Materials Science in Semiconductor Processing 71 (2017) 441–446

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Ultraviolet-assisted annealing for low-temperature solution-processed p-type gallium tin oxide (GTO) transparent semiconductor thin films

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ARTICLE INFO

Keywords:
P-type oxide semiconductor
Gallium tin oxide
Sol-gel spin coating
UV light irradiation
Electrical properties

ABSTRACT

Solution-processed p-type gallium tin oxide (GTO) transparent semiconductor thin films were prepared at a low temperature of 300 °C using ultraviolet (UV)-assisted annealing instead of conventional high-temperature annealing (> 500 °C). We report the effects of UV irradiation time on the structural, optical, and electrical properties of sol-gel derived GTO thin films and a comparison study of the physical properties of UV-assisted annealed (UVA) and conventional thermally annealed (CTA) GTO thin films. The Ga doping content was fixed at 15 at% in the precursor solution ([Ga]/[Sn] + [Ga] = 15%). After a spin-coating and preheating procedure was performed two times, the dried sol-gel films were heated on a hotplate at 300 °C under UV light irradiation for 1–4 h. Each UVA GTO thin film had a dense microstructure and flat free surface and exhibited an average optical transmittance approaching 85.0%. The level of crystallinity, crystallite size, and hole concentration density of the GTO thin films increased with increasing UV irradiation time. In this study, the UVA 4 h thin film samples exhibited the highest hole concentration (9.87×10^{17} cm^{-3}) and the lowest resistivity (1.8 Ω cm) and had a hole mobility of 5.1 cm^2/Vs.

1. Introduction

Metal oxide (MO) semiconductors have drawn significant attention in the fields of flat panel displays, photovoltaic cells, smart sensors, and transparent electronics during last decade, owing to their high carrier mobility, optical transparency, photoactive characterization, mechanical stress tolerance, and good environmental stability compared with crystalline silicon and III-V semiconductors [1–3]. The most developed and utilized MO semiconductors are n-type conductivity. To date, few p-type MO semiconductors have been reported due to localized O 2*p*-dominated valence band (VB) and high density of deep traps near the VB [3]. The development of p-type MO semiconductors with good physical properties could be enabled optoelectronic devices that are more power efficiency and greater circuit complexity [4].

The solution-based approach is recognized as a cost-effective MO thin film deposition technique, which is used for optoelectronic devices and thin-film transistors (TFTs) fabrication, afford large-area deposition, easy make of multicomponent materials, easy control of chemical composition ratios [2,5]. However, the annealing temperature for solution-based MO thin films above 400 °C typically requires for precursor-to-metal oxide conversion, decomposing and removing residual organics, and obtaining reasonable film quality and properties [6,7], which is incompatible with flexible plastic substrates and risk complications for stacked multi-layer structures such as stress and/or crack induced by thermal expansion coefficient mismatch between layers [7,8].

If alternative energy to heat such as microwave, laser, and UV light can be used to effectively remove organic components via break or cleavage of alkoxy groups and form dense MO thin films through activating metal and oxygen atoms to facilitate metal-oxygen-metal (M–O–M) bonds and network formation, the process temperatures will be lowered [9,10]. A UV-assisted annealing process for functional MO thin film fabrication, which combined sol-gel method and UV irradiation technique, is an effective method for preparing MO thin films at a low temperature than the conventional thermal annealing process does [11]. Such a process also was demonstrated to improve the physical properties of MO thin films and to make the fine patterning of MO thin films [12]. UV-assisted annealing of MO precursor films, as developed earlier for dielectric and ferroelectric MO thin films [11,13–15], and recently as introduced for MO semiconductor thin films, gas sensors, and TFTs [6,9,10,16]. For example, Park et al. reported the UV-light annealed indium zinc oxide (IZO) TFTs had a field-effect mobility of 2.4 cm^2/Vs, which is comparable to a device performance of 2.7 cm^2/Vs obtained through thermal annealing [17]. Jo et al. presented that photo-annealed solution-processed indium-gallium-zinc oxide (IGZO) TFTs showed much-reduced threshold voltage (V_T) shift and more

