

Structure and electrical properties of CdIn_2O_4 thin films sputtered at elevated substrate temperatures

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Received 20 November 2003, revised 7 January 2004, accepted 9 January 2004

Published online 11 March 2004

PACS 68.55.Jk, 73.61.Le, 81.15.Cd

A Hall mobility as high as $39.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained for cadmium indate (CdIn_2O_4) thin films deposited by rf reactive sputtering from a Cd–In alloy target. The structural and electrical properties for both as-sputtered and after-annealed thin films were studied as a function of the substrate temperatures. The results revealed that elevated substrate temperatures favour the formation of CdIn_2O_4 thin films with spinel phase. The electrical properties can be understood by a combination of the occupancy of In cations on the tetrahedral vacancies in the spinel unit cell at the elevated substrate temperatures and the formation of oxygen vacancies originating from off-stoichiometry. It can be inferred that the presence of secondary phases in the CdIn_2O_4 thin films deposited in an oxygen-deficient atmosphere is responsible for their electrical properties.

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1 Introduction

Transparent conducting oxides (TCOs) are extensively used as transparent electrodes in photovoltaics, flat panel displays, and electrochromic devices. Although tin-doped indium oxide (ITO) is still the most used and widely studied transparent conductor among the TCOs, and commercial ITO has been prepared with a conductivity of $\sim 5600 \text{ S cm}^{-1}$, carrier mobility of $28.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and carrier density of $1.2 \times 10^{21} \text{ cm}^{-3}$ [1], its electrical and optical characteristics are inadequate for many future applications, and understanding its properties as a function of the exceedingly complex microstructure remains a great challenge [2]. Much progress on research into TCOs, which includes high-performance invisible transistors [3, 4], has occurred recently. It is of particular interest that homogeneously doped $\text{Cd}_{0.95}\text{In}_{0.05}\text{O}$ films have been deposited with a conductivity of $17,000 \text{ S cm}^{-1}$, mobility of $70 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a visible region optical transparency window, considerably exceeding the corresponding parameters for commercial ITOs [5, 6].

Cadmium indate (CdIn_2O_4) is an n-type semiconductor, in which a carrier concentration of about 10^{20} cm^{-3} can be achieved without additional doping. Shannon et al. [7] prepared a single crystal of CdIn_2O_4 , which has the lowest room-temperature resistivity, $5 \times 10^{-6} \Omega \text{ m}$, among ternary TCOs containing Sn or In, such as CdSnO_3 , Cd_2SnO_4 , and In_2TeO_6 . Although a resistivity as low as $3.7 \times 10^{-6} \Omega \text{ m}$ has been achieved for a single-spinel-phase CdIn_2O_4 thin film coated onto a glass substrate using ultrasonic spraying of an aerosol [8], sputtering techniques are still the prevailing methods for deposition of CdIn_2O_4 thin films [9–11].

Wu et al. [10] prepared a CdIn_2O_4 thin film with single spinel phase using rf magnetron sputtering, which had a resistivity as low as $2.3 \times 10^{-6} \Omega \text{ m}$ and a mobility as high as $44.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, according to Haacke [12], a CdIn_2O_4 thin film with single spinel phase has a lower infrared reflectivity,

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whereas a film containing some In_2O_3 phases besides the major CdIn_2O_4 spinel phase reaches 93% infrared reflectivity, equal to the best Cd_2SnO_4 coatings. Although the differences in the optical properties of the two films cannot be explained by different carrier concentrations or mobilities, this experimental fact suggests that under certain conditions the presence of a second phase may have a beneficial effect on the infrared reflectivity of CdIn_2O_4 thin films. Therefore, improving both the electrical and optical properties of thin films will require a deeper understanding of their microstructures. In this paper an attempt is made to correlate the microstructures with the electrical parameters of CdIn_2O_4 thin films prepared by conventional rf sputtering.

Budzynska et al. [13] proposed that the composition of the Ar– O_2 atmosphere during sputtering strongly affects the substrate temperature as a result of inducing plasma heating, and the explanation of the changes in the structure and electrical properties should involve two factors: oxygen partial pressure and substrate temperature. However, previous work has mainly focused on the effect originating from the oxygen partial pressure. The aim of the present paper is to determine the influence of the substrate temperature and post-deposition annealing on the structure and electrical properties of CdIn_2O_4 thin films, as it is established that the fabrication process governs the microstructures and the intrinsic properties.

