Effects of Cr doping on physical properties of amorphous In–Ga–Zn–O films

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ABSTRACT

Amorphous thin films of InGaZnO$_4$ (a-IGZO) doped with Cr have been fabricated by using pulsed-laser deposition (PLD). The electrical, optical and magnetic properties of Cr-doped a-IGZO films grown at 25 °C and 150 °C were investigated. The conductivity, optical transmission and band gap of films are remarkably enhanced by increasing the growth temperature. Conductivity, carrier concentration and mobility decrease with increasing the Cr content. However, the optical transmission and band gap are not significantly affected by Cr doping. Moreover, all Cr-doped films exhibit room-temperature ferromagnetism.

1. Introduction

Amorphous transparent conducting oxides (a-TCOs) are promising materials since their applications on large-area and flexible optoelectronic devices such as thin film transistors (TFTs) used in flat panel displays [1,2]. The most attractive a-TCO should be amorphous InGaZnO$_4$ (a-IGZO) because it has been demonstrated the feasibility of using a-IGZO as the active layers in the high-performance TFTs fabricated on flexible substrates at room temperature[1] and used in large-size panels [3]. IGZO has a complex structure with alternating InO$_2$ and GaZnO$_2$ layers [4]. Crystalline IGZO is a rhombohedral crystal and belongs to the space group of R̄3m. Due to the unique electronic structure in which the conduction paths of carriers in IGZO are composed of extended spherical *s* orbitals of heavy metal cations, the carrier transport is almost not affected by the chemical bond distortion and IGZO exhibits large electron mobility even in amorphous structure. The field-effect mobility of TFTs using amorphous IGZO as the active channel can achieve 100 cm^2 V^{-1} s^{-1} [5].

In the meanwhile, diluted magnetic semiconductors/dielectrics synthesized by introducing transition-metal (TM) ions into conventional III–V and II–VI semiconductors have recently attracted interest due to the potential application of both charge and spin of electrons [6–8]. In addition, wide bandgap oxide semiconductors such as TiO$_2$, ZnO, and SnO$_2$ doped with transition metal including Fe, Co, Ni, Mn, and Cr were extensively investigated owing to the theoretical prediction of room-temperature ferromagnetism [9,10]. Actually, a number of studies on TM-doped oxide semiconductors/dielectrics exhibiting room-temperature ferromagnetism have been reported, such as Co-doped TiO$_2$ [11,12], Co-doped SnO$_2$ [13], Fe-doped SnO$_2$ [14], Co-doped ZnO [15,16] and Mn-doped ZnO [17].

There are many groups devoted to the research and development of a-IGZO based TFTs in recent years. Theoretical calculation of electronic structure [4] and fundamental studies on optical and electrical properties of crystalline and amorphous IGZO films have also attracted much attention [18,19]. Since the feasibility of fabricating high performance TFTs using a-IGZO has been demonstrated, ferromagnetic a-IGZO could be used to construct spin-electronic devices. However, the physical properties of ferromagnetic a-IGZO films doped with transition-metal impurities have rarely investigated [20]. In this article, we report the room-temperature ferromagnetism induced by Cr doping in a-IGZO films. The effects of growth temperature and Cr doping on the electrical, optical and magnetic properties are also investigated.

2. Experiments

The undoped and Cr-doped IGZO films used in this work were grown on double-side polished *c*-cut sapphires by using pulsed-laser deposition (PLD) with Cr-doped IGZO ceramic oxide formed into pellets as the targets prepared by conventional solid state reac-

tions from stoichiometric amounts of In_2O_3, Ga_2O_3, ZnO and Cr_2O_3 powders of 99.99% purity. The Cr content ratio ([Cr]/[In]) of the films is denoted as x at.% and $x = 0$, 2.5 and 5.0 in this study. The temperatures of substrates were kept at room temperature (i.e. 25 °C) and 150 °C. The oxygen pressure was 10^{-2} Torr during PLD. KrF excimer laser was used to ablate the target with energy density of 1.5 J/cm^2 per pulse and repetition rate of 5 Hz. The distance between the targets and substrates was 4–5 cm. The growth rate is about 0.05 nm per pulse and the thickness of the films used in this study is about 130–150 nm. The structure properties of films were examined by high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) using the JEOL JEM-2100F system. The electrical properties including resistivity, carrier concentration and carrier mobility were carried out using the four-probe van der Pauw method. The valence state of Cr ions was investigated by X-ray photoelectron spectroscopy (XPS) analysis using the Thermo VG Scientific ESCALAB 250 system with a Al Kα X-ray source (1486.6 eV). The analysis chamber is equipped with a flood gun used for charge compensation when necessary. The XPS spectra are referenced to the C 1s photoemission line of 284.8 eV. The optical measurements of the films were recorded using a UV–vis double beam spectrometer (JASCO V-570) in the wavelength of 200–900 nm. The room-temperature magnetization vs magnetic field $M(H)$ curves were performed on a Quantum Design superconducting quantum interference device magnetometer.

