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Synthesis and characterization of AgI thin films at low temperature

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ABSTRACT

The growth of AgI (silver iodide) thin films has been performed in aqueous medium using simple chemical method at room temperature (25 °C). Silver nitrate and potassium iodide have been used as source materials. Thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), surface photovoltage (SPV) and optical absorption spectroscopy. Glass and indium doped tin oxide (ITO) coated glass was used as substrates. The thin films were surface homogeneous with mixed β and γ-phases with surface roughness value of 21 nm. Optical transmission on glass exceeds 80% for 150 nm thick film with the direct band gap value of 2.85 eV. The change in crystal phases after transition temperature is studied by SPV measurements.

1. Introduction

Silver iodide (AgI) has become a promising material due to its superionic conducting behavior, and its photosensitive property; hence, it has been extensively studied in the fields of solid-state ionic and photography. Several approaches have been made for the synthesis and study of silver iodide. Pressure induced phase transition which occur within AgI at close to ambient temperature have been studied using powder neutron diffraction by Keen and Hull in 1993 [1]. They described that the rocksalt structured has approximately 10 times more defects in the fast-ionic phase of than in iso-structural AgBr at ambient pressure [2]. Furthermore, Keen has given the superionic behavior of α-phase of silver iodide in detail [3]. Safran et al. [4] have been carried out synthesis of silver iodide by successive vacuum deposition of silver and iodine in a conventional high vacuum system and study of the phases using TEM analysis. Using gas-evaporation method, small particles (140–680 nm) of AgI with the mixture of γ and β-phases have been reported [5]. At ambient temperature, AgI thin film was formed by reaction between silver foil and iodine by Kumar and Sunandana [6] and their structural, electrical and optical properties were studied. Furthermore, they studied the formation of AgI thin films upon the untreated and surface modification of silver foils [7]. Auto-clave method was used for the synthesis of silver iodide nano-crystals at 140 °C [8]. Chemical solution deposition has been carried out for AgI by using homogeneous generation of halide ions by hydrolysis of halo-alcohols [9]. Nano-scale AgI (with grain sizes of 7–9 nm) have been prepared by quenching molten AgI in liquid nitrogen by Wang et al. [10]. They compared the ionic conductivity at room temperature for quenched and normal AgI. Electrochemical method was used to prepare AgI nanowire arrays in the channels of the ordered porous alumina membrane by Wang et al. [11].

Chemical method, namely, successive ionic layer adsorption and reaction (SILAR) involves immersion of the substrate successively in a cation and anion precursor solution. Between the each immersion, rinsing of the substrate with highly purified water is carried out to avoid homogeneous precipitation. The rinsing and adsorption of the precursor ion control the SILAR hence growth of the desired material occurs only on the substrate surface. The SILAR process has advantages over alternative methods of thin film deposition, notably the technique is simple and requires relatively low capital expenditure, films may be deposited at very low temperatures upon a variety of substrates, the process may be easily adapted to large area processing at low fabrication cost. Number of reports is available to grow thin films of CdS, ZnS, PbS, Bi_2Se_3, Sb_2Se_3, CuI and CuSCN [12–14].

Main goal of this research work is to grow AgI thin films at room temperature by SILAR method. We used glass and indium doped tin oxide (ITO) coated glass as substrates. Structural, surface morphological and optical properties are carried out and results are incorporated.

2. Thin film deposition

Merck analytical reagent grade silver nitrate and potassium iodide were used for the synthesis of silver iodide films. The precursors used for the films formation were 5 mM $AgNO_3$ (pH ∼ 4.5)

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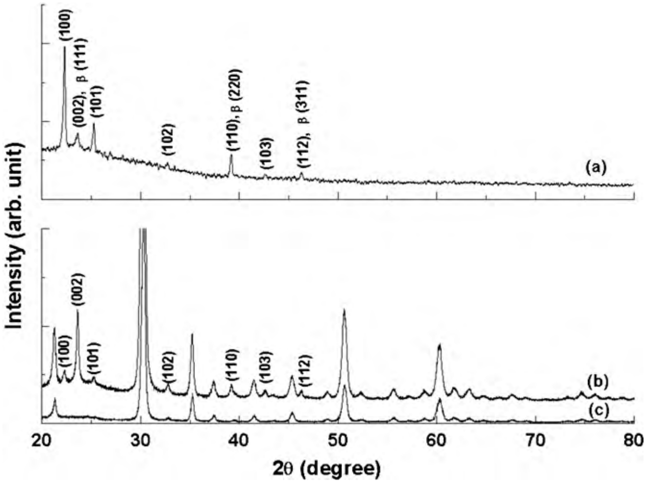

Fig. 1. X-ray diffraction patterns of AgI thin film on (a) glass substrates, and on (b) ITO, with (c) ITO-as a reference.

as cation and 12.5 mM KI (pH ~ 5) as anion. The adsorption and reaction times in cationic and anionic precursor's solutions were experimentally optimized and were 5 and 20 s, respectively. The rinsing time was 20 s in each case. The conductivity of rinsing water was 18 $\mu\Omega^{-1}$ cm^{-1}. Numbers of immersion cycles were repeated until the desired film thickness was obtained. The whole deposition was carried out at room temperature (25 °C).

