

p -type electrical conduction in α -AgGaO₂ delafossite thin films

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(Received 28 December 2005; accepted 26 March 2006; published online 23 May 2006)

Thin films of delafossites of α -AgGaO₂ were prepared on α -Al₂O₃ (0001) and on Si (100) single crystal substrates by pulsed laser deposition. The films have a band gap of 4.12 eV and a transparency of more than 50% in the visible region. The electrical conductivity at 300 K was 3.2×10^{-4} S cm⁻¹. The positive sign of Seebeck coefficient ($+70 \mu\text{V K}^{-1}$) demonstrated the p -type conduction in the films. Transparent p - n heterojunctions on a glass substrate having a structure glass/ITO/ n -ZnO/ p -AgGaO₂ were fabricated. The ratio of forward to reverse current was more than 100 in the range of -2 to $+2$ V. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2204757]

Transparent conducting oxides (TCO's) find wide range of applications.¹ Most known TCO's such as Sn doped In₂O₃ or SnO₂ are n -type conductors. There has been considerable interest in finding p -type electrical conductivity in wide band gap semiconductors. These wide band gap p -type semiconducting oxides with n -type transparent conducting oxides can lead to the development of UV and blue emitting light emitting diodes. The report of p -type conductivity in CuAlO₂ by Kawazoe *et al.*² has aroused much interest in $A^I B^{III} O_2$ delafossite ($A^I = \text{Cu, Ag, Pt and Pd}$; $B^{III} = \text{Al, Ga, In, Fe, Co, Sc, and rare earths}$). Since the report of p -type conductivity in CuAlO₂ films, reports followed by observation of p -type conductivity in transparent of CuScO₂,³ CuGaO₂,⁴ CuYO₂,⁵ and CuCrO₂.⁶ Bipolarity has been reported in the CuInO₂ delafossite⁷ with the realization of transparent p - n homojunction. All oxide transparent p - n junctions and ultraviolet emitting diodes were fabricated using n -ZnO and p -SrCuO₂.⁸ The recent improvement in the growth of high quality p -type ZnO (Ref. 9) has resulted in p - n ZnO based junctions and p - n ZnO light emitting diodes.^{10,11} Rectifying behavior has been reported in delafossite oxide based structures, such as p -CuYO₂/ i -ZnO/ n -ZnO (Ref. 12) p - i - n junction, n -ZnO/ p -CuAlO₂ (Ref. 13 and 14) p - n junction, and n -CuInO₂:Sn/ p -CuInO₂:Ca homojunction.¹⁵ All the p -type delafossites reported so far are all based on copper delafossites except for AgCoO₂.¹⁶ Acceptor doping of AgInO₂ (Ref. 17) has not been successful in inducing p -type conductivity. Among wide band gap semiconductors, p -type TCO's are particularly difficult to dope.¹⁸

In the present letter, we report the growth of silver delafossite thin film with p -type conductivity and moderate transparency in the visible region. The p -type silver delafossites are the α -AgGaO₂ and the thin films were deposited by pulsed laser deposition (PLD) on silicon (100) and α -Al₂O₃ (0001) single crystal substrates. The electrical and optical properties were investigated and the results are presented. The PLD grown AgGaO₂ films were used for the fabrication of transparent p - n heterojunction.

The direct synthesis of α -AgGaO₂ by conventional solid state reaction of the constituent oxides at high temperature was not successful. The sintered disks of α -AgGaO₂ were

prepared by two step process. NaGaO₂, which has an orthorhombic structure, was prepared by solid state reaction¹⁹ of stoichiometric amount of NaCO₃ and β -Ga₂O₃. The reaction was carried out by successive heating at 650, 750, 850, 1000, and 1050 °C for 24 h at each temperature. The β -NaGaO₂ thus obtained is transformed into β -AgGaO₂ by reacting with excess molten AgNO₃ at 280 °C for 24 h under nitrogen atmosphere. The AgGaO₂ obtained through the ion exchange reaction has an orthorhombic structure. The excess AgNO₃ was removed by repeated washing with distilled water. The β -AgGaO₂ is then converted into α -AgGaO₂ by hydrothermal reaction in a Parr bomb at 250 °C. The length of the reaction was four days. The reagents used were β -AgGaO₂ and KOH (1M) solution. The α -AgGaO₂ prepared by direct hydrothermal synthesis contains more silver impurities, where as phase pure α -AgGaO₂ is obtained by the hydrothermal conversion of β -AgGaO₂ into α -AgGaO₂. The result on the synthesis of phase pure α -AgGaO₂ is being published elsewhere.²⁰ The α -AgGaO₂ were pelletized by cold isostatic press and then sintered at 350 °C for 5 h in air.

