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Pulsed laser deposition of p-type α-$AgGaO_2$ thin films

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Abstract

Polycrystalline α-$AgGaO_2$ powders were prepared by the hydrothermal conversion of β-$AgGaO_2$. The β-$AgGaO_2$ was synthesized by the ion exchange reaction between $NaGaO_2$ and molten $AgNO_3$ under nitrogen atmosphere. The α-$AgGaO_2$ thus synthesized was used as the target for pulsed laser ablation. The films grown on α-Al_2O_3 (0001) single crystal substrates are crystalline and are 50% transparent in the visible region. The temperature dependence of conductivity shows a semiconducting behaviour with room temperature conductivity 3×10^{-4} Scm^{-1}. The positive sign of Seebeck coefficient (+70 μVK^{-1}) demonstrated the p-type conduction in the films. Transparent p–n heterojunctions on a glass substrate were fabricated. The structure of the device was glass/ITO/n-ZnO/p-$AgGaO_2$. The ratio of forward to reverse current was more than 100 in the range of −1.5 V to +1.5 V.

Keywords: Pulsed laser deposition; p-type; p–n junction; HRTEM

1. Introduction

There has been considerable interest in finding p-type electrical conductivity in wide band gap semiconductors [1]. These wide band gap p-type semiconducting oxides along with n-type transparent conducting oxides can lead to the development of UV and blue emitting diodes. The report of p-type conductivity in $CuAlO_2$ by Kawazoe et al. [2] has aroused much interest in $A^IB^{III}O_2$ delafossite (A^I=Cu, Ag, Pt and Pd; B^{III}=Al, Ga, In, Fe, Co, Sc, T and rare earths). Since the report of p-type conductivity in $CuAlO_2$ films, reports followed by observation of p-type conductivity in transparent of $CuScO_2$ [3], $CuGaO_2$ [4], $CuYO_2$ [5], $CuCrO_2$ [6]. Bipolarity has been reported in the $CuInO_2$ delafossite [7] with the realization of transparent p–n homojunction. All the p-type delafossites reported so far all based on copper delafossites. Acceptor doping of $AgInO_2$ [8] has not been successful in inducing p-type conductivity. Copper delafossites can easily synthesized by high temperature solid-state reaction. Synthesis of silver delafossites is difficult in one-step solid state reaction [9]. Reagents containing noble metal cations has low free energies of formation which results in decomposition or dissociation at temperatures before the mass diffusion take place. Most of the silver delafossites are prepared by direct reactions in a parr bomb [10] or by ion exchange reaction [8,11]. In this paper we report the low temperature hydrothermal growth of $AgGaO_2$ delafossite compound and growth of thin film by pulsed laser deposition.

2. Experimental details

The α-$AgGaO_2$ was synthesized by the conversion of β-$AgGaO_2$ by hydrothermal reaction. The synthesis of β-$AgGaO_2$ involves two steps viz. synthesis of $NaGaO_2$ precursor followed by the ion exchange reaction to produce the β-$AgGaO_2$. The $NaGaO_2$ precursor was synthesized by solid state reaction [12] of stotiometric amount of $NaCO_3$ and β-Ga_2O_3. The reaction was carried out by successive heating at 650 °C, 750 °C, 850 °C, 1000 °C, and 1050 °C for 24 h at each temperature. The β-$NaGaO_2$ thus obtained is transformed in to β-$AgGaO_2$ by reacting with excess molten $AgNO_3$ at 280 °C for 24 h in nitrogen atmosphere. The $AgGaO_2$ thus obtained has orthorhombic structure. The excess $AgNO_3$ was removed by repeated washing. β-$AgGaO_2$ is then converted in to α-$AgGaO_2$ by hydrothermal reaction in a parr bomb at 250 °C. The length of reaction was four days. The reagents used were β-$AgGaO_2$ and