2 Experimental

CdIn_2O_4 thin films were deposited by rf reactive sputtering using homemade JS-450 sputtering equipment. A 100 mm diameter Cd–In alloy target was used, which was made of 34 at% Cd (99.999% purity) and 66 at% In (99.999% purity). Glass (Corning 7059) plates, measuring 25 mm \times 25 mm \times 1 mm, were used as substrates. Prior to the sputtering, the chamber was evacuated to a base pressure of 2.7×10^{-5} Pa, and a pre-sputtering treatment of the target surface was required to avoid eventual contamination. Deposition conditions, including substrate temperature and oxygen partial pressure, were controlled accurately. Oxygen and argon gases were introduced into the chamber independently through two needle valves in order to control the reactive atmosphere in the chamber. The total pressure of the Ar– O_2 mixture was ~ 0.67 Pa. All samples were sputtered at 10% oxygen concentration in a reactive atmosphere. Substrates were mounted on a water-cooled sample holder with a tungsten lamp, and the substrate temperature was monitored by a Pt–Rh thermoelectric couple attached to the back of the substrate. The distance between the target and substrate was 30 mm, and the rf power was kept in the range 100–400 W. The deposition time was 30 min for all samples. Chosen samples were subjected to post-deposition annealing in a stable Ar gas flow at 300 °C for 60 min.

A thickness of ~ 5000 Å for all samples was controlled during sputtering by an optical monitoring system and also determined by fitting to the transmission spectra. An error of less than 2% was obtained. Structural analysis of the thin films was performed using X-ray diffraction (XRD) with a D/Max-RB diffractometer, which uses the Cu K_α line ($\lambda = 1.50406$ Å). The electrical properties of the thin films were measured at room temperature, except two samples for resistivity measurements in the temperature range 77–300 K. The resistivity of the thin films was measured using a linear four-point probe of 0.625 mm spacing, and conventional Hall measurements were performed under a magnetic field of 10.25 kGs. In order to determine the resistivity of the thin films at low temperature, ohmic contacts were made by evaporating four indium spots on the film surface in a Van der Pauw configuration, and Cu wires were connected to the external circuits using silver paste.

3 Results

3.1 Structural properties

The XRD patterns for as-sputtered CdIn_2O_4 thin films deposited at different substrate temperatures are shown in Fig. 1. The presence of many peaks indicates the polycrystalline structure of the thin films. It can be seen that all films contain a majority of the CdIn_2O_4 phases while a small concentration of In_2O_3 phase still exists. Another possible phase, CdO, the existence of which was predicted by Budzynska et al. [13], is also found. There are two different crystallographic structures of CdIn_2O_4 reported in the litera-

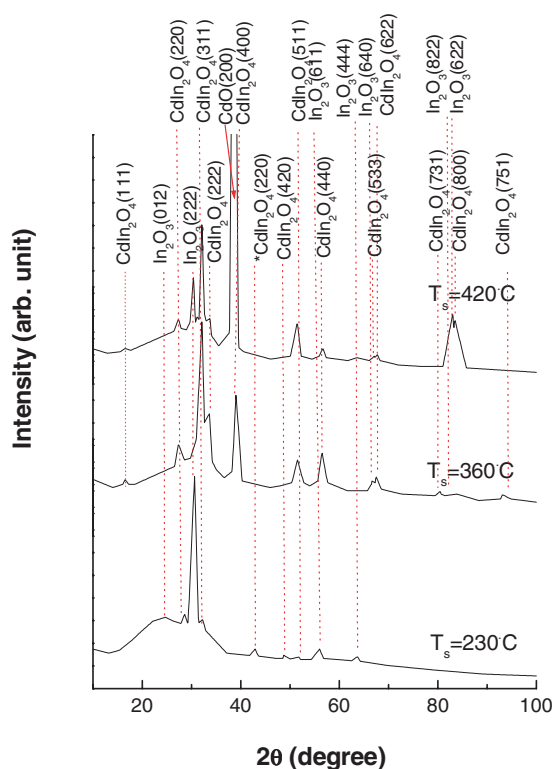


Fig. 1 (online colour at www.interscience.wiley.com) XRD patterns of as-sputtered CdIn₂O₄ thin films deposited at different substrate temperatures (*CdIn₂O₄ is tetragonal phase).

