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Full Length Article

Further improvements in conducting and transparent properties of ZnO:Ga films with perpetual *c*-axis orientation: Materials optimization and application in silicon solar cells

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ABSTRACT

Technologically appropriate device friendly ZnO:Ga films have been prepared at a low growth temperature (100 °C) by changing the RF power (P) applied to the magnetron plasma. Structurally preferred *c*-axis orientation of the ZnO:Ga network has been attained with $I_{(002)}/I_{(103)} > 5$. The *c*-axis oriented grains of wurtzite ZnO:Ga grows geometrically and settles in tangentially, providing favorable conduction path for stacked layer devices. Nano-sheet like structures produced at the surface are interconnected and provide conducting path across the surface; however, those accommodate a lot of pores in between that help better light trapping and reduce the reflection loss. The optimized ZnO:Ga thin film prepared at RF power of 200 W has ⟨002⟩ oriented grains of average size ~10 nm and exhibits a very high conductivity ~200 S cm^{-1} and elevated transmission (~93% at 500 nm) in the visible range. The optimized ZnO:Ga film has been used as the transparent conducting oxide (TCO) window layer of RF-PECVD grown silicon thin film solar cells in glass/TCO/*p*-*i*-*n*-Si/Al configuration. The characteristics of identically prepared *p*-*i*-*n*-Si solar cells are compared by replacing presently developed ZnO:Ga TCO with the best quality U-type SnO_2 coated Asahi glass substrates. The ZnO:Ga coated glass substrate offers a higher open circuit voltage (V_{OC}) and the higher fill factor (FF). The ZnO:Ga film being more stable in hydrogen plasma than its SnO_2 counterpart, maintains a high transparency to the solar radiation and improves the V_{OC}, while reduced diffusion of Zn across the *p*-layer creates less defects at the *p*-*i* interface in Si:H cells and thereby, increases the FF. Nearly identical conversion efficiency is preserved for both TCO substrates. Excellent *c*-axis orientation even at low growth temperature promises improved device performance by extended parametric optimization.

1. Introduction

Transparent conducting oxides (TCOs) e.g., Zinc Oxide (ZnO) [1], Titanium Oxide (TiO_2) [2], Tin Oxide (SnO_2) [3], Tin doped Indium Oxide (ITO) [4], etc are commonly used in thin film silicon solar cells. Among them ZnO have been extensively studied due to its improved electronic, optical, optoelectronic properties and potential applications in nanoscale devices [5–7]. In addition, ZnO is an attractive metal-oxide semiconductor material for ultraviolet and blue light-emitting devices (LEDs) due to having a direct wide band gap of ~3.37 eV (at 300 K) and large exciton binding energy of 60 meV [8–10]. ZnO films are inexpensive, non-toxic, stable under H_2-plasma and usually prepared at low deposition temperature [11]. The electrical characteristics of intrinsic ZnO films are typically *n*-type by virtue of inherent structural defects e.g., oxygen vacancies, zinc interstitials etc. For further *n*-type doping of the ZnO films Ga has been identified as the ideal material as the physical dimension of ionic Zn^{2+} (~0.074 nm) is very close to that of ionic Ga^{3+} (~0.062 nm) than the more abundant ionic Al^{3+} (~0.053 nm) [12]. In addition, Ga is less reactive and more resistant to oxidation compared to Al.

One of the foremost applications of thin-films is in the photovoltaic power devices. For large area applications with moderate energy cost the thin-film technology are truly advantageous [13]. In silicon solar cells ZnO:Ga films are important components which are commonly used as transparent as well as conducting front layer of *p*-*i*-*n* solar cell structures [14–16]. ZnO:Ga front layer is effectively used to avoid a high series resistance to prevent resistive losses over typical distances in the range of few mm [17]. There always remains a trade-off relation between the optical trans-

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parency and electrical conductivity. Therefore, proper optimization of these two characteristic parameters at a device compatible growth temperature is a demanding task. Over and above all these, orientational configuration is another considerable issue, particularly in large area stacked layer devices. Being the top contact layer of solar cells, dominant *c*-axis orientation of the ZnO crystallites could efficiently transport the collected charge carriers of the *p-i-n* device to the external load. Among different deposition techniques RF magnetron sputtering has been quite efficient in device fabrication as it has the advantages of high deposition rate over large deposition areas and it can produce device grade material at moderately low substrate temperature [18].

The present study demonstrates the growth and optimization of very conducting and transparent ZnO:Ga films with preferred *c*-axis orientation by RF magnetron sputtering at low growth temperature and reasonable RF power. The *p-i-n* type silicon solar cells have been made on these oriented crystalline ZnO:Ga films and the optimum efficiency of the device has been compared with similar solar cells prepared on the best quality Asahi U-type SnO_2 coated glass substrate.

2. Experimental

ZnO:Ga thin films were grown by RF magnetron sputtering using Ar as the sputtering gas and a high purity (99.99%) ZnO target doped by 2% Ga. The reactor was evacuated to $\sim 9 \times 10^{-7}$ Torr prior to deposition and subsequently ~3.3 sccm Ar was taken using a mass-flow controller. Corning® Eagle2000™ glass substrates were used and in order to get better film homogeneity, during deposition the substrate was externally rotated at 10 rpm. A set of ZnO:Ga films were prepared at a low substrate temperature, T_S ~100 °C, a fixed pressure, p ~20 mTorr, and by changing the RF power (P) from 50 to 250 W. Films were grown maintaining a typical thickness of ~(400 ± 20) nm.

