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Effect of hydrogen doping on the properties of Al and F co-doped ZnO films for thin film silicon solar cell applications

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ABSTRACT

Aluminum and fluorine co-doped zinc oxide (AFZO) thin films were prepared in Ar + H_2 atmospheres by rf magnetron sputtering at room temperature. The structural, electrical, and optical properties of the prepared films were investigated using X-ray diffraction, scanning electron microscopy, atomic force microscopy, Hall-effect measurement, X-ray photoelectron spectroscopy, and ultraviolet–visible spectrometry, and their dependence on deposition atmosphere (i.e. H_2 / (H_2 + Ar) ratio) was studied. The resulting films showed a (0 0 2) diffraction peak, indicating a typical wurtzite structure, and the optimal film crystallinity was obtained with the H_2 / (H_2 + Ar) ratio of 3%. The electrical resistivity of AFZO films decreased to 9.16×10^{-4} Ω-cm, which was lower than ZnO:Al and ZnO:F films due to double doping effect of Al and F. The resistivity further decreased to below 5×10^{-4} Ω-cm for the AFZO film with the H_2 / (H_2 + Ar) ratio of 3%–5%. All the films regardless of hydrogen content displayed high transmittances (>92%) in the visible wavelength range. Applying the developed AFZO films as front transparent electrodes, amorphous Si thin film solar cells were fabricated and the open-circuit voltage, fill factor, and efficiency of the cell with the hydrogenated AFZO film were improved in contrast to those without the hydrogenated film.

1. Introduction

Transparent conducting oxide films are indispensable materials in optoelectronic industry for application such as solar cells, flat panel displays, light-emitting diodes, electrochromic windows and low thermal emissivity windows [1–5]. Impurity-doped ZnO thin films have attracted considerable attention as transparent conducting oxide (TCO) thin films due to their superior electrical and optical properties in combination with the low material cost and non-toxicity as compared to tin-doped indium oxide (ITO) films [6–10]. Moreover, high electrical and optical stability under hydrogen plasma promoted ZnO thin films as front electrodes in silicon thin film solar cells.

Many cationic dopants such as boron [6], aluminum [7,8], gallium [9,10], indium and titanium [11] have been studied to substitute for Zn to improve the conductivity of n-type ZnO films. Among these dopants, Al-doped ZnO (AZO) thin films have been widely studied as a substitute for ITO films due to low cost and superior stability under hydrogen plasma [12]. Our previous study shows that the resistivity of the sputtered AZO thin film is below 2×10^{-3} Ω-cm, which is remarkably lower than undoped ZnO films with a typical resistivity of 1–100 Ω-cm [13]. Besides, fluorine has attracted attention because it can substitute for oxygen as an anionic dopant in the ZnO atomic structure to provide an extra conducting electron. The ionic radius of fluorine (0.131 nm) is close to that of oxygen (0.138 nm), thus resulting in less lattice distortion in ZnO crystal structure [14,15]. Gordon et al. reported that the substitution of oxygen ions by fluorine ions would perturb the valence band, thereby leaving the conduction band relatively free from scattering, which could enhance carrier mobility and reduce light absorption [16]. Furthermore, there has been particular interest in the role of hydrogen in ZnO because density function theory and total energy calculations suggest that hydrogen should be a shallow donor for improvement of conductivity of ZnO-based films [17–19].

Several methods such as sol–gel [20–22], spray deposition [23], and magnetron sputtering [24–26] had been proposed to prepare the Al and F co-doped ZnO (AFZO) thin films. Among these methods, magnetron sputtering is the most commonly used technique due to high deposition rate at low temperature, high film uniformity, and large area films with strong adhesion. Kim et al. prepared AFZO films by magnetron sputtering of a ZnO:Al_2O_3 target at substrate temperature of 150 °C with Ar/CF_4/H_2 gas mixtures, and annealed in vacuum at 300 °C [24]. They reported that the lowest resistivity of the as-deposited/vacuum-annealed films was about $3.9–4 \times 10^{-4}$/2.9×10^{-4} Ω-cm. Kim et al. used two ceramic targets, i.e. ZnO:Al_2O_3 (3 wt%) and ZnO:ZnF_2 (0–10 wt%), to co-sputter AFZO films with varying fluorine contents to investigate doping effects of fluorine on properties of the films [25]. Their results indicated that the small amount of F addition to AZO films resulted in an improved electrical conductivity by enhancing Hall mobility, and the minimum resistivity was as low as 5.9×10^{-4} Ω-cm.