ture: tetragonal with lattice constants $a = 8.65 \text{ \AA}$, $c = 9.87 \text{ \AA}$ [14] and cubic spinel with $a = 9.11 \pm 0.01 \text{ \AA}$ [15]. It can be seen that, despite the dominant cubic spinel structure in all films, a diffraction peak corresponding to the tetragonal structure can be detected. To the best of our knowledge, this is the first report on the appearance of the tetragonal structure in CdIn₂O₄ thin films.

The lattice parameters of spinel CdIn₂O₄ were determined from the diffraction patterns using Bragg's law and the angular position of the diffraction peaks. The results reveal the parameters are generally greater than those values for CdIn₂O₄ powder. The results for (111) and (220) diffraction peaks are given in Table 1.

The average crystallite size D was calculated using the approximate Scherrer's formula. Calculated values are in the range 500–700 Å, in good agreement with the results of surface morphology studied by scanning electron microscopy [16], and considerably larger than the electron mean free path (20–80 Å). Thus, the scattering of electrons at grain boundaries cannot be considered as the predominant scattering mechanism.

The crystallites in a polycrystalline material usually have preferential orientations. In order to describe these orientations the texture coefficients $TC(hkl)$ for all the planes were calculated. In the present investigation, CdIn₂O₄ spinel phase in thin films exhibits preferential orientations along (111) and (220) diffraction planes, the texture coefficients for which, $TC(111)$ and $TC(220)$, are given in Table 1.

From Fig. 1, it can be clearly seen that the film prepared at a substrate temperature of 230 °C is partially amorphous. The peaks corresponding to CdIn₂O₄ (including tetragonal CdIn₂O₄ phase) and In₂O₃ crystalline phases are embedded in the amorphous matrix. This agrees with the fact that In₂O₃ thin films deposited at low substrate temperature are amorphous [17], and confirms that the lower substrate temperature is disadvantageous to the crystallization of CdIn₂O₄. With the increase of substrate temperature to 360 °C the number of peaks corresponding to In₂O₃ phase decreases. Meanwhile, the peaks corre-

Table 1 Structural data obtained from the (111) and (220) diffraction peaks of spinel CdIn₂O₄ phase in thin films.

deposition conditions	(111)			(220)		
	a (Å)	D (Å)	TC	a (Å)	D (Å)	TC
$T_s = 230 \text{ °C}$, 10% O ₂	—	—	—	8.82469	577.3	1.68149
$T_s = 360 \text{ °C}$, 10% O ₂	9.2734	—	1.40826	9.2037	483.8	0.99188
$T_s = 425 \text{ °C}$, 10% O ₂	9.29592	—	1.65842	9.21784	520.8	0.94559

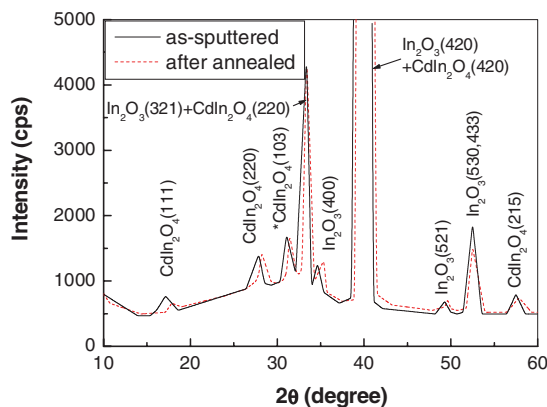
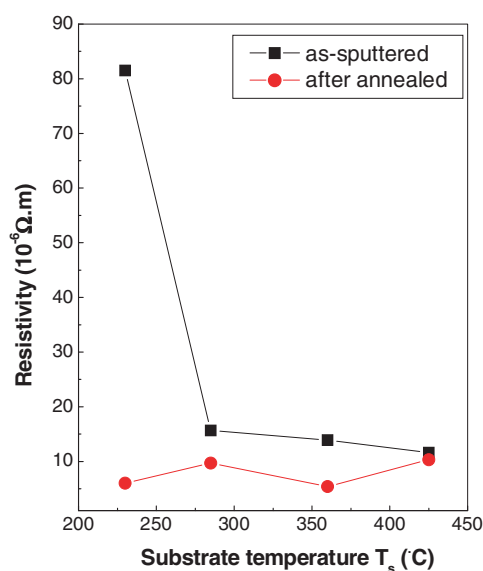