α -AgGaO₂ thin films were prepared on silicon and Al₂O₃ substrates by pulsed laser deposition. The third harmonics (355 nm) of a Q -switched Nd:YAG (yttrium aluminum garnet) laser (Spectra Physics Quanta Ray GCR series) was focused onto a rotating target. The repetition rate of the laser pulse was 10 Hz with a pulse width of 9 ns and the energy density of the laser was 1 J/cm² per pulse. The chamber was initially pumped down to a base pressure of 10⁻⁶ mbar. Oxygen gas was then introduced into the chamber and the working pressure of oxygen was controlled at 0.01 mbar. The substrate to target distance was kept at 3.7 cm. The substrate temperature was kept at 250 °C for silicon substrates and 400 °C when Al₂O₃ was used as substrates. The films were allowed to cool down to room temperature at the same oxygen pressure.

The thickness of the deposited α -AgGaO₂ films was measured using a stylus profiler (Dektak 6M Stylus profiler) as 180 nm. The crystalline nature of the films was identified by x-ray diffraction using Cu K α line. Figure 1 shows the diffraction pattern of β -AgGaO₂ (a), α -AgGaO₂ (b), and the thin film (c). The crystalline phase identified in the thin film sample was found to belong to α -AgGaO₂ of $R\bar{3}m$ space group. The impurity phase in the x-ray diffraction can be

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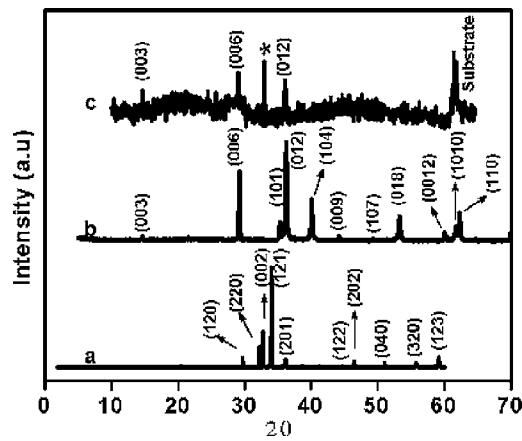


FIG. 1. The x-ray diffraction pattern of (a) β -AgGaO₂ powder, (b) α -AgGaO₂ powder, and (c) α -AgGaO₂ thin film. * indicates (002) peak of the impurity β -AgGaO₂ phase.

identified as the (002) peak of the β -AgGaO₂. The high resolution transmission electron micrograph (HRTEM) of the α -AgGaO₂ films grown under the same deposition conditions of film growth on silicon substrates but on carbon coated copper grids is shown in Fig. 2. The nucleation and growth of the film in the form of nanorods with an average diameter of 20 nm and a length up to 270 nm were observed. The atomic scale images of the films (inset of Fig. 2) show parallel line of ions at intervals of 2.225 Å for most of the grains. This lattice spacing coincides with d spacing of α -AgGaO₂ (104). Similar growth has been observed in nanocrystalline CuAlO₂.²¹ The d spacing observed do not match with that of Ag₂O or β -AgGaO₂. Energy dispersive x-ray analysis shows that the ratio of Ag/Ga is 1.02, which is close to the atomic ratio of α -AgGaO₂. The grains in the films grown on silicon substrates may be very small. Such nanoscale particle and small sample thickness may be the reason for the very weak signal in the x-ray diffraction pattern.