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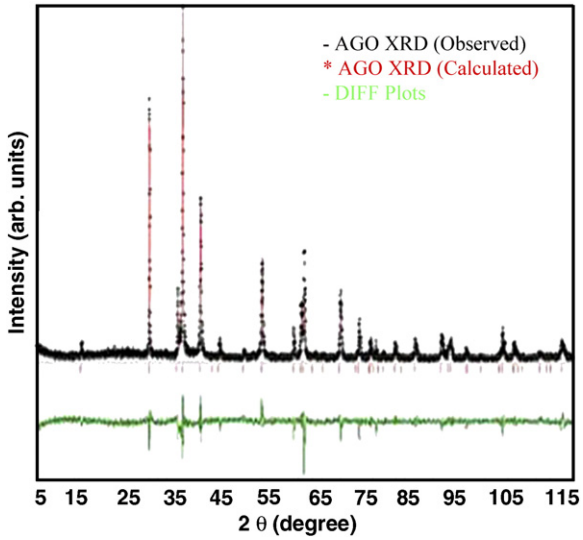

Fig. 1. Calculated, difference plots by Rietveld refinement and observed XRD pattern of α-$AgGaO_2$ obtained by hydrothermal reaction.

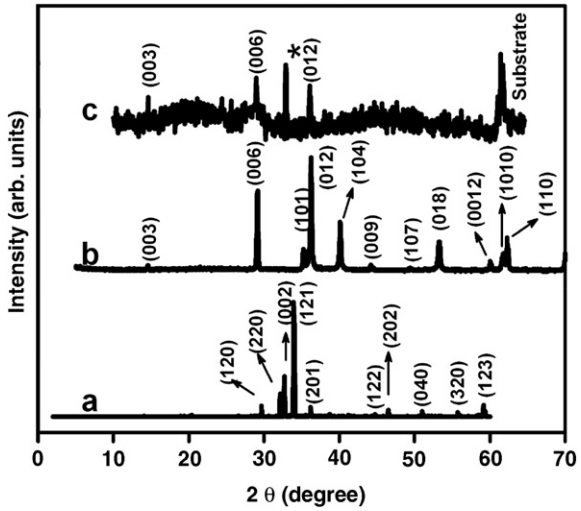

Fig. 3. The X-ray diffraction patterns of (a) β-$AgGaO_2$ powder (b) α-$AgGaO_2$ target and (c) α-$AgGaO_2$ thin film. * Indicates (002) peak of the impurity β-$AgGaO_2$ phase.

