Chapter 5

Hydrothermal synthesis of p-type AgGaO$_2$ and fabrication of n-ZnO/p-AgGaO$_2$ pn junction by pulsed laser deposition

Abstract

The synthesis of p-type delafossite AgGaO$_2$ bulk powder materials by hydrothermal method is described in detail. These powder materials have been characterised by various analytical techniques and the phase purity was confirmed. The silver gallium oxide thus synthesised has been used as the target for the growth of thin films by PLD. All oxide transparent ITO/ZnO/AgGaO$_2$ pn junctions have also been fabricated
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5.1 Introduction

Delafossite type compounds [1] have general formula $A^I B^{III}O_2$ ($A= Cu$, Ag, Pt and Pd; $B= Al$, Fe, Co, Rh, Ga, Sc, In and rare earths). The structure of the delafossite type oxides can be described as the alternate stacking of edge shared $BO_6$ octahedral layers and $A^+$ ion layers perpendicular to c axis (fig1.3chapter 1). Each $A^+$ ion layer is linearly coordinated by two $O^2-$ ions [1]. These delafossites can crystallize in either the rhombohedral 3R (R3m) or hexagonal 2H ($p6_3/mmc$) polytype based on the stacking of the alternate layers of $BO_6$ octahedra and $A^+$ cations. This delafossite class of material has been of renewed interest since Kawazoe et al [2] reported p-type conductivity in transparent thin films of CuAlO$_2$. This was followed by reports of observation of p-type conductivity in transparent conducting films of CuScO$_2$ [3], CuGaO$_2$ [4], CuY$_{1-x}$Ca$_x$O$_2$ [5], CuCr$_{1-x}$Mg$_x$O$_2$ [6] and CuInO$_2$ [7]. Wide band gap semiconductors are difficult to be doped, particularly to p-type [8] and there is no report on p-type silver delafossite in thin film form, except for AgCoO$_2$ [9]. The AgInO$_2$ [10] films doped with tin shows n-type conductivity. The synthesis of silver delafossites by conventional solid state reaction of the constituent oxides at high temperature has been found to be unsuccessful. Hence silver delafossites are generally prepared by cation exchange reaction or by hydrothermal synthesis. The presence of trace amounts of metallic silver in the products has been observed in the attempts to synthesize Ag based delafossites [11]. In the present work, the synthesis of $\alpha$-AgGaO$_2$ by a two step process involving the synthesis of $\beta$-AgGaO$_2$ by ion exchange reaction followed by the hydrothermal conversion of the $\beta$-AgGaO$_2$ into $\alpha$-AgGaO$_2$ is attempted. The trace amount of Ag has been
reduced substantially in the two step synthesis compared to the direct hydrothermal synthesis.

5.2 Synthesis of bulk AgGaO$_2$ powder

β-AgGaO$_2$ was prepared through the ion exchange reaction between β-NaGaO$_2$ and AgNO$_3$. The preparation of β-AgGaO$_2$ involves two steps viz, the synthesis of NaGaO$_2$ precursor and transformation to AgGaO$_2$. The NaGaO$_2$ precursor was synthesized by solid state reaction [12] of stoichiometric amounts of Na$_2$CO$_3$ and β-Ga$_2$O$_3$. The reaction was carried out by successive heating at 650$^\circ$C, 750$^\circ$C, 850$^\circ$C, 1000$^\circ$C, and 1050$^\circ$C for 24 h at each temperature. The β-NaGaO$_2$ thus obtained was transformed in to β-AgGaO$_2$ by reacting with excess molten AgNO$_3$ at 280$^\circ$C for 24 h under N$_2$ atmosphere. The AgGaO$_2$ thus obtained has orthorhombic structure. The excess AgNO$_3$ was removed by repeated washing with distilled water and the β-AgGaO$_2$ was then converted in to α-AgGaO$_2$ by hydrothermal reaction in a parr bomb at 250$^\circ$C. The reaction was continued for four days. The reagents used were β-AgGaO$_2$ and KOH(1 M) solution. X-ray diffraction (XRD) studies were carried out with Rigaku diffractometer in Brag-Brentano geometry (θ–2θ) using CuK$_\alpha$ radiation. The electrical conductivity of the sintered pellets was measured from 300 K to 70 K by two probe technique using Keithley source measure unit. Silver paste was used as the electrodes and ohmic nature of the contacts was confirmed before the measurements. Diffuse reflectance spectra of powder samples at room temperature with MgO as reference were recorded using Ocean optics SD 2000 fiber optic spectrophotometer. The thermo power measurements were carried out on the sintered pellets by producing a temperature difference on either side of the pellet and measuring the thermo emf produced.
5.2.1 Characterisation of the AgGaO₂ powder material

