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Texture optimization process of ZnO:Al thin films using NH_4Cl aqueous solution for applications as antireflective coating in thin film solar cells

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ABSTRACT

ZnO:Al thin films varying the thickness from 80 to 110 nm were deposited on polished float zone <100> Si wafers by radio frequency magnetron sputtering at 100 °C. To texturize these surfaces with the aim of being used as antireflective coating, a wet etching process based on NH_4Cl was applied. Taking into account that the layer thickness was small, the control of the etch parameters such as etchant concentration and etching time was evaluated as a function of the textured film properties. An appropriate control of the etching rate to adjust the final thickness to the 80 nm required for the application was realized. Using NH_4Cl concentrations of 10 wt.% and short times of up to 25 s, an increase of the film roughness up to a factor of 5.6 of the as-deposited films was achieved. These optimized textured films showed weighted reflectance values below 15% and considerable better electrical properties than the as-deposited 80 nm-thick ZnO:Al films.

1. Introduction

Zinc oxide (ZnO) thin films are attracting much attention because of its low toxicity, their high transparency in visible and near-UV spectral region as well as their wide band gap and high conductivity. Because of all these properties, ZnO results in a very attractive and reliable alternative to be used as transparent conductive oxide in devices such as flat panel display and thin film solar cells. Specifically, one of the potential uses of the ZnO is as antireflection coating (ARC) for silicon based solar cells.

Several deposition techniques for ZnO such as chemical vapor deposition [1,2], vacuum evaporation [3], sol–gel method [4–6] and magnetron sputtering [7,8] have been widely used. Among them, radio-frequency (RF) magnetron sputtering shows several advantages in comparison with other deposition methods such as low temperature, high deposition rates and good adhesion to the substrate. Taking this into account, ZnO material deposited by magnetron sputtering would result a low cost effective solution for the ARC application than other materials commonly used such as silicon nitride (SiN_x). The standard SiN_x ARC is deposited usually by plasma enhanced chemical vapor deposition and reduces the weighted reflectance on a planar surface from 35% to 10% [9].

The two most important parameters in the ARC design are the refractive index, n, and the layer thickness, d. This last parameter should be that value that goes to zero the reflectance at the wavelength where the response of the device is maximum [10]. For the particular case of the silicon solar cells, the refractive index of the ARC is close to 2.0 and the thickness, around 80 nm, which reduces the reflectance losses to a wavelength of around 600 nm [11]. The role of an ARC on a solar cell is to minimize the reflectance losses and maximize the light-trapping ability to achieve the maximum photocurrent for the incident solar spectrum.

On the other hand, the properties of the thin film silicon solar cells, i. e. heterojunction silicon solar cells (SHJ), can be also improved significantly using previously textured silicon wafers. The texturing is important for improving the device current output by reducing the surface reflection. Anisotropic etching with hot alkaline solutions is commonly used in the industrial production of the solar cells. With appropriate process parameters, wet chemical mixtures of KOH (or NaOH) and IPA (isopropyl alcohol) forming random pyramids on the surface of (100) oriented c-Si wafers [12–14]. Under optimized conditions, average weighted reflectance around 13%, without any antireflection coating could be obtained regardless the initial silicon surface [15].

With the attempt to further optimize the SHJ solar cell, the role of texturing the ARC surface to be combined with the textured silicon wafers is evaluated. Most of the effort is placed on tuning the textured process parameters to control the final surface morphology of ZnO:Al (AZO) thin films with thicknesses ranging for 80 to 110 nm de. Taking into account the small thickness of the films, the etching process optimization requires a very precise and exhaustive control of parameters such as the etching rate and the pH of the aqueous solution. The relationship between these parameters and the structural, electrical and optical properties of the final textured films is established.

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It has to be pointed out that to divide the effects due to the high size of the features showed by the textured silicon wafers, the optimization etching process is performed on polished wafers.

2. Experimental details

The AZO thin films were deposited on polished resistive float zone <100> Si wafers (resistivity $> 10^4\ \Omega$ cm) at 100 °C, a working pressure of 0.7 Pa, a discharge power density of 1.3 W cm^{-2} and a distance between the substrate and the target of 74 mm [16]. The AZO layer thicknesses used for the study were ranging from 80 to 110 nm taking into account its application as antireflective coatings (ARC) in silicon-heterojunction solar cells. On the other hand, the low temperature used for the deposition, 100 °C, is to avoid possible damages in the device structure deposited previously to the ARC. The sputtering system used for the film deposition is a commercial MVSystem equipment with one cathode operated by RF power. The 76.2 mm diameter ceramic target ($ZnO{:}Al_2O_3$, 98%:2% wt) from Williams Advanced Materials (WAM) showed a purity of 99.995% and a density of 6.6 g/cm^3. The base pressure was 3.0×10^{-5} Pa and the flow rate of the Argon, controlled by mass flow controller (MFC) was set to 30 sccm.