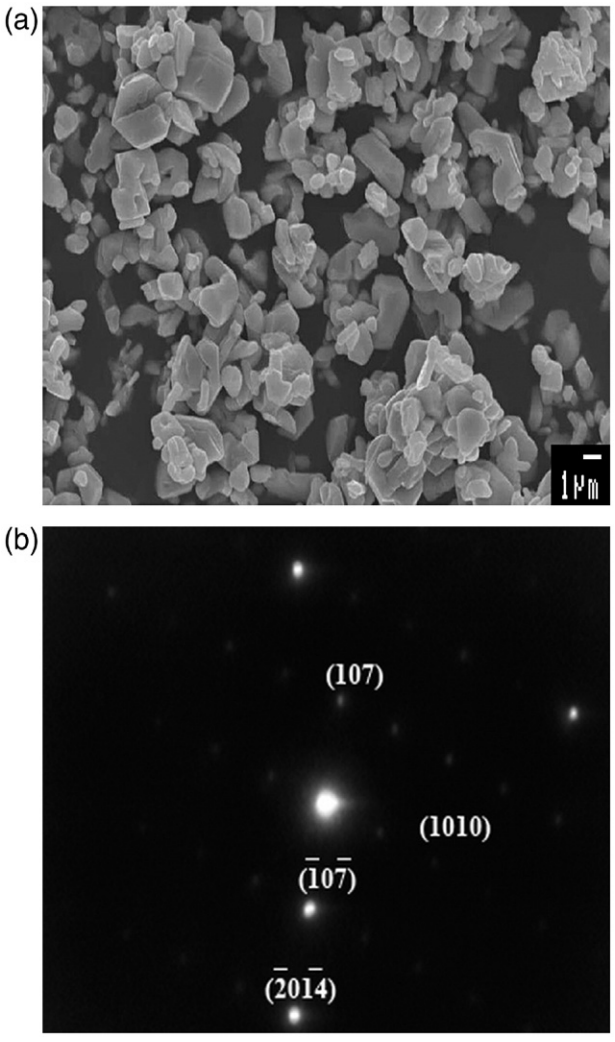

Fig. 2. SEM image (a) and electron diffraction pattern (b) of the α-$AgGaO_2$ powder grown by hydrothermal reaction.

KOH (1M) solution. The α-$AgGaO_2$ were pelletized by cold isostatic press and then sintered at 350 °C for 5 h in air. Thin films of α-$AgGaO_2$ were grown on Si (100) and Al_2O_3 substrates by pulsed laser deposition. The third harmonics (355 nm) of a Q-switched Nd: YAG laser (Spectra physics Quanta ray GCR series) was focused on to a rotating target. The repetition rate of the laser pulse was 10 Hz with pulse width of 9 ns and energy density of the laser pulse was 1 J/cm^2. The chamber was initially pumped down to 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 for Al_2O_3 substrates. The films were allowed to cool down to room temperature at the same oxygen pressure. The thickness of

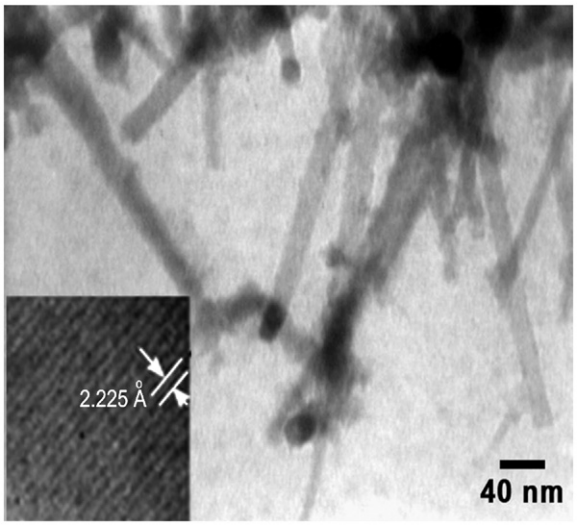

Fig. 4. TEM picture of α-$AgGaO_2$ thin film grown on carbon coated copper grid and inset shows the atomic scale image of the film.

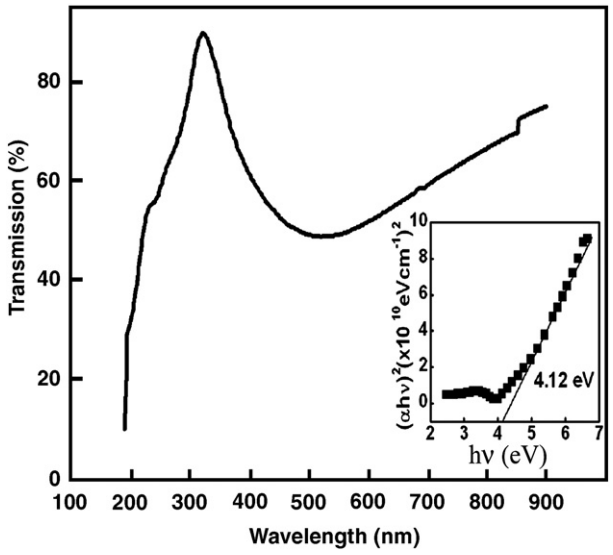

Fig. 5. Transmission spectra of the α-$AgGaO_2$ thin film. Inset shows the plot of $(\alpha h\nu)^2$ vs. hν.