The x-ray diffraction patterns of the synthesized NaGaO₂ and β-AgGaO₂ are shown in (Figure 5.1). The orange β-AgGaO₂ has orthorhombic structure similar to β-NaGaO₂ with $a=5.5645\, \text{Å}$, $b=7.1522\, \text{Å}$ and $c=5.4697\, \text{Å}$. All the observed peaks can be indexed to that of the β-AgGaO₂[13] and NaGaO₂[14]. The structure of 3R α-AgGaO₂ is described in space group R3m 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-AgGaO₂ was refined by Rietveld analysis. Figure 5.2 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 possible phases of AgGaO₂, Ag₂O and Ga₂O₃.

![Figure 5.1. Powder X-ray diffraction patterns of orthorhombic NaGaO₂, β-AgGaO₂ and α-AgGaO₂.](image-url)
However, the refinement result did not fit with the observed X-ray diffraction pattern. The structure refinement performed on a single phase of delafossite type confirms the conversion of $\beta$-AgGaO$_2$ to $\alpha$-AgGaO$_2$ by hydrothermal conversion.

![Graph](image)

Fig.5.2. Calculated, and difference plots by Rietveld refinement and observed XRD pattern of $\alpha$-AgGaO$_2$ obtained by hydrothermal reaction.

The scanning electron micrograph (SEM) image in figure 5.3 shows that the particle size of light green $\alpha$-AgGaO$_2$ crystallite ranges from 1 $\mu$m to 3$\mu$m. The scanning electron microscopy (SEM) study shows that the morphology of the AgGaO$_2$ compound is hexagonal. The energy depressive X-ray (EDX) analysis shows that the compound is close to stoichiometry with Ag/Ga ratio 1.02. The presence of any secondary phases other than the $\alpha$-AgGaO$_2$ was not detected by powder XRD. The electron diffraction pattern shown in fig.5.4 can be indexed to the planes of $\alpha$-AgGaO$_2$. 

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Fig. 5.3. The SEM picture of $\alpha$-AgGaO$_2$ powder grown by hydrothermal reaction

Figure 5.4 The electron diffraction pattern of the AgGaO$_2$ powder grown by hydrothermal reaction.
Inset of figure 5.5 shows the diffuse reflectance spectrum of $\alpha$-AgGaO$_2$ powder in the visible region using MgO as the reference. The band gap of the $\alpha$-AgGaO$_2$ powder sample was found to be 4.4 eV from the plot of $\{(k/s)h\nu\}^2$ vs $h\nu$ (fig.5.5) where $k$ and $s$ denote the absorption and scattering coefficients respectively and $h\nu$ the photon energy. The ratio $k/s$ was calculated from the reflectance spectrum via the Kubelka-Munk equation [15, 16].

Fig.5.5 Plot of $\{(k/s)h\nu\}^2$ vs $h\nu$ for $\alpha$-AgGaO$_2$ giving a band gap of 4.4 eV.
Inset shows the diffuse reflectance spectrum of $\alpha$-AgGaO$_2$. 
Fig 5.6. Temperature dependence of the dc electrical conductivity of $\alpha$-AgGaO$_2$

The inset shows the result of Seebeck coefficient measurement of $\alpha$-AgGaO$_2$

The temperature dependence of the electrical conductivity of undoped $\alpha$-AgGaO$_2$ was studied in the temperature range of 300 K to 50 K by using sintered pellet of $\alpha$-AgGaO$_2$. The pellets (1cm diameter) for electrical conductivity studies were synthesized by mixing the $\alpha$-AgGaO$_2$ powder with poly vinyl alcohol and applying a pressure of 5 tones. The electrical contacts were made using silver paste and the ohmic nature of the contact was confirmed by studying the current voltage characteristic. The conductivity of $\alpha$-AgGaO$_2$ bulk powder samples at room temperature was $\sim$1x10$^{-6}$Scm$^{-1}$. The conductivity of $\alpha$-AgGaO$_2$ samples do not show appreciable dependence on temperature (fig.5.6). At higher temperature, there is an increase in conductivity and the contribution of increased
conductivity seems to have started around room temperature. The temperature dependence of conductivity shows a semiconducting behavior (Fig 5.6). The undoped samples show very low conductivity which can be enhanced by replacing the trivalent Ga ion by divalent impurity or by oxygen intercalation. The oxygen annealing at atmospheric pressure increases the conductivity to $1 \times 10^{-5} \text{S cm}^{-1}$. The type of conductivity was determined from the thermoelectric power measurement using the set up similar to the one reported in literature [17] (Inset of Fig.5.6) The positive sign of Seebeck coefficient (+254 $\mu$V/K) confirms that holes are responsible for electrical conduction.