The texturing process of the as-deposited AZO films was performed using a diluted NH_4Cl aqueous solution with concentration ranging from 5 to 20 wt.%, where the pH varies from 4.65 to 4.34, respectively. The aqueous solution was prepared by dissolving NH_4Cl powder, with a purity of 99.5%, in deionized water ($\rho > 18$ MΩ-cm) at room temperature. The etching mechanism of ZnO in diluted NH_4Cl solution can be found in Ref. [17–19]. Taking into account the thickness range used for this application, the optimization of the etching process would require a precise etching rate control that it is performed basically with an exhaustive control of the aqueous solution pH. Besides, the AZO deposition at so low temperatures leads to films with a less dense structure [20], and hence, the lack of a compact morphology would increase the etching rate [21], making much more difficult to control the etching process [22]. For these reasons, the choice of the acid was based on its low and controllable etch rate in comparison with other acids commonly used as HCl [17].

The surface morphology was evaluated by a standard atomic force microscope (AFM) (Multimode SPM, Veeco-Digital Instruments) operated in contact mode and using silicon nitride AFM probes (NP-S model from Veeco). The roughness of the films was quantified by the value of the Root Mean Square (RMS) deviation of the AFM measured height from the mean data plane in AFM $10 \times 10\ \mu m^2$ images. On the other hand, the grain size is estimated from the AFM images in areas of $2 \times 2\ \mu m^2$.

The optical performance of the as-deposited and textured AZO films was evaluated by the weighted reflectance R_p following the equation

$$R_p = \frac{\int_{400}^{1100} R_{hem}(\lambda) \times e(\lambda) \times d\lambda}{\int_{400}^{1100} e(\lambda) \times d\lambda} \quad (1)$$

where $R_{hem}(\lambda)$ is the hemispherical reflectance as a function of the wavelength, measured in a Perkin-Elmer Lambda 1050 UV/Visible/NIR spectrophotometer with an integrating sphere of 6 mm illuminating from the ARC side, and $e(\lambda)$ the global spectral AM1.5 G irradiance. The ARC layer thickness was estimated from the following equation

$$n \times d = \lambda_{min}/4 \quad (2)$$

where λ_{min} is the wavelength at which the hemispherical reflectance, R_{hem}, reaches a minimum value.

Finally, the electrical sheet resistance R_s of the films was determined from the four-point probe method using a commercial Veeco Instrument system.

3. Results and discussion

3.1. As-deposited ZnO:Al films properties

Table 1 summarizes the structural, electrical and optical properties of the as-deposited AZO thin films (samples #1 to #4) with the different thicknesses studied. It has been to point out the small difference between the value of the thicknesses, but in spite of this, and as it will be showed later, this difference is enough to obtain significant differences in the film properties. It has to be pointed out the considerable electrical improvement achieved when increasing the AZO thickness. A slight increase of the grain size, from 23 to 32 nm, was observed with the layer thickness, according to the obtained by other authors [23], and the RMS values remained relatively close to the substrate one, 1.4 nm. Finally, the R_p values increased also with the thickness due to the displacement of the R_{hem} spectrum to larger wavelengths, as it is shown in Fig. 1. It has to be emphasized that taking into account the ARC properties defined in the introduction section, the AZO film used in the heterojunction solar cells as ARC was the sample 1. For this reason, it has been considered as the reference sample.

3.2. Etching process control

Several are the requirements that the textured AZO thin films should fulfill in order to be applied as ARC in the solar device. Between them, the final textured thickness should be close to 80 nm, the R_p values, as low as possible, and finally, its electrical properties, reasonably good. In order to achieve all these requirements, a good control of the etching process is required. For this reason, in the present work the etching characteristics were studied systematically for the different etchant concentrations and layer thicknesses used. In this sense, the estimation of the etching rate as function of the as-deposited film thickness found a decreasing linear dependence with that parameter. In the particular case of using an aqueous solution with a pH of 4.49, that corresponds to a 10 wt.% of NH_4Cl concentration, the etching rate values were ranging from 0.80 ± 0.06 to 0.49 ± 0.03 when the film thickness increased from 81 to 105 nm. This tendency observed was attributed to the increase of the grain size with the layer thickness and hence, of its compactness [23]. Therefore, it can be supposed that tendency would be similar using different chemical etchant concentration. Fig. 2 displays the dependence of the etch depth and the RMS of the etched surface both with the etching time for the sample of 91 nm-thick in the case of using a pH solution of 4.49. As it is shown, the roughness increased linearly with the etch depth during all the range of the etching time used. On the other hand, it must be noted the no etch depth saturation with the etching time was achieved, indicating that the etch process can be easily controlled with high reproducibility and at a constant average etch rate of 0.65 ± 0.7 nm/s. Fig. 3 shows the

Table 1
Description of the structural, electrical and optical properties of the as-deposited AZO films on float zone <100> silicon wafers.

Sample	Thickness (nm)	RMS (nm)	Grain size (nm)	R_{sheet} (Ω/sq)	R_p (%)
#1	81 ± 2	2.6	23 ± 1	630 ± 44	10.9
#2	91 ± 1	1.8	24 ± 3	184 ± 13	12.5
#3	93 ± 3	1.5	23 ± 2	178 ± 5	13.6
#4	105 ± 3	2.4	32 ± 4	183 ± 11	15.8