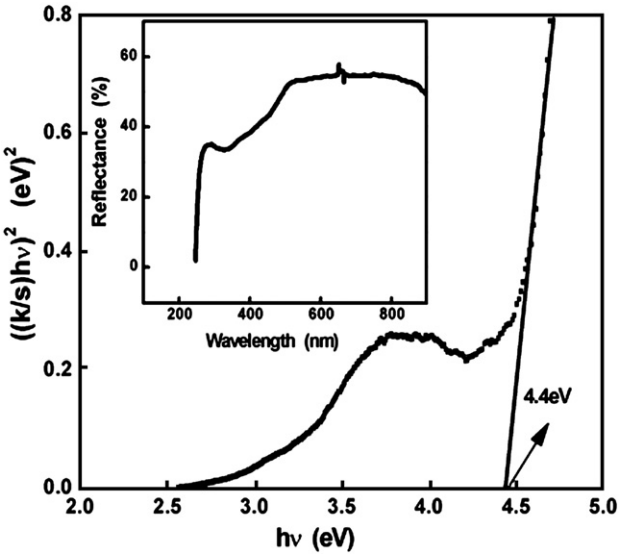

Fig. 6. The plot of $\{(k/s)\,h\nu\}^2$ vs. hν for α-$AgGaO_2$ giving a band gap of 4.4 eV. and inset shows diffuse reflectance spectra of the powder sample.

the deposited films (~200 nm) was measured using a stylus profiler (Dektak 6M). The crystalline nature of the films was identified by X-ray diffraction (Rigaku X-ray Diffractometer) using Cu K_α line.

3. Results and discussion

The X-ray diffraction pattern of α-$AgGaO_2$ synthesized in the laboratory is shown in Fig. 1. The structure of 3R α-$AgGaO_2$ is described in space group $R\bar{3}m$ with Ag at 0 0 0, Ga at 0 0 1/2, and oxygen at 0 0 z where $z=0.1061$. The structure of α-$AgGaO_2$ was refined by Rietveld analysis. Fig. 1 shows the fitting profile calculated by Rietveld refinement, the observed X-ray diffraction data and their difference plot. Rietveld analysis was also carried out with three phases such as the delafossite $AgGaO_2$, Ag_2O and Ga_2O_3. However, the refinement result did not fit with the observed X-ray diffraction pattern. The structure refinement performed on a single phase of delafossite structure confirms the conversion of β-$AgGaO_2$ to α-$AgGaO_2$ by hydrothermal conversion. The scanning electron micrograph (SEM) image in Fig. 2(a) shows that the particle size of light green α-$AgGaO_2$ crystallize range from 1 μm to 3 μm. The electron diffraction (Fig. 2(b)) pattern can be indexed to the planes of α-$AgGaO_2$.

Thin films of α-$AgGaO_2$ were grown on Si substrate at 250 °C, while deposition on Al_2O_3 or glass substrates were carried out at 400 °C. Fig. 3 shows the X-ray diffraction pattern of α-$AgGaO_2$ grown on Si substrate at 250 °C along with the diffraction patterns of bulk β-$AgGaO_2$ and α-$AgGaO_2$. The crystalline phase identified in the sample was found to belong to α-$AgGaO_2$ of $R\bar{3}m$ space group. An impurity phase was also detected in the X-ray diffraction pattern. This diffraction peak can be identified as the (002) peak of the β-$AgGaO_2$. The high resolution transmission electron micrographs (HRTEM) of the α-$AgGaO_2$ films grown under the same deposition conditions of film growth on silicon substrates but on carbon coated copper grids is shown in Fig. 4. 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. 4) 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-$AgGaO_2$ (104). Similar growth has been observed in nanocrystalline $CuAlO_2$ [13]. The d spacing observed does not match with that of Ag_2O or β-$AgGaO_2$. Energy dispersive X-ray analysis shows that the ratio of Ag/Ga is 1.02, which is close to the atomic ratio of α-$AgGaO_2$. 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. Fig. 5 shows the optical transmittance of α-$AgGaO_2$ films in the visible region. The films have more than 50% transmission in the visible region. The inset of Fig. 5 shows the

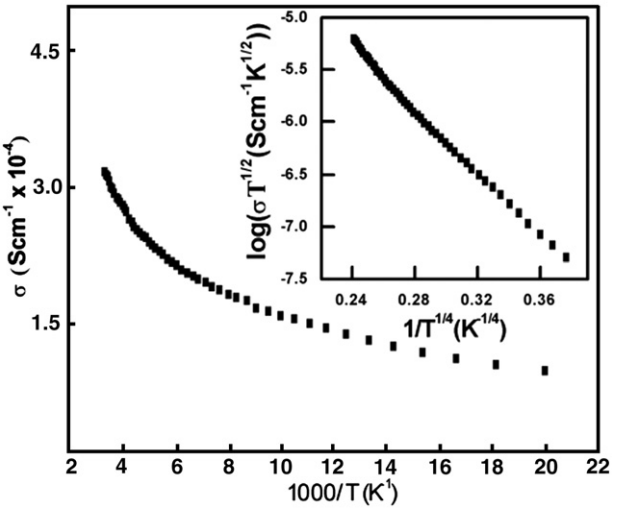

Fig. 7. Conductivity σ vs. $1/T$ and inset shows log $\sigma T^{1/2}$ vs. $1/T^{1/4}$ of the $AgGaO_2$ thin film.

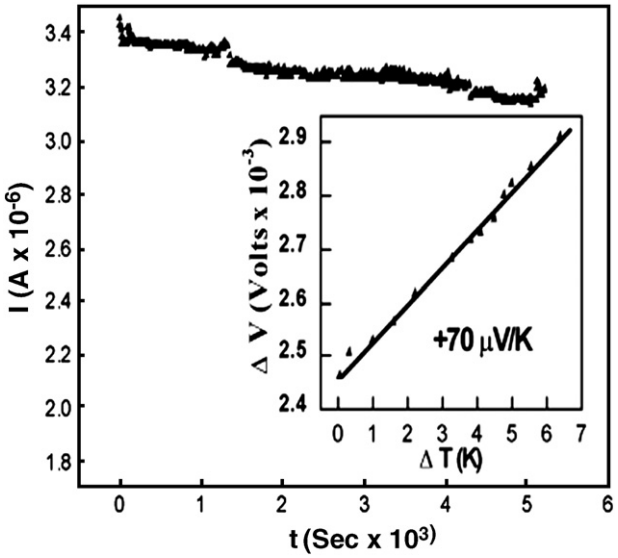

Fig. 8. The variation of current (I) of α-$AgGaO_2$ under a steady dc potential of 500 mV over a time of two hours and inset shows the variation of thermo emf of the film with ΔT.

plot of $(\alpha h\nu)^2$ vs. $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. From the plot optical band gap is estimated as 4.12 eV. The band gap of α-$AgGaO_2$ powder sample was estimated by recording the diffuse reflectance spectrum of the sample (inset of Fig. 6) in the visible region using MgO as the reference. The band gap was found to be 4.4 eV from the plot of $\{(k/s)/h\nu\}^2$ vs. $h\nu$ (Fig. 6), where k and s denotes the absorption and scattering coefficients and $h\nu$ the photon energy. The ratio k/s was calculated from the reflectance spectra via the Kubelka–Monk equation [14,15].