Figure 3 shows the optical transmittance of the α -AgGaO₂ films in the visible region. The films have more than 50% transparency in the visible region. The inset shows the plot of $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. The optical band gap is estimated as 4.12 eV. The dc electrical conductivity of the samples was studied in the range of 50 to 300 K. The room temperature conductivity (σ) of the undoped AgGaO₂ films was 3.2×10^{-4} S cm⁻¹. The activation energy at high tem-

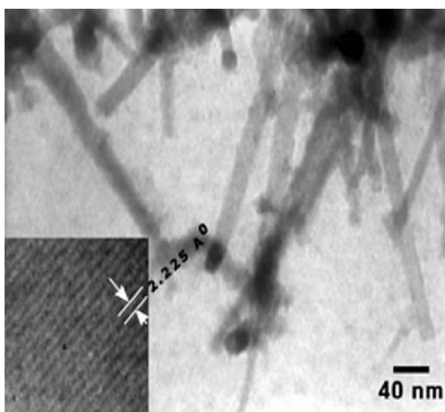


FIG. 2. TEM picture of α -AgGaO₂ thin film grown on carbon coated copper grid and the inset shows the atomic scale image of the film.

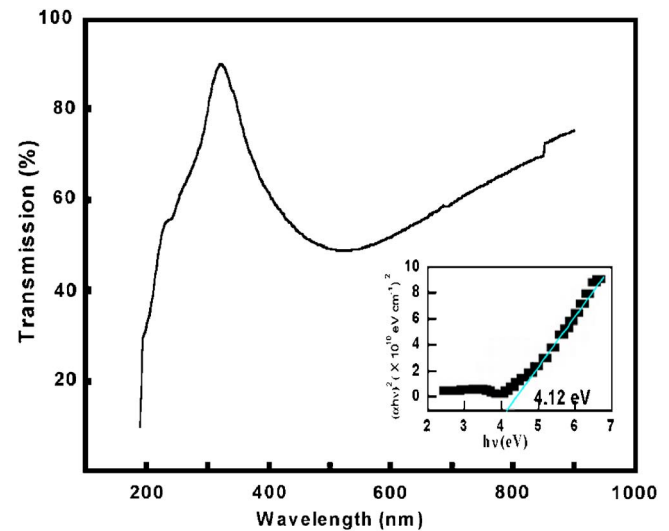


FIG. 3. (Color online) Transmission spectra of the α -AgGaO₂ thin film. Inset shows the plot of $(\alpha h\nu)^2$ vs $h\nu$.

perature is 68 meV. The σ vs $1/T$ plot is not well fitted by a straight line (shown in Fig. 4). However, the $\log \sigma T^{1/2}$ vs $1/T^{1/4}$ plot (inset of Fig. 4) is close to a straight line, suggesting that a variable range hopping²² is dominant in positive hole conduction at the top of valence band which is observed in similar delafossite materials.^{4,6} The type of carriers responsible for conduction are holes which were identified from the Seebeck coefficient measurement. The positive Seebeck coefficient of $70 \mu\text{V K}^{-1}$ at room temperature indicates that the conduction is p type. The x-ray diffraction shows the presence of β -AgGaO₂ impurity phase and the film is composed of nanosize particles. The conductivity of the β -AgGaO₂ bulk (2.5×10^{-7} S cm⁻¹) (Ref. 23) is smaller than that of α -AgGaO₂ bulk samples 1×10^{-6} S cm⁻¹ (Ref. 20) pelletized under similar conditions. The contribution from the impurity phase for the conductivity of the film may be very small. The Ag⁺ ions contributing to the conductivity have been estimated by measuring the transference number using the dc polarization method.²⁴ The electron beam evaporated gold forms the blocking electrodes. The variation of current has been noted under a steady dc potential of