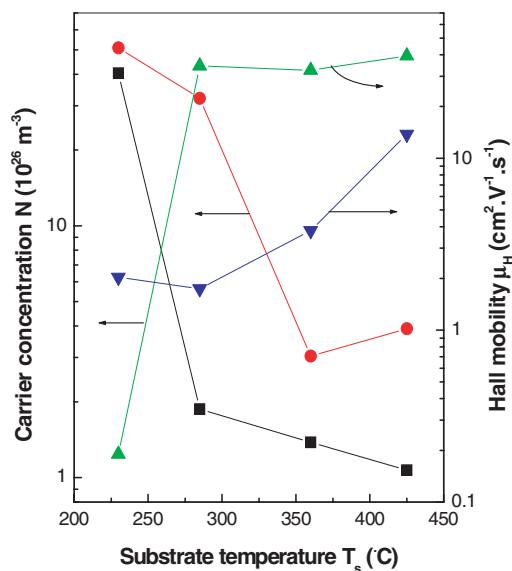
Fig. 2 (online colour at www.interscience.wiley.com) XRD patterns of as-sputtered and after-annealed CdIn_2O_4 thin films deposited at a substrate temperature of 425 °C and 25% oxygen partial pressure (* CdIn_2O_4 is tetragonal phase).

sponding to both CdIn_2O_4 and In_2O_3 crystalline phases are much narrower, indicating the crystallization of the amorphous phase. The number of peaks corresponding to spinel CdIn_2O_4 increases, (220) preferential orientation decreases, (111) orientation increases, and tetragonal CdIn_2O_4 phase disappears. At a substrate temperature of 425 °C the peak corresponding to the CdO phase appears, which has a distinguishable (100) preferential orientation.

Post-deposition annealing in a reducing atmosphere does not lead to fundamental changes in the crystal structure of the thin films, which can be verified by the fact that annealing does not result in the formation of new secondary phases. Annealing enhances the ordering processes, which include an increase in the preferential orientations and in the grain size for both CdIn_2O_4 and In_2O_3 phases, as shown in Fig. 2. In addition, it can be seen that the angular positions of the diffraction peaks increase, indicating the shrinkage of the lattice.



a)



b)

Fig. 3 (online colour at www.interscience.wiley.com) a) Resistivities of as-sputtered and after-annealed CdIn_2O_4 thin films deposited at different substrate temperatures. b) Carrier concentrations and Hall mobilities of as-sputtered and after-annealed CdIn_2O_4 thin films deposited at different substrate temperatures (■, ▲ as-sputtered; ●, ▼ after-annealed).

3.2 Electrical properties

In the temperature range 77–300 K the change of the resistivity with temperature was measured. The change is very small, from 5.47×10^{-5} to $5.35 \times 10^{-5} \Omega \text{ m}$ at 77 and 300 K, respectively, for a thin film deposited at a substrate temperature of 425 °C and an oxygen partial pressure of 25%. This reveals that CdIn₂O₄ thin films are highly degenerated.

The resistivity of thin films sputtered at different substrate temperatures is shown in Fig. 3a. The influence of post-deposition annealing is also shown. It is quite obvious that annealing CdIn₂O₄ thin films in an argon atmosphere can effectively reduce their resistivities, regardless of any deposition conditions. When the substrate temperature is increased from 230 to 285 °C the resistivity of as-sputtered films drops drastically from 8.17×10^{-5} to $1.59 \times 10^{-5} \Omega \text{ m}$, being a reflection of the crystallization of the amorphous phase, in accordance with the changes of lattice parameters.

