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Comparable study on the effect of diluted NH_4Cl solution on the postdeposition surface texture of as-deposited aluminum-doped zinc oxide films by direct current pulse and direct current reactive magnetron sputtering

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ABSTRACT

Effect of 5.0% diluted NH_4Cl aqueous solution was comparably investigated on the postdeposition surface texture of the as-deposited smooth aluminum-doped zinc oxide (AZO) films by direct current pulse reactive magnetron sputtering (DCP-sputtering) and direct current reactive magnetron sputtering (DC-sputtering). The as-deposited AZO films by DCP-sputtering showed an effective surface texture for light trapping upon the etching of 5.0% diluted NH_4Cl solution, while the as-deposited AZO films by DC-sputtering demonstrated an obscure surface texture upon the same etching treatment. The different result might be attributable to a big difference in film strain and film compactness. The formation of interstitial Zn, interstitial Al and grain boundary is the key to realize effective surface texture for the as-deposited AZO films.

1. Introduction

Since CdO film was first reported by Bakdeker in 1907, transparent conductive films based on SnO_2, In_2O_3, and ZnO have been extensively investigated. ZnO transparent conductive film has a wider band gap of 3.37 eV and a larger exciton binding energy of 60 meV compared with SnO_2 and In_2O_3. In addition, ZnO is more stable in a hydrogen plasma environment [1,2]. ZnO film, thereafter, has been widely studied for their practical applications as flat panel displays, transparent electrodes and window materials in solar cells [3–5]. In particular, aluminum-doped zinc oxide (AZO) is a nice transparent conductive material [3,5]. Its electrical resistivity is on the order of $10^{-4}\,\Omega$ cm [1,6], while its average optical transmissivity is more than 85% in visible region [2,7]. AZO films are able to be deposited by many methods including sputtering, pulsed laser deposition, and reactive evaporation [8]. Among the deposition techniques, the magnetron sputtering technique including radio frequency, middle-frequency and direct-current magnetron sputtering have been widely used due to its high deposition rate and stability for large area AZO film. Magnetron-sputtered AZO films have been applied to CIS film solar cells as standard front TCO contact [9], and silicon film solar cells as alternative TCO contact [10,11], and other film devices. Agashe et al. [12] found out that radio frequency-sputtered AZO films have much lower parasitic absorption with similar conductivity values by using sputtering targets with a low amount of alumina. middle-frequency-sputtered AZO films from Zn:Al alloy target have low cost [13]. They have been successfully applied as substrates for large area a-Si:H solar modules [14]. As front contact and back contact of silicon film solar cells with p-i-n structure, magnetron-sputtered AZO films have to combine low series resistance (i.e. high conductivity) and high transparency (i.e. low carrier concentration to avoid absorption losses in the red and near-infrared wavelength region) in the visible (400–800 nm) and also in the NIR spectra range (800–1100 nm) for microcrystalline silicon. In addition, AZO surface texture is required to provide an efficient light trapping to enhance the intrinsically low absorption of microcrystalline silicon in the long wavelength ($\lambda > 850$ nm)

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[11,15]. The mechanism is realized by efficiently scattering light to extend the effective path length within the active silicon layers [16,17]. For sputtered AZO films, the surface texture is realized by the combination of an optimized deposition condition and a postdeposition wet-chemical etching in diluted acid or bases [18,19]. Kluth et al. [19] found out that textured AZO films by wet-chemical etching in 0.5% diluted hydrochloric acid (HCl) showed that a craterlike surface topography with a typical lateral length scale of 1–2 μm and depth of 200–400 nm develops in a self-organized fashion. This etching behavior is sensitively affected by the structural properties of the as-deposited AZO films. Berginski et al. [20] and Hüpkes et al. [3] once reported individually that a well-textured AZO film is able to be performed by 0.5% diluted HCl solution. However, the etching process and surface morphology are difficult to control due to its high etching rate even if the solution concentration is drastically reduced [21]. 5.0% diluted NH_4Cl solution was used to perform the surface texture of as-deposited AZO films by DCP-sputtering and DC-sputtering on purpose of slowing down the etching rate. DCP-sputtering technique uses a middle-frequency (40 kHz) direct current pulse signal with a 80% voltage duty rather than a middle-frequency alternating signal used in MF-sputtering. It is expected to enhance its deposition rate and uniformity for large area films.

This article addressed the effect of 5.0% diluted NH_4Cl solution on the postdeposition surface texture of the as-deposited AZO films by DCP-sputtering and DC-sputtering. The results indicated that the film surface texture was sensitive to the structural properties of the as-deposited AZO films. The structural-dependent surface texture with respect to the surface roughness, feature size and shape developed during the etching process. The different surface texture might originate from the structural difference of the as-deposited AZO films by DCP-sputtering and DC-sputtering even if the uniform etching is carried out.

