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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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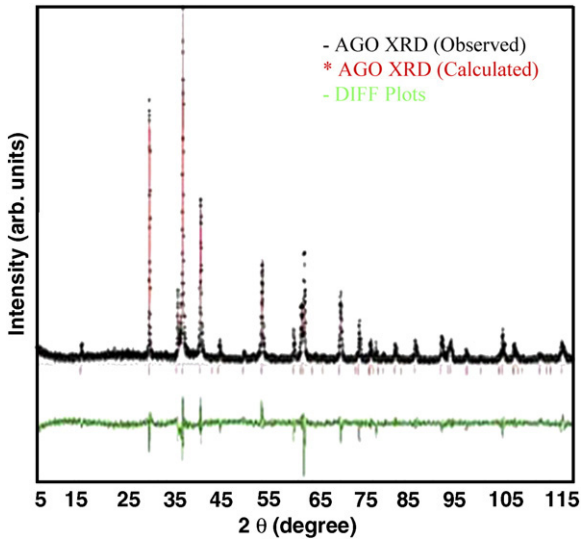

Fig. 1. Calculated, difference plots by Rietveld refinement and observed XRD pattern of α-$AgGaO_2$ obtained by hydrothermal reaction.

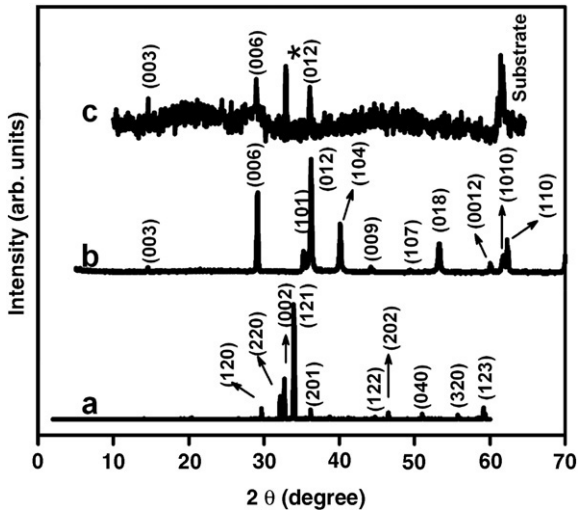

Fig. 3. The X-ray diffraction patterns of (a) β-$AgGaO_2$ powder (b) α-$AgGaO_2$ target and (c) α-$AgGaO_2$ thin film. * Indicates (002) peak of the impurity β-$AgGaO_2$ phase.

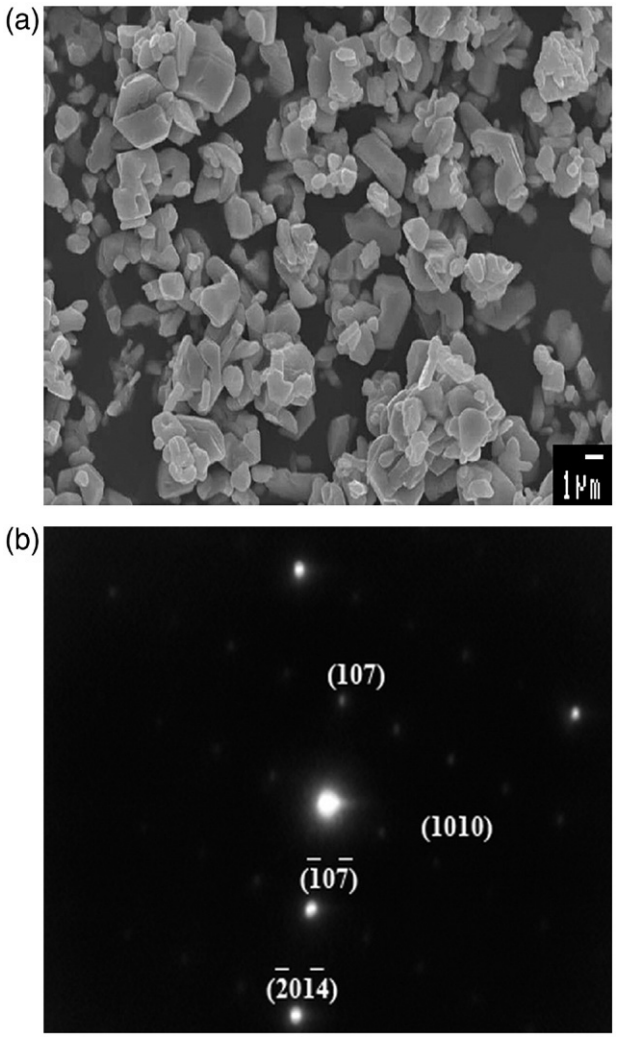

Fig. 2. SEM image (a) and electron diffraction pattern (b) of the α-$AgGaO_2$ powder grown by hydrothermal reaction.

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

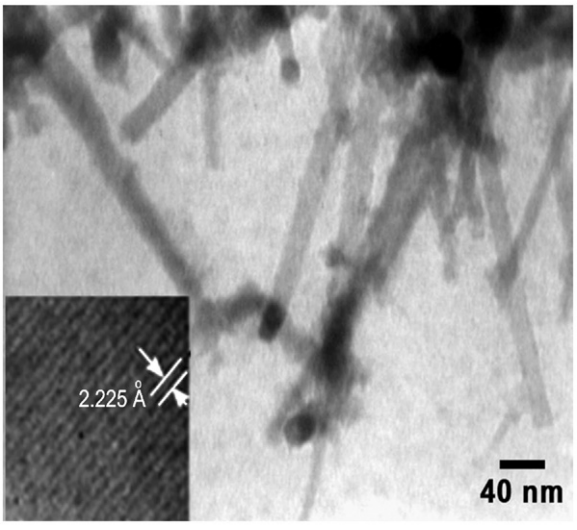

Fig. 4. TEM picture of α-$AgGaO_2$ thin film grown on carbon coated copper grid and inset shows the atomic scale image of the film.