3. Results and discussion

The HRTEM images and SAED patterns of undoped and 5.0 at.% Cr-doped IGZO films grown at 150 °C are shown in Fig. 1(a) and (b), respectively. There is no clear crystalline structure observed in the HRTEM images of both films. Moreover, except the diffraction spots of sapphire substrates, the SAED patterns show no diffraction signal from films. The results indicate amorphous structures of both films. Since the undoped and 5.0 at.% Cr-doped IGZO films grown at 150 °C are amorphous, the films grown at room temperature and 2.5 at.% Cr-doped IGZO films are believed to be amorphous.

The room-temperature resistivity, carrier concentration and mobility of amorphous films used in this study are listed in Table 1. The resistivities of films grown at 25 °C are much higher than those of films grown at 150 °C. Moreover, Cr doping reduces the carrier concentration and mobility, and thus increases resistivity of films. The 5.0 at.% Cr-doped a-IGZO film grown at 25 °C is insulating.

The temperature dependent resistivities, $\rho(T)$, of films grown at 150 °C were carried out to investigate the effect of Cr doping on the electrical transport properties of a-IGZO films. As shown in Fig. 2(a), nearly degenerate conduction is observed in the undoped a-IGZO film. The resistivities of Cr-doped films increase monotonically with decreasing temperature. Furthermore, $\rho(T)$ curve of the film doped with 5.0 at.% Cr obeys the $\rho(T) \sim \exp(T^{-1/4})$ relationship which is generally attributed to the variable-range-hopping (VRH) conduction, rather than the thermally activated conduction,
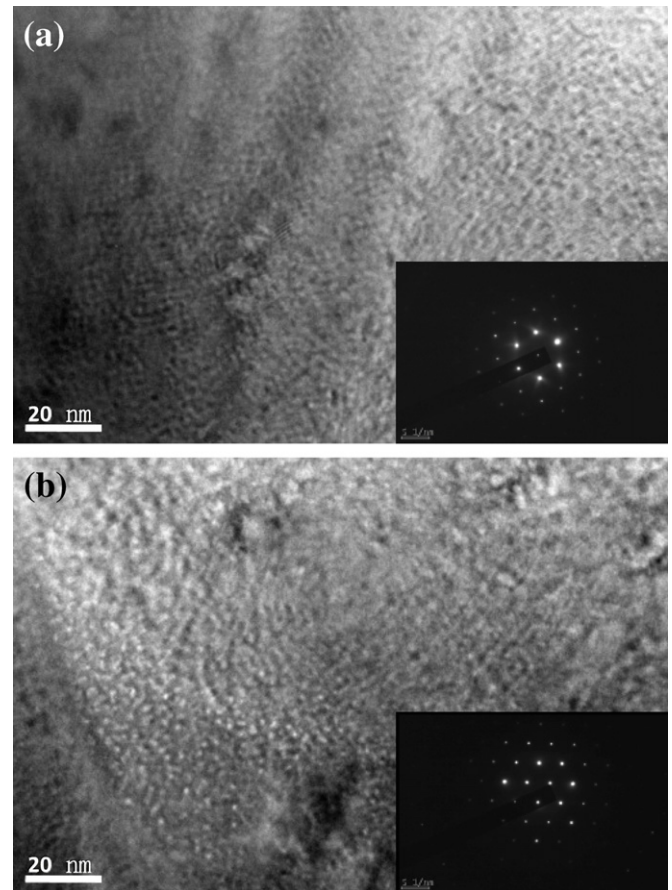

Fig. 1. HRTEM images and SAED patterns (inset) of (a) undoped and (b) 5.0 at.% Cr-doped IGZO films grown at 150 °C.