The optical transmission and reflection of the ZnO:Ga films grown on glass substrates were measured by a double-beam spectrophotometer (Hitachi 330). The X-ray diffraction study was performed by a Cu-Kα X-ray radiation (**λ** ~1.5418 Å) source connected to a Bragg diffraction setup (Seifert 3000P). The surface structure of the films was studied by atomic force microscope (Veeco di CP-II) and a field emission scanning electron microscope (JEOL JSM-6700F). The photoluminescence emission was measured at room temperature, using 370 nm wavelength excitation. The electrical conductivity at room-temperature was measured by four-probe method. The Si solar cells of $1 \times 1\,cm^2$ area were deposited on optimized ZnO:Ga films and were characterized by standard I–V set up with solar simulator (Wacom) creating AM1 illumination. The individual external quantum efficiency (EQE) of the single junction silicon solar cells were measured with appropriate DC bias light and using monochromatic probe light.

3. Results

The X-ray diffraction study has been performed to monitor the changes in the nature of crystallographic orientation of the ZnO:Ga films on varying the applied RF power during its growth. Fig. 1 demonstrates that the ZnO:Ga film prepared at a low RF power of 50 W exhibits a very sharp and intense peak at around 2θ ~34.4°, corresponding to the ⟨002⟩ crystallographic plane of ZnO. The other two peaks at around 2θ ~36.2° and 62.9° which are associated to the ⟨101⟩ and ⟨103⟩ crystallographic planes of ZnO are relatively small. With the increase in applied RF power the ⟨101⟩ peak disappeared, while the width of other two peaks gradually widened; however, maintaining the dominance of ⟨002⟩ crystallographic orientation in the network. In order to make a quantitative estimation,

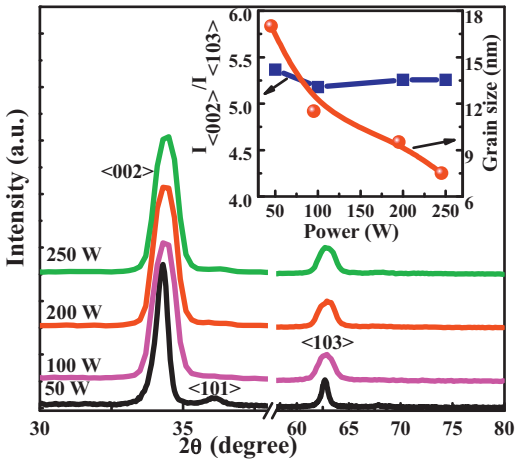

Fig. 1. XRD spectra of ZnO:Ga films grown by magnetron sputtering at RF power (P) changing from 50 to 250 W. Inset presents the variations in the intensity ratio, $I_{\langle 002\rangle}/I_{\langle 103\rangle}$, and the average grain size along ⟨002⟩ orientation with applied RF power.

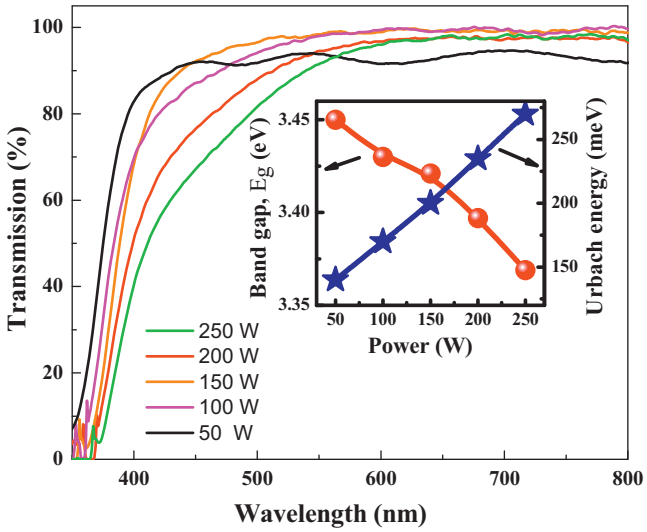

Fig. 2. Optical transmission spectra of ZnO:Ga films grown at different RF powers. Inset shows the variations of optical band gap, E_g, and the Urbach energy, E_0, of the ZnO:Ga prepared at different RF powers.

the ratio of the intensity of ⟨002⟩ and ⟨103⟩ peaks are plotted at the inset in Fig. 1 which demonstrates an almost identical *c*-axis preferred orientation by $I_{\langle 002\rangle}/I_{\langle 103\rangle}$ ~5.3. The average grain size (*D*) in the network has been estimated by using the FWHM (β) of the dominant ⟨002⟩ XRD peak, via Scherer's formula:

$$D = 0.9\lambda/\beta\cos\theta,$$

and plotted at the inset in Fig. 1. A systematic lowering in the average grain size from 18 to 8 nm has been evidenced during increase in RF power while the growth orientation remains identically preferred along the *c*-axis.

The optical transmission spectra in the UV–vis region for the ZnO:Ga films grown at different RF power is shown in Fig. 2. The film grown at P = 50 W exhibits a high transmission >90% from optical wavelength above 430 nm. At higher P the films attain a maximum transmission as high as 98%; however, above 90% transmission is obtained at relatively higher wavelength, e.g., it starts at 540 nm in case of film grown at P = 250 W. The optical density data were estimated from the transmission and reflection measurements. Considering the parabolic nature of the band edge, the absorption coefficient could be presented by Tauc's formula: