Formation of ZnO by Annealing of Thermally Evaporated Zinc in Oxygen Ambient for Solar Cell Application

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Abstract- Zinc oxide films have been formed from thermally evaporated zinc films on polished and textured silicon wafers after heat treatment at temperatures between 400-900°C for 10min in oxygen ambient. These ZnO films show crystalline structure and the values of their refractive index are found to increase slightly from 1.85 for films annealed at 400°C to 2.05 for the films annealed at 900°C. The films formed at a heat-treatment of 450°C have a refractive index value of 1.9. These films have a direct band gap of 3.3eV that corresponds to the absorption edge at 376nm. Consequently these films are highly transparent in the entire 400-1200 nm range and are useful for silicon solar cell application. ZnO films of 80nm thickness on textured silicon exhibit an average reflectivity of ~4 % over the 400-1100nm range; however, the lowest reflectivity is found to be 2.3%. Surface morphological studies have been carried out using SEM for the ZnO thin films deposited on polished silicon wafers. The grain size of ZnO film was found to be ~20nm corresponding to annealing at 450°C. XRD analysis has been done for investigating the crystallographic structure and grain size of the ZnO thin films. The grain size of the ZnO thin films increases with heating temperature from 20nm corresponding to an annealing temperature of 400°C to 42nm corresponding to annealing at 900°C.

Keywords – ZnO, thin films, thermal evaporation, antireflection coating

I. INTRODUCTION

Zinc oxide (ZnO) is a wide band gap (3.37eV) compound semiconductor, has a stable wurtzite structure with lattice spacing a = 3.25Å nm and c = 0.521Å and has a large excitation binding energy ~60meV at room temperature [1]. It is attractive for application in transparent electronics, ultraviolet (UV) light emitter, piezoelectric devices, chemical sensors and spintronics [2]. Due to its high transmission and matching refractive index in 350-1200nm wavelength range it is quite suitable for application as antireflection coating to silicon solar cells. Several techniques have been used to prepare ZnO thin films, viz. pulse laser deposition (PLD) [3], metal organic chemical vapor deposition (MOCVD) [4], molecular beam epitaxy (MBE) [5], DC magnetron sputtering [6], hybrid beam deposition (HBD) [7], spray pyrolysis [8], sol-gel technique [9] and thermal evaporation technique [10]. Formation of ZnO thin films from thermal evaporation of Zn metal in vacuum and its oxidation at 400°C has been reported by Tripathi et. al. [10]. H. Kavak and R. Esen [11] have grown ZnO thin films by pulsed filtered cathodic vacuum arc deposition. S. K. Panda and C. Jacob [12] synthesized Needle-like zinc oxide ZnO nanostructures on silicon wafer, respectively via thermal evaporation of metallic zinc followed by a thermal annealing in air. S. K. Panda et al [13] have grown ZnO nanotetrapods on p-type Si (111) substrate by oxidizing zinc pieces in air by thermal evaporation technique without the presence of any catalyst. Thermal evaporation is relatively a low cost and simple technique that can be applied to low melting point, low decomposition or low sublimation point oxides [13]. The ZnO thin films have been used as antireflection
coating on silicon solar cells [14,15]. Despite its obvious economic advantages and simplicity, thermal evaporation technique has received very little attention from research groups. In this paper, we present the growth and characterization of zinc oxide nanostructures prepared by thermal evaporation. In the present work we have deposited zinc oxide thin film on both polished and textured silicon wafers by thermal evaporation of zinc in vacuum followed by its oxidation at 400-900°C temperature range in oxygen ambient and have investigated their optical properties for their possible application as antireflection coatings for silicon solar cells. We are the first to investigate the ZnO thin films by thermal evaporation of Zn metal in vacuum and annealed in O₂ ambient as antireflection coating for solar cell application as ZnO coatings are cost effective in comparison with Si₃N₄ layers and have great potential to replace Si₃N₄ antireflection coatings in silicon solar cells.

II. EXPERIMENTAL

Monocrystalline silicon wafers of Cz Boron doped p-type silicon wafers of 50mm diameter, 300μm thickness, <100> oriented and 1ohm-cm base resistivity were used as a starting material for the experiment. Some of the wafers were chemically polished on both sides and some were textured in a 2% NaOH solution at 80°C after damage removal in 20% NaOH. A single layer ZnO AR coating was applied on the front surface of the cell, as described below.

The polished and textured wafers were cleaned in acetone and ethanol successively and then rinsed in DI water. Zn metal layer was deposited by thermal evaporation on a few polished silicon wafers and textured wafers under a vacuum of 10⁻⁶ mb. After that the wafers were kept in vacuum for 18hr for stabilization of Zn film. Subsequently the wafers were heated at different temperatures in the range of 400-900°C in an oxygen ambient to convert Zn into ZnO. Zn films of the same thickness were deposited on all the wafers. Different wafers were heat treated at different temperatures in the above range. The refractive index and thickness of ZnO films coated on polished silicon wafers were measured at λ = 632.8 nm using an ellipsometer Gaertner model L117. A few number of Zn films were deposited similarly on quartz substrates and were likewise heat treated but at a temperature of 450°C only for 10min in oxygen ambient to form ZnO on the quartz substrates. The transmittance values of these ZnO films were measured at different wavelengths in 300-1200nm range with a spectrophotometer Shimadzu model UV-3101PC.

