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Effect of doping on structural, optical and electrical properties of nanostructure ZnO films deposited onto a-Si:H/Si heterojunction

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ABSTRACT

We investigated the structural; optical and electrical properties of ZnO thin films as the n-type semiconductor for silicon a-Si:H/Si heterojunction photodiodes. The ZnO film forms the front contact of the super-strata solar cell and has to exhibit good electrical (high conductivity) and optical (high transmittance) properties. In this paper we focused our attention on the influence of doping on device performance. The results show that the X-ray diffraction (XRD) spectra revealed a preferred orientation of the crystallites along *c*-axis. SEM images show that all films display a granular, polycrystalline morphology and the ZnO:Al exhibits a better grain uniformity. The transmittance of the doped films was found to be higher when compared to undoped ZnO. A low resistivity of the order of $2.8 \times 10^{-4}\ \Omega$ cm is obtained for ZnO:Al using 0.4 M concentration of zinc acetate. The photoluminescence (PL) spectra exhibit a blue band with two peaks centered at 442 nm (2.80 eV) and 490 nm (2.53 eV). It is noted that after doping the ZnO films a shift of the band by 22 nm (0.15 eV) is recorded and a high luminescence occurs when using Al as a dopant. Dark *I–V* curves of ZnO/a-Si:H/Si structure showed large difference, which means there is a kind of barrier to current flow between ZnO and a-Si:H layer. Doping films was applied and the turn-on voltages are around 0.6 V. Under reverse bias, the current of the ZnO/a-Si:H/Si heterojunction is larger than that of ZnO:Al/a-Si:H/Si. The improvement with ZnO:Al is attributed to a higher number of generated carriers in the nanostructure (due to the higher transmittance and a higher luminescence) that increases the probability of collisions.

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1. Introduction

Heterostructures such as TCO/a-Si:H/c-Si have considerable potential for low cost high efficiency solar cells above 21% has been demonstrated [1]. The properties of such cells are strongly influenced by both the electronic properties of the a-Si:H/c-Si heterojunction and the TCO/a-Si:H contact. At present, the most important research area in the field of a-Si:H based solar cells is considered to be further development and implementation of efficient light trapping. Light trapping techniques help to capture light in the desired parts of a solar cell, which are the absorber layers, and prevent it from escaping. Efficient light trapping in a-Si:H silicon solar cells is based on scattering of light at rough interfaces resulting in a longer average optical path through the absorber layer. This ensures efficient light confinement that substantially enhances light absorption in the absorber layer and increases the photocurrent of the solar cell. Transparent conductive oxide films (TCO) play a central role in light trapping approaches and, at present, determine the efficiency of the state-of-the-art solar cells. The development of TCO materials with required optical and electrical properties and optimal surface texture is today the most important issue in the field of thin film silicon solar cells. Among TCO films, Zinc Oxide (ZnO) has been widely studied in recent years for solar cells application. it is an inexpensive semiconductor with a direct large band gap of about 3.37 eV and hexagonal wurtzite structure [2]. ZnO is an n-type semiconductor and its electrical conductivity is due to an excess of zinc at interstitial positions [3]. This can be modified thoroughly by an appropriate doping process, either by cationic [4] or anionic [5] substitution. The electrical conductivity of ZnO thin films can be improved by cationic substitution with positive trivalent atoms. Usually group-III elements, such as In, Al or Ga, are used as the dopant to produce conducting ZnO and there are several reports on doped samples [22–24]. Different methods have been proposed to deposit ZnO films such as RF magnetron sputtering [6], chemical vapor deposition (CVD) [7], sol–gel method [8], thermal evaporation [9] and spray pyrolysis [10]. In this study, a undoped and doped ZnO film were deposited on a-Si:H/Si heterojunction using the spray pyrolysis technique. This method has a several advantages such as is cheap and simple method with high purity, excellent control of chemical uniformity, and stoichiometry in multi-component system. The other advantage of the spray pyrolysis method is the easy adaptation for the production of large-area films. With our deposition system, uniform ZnO layers can be deposited on a $10 \times 10\ cm^2$ large area. Structural, electrical and optical studies were carried out to analyze the nanostructural features of the ZnO (ZnO:Al or ZnO:In)/Si and ZnO (ZnO:Al or ZnO:In)/a-Si:H/Si heterojunction using several analytical methods. The objective of this study was to fabricate a high-efficiency a-Si:H/c-Si solar cell by the enhancement of properties of ZnO films with doping.

2. Experimental

The ZnO/a-Si:H(n)/c-Si(p) structures were prepared using standard process the c-Si-wafers were pre-treated by a HF-dip (5%HF:H_2O) before a-Si:H was deposited. For the a-Si:H deposition we used the DC sputtering-technique. The substrate temperature during deposition was 210 °C. The deposition rate amounted to 7 nm/min. Contact to the a-Si:H emitter is provided by a transparent conductive oxide consisting of a 90 nm thick ZnO (ZnO:Al and ZnO:In) prepared by chemical spray pyrolysis deposition. The precursor used was dehydrated zinc acetate (Zn $(C_2H_3O_2)_2.2H_2O$) dissolved in a methanol/water mixture with proportions of 2:3 and 1:3 by volume. A few drops of acetic acid were added to the aqueous solution to prevent formation of hydroxides. The aluminium and indium chloride were the doping sources. The concentration of zinc acetate was 0.4 M and the Al/Zn and In/Zn ratios were 2 at.% in the starting solution. These layers were deposited onto (100) p-type crystalline Si (1 Ω cm), a-Si:H/Si and glass substrates. In this process, nitrogen was used as the carrier gas. The spray rate and temperature were constant at 15 ml/min and 480 °C respectively. The micro-crystalline structure of the deposited ZnO films was determined by the θ–2θ X-ray diffraction technique (XRD) using an *Advanced D8 Bruker AXS diffractometer* with the Cu-Kα (1.5418 Å) radiation. The curves were measured in symmetrical Bragg geometry in the (20–90°) 2θ range. The optical properties were studied by measuring the optical absorbance and transmittance spectra, in the range 250–2500 nm, with a