The dc electrical conductivity of the samples was studied in the range 50 K to 300 K. The room temperature conductivity (σ) of the undoped $AgGaO_2$ films was 3.17×10^{-4} Scm^{-1} (Fig. 7). The activation energy at high temperature is 68 meV. The log (σ) vs. $1/T$ plot is not well fit by a straight line. However the log ($\sigma\, T^{1/2}$) vs. $1/T^{1/4}$ plot (inset of Fig. 7) is close to a straight line suggesting a variable range hopping [16] is dominant in positive hole conduction at the top of valance band which is observed in similar delafossite materials [4,6]. The types of carriers responsible for conduction are holes which was identified from the Seebeck coefficient measurement. The positive Seebeck coefficient of 70 μVK^{-1}(inset of Fig. 8) at room temperature indicates the conduction is p-type. The X-ray diffraction shows the presence of β-$AgGaO_2$ impurity phase and the film is composed of nanosize particles. The conductivity of the β-$AgGaO_2$ bulk (2.5×10^{-7} Scm^{-1}) [17] is smaller than that of α-$AgGaO_2$ bulk samples (1×10^{-6} Scm^{-1}) [18]. 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, $t=\frac{\sigma_0-\sigma_\infty}{\sigma_0}$ (σ_0 is the conductivity at $t=0$ and σ_∞ is the saturated conductivity) using the dc polarization method [19]. The evaporated gold (1.5 μm thick) forms the blocking electrodes. The variation of conductivity has been noted under a steady dc potential of 500 mV over a time of two hours. The variation in conductivity is very small (Fig. 8) and the estimated transference number is 0.03 indicating 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 glass/ITO/n-ZnO/p-$AgGaO_2$. The indium tin oxide thin film was deposited by rf magnetron sputtering as described elsewhere [20]. The undoped ZnO was deposited on to the ITO coated glass substrates by PLD at an oxygen partial pressure of 10^{-4} mbar and at 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 substrate temperature was kept at 400 °C. The ZnO films deposited by PLD has transparency greater than 85% in the visible region and the conductivity is 44 Scm^{-1}. Depositing the p-type $AgGaO_2$ over the ZnO completed the device. The ITO/ZnO contact is ohmic (inset of Fig. 9). The typical current voltage (I–V) characteristics of the p–n heterojunction diode is shown in Fig. 9. 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 V to 1.1 V from junction to junction.

4. Conclusion

p-type delafossites $AgGaO_2$ were synthesized by a three step process which involves the synthesis of β-$NaGaO_2$ followed by ion exchange reaction producing β-$AgGaO_2$. The β-$AgGaO_2$ has been converted to α-$AgGaO_2$ by hydrothermal reaction. This bulk powder was used for the growth wide band gap α-$AgGaO_2$ p-type conducting thin film by pulsed laser deposition. The room temperature conductivity was measured as 3.17×10^{-4} Scm^{-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.

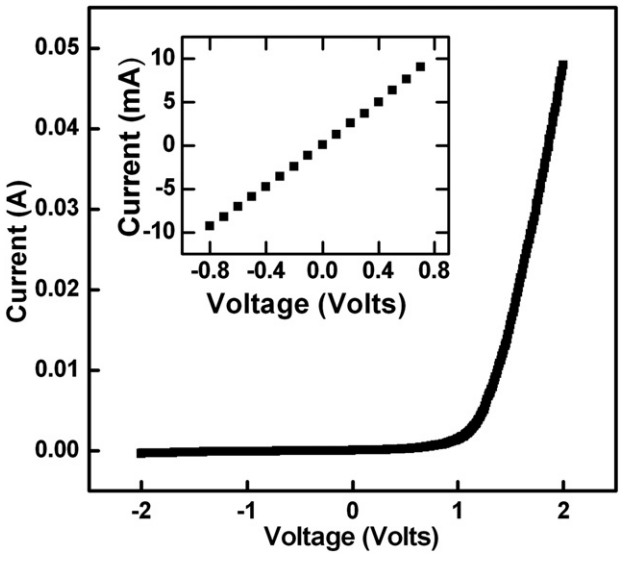

Fig. 9. The current–voltage characteristics for the $AgGaO_2$/n-ZnO p–n heterojunction and inset shows ohmic nature of ITO/ZnO contact.

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