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Band engineered Al-rich InAlN thin films as a promising photoanode for hydrogen generation from solar water splitting

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ABSTRACT

In this study, Al-rich InAlN thin films were grown at different substrate temperatures (T_s) by plasma-assisted dual source reactive evaporation and effects of the parameter on indium incorporation, morphology, structural and optical properties of the alloys were investigated. It was shown that indium content of the films increases at higher substrate temperature and the bandgap is decreased from 3.54 to 2.76 eV as T_s increases from 150° to 400 °C, respectively. The photoelectrochemical (PEC) activity of the deposited films targeted for solar water splitting application was examined in the presence of simulated solar irradiation of AM 1.5 G (100 mW/cm2). The PEC measurements revealed a massive improvement in the photocurrent density for the InAlN sample deposited at T_s = 400 °C compared with the films grown at 150 °C. From the Mott-Schottky (MS) plots it was concluded that by increasing T_s up to 400 °C, charge transport during PEC process could be facilitated. It was shown that Al-rich InAlN with selected band gap and band alignments could be a potential candidate for PEC water splitting.

1. Introduction

Group III-nitride materials have been identified as efficient semiconductor photoelectrodes in electrolysis (photoelectrolysis) of water to supply clean and renewable hydrogen energy [1–4]. This is due to the fact that the bandgap of III-nitride compounds can be adjusted across the entire solar spectrum and, more importantly, the valence and conduction bands of the semiconductors can be aligned close to the water redox potentials which is a crucial prerequisite for efficient charge transfer between photoelectrode and water-based electrolyte. Moreover, the inherent chemical stability of III-nitride semiconductors against corrosion in aqueous solutions further demands their use as a promising photocatalyst [5]. Recently, InGaN with the tunable bandgap of 0.7 − 3.4 eV has been extensively reported as an excellent visible-light responsive photocatalyst. Gopalakrishnan *et al.* achieved photocurrent density of ~32 mA/cm^2 at 1.0 V against Pt counter electrode for the InGaN nanowires [6]. A 3D epitaxial GaN-InGaN core − shell rod array with indium content of 30% was synthesized by Caccamo *et al.* [3] for enhanced visible light driven water splitting. Ganesh *et al.* [7] observed that the photocurrent density of monolithic InGaN/GaN multi-quantum well structures depends on indium content and the photocurrent density increases with increase of indium concentration.

However, very little studies has been devoted so far to photoelectrochemical (PEC) properties of InAlN for water splitting. Depending on the indium (or aluminum) content in the structure of the trinary alloy, the bandgap of InAlN can be widely tuned from 0.7 to 6.2 eV [8] which covers a large portion of the solar light. In addition, it has been theoretically shown that valence and conduction bands of InAlN in Al-rich regime appropriately straddle the H^+/H_2 and O_2/H_2O redox potentials [9]. Hence, the tunable bandgap energy and band alignments of InAlN in the range that meets water splitting requirement, enable the alloy to be a potential candidate for production of H_2 fuel via PEC water splitting technique.

Here, Al-rich InAlN thin films were successfully grown by plasma-assisted dual-source reactive evaporation method and the effect of substrate temperature on the structural, compositional, morphological and optical properties of the as-grown films was studied. We investigate PEC behavior of the samples and the corresponding potential for H_2

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generation via water splitting under simulated sun illumination.

2. Experimental methods

InAlN thin films were prepared on Si(111) and quartz (for optical measurements) substrates by a home-built plasma-assisted dual source reactive evaporation system which was introduced in our previous work [10]. The Si and quartz substrates were separately cleaned, prior the deposition, using different cleaning procedures as described elsewhere [10,11]. Prior to actual deposition, the substrate surface was bombarded by hydrogen plasma (RF power 15 w) for 10 min and at a fixed hydrogen flow rate of 100 sccm to activate the surface bonds. The deposition process was carried out in three steps: (1) purified nitrogen gas (99.99999%) with the flow rate of 60 sccm was introduced in the camber and N_2 plasma (RF power: 200 W) was generated and stabilized for 5 min (2) the first filament (filament to substrate distance: 1 cm) that holds Al wire was heated to 1650 °C and then immediately cooled down to 1450 °C to decrease evaporation rate. (3) The second filament (filament to substrate distance: 1.5 cm) that holds In wire was promptly heated to around 1000 °C and the growth of InAlN films was conducted under N_2 plasma and by evaporating of Al and In wires for 5 min. Finally, the second filament was switched off, the first one was cooled down to 1300 °C and the prepared samples were in-situ annealed for 30 min under N_2 plasma (RF power: 50 W). The substrate temperature (T_s) during the deposition process was varied as the growth parameter in this work and the experiments were carried out at different substrate temperature of 150, 200, 250, 300, 350 and 400 °C.

The Raman spectra of the grown InAlN films were recorded by Renishaw inVia Raman Microscope using a laser excitation wavelength of 514 nm. The structural properties of the films were investigated by X-ray diffraction (XRD), PANalytical Empyrean X-ray diffractometer, Cu K_α X-ray radiation $\lambda = 1.54060$ Å. The surface morphology and elemental composition of the prepared samples were examined by a Hitachi SU 8000 scanning electron microscope and an energy-dispersive X-ray spectroscopy (EDX) accessory of BrukerXFlash6|100 attached to the microscope. The bonding configuration of the samples was investigated by X-ray photoelectron spectroscopy (XPS, PHI Quantera II). The thickness of the grown thin films was measured using a surface profiler (KLA-Tencor). An UV–vis spectrophotometer (Lambda 750, PerkinElmer) was employed to measure the optical transmittance and reflectance of the InAlN/quartz thin films.