2. Experimental details

The AZO films were first deposited on glass substrate by DCP-sputtering and DC-sputtering techniques at different gas flow rate ratios of oxygen to argon (OTA = $[O_2]/[Ar]$). They were then textured by the 5.0% diluted NH_4Cl aqueous solution for different etching times at room temperature. A large-size and high-purity (>99.999%) rectangular Zn–Al metal alloy target with an Al content of 3.0 wt% was used as a sputtering target in order to simulate the real production condition. The glass substrate was first pretreated and rinsed sequentially with acetone and alcohol in an ultrasonic bath for 10 min prior to the deposition of high-quality AZO film. The substrate was then put into an ultrahigh vacuum chamber previously evacuated to a base pressure below 4×10^{-4} Pa and heated to 300 °C to obtain a clean substrate surface. The optimized deposition parameters for DCP-sputtering and DC-sputtering were listed as Table 1.

The film crystalline structure was measured by X-ray diffractometry and the electrical resistivity by four-point probe. The optical transmissivity and reflectivity were measured in air with spectrophotometry (Shimadzu UV-3150). The surface topography and feature size were determined with cold-field emitting scanning electron microscopy (JSM-6700). The film thickness was obtained by using a profilometer. All measurements above were performed at room temperature.

Table 1
Optimized deposition parameters for DCP-sputtering and DC-sputtering.

	T_s (°C)	Deposition time (h)	OTA	Film thickness (nm)
DCPMS	250	3	1.2/18	600
DCMS	200	0.5	3.0/18	300

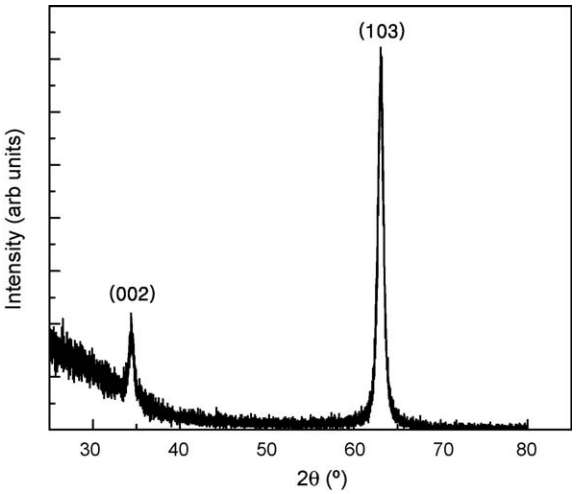

Fig. 1. XRD pattern of the as-deposited AZO film by DCP-sputtering for 3 h.

3. Results and discussions

3.1. Structural properties

XRD pattern of the as-deposited AZO film by DCP-sputtering for 3 h is shown as Fig. 1. The AZO film exhibited two obvious wurtize characteristic ZnO-(0 0 2) and (1 0 3) diffraction peaks indicating a non-oriented polycrystalline structure. It was noted that the integrated intensity of (1 0 3) diffraction peak was at least two times larger than that of (0 0 2) diffraction peak, showing no (0 0 2) *c*-axis predominantly orientated AZO film. This result is different from that reported previously [22–24], which might be attributed to the transition of crystalline face energy and the growth mode from vertical growth along (0 0 2) orientation to lateral growth along (1 0 3) orientation during 3 h deposition [25]. Fig. 2 demonstrated the XRD pattern of the as-deposited AZO film by DC-sputtering for 0.5 h. In contrast, the AZO film has a clear *c*-axis preferential orientation perpendicular to substrate surface. In addition, no other diffraction peaks, resulting from Zn_2O_3, Al_2O_3 and AlN, were observed in both Figs. 1 and 2.

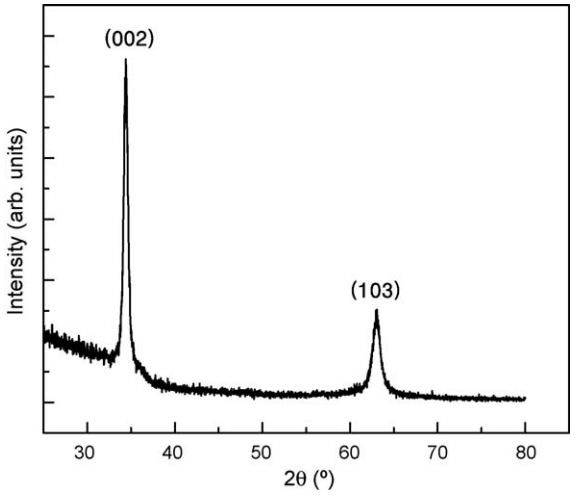

Fig. 2. XRD pattern of the as-deposited AZO film by DC-sputtering for 0.5 h.