$\rho(T) \sim \exp(1/T)$, as shown in Fig. 2(b). Takagi et al. reported that VRH conduction is observed in a-IGZO films with carrier concentration $< 10^{15}$ cm^{-3} and room-temperature resistivity $> 10^4$ Ω cm [18]. However, in this study, the carrier concentration of the 5.0 at.% Cr-doped a-IGZO film is $\sim 1.9 \times 10^{19}$ cm^{-3} which seems to be too high for the VRH mechanism. Although the high concentration of Cr ions may result in the VRH conduction, it needs more studies to determine the exact transport mechanism in the Cr-doped a-IGZO films. Nevertheless, it can be deduced that the major effect of Cr doping on the electrical properties of a-IGZO films is to reduce the carrier mobility. On the other hand, Orita et al. calculated the electronic structure of IGZO [4] and concluded that the InO_2 layers serve as the transport paths in IGZO. Since the most stable oxide of Cr is Cr_2O_3, the reduction of carrier mobility implies that Cr ions with valence of 3+ doped in a-IGZO films have mainly been incorporated into the In^{3+} sites and the scattering or localization of carriers is increased. As a result, the carrier mobility is reduced.

In order to determine the valence state of Cr ions, XPS measurements were conducted on all Cr-doped samples (Samples 2, 3, 5, and 6). The measured Cr 2p spectra are shown in Fig. 3. Possibly because of low intensity of spectra resulted from low concentration of Cr doping, the curves are very rough. Nevertheless, peaks at around 576.7 eV can be obviously observed and are attributed to the Cr 2p$_{3/2}$ level. Moreover, the intensity of the Cr 2p$_{3/2}$ peaks of both 5.0 at.% Cr-doped films (Samples 3 and 6) are higher than those of 2.5 at.% Cr-doped films (Samples 2 and 5). Since the binding energy of Cr^{3+} and Cr^{6+} are 576.5 eV and 579.3 eV, respectively [21], the valence of Cr doped in the a-IGZO films is confirmed to be 3+ by the Cr 2p$_{3/2}$ peaks located at around 576.7 eV observed in XPS.
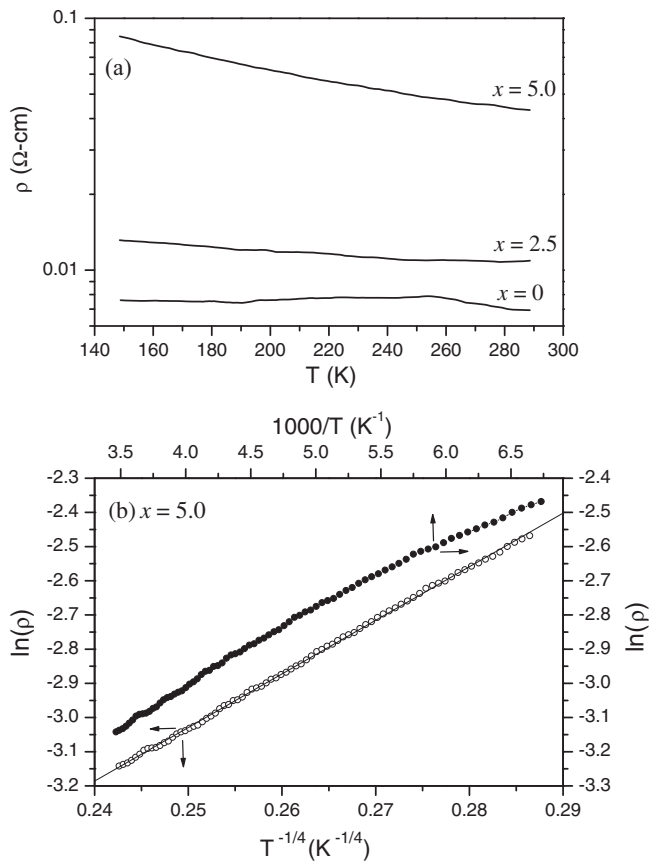
Table 1
Electrical properties of films used in this study. The x, T_S, ρ, n and μ are the Cr content ratio ([Cr]/[In]), growth temperature, resistivity, carrier concentration and carrier mobility of the films, respectively. N/A means that the value is not available owing to limits of the equipment.