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In this paper, we use a single ceramic ZnO target containing Al_2O_3 (1 wt%) and ZnF_2 (1.5 wt%) to fabricate hydrogenated AFZO thin films by rf-magnetron sputtering in Ar + H_2 atmospheres at room temperature. The structural, optical, and electrical properties of hydrogenated AFZO thin films are investigated with various H_2 flow rates. The superstrate p-i-n amorphous Si (α-Si) thin film solar cells using the AFZO thin films as the front transparent electrodes are developed and their current–voltage characteristics are measured.

2. Experimental details

The ZnO powder (99.999%), Al_2O_3 powder (99.999%) and ZnF_2 powder (99.995%) were mixed with the ratio of 97.5 wt%, 1.0 wt%, and 1.5 wt%, respectively, and then ball milled for 24 h in alcohol. After being dried and ground, the powders were uniaxially pressed into pellets of 3 mm thickness and 52 mm diameter. The pressed targets were sintered at 1060 °C for 3 h to prepare the ceramic target for sputtering. Glass substrates (Corning Eagle XG) were cleaned ultrasonically with isopropyl alcohol (IPA) and deionized (DI) water, and then dried under a blown nitrogen gas. AFZO films of approximately 330 nm were deposited on glass substrates by using an rf-magnetron sputtering system at an rf power of 80 W at room temperature. The working distance from the target to substrates is 8 cm. Ar or Ar + H_2 were introduced into the chamber and the working pressure was controlled at 0.667 Pa (5 mTorr) with the different H_2 / (H_2 + Ar) ratios of 0–10%. During sputtering, the substrate holder was spun at 10 rpm for a better film uniformity.

The structure of the films was analyzed by X-ray diffraction (XRD) (PANalytical) with Cu-Kα radiation (λ = 1.54056 Å, θ–2θ scan mode). The electrical resistivity, Hall mobility, and carrier concentration were determined by Hall-effect measurement (Ecopia, HMS-300) using the Van der Pauw method. The morphology of AFZO films was observed using a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700F) and an atomic force microscope (AFM) (Veeco, D3100). The optical transmittance was obtained by a UV–visible spectrophotometer (JASCO, V–570). X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, PHI 5000 Versaprobe) characterization was made after surface pre-cleaning for 30 s. The pre-cleaning of the samples used Ar^+ ion sputtering with an operation voltage of 2 kV and a sputtering rate of 12.5 nm/min in SiO_2. Wide-scan spectra in the 0–1100 eV kinetic energy range were recorded in 1 eV steps. Detailed spectra of the core level lines were recorded in 0.2 eV steps.

Thin film solar cells were fabricated using a single-chamber plasma enhanced chemical vapor deposition system at 200 °C with an rf power of 20 W and a working pressure of 93.31 Pa (0.7 Torr) on a 0.2%-HCl etched AFZO thin films with a thickness of about 800 nm. The thicknesses of the p/i/n α-Si layers are about 20/400/50 nm. The detailed fabrication processes have been reported previously [27]. The current–voltage characteristics of the fabricated solar cells were measured under an illumination intensity of 300 mW/cm^2 and an air mass (AM) 1.5G spectrum.

3. Results and discussion

Fig. 1 shows the deposition rates of AFZO:H thin films as a function of H_2/(Ar + H_2) ratio. The decreased deposition rate with the increasing H_2 ratio is due to the gas dilution effect and possible chemical reaction of hydrogen with oxygen in the plasma ambient. Fig. 2 exhibits the XRD patterns of AFZO:H thin films with various H_2/(Ar + H_2) ratios. All the AFZO:H films showed a (0 0 2) diffraction peak, indicating a typical wurtzite structure with a preferential orientation of the c-axis perpendicular to the substrate. No Al_2O_3 and ZnF_2 phase existed in the XRD patterns. With increasing the H_2/(Ar + H_2) ratio, the intensity of the (0 0 2) peak increased first and then decreased as the hydrogen ratio was larger than 3%, indicating the AFZO films incorporated with small amount hydrogen possessed better crystallinity. This phenomenon results from excess hydrogen may adsorbed on the growing

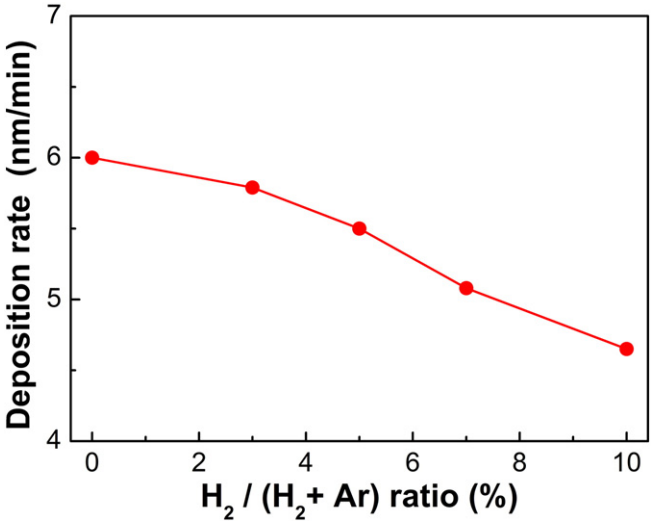

Fig. 1. Deposition rate of AFZO:H thin films as a function of H_2/(H_2 + Ar) ratio.

surface, restraining further crystal growth with preferred orientation and leading to poor crystallinity of the films [28]. Liu et al. also reported that the H_2 flow rate should be controlled in a small range to grow good crystallinity AZO thin films [29]. Table 1 lists the structural parameters of AFZO films calculated from the XRD results (as shown in Fig. 2). The grain sizes of the AFZO films with different H_2/(Ar + H_2) ratios are evaluated from the full-width at half-maximum (FWHM) of the (0 0 2) peak using Scherrer's formula [30]. The crystalline plane distance, d, is calculated from the Bragg diffraction equation: λ = 2dsinθ, where λ is the X-ray wavelength (1.54056 Å) and θ is the diffraction angle of the (0 0 2) peak. The lattice constant, c, is equal to 2d for the (0 0 2) diffraction peak. The residual film strain (ε) can be estimated by the relative changes of the lattice constant and is associated with the diffraction peak displacement, that is, $\varepsilon = [(c_{film} - c_{bulk}) / c_{bulk}]$, where c_{bulk} is the unstrained lattice parameter measured from bulk ZnO [31]. In the AFZO films, Al (or F) is expected to substitute Zn (or O) in its lattice site, thus shifting the (0 0 2) peak position to higher 2θ values, owing to the smaller ionic radius of Al^{3+} (or F^-) than Zn^{2+} (or O^{2-}) [14,32]. In this work, the (0 0 2) peak position of the AFZO films is situated at 2θ = 34.41°, which almost consists with hexagonal ZnO of 34.42° with the wurtzite structure (JCPDS 36-1451) [33] and is smaller than that of AZO films (around 34.5°) [29,32]. This fact implies that many F atoms maybe situate in interstitial sites rather than substitute for O^{2-} ions. In the AFZO:H films, the (0 0 2) peak shifted toward lower

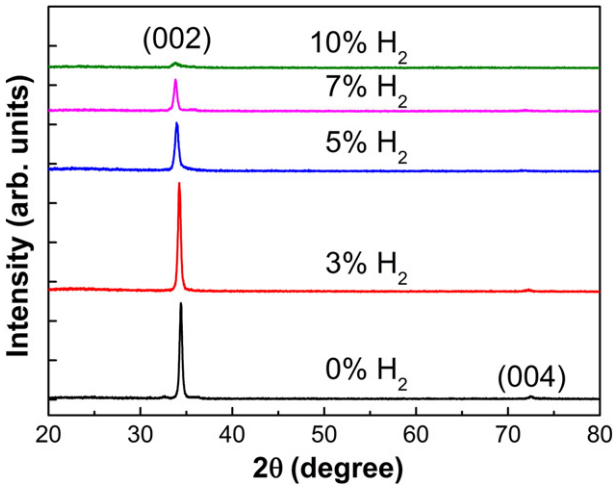

Fig. 2. XRD pattern and of AFZO:H thin films prepared with different H_2/(H_2 + Ar) ratios.