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Characterization of low-temperature solution-processed indium–zinc oxide semiconductor thin films by KrF excimer laser annealing

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Abstract

We have employed KrF excimer laser annealing (ELA) treatment on sol–gel derived indium–zinc oxide (IZO) precursor films to develop a method of low thermal-budget processing. As-coated IZO sol–gel film was dried at 150 °C and then annealed using KrF excimer laser irradiation under ambient air. The laser irradiation energy density was adjusted to 150, 250, 350, and 450 mJ/cm^2 to investigate the effects of laser irradiation energy density on the microstructure, surface morphology, optical transmittance, and electrical properties of laser annealed IZO thin films. Results of GIXRD and TEM-SAED indicated that the ELA IZO thin films had an amorphous phase structure. The surface characteristics and electrical properties of laser annealed IZO thin films were significantly affected by the laser irradiation energy density. It was found that the dried IZO sol–gel films irradiated with a laser energy density of 350 mJ/cm^2 exhibited the flattest surface, the highest average optical transmittance in the visible region, and the best electrical properties among all ELA samples.

Keywords: A. Films; A. Sol–gel processes; C. Electrical properties; E. Functional applications

1. Introduction

Oxide-based semiconductor thin films have been used for thin-film transistors (TFTs), ring oscillators, thin-film solar cells, nonvolatile memories, ultraviolet (UV) detectors, gas sensors, etc. Most studies continue to focus on the development of active channel materials for the driving elements of high resolution active-matrix flat-panel displays (AMFPDs) [1,2]. In particular, multicomponent oxide semiconductor thin films are widely recognized as suitable channel layer materials for TFTs [3–5]. Both indium–zinc oxide (IZO) and zinc–tin oxide (ZTO) are commonly investigated as the basic compositions in studies on improving the performance of TFTs by substituting charge-controlling cations and by adjusting different process parameters; however, IZO-based TFTs exhibit a higher field-effect mobility than ZTO-based TFTs [6,7].

Solution-process thin film deposition methods, such as spin coating and slit-coating, could provide the advantages of simple equipment, easy composition adjustments, high throughput, and low-cost manufacturing as compared to vacuum deposition methods such as rf magnetron sputtering and pulsed laser deposition [8,9]. In addition, solution-processes such as roll-to-roll coating and ink-jet printing offer the possibility of selective area deposition and direct patternability without the need for photolithography [10]. Although solution-processes are promising candidates for fabricating low-coat and high performance optoelectronic devices, subsequent heat treatment at a relatively high temperature ($\geq$ 300 °C) is needed to remove organics and hydroxyl groups in the precursor solutions of metal oxide semiconductors, as well as to improve the densification and electrical properties, thus restricting their applicability to larger-areas and the flexibility of application [7,11,12].

Recently, excimer laser irradiation and ultraviolet (UV) light irradiation techniques have been utilized to densify and modify sol–gel derived oxide semiconductor thin films at a low temperature as an alternative to conventional heat-treatment [13–16]. Excimer laser annealing (ELA) treatment was developed for

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preparing of low-temperature solution processed oxide thin films because excimer laser beams, which have extremely short pulse widths, can selectively increase the temperature of the sol–gel derived precursor films, and because most of the laser energy is absorbed in the films, causing densification of the precursor films (thermal influence) [14,17,18]. In addition, excimer laser irradiation is expected to have a direct photo-induced influence, which leads to rapid densification of the precursor films without the substrate being affected [15]. ELA treatment allows low thermal-budget processing and heating confinement near the surface region of the oxide films with negligible thermal damage to the substrate [19]. Therefore, solution-processed oxide semiconductor thin films employing ELA treatment may be suitable for application in the active matrix backplanes of flexible displays.

In this study, we discuss a method that can be used to obtain transparent IZO semiconductor thin films from sol–gel derived IZO precursor films on alkali-free glass substrates using KrF excimer laser annealing. We also report how changes in the energy density of excimer laser irradiation affect the microstructure, surface morphology, visible optical transmission, and electrical properties of the ELA IZO films.