Figure 3b shows the measured carrier concentrations and Hall mobilities for thin films deposited at different substrate temperatures, also showing the influence of annealing. It can be seen that annealing enhances the carrier concentrations and reduces the Hall mobilities. The decrease of carrier concentrations and the increase of Hall mobilities for as-sputtered films with the increase of substrate temperature from 230 to 285 °C are in very good agreement with the changes of resistivities and structural characterizations. The as-sputtered film deposited at 425 °C has the highest Hall mobility of $39.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

4 Discussion

The essential requirement for the electronic structure of an n-type TCO material is that electric current is transported by electrons introduced into the conduction band and the conduction band must constitute an extended state. The ideal crystal structure for the desired electronic structure consists of linear chains of edge-sharing oxygen octahedra. Because the rutile structure also consists of linear chains of edge-sharing octahedra running in parallel along the *c*-axis, chains of this type are often referred to as ‘rutile chains’. Kawazoe and Ueda [18] concluded that the lattices for TCOs must contain structural units consisting of rutile chains. This conclusion concurred with the results reported by Shannon et al. [7], who noted a correlation between edge-sharing octahedral chains of Cd²⁺, In³⁺, and Sn⁴⁺ and transparent conductivity.

Spinel belongs to the cubic system, and contains rutile chains running along $\langle 110 \rangle$ directions. The chemical formula of spinel oxides is expressed as AB₂O₄, where A and B are divalent and trivalent cations, respectively. The crystallographic unit cell contains 32 cubic closed packed oxygen ions (eight chemical formula units). There are equivalent positions in this cell for 8 tetrahedral cation sites and for 16 octahedral cation sites. Twenty-four cations are distributed over the cation sites. The total numbers of tetrahedral and octahedral vacancies between the oxygen layers in the unit cell are 64 and 32, respectively. Therefore, seven-eighths of the tetrahedral and one-half of the octahedral vacancies remain unoccupied.

The cation distribution (e.g. normal, random, or inverse) on the CdIn₂O₄ spinel lattice imposes an important effect on the electrical properties. Wei and Zhang [19] showed by first principles band structure calculations that the fundamental band gaps in spinel CdIn₂O₄ are dependent on the inversion parameters. Normal CdIn₂O₄ (calculated to be more stable than inverse CdIn₂O₄) was predicted to have a fundamental band gap 1.07 eV larger than inverse CdIn₂O₄. A normal cation distribution means that the majority of Cd is distributed on the tetrahedral planes, while the majority of In is distributed on the octahedral planes. If one assumes that the CdIn₂O₄ spinel is a completely normal spinel, then all of the tetrahedral cation sites are filled by Cd. The atom location by channelling enhanced microanalysis (ALCHEMI) experiments performed by Brewer et al. [20] revealed that CdIn₂O₄ is a normal-type spinel. However, this normal-type distribution evolves towards a more random distribution at elevated substrate temperatures.

Now consider the cation redistribution reaction in stoichiometric CdIn₂O₄:



where the subscript denotes the site on which the species rests and the superscript the charge of the species in question relative to the ideal crystal lattice (‘x’ for a neutral charge, a prime for a negative charge, and ‘·’ for a positive charge). Since there is a balance of positive and negative species, i.e. $[\text{Cd}_{\text{In}}'] = [\text{In}_{\text{Cd}}']$ (where the square brackets are used to show that the concentration of the species is being considered),

the reaction takes place without contributing to carrier production. This corresponds to the overall In: Cd ratio being maintained at precisely 2:1. If instead there is considerable cation off-stoichiometry, such that In: Cd is greater than 2:1, the excess of positive over negative species will now contribute to carrier production:

$$n = \{[\text{In}_{\text{Cd}}'] - [\text{Cd}_{\text{In}}']\} > 0. \quad (2)$$

The results reported by Budzynska et al. [13] and Cheng et al. [21], who measured the compositions of CdIn_2O_4 films using electron X-ray microprobe analysis and AES analysis, respectively, revealed that thin films prepared by means of sputtering were non-stoichiometric. This assumption is further supported by the observed increases in lattice parameters as a result of elevated substrate temperatures.