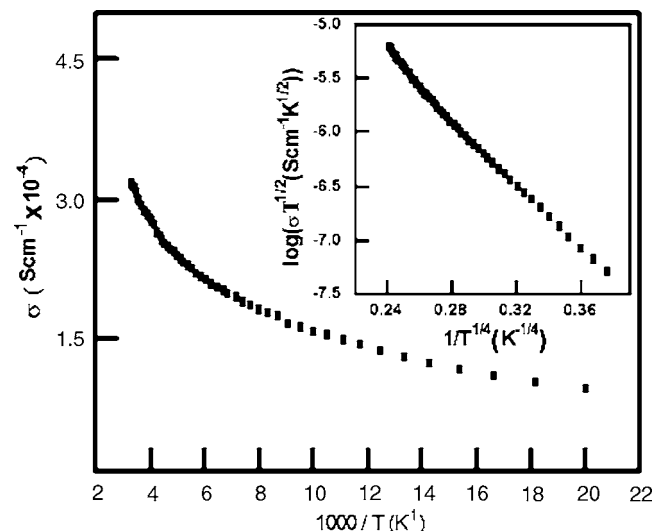


FIG. 4. Conductivity σ vs $1/T$ and inset shows $\log \sigma T^{1/2}$ vs $1/T^{1/4}$ of the AgGaO₂ thin film.

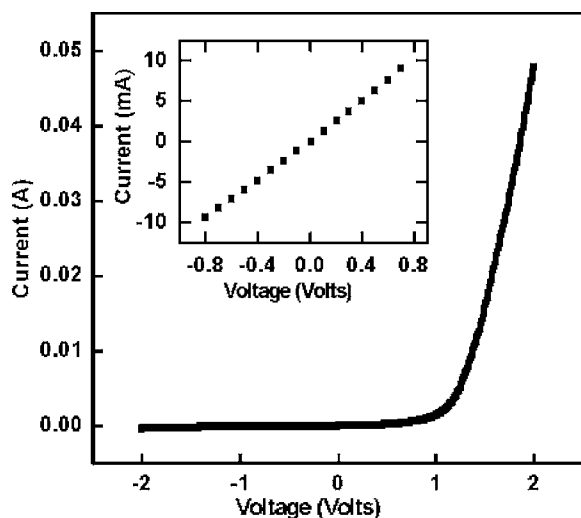


FIG. 5. The current voltage characteristics for the $\text{AgGaO}_2/\text{n-ZnO}$ p - n heterojunction. Inset shows Ohmic nature of ITO/ZnO contact.

500 mV over a time of 2 h. The variation in current is very small and the estimated transference number is 0.03, indicating that the ionic contribution to conductivity is negligible. The possible application of p -type TCO has been demonstrated by fabricating a p - n junction. The transparent heterojunction diodes have a structure $\text{glass/ITO/n-ZnO/p-AgGaO}_2$. The indium tin oxide thin film was deposited by rf magnetron sputtering as described elsewhere.²⁵ The undoped ZnO was deposited onto the ITO coated glass substrates by PLD at an oxygen partial pressure of 10^{-4} mbar and at a laser power of 2 J/cm^2 for 20 min, resulting in a film of 200 nm thickness. The target to substrate distance was 5.5 cm and the substrate temperature was kept at 400°C . The ZnO films deposited by PLD have a transparency greater than 85% in the visible region, and the conductivity is 44 S cm^{-1} . Depositing the p -type AgGaO_2 over the ZnO completed the device. The ITO/ZnO contact is Ohmic (inset of Fig. 5). The typical current voltage (I - V) characteristics of the p - n heterojunction diode is shown in Fig. 5. The n -ZnO/ p - AgGaO_2 junction shows a rectifying characteristics with the forward current to reverse current ratio larger than 100 at applied voltage of -1.5 to $+1.5$ V. The turn on voltage of the device varied from 0.9 to 1.1 V from junction to junction.

In conclusion, we have grown wide band gap α - AgGaO_2 p -type conducting thin film by pulsed laser deposition. The room temperature conductivity was measured as

$3.2 \times 10^{-4} \text{ S cm}^{-1}$ and the optical band gap was estimated as 4.12 eV.

A transparent p - n junction thin film diode on glass substrate was fabricated using p -type α - AgGaO_2 and n -ZnO.

This work is Supported by Board of Research in Nuclear Science, Government of India. One of the authors (K.A.V.) thanks Department of Science and Technology for the financial assistance under women scientist scheme. The authors thank Professor P. V. Sathyam and Ummanda of Institute of Physics, Bhubaneswar for the TEM images and Dr. L. M. Kukreja of Raja Ramanna Centre for Advanced Technology, Indore for discussion.

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