We have not yet applied such antireflection coatings on solar cells. We will apply the above ZnO films on silicon solar cells and this work will be reported separately elsewhere.

III. RESULT AND DISCUSSION

The refractive index and thickness of ZnO films as a function of heat treatment temperature are plotted in Fig 1.
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The index of pulse filtered cathodic vacuum arc deposited ZnO films decreased with heat treatment temperature whereas, Ali et. al [13] have also found that the refractive index of electron beam evaporated ZnO thin films in the visible region decreases with heat treatment temperature. The matching refractive index value for ZnO films to act as a single layer antireflection coating on silicon solar cells is 1.9 which was obtained at a heat-treatment temperature of 450°C.

![X-ray diffraction pattern of ZnO film](image)

Figure 2. X-ray diffraction spectra of thermally evaporated Zn film heat-treated at 450°C in O2 ambient. (2a) SEM micrograph of ZnO thin films corresponds to heat treatment 450°C. (2b) Variation of grain size of ZnO thin films with the heat treatment temperature in the

An X-ray diffraction pattern of ZnO film formed on textured monocrystalline silicon is shown in Fig 2. Three different peaks correspond to (100), (101) and (110) planes. The intensity of (100) peak is very high. The above three peaks matched with standard XRD data (2000 JCPDS-International Centre for Diffraction Data PCPDFWIN v. 2.1) of zinc oxide films. The grain sizes were calculated from XRD data using well known Scherrer formula. The SEM micrograph shown in Fig 2a (inset of Fig 2) shows the grain size of ZnO thin films annealed at 450°C is ~20nm. Fig 2b (inset of Fig 2) shows the grain size corresponding to (100) orientation increases from ~20nm for the heat treatment temperature of 400°C to ~42nm corresponding to the heat treatment temperature 900°C. Senadin et. al [12] has also found the same dependence of grain size of pulse filtered cathodic vacuum arc deposited ZnO films with heat treatment temperature.

Optical transmittance of a ZnO film formed on a quartz substrate of 2mm thickness after heat-treatment of a vacuum deposited Zn film at 450°C for 10min in oxygen ambient is shown in Fig 3. The transmittance of this film is ~90% in 400-1100nm wavelength range. It may be pointed out that the ZnO films are highly transparent and the above measured value of transmittance is due to nearly 9.6% loss of intensity as a result of reflection at air-ZnO interface for normal incidence. This transmittance vs. wavelength data of Fig. 3 was used to calculate the absorption coefficient $\alpha$ which was in turn used to determine the band gap of ZnO film. The plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for the determination of the direct band gap of ZnO film is shown in the inset of Fig 3. The direct band gap is found to be 3.3eV.
Among the ZnO films formed on polished and textured silicon wafers by heat treatment at 450°C the films of thickness 80nm showed minimum reflectance. The variation of reflectivity of polished and textured silicon wafers with and without such ZnO coated films of 80nm thickness is depicted as a function of wavelength in 400 < λ < 1100nm range in Fig.4. The average reflectivity of 80nm thick ZnO films on polished and textured silicon is found to be ~10% and ~4%, respectively. Thus ZnO films formed by heat-treatment of vacuum deposited Zn films at 450°C in oxygen ambient are quite suitable for use as a single layer antireflection coating on textured silicon solar cells.

Figure 3. Optical transmittance in 300-1200nm wavelength range of ZnO thin film formed at 4500C from vacuum deposited Zn film on a quartz substrate. The plot of (αhυ)² vs. photon energy (hυ) for determination of direct band gap is shown in the inset.

Fig 4. Variation of reflectivities of (1) polished monocrystalline silicon, (2) textured monocrystalline silicon, (3) ZnO coated polished monocrystalline silicon and (4) ZnO coated textured monocrystalline silicon wafers in 400-1100nm range. The ZnO films correspond to heat-treatment temperature of 4500C.
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IV. CONCLUSION

ZnO thin films with refractive index in the range 1.85-2.05 have been fabricated on polished and textured silicon wafers from vacuum deposited Zn films followed by their heat-treatment at temperatures between 400 to 900°C in oxygen ambient. These films have a direct band gap of 3.3 eV that corresponds to the absorption edge at 376 nm. Consequently these films are highly transparent in the entire 400-1200 nm wavelength range which is useful for silicon solar cells. The films formed at heat-treatment of 450°C have a refractive index value of 1.9 which is ideal for their use as a single layer AR coating on silicon solar cells. ZnO films of 80 nm thickness on textured silicon exhibited a very low reflectivity of 2.3% in 400 < λ < 1000 nm range and an average reflectivity of ~4% over the 400-1100 nm range. This indicates that the so formed ZnO films can act as good antireflection coatings for silicon solar cells.

REFERENCE