Structural study was carried out using Bruker D8 advance X-ray diffractometer (Cu-K$_\alpha$ radiation, $\lambda = 1.5406$ Å) with scanning angles in the range of 20–80° in grazing incidence mode (1°). LEO1530 (Gemini) FE-SEM scanning electron microscopy (SEM) unit with Schottky field emission and acceleration voltage of 7 kV was used for surface morphological study. In order to get the surface roughness, atomic force microscopy (AFM) images were recorded in contact mode with a Nanoscope IIIa scanning probe microscope using commercial n$^+$-silicon cantilevers with a typical spring constant of 0.2 N/m. With an integration sphere using Cary 500, optical transmissions and reflection spectrum were recorded. Dektak 3030 unit measured the thickness of the films. Spectral dependent PV measurements were carried out in the arrangement of a parallel plate capacitor as described recently [15]. PV spectra were measured by using halogen lamp with a quartz prism monochromator for the excitation and a chopper for modulation (modulation frequency 7 Hz, signal detected with a lock-in amplifier). In the PV spectra the PV signal is given as the amplitude irrespective to the sign. The PV spectra are not normalized to the incident photon flux of halogen lamp. PV spectroscopy was performed to get information about both E_g and E_t, the energy value of exponential tail states. Measurements were carried out at different temperatures under low pressure conditions (5×10^{-5} mbar) to prevent the oxidation of the film.

3. Results and discussion

The obtained AgI films were pale yellow in colour. Generally, at room temperature, the AgI material has two phases: β-phase corresponding to hexagonal wurtzite type structure and γ-phase with a cubic zinkblende structure [7]. The X-ray diffraction patterns of AgI film deposited on glass and ITO coated glass substrates are shown in Fig. 1. The broad hump is due to amorphous glass substrate (Fig. 1a). In both cases, the films were polycrystalline and presumably hexagonal crystal structure corresponding to β-phase although co-existence of cubic γ-phase could not be excluded thoroughly since three peaks at 23.71°, 39.20° and 46.30° are superimposed. Preferred orientation of AgI on glass is observed along (1 0 0) reflection at 2θ angle 22.34° whereas (0 0 2)/(1 1 1) reflection at 23.70° for the films on ITO substrate. Crystal size of AgI thin film is determined for (1 0 0) specific orientations by using Scherrer's formula as

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of light used, β is the half width of central maxima and θ is the Bragg's angle. Crystal sizes are found to be 48 and 35 nm for AgI films deposited on glass and ITO substrates, respectively.