Sample no.	x (at.%)	T_S (°C)	ρ (Ω cm)	n (cm^{-3})	μ (cm^2 V^{-1} s^{-1})
1	0	25	1.8×10^2	N/A	N/A
2	2.5	25	2.4×10^2	N/A	N/A
3	5.0	25	N/A	N/A	N/A
4	0	150	6.8×10^{-3}	3.1×10^{19}	29.0
5	2.5	150	11.9×10^{-3}	2.6×10^{19}	21.6
6	5.0	150	45.6×10^{-3}	1.9×10^{19}	7.1

Fig. 2. (a) Temperature (T) dependence of electrical resistivity (ρ) in x at.% Cr-doped a-IGZO films grown at 150 °C and (b) $\ln(\rho)$ vs $T^{-1/4}$ and $\ln(\rho)$ vs $1000/T$ plots for 5.0 at.% Cr-doped a-IGZO films grown at 150 °C.
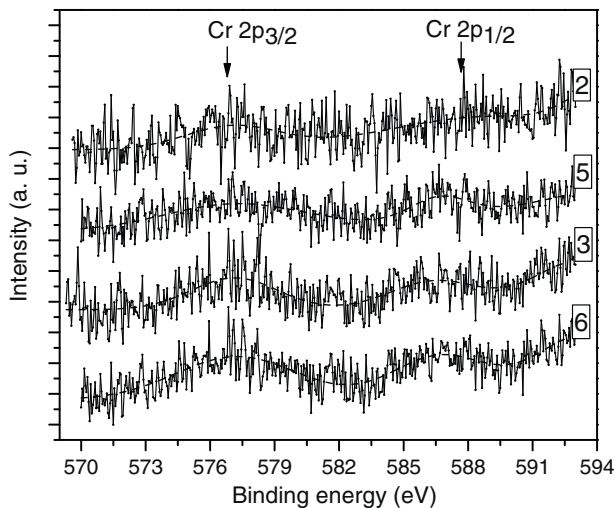

Fig. 3. XPS Cr 2p spectra of the Cr-doped a-IGZO films. The figures denote the sample numbers (listed in Table 1). The peaks located at around 576.7 eV are attributed to Cr $2p_{3/2}$ level. The smoothing lines (dash lines) are obtained by means of curve fitting using Gaussian functions and the backgrounds are not subtracted.

The XPS results exclude the existence of CrO_2, a room-temperature ferromagnetic material, in our Cr-doped IGZO films.

The transmission spectra of all films are illustrated in Fig. 4(a). The transmission of films grown at 150 °C exceeds 80% in the visible range (400–700 nm), which are much higher than those of films grown at 25 °C. The improvement in the transmission can be attributed to the reduction of defect states of films due to raising

the growth temperature. Moreover, it is clear that the absorption edges of a-IGZO films grown at 25 and 150 °C are both not significantly affected by Cr doping. The results further indicate the substitution of Cr^{3+} ions for In^{3+} ions. Furthermore, the optical band gaps (E_g) of these films can be estimated by the relationship between absorption coefficient (α) and photon energy ($h\nu$) of the form $(\alpha h\nu) \sim (h\nu - E_g)^r$ with $r = 2$ suggested by Tauc for amorphous semiconductors [22,23]. The optical band gaps of films grown at 25 and 150 °C are about 2.0 and 3.1 eV, respectively, obtained by linear extrapolation of $(\alpha h\nu)^{0.5}$ to the $h\nu$-axis, as depicted in Fig. 4(b).