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http://dx.doi.org/10.1016/j.mssp.2017.09.008
Received 12 July 2017; Received in revised form 3 September 2017; Accepted 7 September 2017

immediate V_T recovery as compared to thermally annealed TFTs [18]. Hwang et al. utilized a UV photo-annealing process to fabricate sol-gel zinc tin oxide (ZTO) TFTs at a low temperature of 250 °C [19]. They proposed a combined UV irradiation and vacuum annealing improved electrical performance of the ZTO TFTs with the mobility of 2 cm^2/Vs. Leppäniemi et al. showed that amorphous IZO thin films annealed at 250 °C with UV irradiation yield enhancement-mode TFFs with saturation mobility of 1 cm^2/Vs [20].

The reports based on UV-assisted annealing almost focused in the development of n-type MO semiconductor thin films and devices. SnO_2 is an n-type semiconductor and a wide bandgap of 3.6–4.0 eV [21,22]. Recently, p-type SnO_2-based thin films were prepared using a lower valence cation as acceptor dopant (e.g. Al, Ga, In, Sb, and Li), which produces a hole and increases the hole concentration density [23,24]. Yang et al. reported that p-type transparent conducting Ga-doped SnO_2 (GTO) thin films were grown using reactive rf magnetron sputtering and applied to transparent p-n homojunction diode [25]. Mao et al. also reported structural, electrical, and optical properties of p-type GTO thin films synthesized by spray pyrolysis [24]. Our previous work reported that the conductivity type of Ga-doped SnO_2 (GTO) thin films changed from n-type to p-type, which occurred at 10% Ga doping content and when the Ga doping level was 15%, the GTO thin films exhibited the highest hole concentration density of 1.70×10^{18} cm^{-3} [26]. In this study, we introduce the UV-assisted annealing process for preparing the p-type GTO semiconductor thin films at a low thermal budget. The effects of UV irradiation time are evaluated from the structural features, optical and electrical properties of the annealed GTO gel films. In addition, comparison of physical properties of GTO semiconductor thin films prepared by UV-assisted annealing (UVA) and conventional thermal annealing (CTA) is also reported in this paper.

2. Experimental procedure

P-type gallium-doped tin oxide (GTO) thin films with 15 at% Ga doping content were prepared on pre-cleaned alkali-free glass substrates (Asahi Glass AN-100, with a thickness of 0.5 mm) by the sol-gel spin-coating process. A precursor solution was synthesized by dissolving tin (II) chloride dehydrate and gallium (III) nitrate hydrate in 2-methoxyethanol (2-ME) solvent, and then a stabilizer of monoethanolamine (MEA) was added to the blended solution. The concentration of metal ions in the resultant solution was 0.5 M; the molar ratio of MEA to metal ions was 0.3. The synthesis procedure of the coating solution was described in our previous paper [26]. The spin coating was carried out at 3000 rpm for 30 s, followed by heating at 300 °C for 10 min to evaporate the solvent, water, and organic compounds before the next layer was deposited. To obtain the desired film thickness (> 100 nm), the spin coating and drying procedures were performed two times for the CTA and UVA processes, respectively. The dried GTO sol-gel films were cured with two different annealing processes. One was conventional thermal annealing (CTA), in which the dried sol-gel films were annealed in oxygen ambient at 520 °C for 1 h in a quartz tube furnace. The other was ultraviolet-assisted annealing (UVA), in which the dried sol-gel films were cured on a pre-heated ceramic hot plate at 300 °C under UV irradiation for 1–4 h using UVC lamps with a peak intensity of 253.7 nm. The power density of the UV irradiation was approximately 4.5 mW/cm^2.