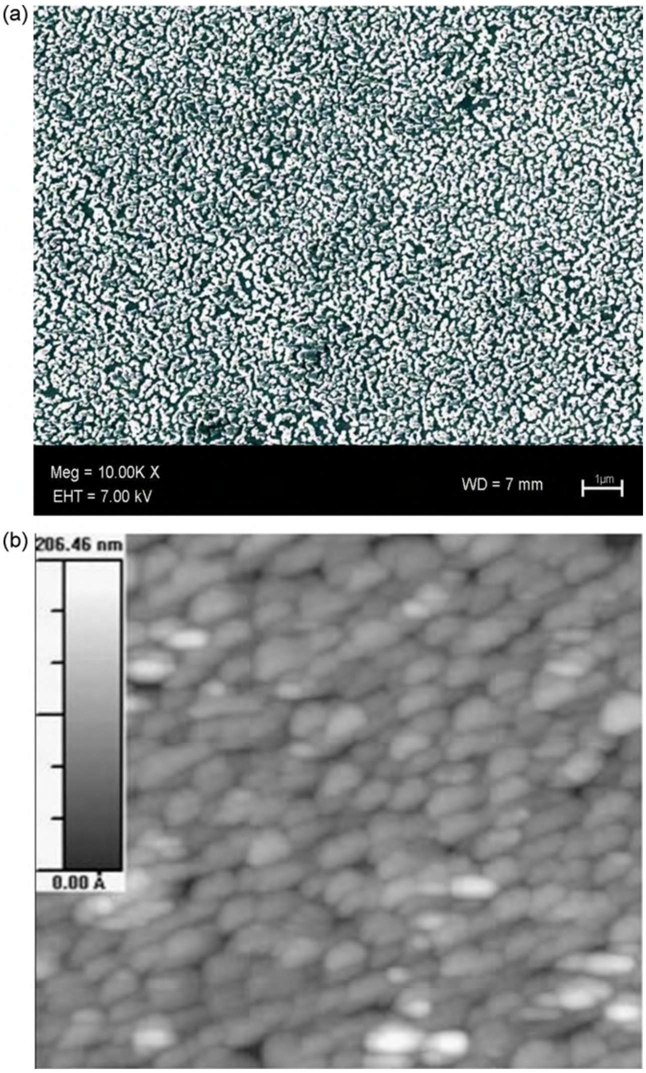

Fig. 2. AgI thin film on the glass substrate (a) SEM image and (b) top-view AFM image.

Fig. 2a shows surface morphology of the film on the glass substrate using SEM analysis. Random distribution of the grains is clearly seen from the image with most of the surface coverage.

Top-view AFM image of AgI on glass is shown in Fig. 2b. AFM image shows film has a dense microstructure on glass. The root-mean-square (r.m.s.) roughness was obtained over 5 μm^2 area as 22 nm.

Optical measurements have been performed for AgI thin film deposited on the ITO coated glass substrate. The optical transmission was above 80% for 150 nm thick AgI film (not shown here) for the wavelength values greater than the wavelength corresponding to E_g. The square of the absorption coefficient (α), against energy ($h\nu$) from optical absorption for the AgI is shown in inset of Fig. 3.

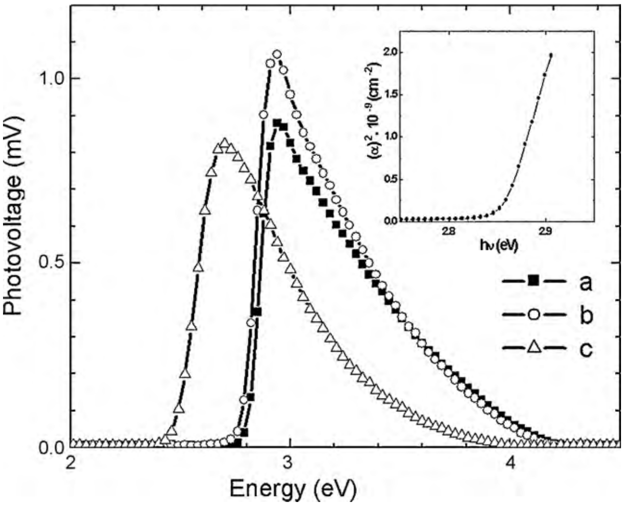

Fig. 3. Photovoltage spectra of AgI thin films on ITO (a) at R.T. (filled square), (b) at 100 °C (open circle) and (c) at 200 °C (open triangle). The inset shows the variation of (absorption coefficient)^2 versus photon energy for AgI films on ITO substrate at R.T.

The linear nature of the plot indicates that the AgI material is a direct band gap material. The extrapolation of linear part of the curve to the energy axis gives the direct band gap, E_g as 2.85 eV. This value is in good agreement with value reported earlier [8].

Fig. 3 compares PV spectra of AgI thin film on ITO at room temperature, 100 °C and 200 °C. For the AgI at ambient temperature the PV signal at about 2.8 eV increased strongly corresponding to the onset of strong absorption at the band edge. The value of the E_g obtained from PV spectra (2.84 eV), is in the good agreement with the result obtained from the optical measurements. After reaching the temperature of 100 °C, the value of the band gap was shifted only slightly towards lower energy due to the temperature dependence of the band gap of the respective phase. This indicates no occurrence of the phase transition. In contrast, a strong change of the band gap was observed between 100 °C and 200 °C. The change of the crystal phase from β, γ to α at higher temperatures is known from literature [6,16]. The decrease of E_g from 2.84 to 2.53 eV between 100 °C and 200 °C indicates the transition to the α-phase of AgI in our experiments.

4. Conclusions

In this study, we showed the synthesis of polycrystalline AgI thin films on glass and ITO by simple SILAR method from week acidic medium at room temperature. The obtained films were mixed β- and γ-phases with optical band gap 2.85 eV. Well coverage of AgI is observed on glass substrates. PV spectra with increase in temperature from ambient to 200 °C film showed shift in band gaps from around 2.84 to 2.53 eV attributed to change in crystal phases from β, γ to α due to well known transition temperature at 147 °C.

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