Fig. 5 shows the field dependence of magnetization $M(H)$ curves measured at 300 K for the Cr-doped a-IGZO films. All films obviously exhibit room-temperature ferromagnetism. For films grown at 25 °C, the magnetization of the a-IGZO film doped with 5.0 at.% Cr is larger than that of the 2.5 at.% Cr-doped film. It seems that higher concentration of magnetic ions results in larger magnetization. Since the 2.5 and 5.0 at.% Cr-doped a-IGZO films are highly resistive and insulating, respectively, the bound magnetic polarons may play an important role in the ferromagnetic interaction in these films [24,25]. On the other hand, for films grown at 150 °C, the magnetization of the 2.5 at.% Cr-doped film is larger than that of the film doped with 5.0 at.% Cr. It is noted that the carrier concentration and mobility of the former are larger than those of the latter although both of them are conductive. It implies that the delocalized carriers may be crucial for the ferromagnetism of films grown at 150 °C [9]. Furthermore, the nearly negligible difference between $M(H)$ curves of 5.0 at.% Cr-doped a-IGZO films grown at 25 and 150 °C reveals that magnetic property of a-IGZO films doped with high concentration of Cr is almost not affected by the carrier concentration and mobility. One possible reason is that although the
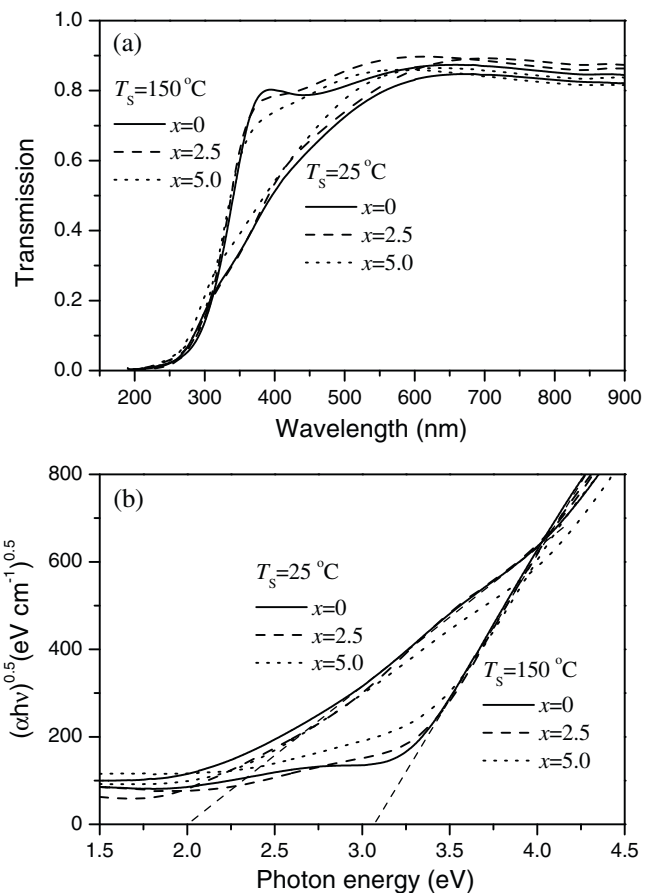

Fig. 4. (a) Transmission spectra and (b) $(\alpha h\nu)^{0.5}$ vs $h\nu$ plots for x at.% Cr-doped a-IGZO films. T_S denotes the growth temperature of films.
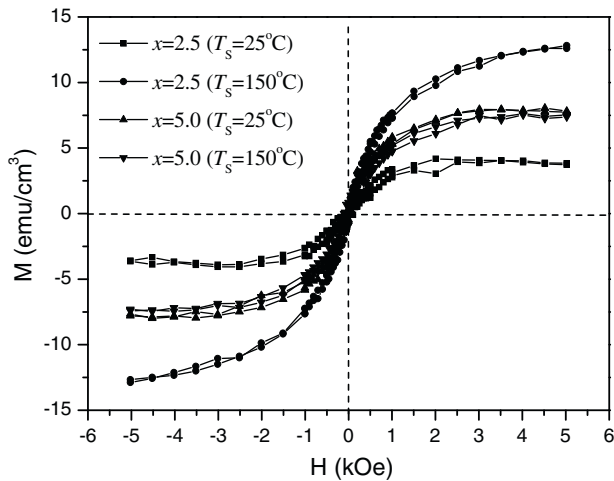
Fig. 5. Field (H) dependent magnetization (M) of x at.% Cr-doped a-IGZO films measured at room temperature. T_S denotes the growth temperature of films. The magnetic fields were applied parallel to the plane of films.

relative high growth temperature (i.e. 150 °C) remarkably increases the carrier concentration in the film, the scattering of delocalized electrons is increased by Cr^{3+} ions doped in the InO_2 layers which are the conduction paths. Therefore, carrier-mediated exchange exhibits no or few contribution to the ferromagnetism of 5.0 at.% Cr-doped a-IGZO films. Another possible mechanism which explains that the magnetization of 5.0 at.% Cr-doped films is smaller than that of 2.5 at.% Cr-doped films grown at 150 °C is the antiferromagnetic dopant–dopant interactions at close proximity [26]. However, due to the amorphous structure, the mechanism of ferromagnetism observed in the Cr-doped a-IZGO films is more complex than that of other TM-doped crystalline oxide semiconductors such as SnO_2, ZnO, and TiO_2. The interplay among the ferromagnetic interaction, electronic structure and lattice ordering in amorphous diluted magnetic semiconductors is attractive.

4. Conclusions

In conclusion, the electrical, optical and magnetic properties of a-IGZO films doped with Cr prepared by using pulsed laser deposition were investigated. The electrical properties including conductivity, carrier concentration and mobility of a-IGZO films are reduced by Cr doping. Nevertheless, the optical band gap and transmission of a-IGZO films are not significantly affected by Cr doping. Furthermore, all Cr-doped films exhibit room-temperature ferromagnetism.

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