2. Experimental

A 0.3 M metal acetate precursor solution of InZnO (IZO) was synthesized by dissolving indium acetatehydrate [$In(OAc)_3 \cdot xH_2O$] and zinc acetate dihydrate [$Zn(OAc)_2 \cdot 2H_2O$] in 2-methoxyethanol (2-ME) solvent, and then diethanolamine (DEA) and acetylacetone (Acac) were added to the mixed solution as sol-stabilizers for long-term solution stability. The molar ratio of In:Zn was maintained at 2:3, and the molar ratio of metal ions:DEA:Acac was determined to be 1:4:4. The resultant solution was stirred at 60 °C for 24 h to promote the dissolving process. After a clear and transparent solution was obtained, the as-synthesized solution was aged for 1 week before being used as the coating solution. The IZO sol–gel films were deposited onto pre-cleaned alkali-free glass (NEG OA-10, 0.7 mm thick) by spin coating at 500 rpm for 10 s and 1000 rpm for 30 s, after which they were immediately dried in a box-type oven at 150 °C for 20 min under ambient air to solidify the IZO films. After four cycles of the spin coating and drying procedures, the dried sol–gel films were annealed by excimer laser irradiation treatment at room temperature in an atmospheric environment by setting the glass/dried sol–gel film sample on a stage. The top surfaces of the dried sol–gel films were irradiation by KrF excimer laser with a wavelength of 248 nm using a Lambda Physik Compex 301F laser source. The laser beam was modified to a rectangular shape ($1.0 \times 30\ mm^2$), and the laser irradiation energy density was adjusted from 150 to 450 mJ/cm^2 (step = 100 mJ/cm^2). The experimental setup for the KrF excimer laser annealing process is presented in Fig. 1. The number of impinging shots was kept at 15, and the frequency of the laser shots was fixed at 7 Hz.

The structure of the ELA IZO thin films was identified by grazing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM, JEOL JEM-2010). The diffraction

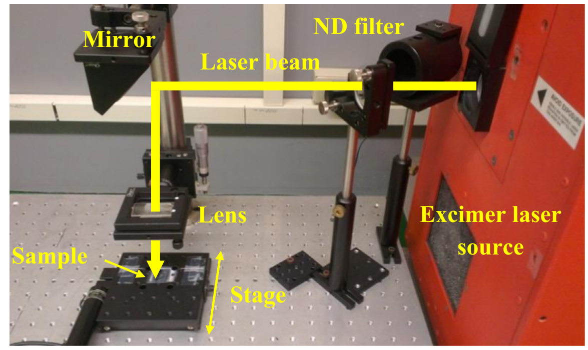

Fig. 1. Photograph of experimental setup used for KrF excimer laser annealing of sol–gel derived IZO precursor films.

spectra were examined with a Bruker D8 SSS X-ray diffractometer using CuKα radiation ($\lambda = 1.5406$ Å) with a grazing incidence angle of 0.8°. Cross-sectional micrographs of IZO thin films were acquired using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM), and the elemental composition was verified by energy dispersive X-ray spectrometry (EDS). The thickness of the dried IZO sol–gel film was measured using an alpha-step surface profile (KLA Tencor AS500); the thicknesses of ELA thin film samples were evaluated from cross-sectional SEM images. The surface morphology of the IZO thin films was characterized by scanning probe microscopy (SPM, Digital Instrument NS4/D3100CL/MultiMode) in tapping mode. Optical transmissions of the dried sol–gel film, glass, and glass/thin film samples were recorded by a Hitachi U-2900 UV–vis spectrophotometer. The electrical properties of each IZO thin film were measured by an Ecopia HMS-3000 Hall effect measurement system using the van der Pauw configuration with a magnetic field of 0.5 T at room temperature.

3. Results and discussion

The maximum processing temperature of solution-processed oxide semiconductor thin films may be lowered to 150 °C. Such thin films will be compatible with flexible polymeric substrates used in flexible optoelectronic and electronic devices [20]. Our previous report found that the organic compounds in the IZO-based sol were completely removed when the heating temperature exceeded 450 °C [21]. Heating the as-coated IZO-based sol–gel film to 150 °C can evaporate solvents with a low boiling point, vaporize water, and decompose some of the stabilizing agents, while as the same time solidifying as-coated sol–gel film. Tsang et al. reported that baking obviously enhanced the excimer laser energy absorption of sol–gel derived ZnO-based precursor films [15]. Thus, in this study, the authors chose a drying temperature of 150 °C for the as-coated IZO sol–gel films.

A comparison of the variation of absorption coefficients with wavelength for the dried IZO sol–gel film and the alkali-free glass in the ultraviolet (UV) light range is presented in Fig. 2. Film thickness, as measured using the α-step surface