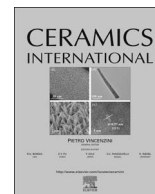




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Electrical and optical properties of hydrogen plasma treated molybdenum-doped indium oxide films synthesized by polymer-assisted deposition method

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ABSTRACT

In this paper, the effects of hydrogen (H₂) plasma treatment on the molybdenum (Mo)-doped indium oxide (InO) thin film that was formed on glass using the polymer-assisted deposition (PAD) process were investigated. The sheet resistance for the sample treated at the ICP power of 15 W was quenched to 167 Ω/sq. from the 680 Ω/sq. for the as-deposited sample. Compared with the as-deposited sample, both the mobility and the concentration of the sample treated at the 15 W ICP power were also increased simultaneously, resulting in an increased conductivity. From these results, it was concluded that the H₂ plasma treatment is an efficient method for the enhancement of the electrical property, as well as to remove nano-sized cracks on the surface of the PAD-Mo-doped InO without a deterioration of the optical transmittance.

1. Introduction

Transparent conductive oxides (TCOs) including the single and multilayer sandwiched structure have been investigated for transparency for the fabrication of solar cells, liquid crystal displays, and light emitting diodes (LEDs) [1]. The combination of physical properties, such as the high transparency and the high carrier concentration can be obtainable if the energy bandgap of materials is large with a high electrical conductivity. Among the other materials, the impurity-doped-InOs are potential materials, as they display a high conductivity with a wide bandgap. The representative materials are tin-doped InO (indium tin oxide, ITO) [2,3], gallium- and zinc-doped InO (IGZO) [4], tin- and zinc-doped InO (ITZO) [5], and molybdenum-doped InO (MIO) [6].

In particular, tin doping can effectively enhance the electron concentration of InO thin films with a sound transmittance in the visible light region and a high conductivity without a significant change of the physical properties in the visible light region [3]. However, the decreased transmittance in the near-infrared region relative to that of the visible region of ITO [7,8] remains a problem. Mo-doped InO (MIO) has a high mobility and a high transmission in the near infrared region [6], and it therefore shows a great potential for its use in infrared optoelectronic devices, such as nanocrystalline-silicon solar cells [9].

On the other hand, the synthesis of thin films using polymer assisted deposition (PAD) contains spin-coating that coated a solution including a compound of metal ion bound to a polymer [10] on the substrate. Proper polymers contain polyethyleneimine and polyacrylic acid. By changing the amount of polymer that is contained in the PAD solution, the viscosity of PAD solution can be adjusted to the requirement for a specific solution process, such as sol-gel, inkjet printing, or spin-coating. Additionally, the polymer can contribute to the uniform distribution of the metal ions in the solution and the formation of composite metal-oxide films without cracks. Similar to the other solution methods for the formation of thin films, PAD [11] is more economical than that of the semiconductor processing such as vacuum deposition methods [12]. Alternatively, lowering the processing temperatures is effective for attainment of high-quality films with a high optical transmittance and conductivity for the fabrication of printable and flexible optoelectronics. Therefore, the high-temperature annealing of PAD-grown MIO electrodes is not suitable. Previously, an H₂ plasma surface treatment at room temperature had been reported to increase the electrical conductivities of InO-based TCOs, including ITO [13] and IGZO [14] that had been deposited by sputtering, ITZO [15] that had been deposited by spin-coating, and Ti-doped InO that had been deposited by PAD [16] without a degradation of optical transparency.

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In this study, the enhanced optical and electrical properties of PAD-prepared Mo-doped InO thin films in terms of the H₂ plasma treatment at room temperature are reported.

2. Experimental

MIO thin films (130 nm ± 10 nm) were deposited on glass substrates using PAD. Indium nitrate hydrate (Sigma Aldrich) and ethylenediamine tetraacetic acid (EDTA; Sigma Aldrich) were dissolved in 40 ml of deionized water. This solution was mixed with the same amount of polyethyleneimine (PEI, Sigma Aldrich) to coordinate the anionic In-EDTA complex. Ammonium molybdate tetrahydrate (Sigma Aldrich) was used as a molybdenum dopant source. Both the In- and Mo-polymer solutions were filtered and concentrated using an Amicon filtration unit containing a membrane filter that is designed to pass materials with a molecular weight > 10,000g/mol. The Mo-polymer solution was supplemented to the In-polymer solution to maintain a Mo concentration of 2 at% in the entire mixed solution. The final solution was coated by a spinner on the glass substrate at a rate of 2000 rpm for 60 s. Before the spin coating, by using acetone, ethanol, and boiled isopropanol, the glass substrates were ultrasonically cleaned sequentially. The coated films were loaded in a tubular furnace under an oxygen (O₂) atmosphere. They were then heated gradually from a room temperature to optimized temperature at a rate of 2 °C/min and kept at that temperature for 1 h to decompose the polymer in the films. A detailed polymer-assisted deposition procedure is available in the literature [17].

After the deposition process, the samples were loaded in a home-made inductively coupled plasma (ICP) system with a 1.5 kW ICP power source and treated with H₂ plasma. The H₂ plasma treatment was conducted for 1 min at ICP source powers of 15, 100, 300, and 500 W under the operating pressure of 5.7 mTorr and H₂ flow rate of 85 standard cubic centimeters per minute (sccm).

The sheet resistance of the plasma-treated samples was measured using a four-point probe (FPP-RS8 (1G) 1 mΩ/sq by Dasol ENG). The conductivity, mobility, resistivity, and sheet-carrier concentrations were analyzed using the Hall effect measurement (HMS-2000 by ECOPIA) in a Van der Pauw configuration.