5.3 Growth of AgGaO$_2$ thin films by PLD

$\alpha$-AgGaO$_2$ thin films were prepared on silicon and Al$_2$O$_3$ substrates by pulsed laser deposition. The third harmonic (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 was 1 J/cm$^2$ per pulse. The chamber was initially pumped down to base pressure of $10^{-6}$ mbar. Oxygen gas was then introduced in to 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$^\circ$C for silicon substrates and at 400$^\circ$C when Al$_2$O$_3$ was used as substrates. The details of experimental set up are discussed in section 2.3.3. The films were allowed to cool down to room temperature at the same oxygen pressure. The thickness of the deposited $\alpha$-AgGaO$_2$ 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 CuK$_\alpha$ line.
Fig 5.7 The x-ray diffraction patterns of a) $\alpha$-AgGaO$_2$ powder, b) $\beta$-AgGaO$_2$ powder, and c) $\alpha$-AgGaO$_2$ thin film. * indicates (002) peak of the impurity $\beta$-AgGaO$_2$ phase.

Figure 5.7 shows the diffraction patterns of $\beta$-AgGaO$_2$ (a) $\alpha$-AgGaO$_2$ (b) and the thin film (c). The crystalline phase identified in the sample was found to belong to $\alpha$-AgGaO$_2$ of R3m space group. A small impurity phase was also detected. The high resolution transmission electron micrograph (HRTEM) images of the $\alpha$-AgGaO$_2$ films grown on carbon coated copper grids, under the same deposition conditions of film growth on silicon substrates are shown in figure 5.8. The nucleation and growth of the film in the form of nanorods with average diameter 20 nm and length up to 270 nm were observed. The atomic scale images of the films (inset of Fig. 5.8) show parallel lines of ions at intervals of 2.225 A$^\circ$ for most of the grains. This lattice spacing coincides with d spacing
of $\alpha$-AgGaO$_2$ (104). Similar growth has been observed in nano crystalline CuAlO$_2$ [19]. The d spacing observed does not match with that of Ag$_2$O or $\beta$-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 $\alpha$-AgGaO$_2$. The grains in the films grown on silicon substrates may be very small also and such nanoscale particles and small sample thickness may be the reason for the very weak signal in the x-ray diffraction pattern.

Figure. 5.8. TEM picture of $\alpha$-AgGaO$_2$ thin film grown on carbon coated copper grid and the inset shows the atomic scale image of the film.
Figure 5.9. Transmission spectrum of the $\alpha$-AgGaO$_2$ thin film. Inset shows the plot of $(\alpha \ h\nu)^2$ vs $h\nu$.

Figure 5.9 shows the optical transmittance of the $\alpha$-AgGaO$_2$ films in the visible region. The films have transparency more than 50% in the visible region. The inset shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$, where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. The optical gap energy is estimated as 4.12 eV. The dc electrical conductivity of the samples was studied in the temperature range 50 K to 300 K. The room temperature conductivity of the undoped AgGaO$_2$ films was $3.17 \times 10^{-4}$ Scm$^{-1}$. The activation energy at high temperature is 68 meV. The $\sigma$ vs. $1/T$ plot is not well fitted by a straight line (shown in Fig. 5.10). However the log $\sigma T^{1/2}$ vs. $1/T^{1/4}$ plot (inset of Fig. 5.10) is close to a straight line suggesting that a variable range hopping [20] is dominant in positive hole conduction at the top of valance band which is observed in similar delafossite
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materials [4,6]. The contribution from the impurity phase for the conductivity of the film may be very small. The Ag$^+$ ions contributing to the conductivity has been estimated by measuring the transference number, $t = \frac{\sigma_0 - \sigma_\infty}{\sigma_0}$ ($\sigma_0$ is the conductivity at t = 0 and $\sigma_\infty$ is the saturated conductivity) using the dc polarization method [21]. The evaporated gold (1.5 μm thick) forms the blocking electrode. The variation of conductivity has been noted under a steady dc potential of 500 mV over a time of two hrs. The variation in conductivity is very small (Fig. 5.11) and the estimated transference number is 0.03 indicating the ionic contribution to conductivity is negligible. [21]

![Graph](image)

Figure. 5.10 Conductivity $\sigma$ vs $1/T$ and inset shows log ($\sigma T^{1/2}$) vs $1/T^{1/4}$ of the AgGaO$_2$ thin film.
Figure 5.11. The variation of current (I) of α–AgGaO₂ under a steady dc potential of 500 mV over a time of two hrs and inset shows the variation of thermo emf of the film with ΔT.

