg doped IZO film. However, more systematic experiments on the band gap engineering have not been performed.

On the basis of the band gap modulation as mentioned above, this study focused on the effect of Mg doping in the In_2O_3–ZnO (IZO) system to determine whether the band gap could also be adjusted in the same system. The thin films of the IZO ($k=3$) were deposited on glass substrates as a function of the Mg content. The lattice constant, optical transmittance, band gap energy and other electrical characteristics of the thin films were analyzed.

2. Experimental procedure

Targets of the $In_2O_3(Zn_{1-x}Mg_xO)_3$ for thin film deposition were prepared through the general solid state reaction process using high purity chemicals of In_2O_3 (Samsung Corning, Korea, 99.9%), ZnO (Aldrich, USA, 99.9%) and MgO (High Purity Chemicals, Japan, 99.9%). The amount of the dopant of MgO in the In_2O_3 $(Zn_{1-x}Mg_xO)_3$ was varied in the rage $x=0$–0.5 with an interval of 0.1. The weighed powders were wet mixed for 24 h in a plastic jar with zirconia balls and ethanol. After drying, the powder was formed into 6.5 cm diameter cakes by a sequential process of uniaxial pressing, followed by cold isostatic pressing (CIP). Subsequent CIP of the green compact was conducted at 100 MPa for 5 min. The cakes were sintered at 1300 °C for 4 h at a heating rate of 5 °C/min followed by furnace cooling.

The substrate of the soda–lime glass was cleaned in TCE (Trichloroethylene), acetone and ethyl alcohol in a sequence by an ultrasonic cleaner, then dried with nitrogen gas. Thin films of the $In_2O_3(Zn_{1-x}Mg_xO)_3$ were deposited on the glass substrates at 300 °C by using rf magnetron sputtering in pure Ar gas, whereas the oxygen partial pressure (Ar:O_2 ratio) of the deposition ambient was changed for the case of the $x=0.2$ samples. Prior to the deposition, the chamber was evacuated to a background pressure of 1.0×10^{-6} Torr initially, and both the working pressure and the rf power were fixed to 10 mTorr and 50 W, respectively. A low incident beam X-ray diffraction with nickel-filtered Cu-Kα radiation (Phillips, X'Pert PRO-MRD, Netherlands) was used for the phase identification of the thin films. Electrical characteristics of the thin films were analyzed using a Hall effect measurement system (Ecopia, HMS-3000) in a constant magnetic field of 1 T at room temperature. The optical characteristics were determined using a UV/VIS/NIR spectrophotometer (Philips, CARY 5G, Australia).

3. Results and discussion

The X-ray diffraction patterns of the thin films deposited at 300 °C as a function of the Mg content in $In_2O_3(Zn_{1-x}Mg_xO)_3$ ($x=0$–0.5) are presented in Fig. 1. The result of the X-ray diffraction showed that only one diffraction peak corresponded to the (0015) plane of $In_2O_3(ZnO)_3$ ($k=3$) appeared around $2\theta=31^\circ$ which implies that the films are preferentially oriented along the [001] direction. The *c*-axis orientation of the $In_2O_3(ZnO)_k$ thin films has been reported elsewhere [5,6]. The peak position of the (0015) plane moved to a higher diffraction angle with an increase of the Mg content, which signifies that the lattice constant of the *c*-axis of $In_2O_3(Zn_{1-x}Mg_xO)_3$ decreased. On the other hand, (0015) diffraction intensity decreased as the content of Mg increased, then disappeared finally at $x=0.5$ and an amorphous like broad peak around $2\theta\approx40^\circ$ was observed.

It is generally accepted that the crystallization and/or crystallinity is retarded as the number of components (species) increases in a system [17], since increasing the number of components results in an increase of entropy. This phenomena has been observed in the thin films of indium zinc oxide (IZO), indium zinc gallium oxide (IZGO), and indium zinc antimony oxide (IZAO). In this case, a higher thermal activation energy is necessary for crystallization.

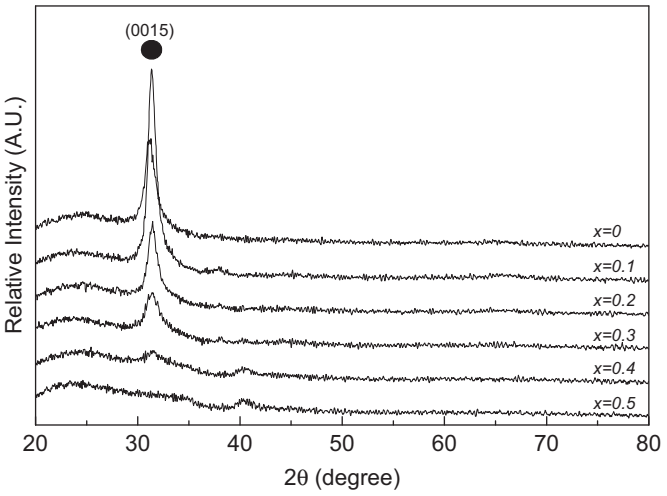

Fig. 1. XRD patterns of $In_2O_3(Zn_{1-x}Mg_xO)_3$ [$x=0$–0.5] thin films deposited in pure Ar on the glass substrate at 300 °C.