Contact was made by depositing Al electrodes on top of the films and on the bottom of Si substrate using the thermal evaporation method. The PEC study of the InAlN thin films was conducted on a PAR-VersaSTAT 3 electrochemical work station using a conventional three-electrode system. The thin films were employed as the working electrode whereas Pt and Ag/AgCl were used as counter and reference electrode, respectively. Phosphate buffer solution (PBS, 0.1 M) with a pH of 7.2 was used as the electrolyte. Before illumination, N-gas was purged for 30 min. A 150-W Xenon arc lamp (Newport, Model 69907) containing a simulated AM 1.5 G filter was employed as the light source for all the experiments.

3. Results and discussion

The Raman spectra of the InAlN thin films grown at different substrate temperatures are shown in Fig. 1(a). It has been reported in the literatures that the A_1(LO) phonon modes of AlN and InN are located at 890 [12] and 586 cm^{-1} [13], respectively. The Raman peak of the sample deposited at 150 °C is observed at 868 cm^{-1} which is assigned to A_1(LO) phonon mode of Al-rich InAlN [14]. By increasing the substrate temperature, the peak is blue-shifted to 858, 846, 843, 834 and 827 cm^{-1} for samples grown at T_s = 200, 250, 300, 350 and 400 °C, respectively. This shows that when the substrate is heated, the In content of the Al-rich InAlN films is increased. Besides, it is obviously seen that Raman features of all films are very broad which could be due

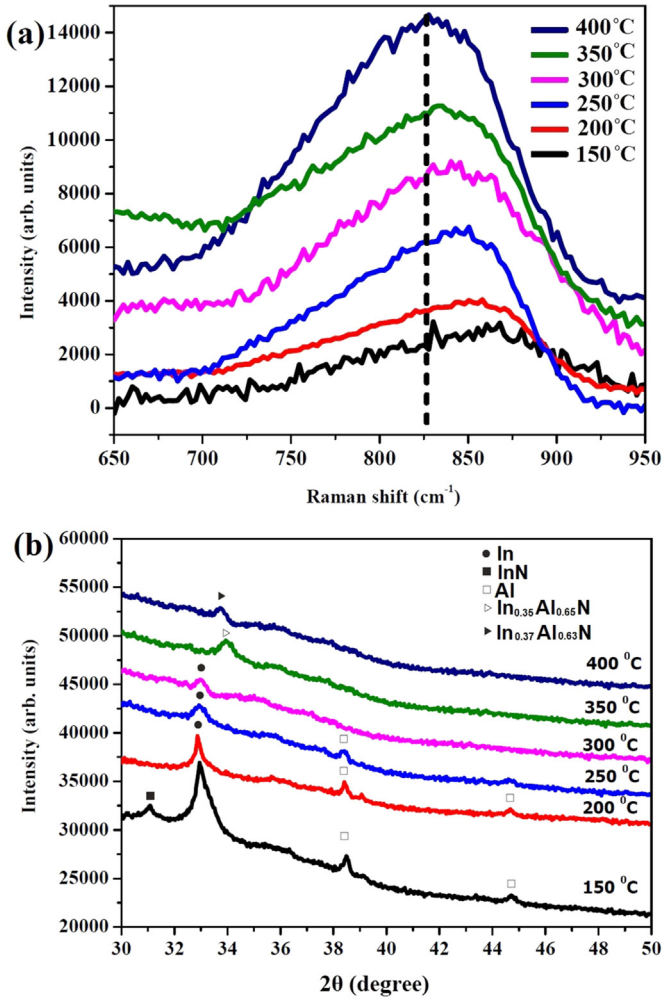

Fig. 1. (a) Raman spectra and (b) XRD pattern of the InAlN thin films deposited at different substrate temperatures.

to large AlN-InN lattice mismatch and unstable nature of Al-rich InAlN thin films [15]. However, Raman results show that at higher substrate temperature the intensity of A_1(LO) is increased and, hence, the structural properties of the films improves.

Fig. 1(b) shows XRD spectra of InAlN films grown at various T_s. The spectra of the films deposited at T_s = 150, 200, 250 and 300 °C show no diffraction peaks assigned to crystalline InAlN. Phases of crystalline Al and In grains are observed from XRD patterns of the InAlN films grown at the substrate temperatures of 150, 200, 250 and 300 °C. Besides, the XRD spectrum of the films grown at T_s = 150 °C presents a diffraction peak corresponding to InN which shows that phase separation occurs at the lowest substrate temperature of 150 °C. The XRD spectra of the InAlN samples deposited at substrate temperatures of 350 and 400 °C show peaks at 2θ = 33.9° and 33.8°, respectively, which are assigned to (002) plane of wurtzite $In_{0.35}Al_{0.65}N$ and $In_{0.37}Al_{0.63}N$ based on Vegard's law:

$$c_{In_xAl_{1-x}N} = xc_{InN} + (1-x)c_{AlN}, \quad (1)$$

where $c_{InN} = 5.793\text{Å}$ and $c_{AlN} = 5.012\text{Å}$ are the c lattice constants of crystalline InN and AlN, respectively [16]. This obviously confirms that Al-rich InAlN films have been grown and the In content of the films increases as the substrate temperature is increased.

The field emission scanning electron microscope (FESEM) images of the Al-rich InAlN samples are depicted in Fig. 2(a-f). It is clearly seen that the morphology of the samples strongly depends on substrate temperature. Surface morphology of the films grown at T_s = 150 °C