The crystal structures of the as-prepared GTO thin films were studied with an X-ray diffractometer (XRD, Bruker D8 SSS) with Cu Kα radiation. Morphology and surface features of the GTO thin films were examined by scanning probe microscopy (SPM, Digital Instrument NS4/D3100CL/MultiMode) in the tapping mode. Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was utilized to examine the microstructures of the films. The optical transmittance of the glass/GTO thin film samples was recorded in the wavelength range of 200–1000 nm using a Hitachi U-2900 ultraviolet-visible (UV–Vis) spectrophotometer. A Hall measurement system (Ecopia HMS-3000) was used to measure the electrical properties using the van der Pauw configuration at room temperature. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 VersaProbe) was performed to determine the chemical compositions and bonding states of elements of the GTO thin films.

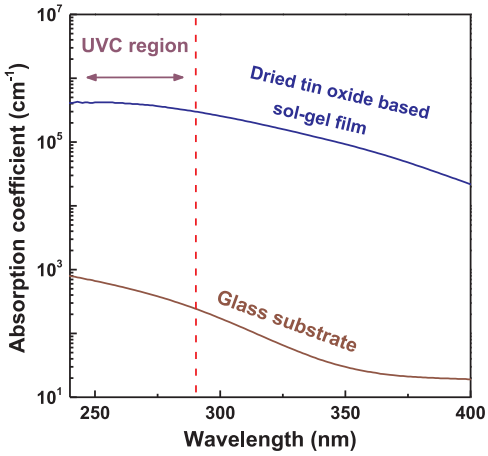

Fig. 1. Comparison of absorption coefficient spectra of the dried tin oxide based sol-gel film and the alkali-free glass in the ultraviolet (UV) wavelength region.

3. Results and discussion

Fig. 1 shows the absorption coefficient spectra of the dried tin oxide based sol-gel film and the alkali-free glass (Asahi Glass AN-100) in the UV region, obtained from the corresponding optical transmittance spectrum. The absorption coefficient (α) is defined as $\alpha = (1/t) \ln (1/T)$, where t is the thickness of the measured sample and T is the optical transmittance. The thickness of the dried tin oxide based sol-gel film was about 130 nm, evaluated with an α-step surface profile meter, and the thickness of the glass was 500 μm. It clearly shows that the absorption coefficient decreased with increasing measured wavelength, and the magnitude of the absorption coefficient of the dried MO sol-gel film was much higher than that of glass in the whole measured region. In addition, the absorption coefficient of the dried sol-gel film was 4.19×10^5 cm^{-1} at a wavelength of 254 nm, which is approaching three orders of magnitude higher than that of the glass substrate (6.16×10^2 cm^{-1}). Therefore, it may be concluded that most of the short-wavelength ultraviolet (UVC) light energy was absorbed in the dried tin oxide based sol-gel film and selectively increased the temperature of the MO gel film, which is essential for the development of a process with a low thermal budget.

Previous studies utilized low-temperature fabrication to produce solution-processed functional MO thin films by combining the sol-gel method and UV irradiation [19,20,27]. This approach was adopted mainly owing to photo energy induced photochemical activation, which results in the dissociation of alkyl group-O bonds and easy elimination of organic compounds from the gel films, as well as the efficient conversion and formation of M–O–M bonds at low temperature [15]. Kim et al. discovered that near-complete condensation and densification of MO films require both UV photo-activation and moderate heating [9]. Park et al. demonstrated that a sufficient amount of heat should be maintained to evaporate organics during the UV irradiation procedure because the condensation of the MO gel films is accompanied by volatile organic residues [17].

XRD patterns of the conventional thermally annealed (CTA) thin film and dried sol-gel films annealed by UV-assisted annealing (UVA) for different times are presented in Fig. 2. The intensity of the diffraction peaks was enhanced with increasing UV irradiation time due to increased atomic diffusion, lead to an improved degree of crystallization. In addition, the three diffraction peaks corresponded with the