X-ray photoelectron spectroscopy (XPS, K-Alpha by Thermo Fisher Scientific Co. Ltd) that was equipped with an Al K_α X-ray source was used to analyze the surface compositional changes on the MIO films. The crystalline structure was analyzed by X-ray diffraction (XRD, X'Pert-PRO MPD by PANalytical B. V.) in θ–2θ geometry. Field emission scanning electron microscopy (FE-SEM, S-4800 by Hitachi) and ultraviolet-visible-infrared (UV–VIS–IR) spectroscopy (V-670 spectrophotometer by JASCO) were used to observe surface morphology and analyze the light transmission, respectively.

3. Results and discussion

Fig. 1 shows the sheet resistance and sheet carrier concentration of the MIO films as a function of the ICP power. The sheet resistance decreased significantly after the treatment at 15 W of ICP power, and then increased at the powers above 15 W (Fig. 1(a)). The as-deposited sample showed a sheet resistance of 680 Ω/sq; however, this sheet resistance was decreased rapidly to 167 Ω/sq when the sample was treated at the ICP source power of 15 W, which is comparable to that of the printed ITO films [18], indicating that the H₂ plasma treatment is an effective method. As the ICP power was increased above 15 W, the sheet resistance of the samples increased by 202 Ω/sq, 205 Ω/sq, and 208 Ω/sq for the samples treated at 100 W, 300 W, and 500 W, respectively, suggesting an optimal source power condition for plasma surface treatments.

Aside from the sheet resistance, the Hall mobility and the sheet-carrier concentration as functions of ICP power increment are also important factor in terms of their use as TCOs and are shown in

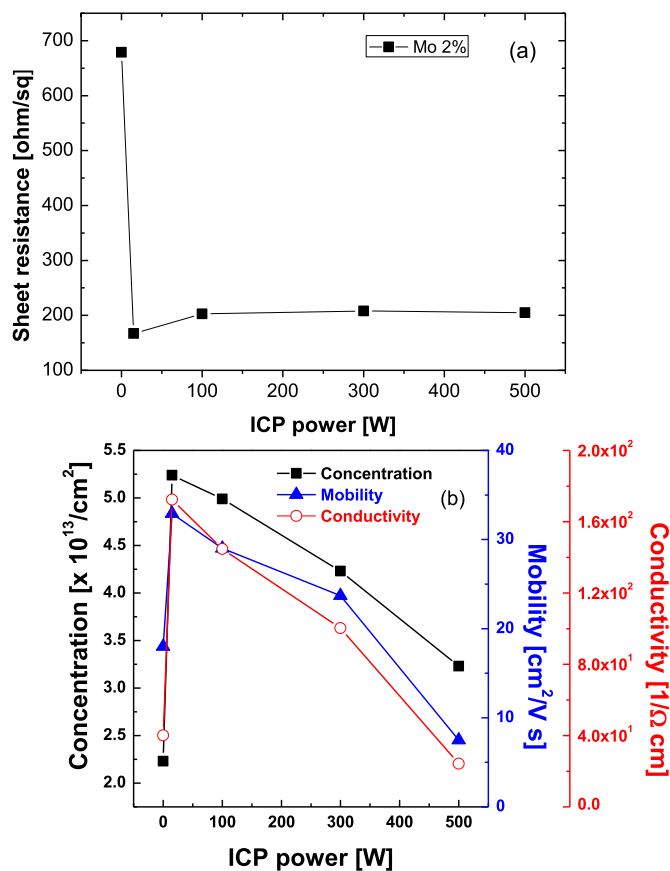


Fig. 1. (a) Sheet resistance and (b) carrier concentration, Hall mobility, and resistivity of H₂ plasma-treated PAD-MIO as a function of the ICP source power.

Fig. 1(b). The resistivity exhibited a similar tendency to that of the sheet resistance while the sheet-carrier concentration increased when the H₂ plasma was used to treat the sample surface. The decrease in the resistivity and sheet resistance of the MIO film when the samples were exposed to ICP powers up to 15 W, can be attributed to the simultaneous increase in the sheet concentration and the Hall mobility. Compared with the as-deposited sample, with a sheet concentration of $2.2 \times 10^{13}/\text{cm}^2$ and a Hall mobility of 18.0 $\text{cm}^2/\text{V s}$, the MIO film that had been treated with an ICP power of 15 W showed a sheet carrier concentration of $5.2 \times 10^{13}/\text{cm}^2$ and a Hall mobility of 32.9 $\text{cm}^2/\text{V s}$. Hydrogen can make a shallow donor level in the band gap of a ZnO film [19] and can penetrate the films from the H₂ plasma stream; therefore the H₂ plasma-treated MIO films showed higher mobilities and carrier concentrations, which correspond to the previous studies [13–16]. It is well known that the electron concentration could be increased due to the oxygen vacancies. When O atom is lost from the oxide lattice, a doubly charged oxygen vacancy and two free electrons are created [20]. Also, the mobility of the TCO films depends on the carrier concentration, since the carrier transport is governed by the percolation conduction over the trap states and is enhanced at the high carrier concentrations through the filling of the trap states [4]. Therefore, the increase in the carrier mobility of the sample that was treated at 15 W of ICP power can be attributed to the increase in oxygen vacancies. Furthermore, the rapid increase in the conductivity of the MIO film that was treated at 15 W of ICP power could be attributed to the simultaneous increase in the carrier mobility and the concentration. Alternatively, the entire degradation of the electronic properties that are observed in the film, when the samples were exposed to plasma powers over 15 W, is due to the surface damage and/or the surface structural changes from the chemical reaction between the hydrogen and the surface oxygen atoms.

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