According to Tahar et al. [17] and Freeman et al. [22], the effect of annealing in a reducing atmosphere can be quite reasonably explained by the predominance of oxygen-array vacancies V_{O} originating from the off-stoichiometry for thin films prepared at a lower oxygen partial pressure. At high V_{O} concentration a V_{O} impurity band forms and overlaps the conduction band at the bottom of the band, producing a degenerate semiconductor. The oxygen vacancies act as doubly ionized donors and contribute a maximum of two electrons to the electrical conductivity as shown in the following equation:



The material can be represented as $\text{CdIn}_2\text{O}_{4-x}$.

The results of Morozova et al. [23], who performed thermogravimetric investigations of CdIn_2O_4 bulk material in air using a UVT-1 balance, revealed that the weight loss occurring in the temperature range 480–770 K corresponds to the decomposition of cadmium carbonate and the thermal desorption of oxygen with some changes in the stoichiometry of the compound. This confirms that the increase of carrier concentration comes from oxygen vacancies when CdIn_2O_4 thin films are subjected to post-deposition annealing. In fact, an increase of carrier concentration with the shrinkage of the lattice occurs corresponding to post-deposition annealing.

An increase of charged defects, however, in the form of compositional impurities, such as singly charged In on Cd sites and doubly charged oxygen vacancies, leads to charged impurity scattering and a decrease in the electron mobility. Therefore, the scattering of conduction band electrons by ionized impurity centres may contribute to the decrease of Hall mobility after annealing of CdIn_2O_4 thin films in an argon atmosphere.

Figure 4 shows the dependence of Hall mobility on the carrier concentration for CdIn_2O_4 thin films. Assuming that all the carriers originate from doubly charged oxygen vacancies, the calculated mobilities based on scattering by ionized impurities are also shown, according to relations described in Refs. [17, 24–26]. It can be seen that the decrease of Hall mobility μ_{H} with increasing carrier concentration N is in accord with the semiconductor theory for homogeneous samples with high carrier concentration. However, the absolute values for the calculated curves are larger than those for the experimental ones. The

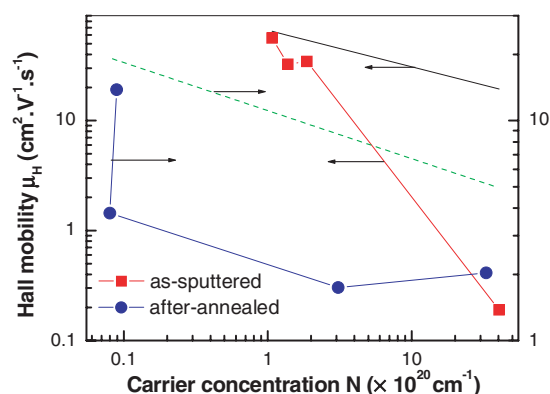


Fig. 4 (online colour at www.interscience.wiley.com) Hall mobility vs. carrier concentration: experimental data and calculated mobilities based on scattering by ionized impurities (solid curve: experimental values and dashed curves: calculated values).

result reveals that, in addition to ionized impurities, other mechanisms of scattering also have to be taken into account.

The origin of these discrepancies has not yet been identified, but the presence of varying amounts of secondary phases in the films may be a major factor. The secondary phases along the grain boundaries are suspected of influencing the mobility significantly. The presence of small grain sizes of secondary phases at the grain boundaries of CdIn₂O₄ matrix is a necessary condition to explain the scattering effect originating from grain boundaries. Grain boundaries of the secondary phases might act as a barrier height that obstructs the motion of conductive electrons in the conduction band. It therefore appears likely that the electrical properties of these films are largely determined by their multiphase composition.

5 Conclusion

Although a Hall mobility as high as 39.4 cm² V⁻¹ s⁻¹ was obtained, CdIn₂O₄ thin films prepared by rf reactive sputtering were found to contain a small concentration of secondary phases of In₂O₃ and CdO. The presence of either phase may affect the electrical properties of the thin films and mask the intrinsic properties of spinel CdIn₂O₄. These films are far from optimized with respect to composition and microstructure; however, their behaviours suggest that further improvements can be anticipated by the control of the deposition–microstructure–properties relationship. If this were the case, the post-deposition heat treatment might be unnecessary and even more attractive transparent electrode properties could be expected as a result of the potentially higher electron mobility.

Acknowledgement This work was supported by the National Science Foundation of China (NSFC) under Grant No. 60378022.

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