Figure 5.12 The structure of the n-ZnO/p-AgGaO₂ pn junction

The carriers responsible for conduction are holes which was identified from the Seebeck coefficient measurement. The positive Seebeck coefficient of 70 μVK⁻¹ at room temperature indicates that the conduction is p-type. 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-AgGaO₂ as shown in Fig. 5.12.

The indium tin oxide thin film was deposited by rf magnetron sputtering in our laboratory [22]. The parameters used for the deposition of ITO are briefly described here. Indium tin oxide films were deposited by rf magnetron sputtering of ITO target containing 95 wt.% of In₂O₃ and 5 wt.% of SnO₂. The target used for sputtering was prepared from In₂O₃ (99.99% pure) and SnO₂ (99.999% pure) powders. The powders were mixed in a mechanical shaker for 1 hour, pressed into pellets of two-inch diameter and then sintered at 1300 °C for 6 hours in air. The rf sputtering was carried out in a vacuum chamber in which high vacuum of the order of 2 x 10⁻⁵ mbar was created by means of an oil diffusion pump backed by a rotary pump. The rf power was delivered to the target material by an rf generator (13.56 MHz) through an impedance matching network. Glass slides of dimension 2.5 cm x 1 cm were used as the substrates. The substrates were kept above the target at a distance of 4 cm, which was found to be optimum for the growth of good quality crystalline films [23]. Initially the substrate was heated to the required temperature. After attaining the required substrate temperature, high purity argon gas was allowed to flow into the chamber and it was adjusted by a mass flow controller to maintain the argon pressure at 0.01 mbar. The films were deposited at an rf power of 30W. The target was pre-sputtered for 10 minutes before each deposition in order to remove any contaminants and to eliminate any differential sputtering effects. By keeping all other parameters the same, sputtering was carried out for various substrate temperatures ranging from room temperature to 300°C. For films deposited at room temperature, the temperature.
of the substrate increased by 20 to 50 degrees during deposition. But when the films were deposited on the preheated substrates, the temperature of the substrate was maintained at the specified value by controlling the power applied to the heating coil. The sputtering time was adjusted such that all the films used in this study were of thickness 220 nm. Table shows the properties of ITO thin films deposited at various substrate temperatures. The lowest resistivity was obtained when the substrate temperature was 150°C. Hence ITO electrodes for the device fabrication were deposited at a substrate temperature of 150°C.

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 a laser power of 2 J/cm² for 20 minutes 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 films were crystalline with (002) planes parallel to the substrate surface, indicating that growth was along c-axis. The ZnO films deposited by PLD have transparency greater than 85% in the visible region, band gap of 3.28 eV, and conductivity of about 44 S cm⁻¹. The conditions for the growth ZnO layer by PLD had been optimized in the laboratory [25]. Depositing the p-type AgGaO₂ over the ZnO completed the device. The ITO/ZnO contact is ohmic (inset b of Fig. 5.13). The typical current voltage (I-V) characteristics of the p-n heterojunction diode is shown in Fig. 5.13. The n-ZnO/p-AgGaO₂ junction shows a rectifying characteristic with the forward current to reverse current ratio larger than 100 at applied voltage of −1.5 to +1.5 volts. The turn on voltage of the device varied between 0.9 volt to 1.1 volt from junction to junction.
Figure 5.13. The current voltage characteristics for the AgGaO$_2$/n-ZnO p-n heterojunction. Inset shows Ohmic nature of ITO/ZnO contact.

### 5.4 Conclusion

The single phase $\alpha$-AgGaO$_2$ bulk powders were grown by a low temperature hydrothermal process. The synthesised samples do not show any impurity phases. The DRS studies show that the material has wide band gap while the thermopower measurements show that the carriers responsible for conduction are holes. These studies indicate the possibility of using this material as p-type material in thin film form for transparent electronics. We have grown wide band gap $\alpha$-AgGaO$_2$ p-type conducting thin film by pulsed laser deposition. The room temperature conductivity was measured as $3.17 \times 10^{-4}$
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Scm$^{-1}$ and the optical band gap was estimated as 4.12 eV. The transparency of the PLD deposited $\alpha$-AgGaO$_2$ film is around 60%. A transparent p-n junction thin film diode on glass substrate was fabricated using p-type $\alpha$-AgGaO$_2$ and n-ZnO.

References
13. JCPDS Card no. 21-1076.
14. JCPDS Card no 51-1132.