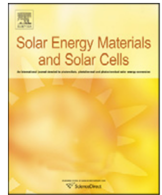
Solar Energy Materials & Solar Cells 95 (2011) 2327–2334

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



High quality ZnO and Ga:ZnO thin films grown onto crystalline Si (1 0 0) by RF magnetron sputtering

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ARTICLE INFO

Article history:
Received 13 December 2010
Accepted 1 April 2011
Available online 6 May 2011

Keywords:
Transparent conductive oxides
Ga-doped ZnO
Silicon solar cells
Microstructural characterization

ABSTRACT

Undoped and 2% Ga-doped ZnO films have been deposited by RF magnetron sputtering onto single crystal Si (1 0 0) substrates equivalent to the commercial Si solar cells. The same films were also grown on amorphous silica substrates to complete their characterization. The films have been characterized by X-ray diffraction, electrical and optical measurements, X-ray photoelectron spectroscopy, Raman microspectroscopy and scanning and high-resolution transmission electron microscopy. Films present a very good quality crystalline wurtzite structure with the *c*-axis perpendicular to the substrate, with continuity of the (0 0 0 2) planes along the whole film, as shown by transmission electron microscopy. The doped sample shows an increase of two orders of magnitude of the electrical conductivity, an optical transmittance bigger than 85% along the visible spectrum, a diminution of the grain size in the direction parallel to the substrate and a lower surface roughness. The Ga-cations act only as substitutional impurities, they are homogeneously distributed in the whole film, maintaining the wurtzite structure and increasing the carrier density. The formation of any spurious phase or segregation of Ga_2O_3 clusters that can act as carrier traps can be discarded. The characterization results allow us to conclude that the doped film has improved electrical and optical properties with respect to the undoped one. Therefore, the Ga-doped films are very suitable candidates as transparent conducting electrodes for solar cells, displays and other photoelectronic devices.

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1. Introduction

Transparent conducting oxide (TCO) thin films have been extensively studied [1], because they exhibit both high optical transmission and good electrical conductivity, and have practical applications for transparent electrodes in photoelectronic devices such as solar cells and flat panel displays. In that sense, the efficiency of solar cells could be enhanced by using a TCO top layer acting both as a transparent electrode and antireflective coating. Doped zinc oxide (ZnO), among others, was already proposed as a non-toxic and cheap alternative to ITO (In_2O_3:SnO_2) ten years ago [2]. Problems to be addressed are the optimization of the deposition method – large area substrates and a high deposition rate – and the influence of dopant concentration on the microstructure, conductivity and optical properties.

Doping of ZnO with trivalent cations improves its electrical properties by introducing free charge carriers. Different dopants can be added to the ZnO structure such as: Al [3,4], Co [5] and In [6], among others. One of the most interesting is gallium because Ga-doped ZnO powders were reported to have conductivities as high as 300 Ω^{-1} cm^{-1} [7] and Ga-doped films showed optical transmittance values higher than 85% in the visible spectrum [8]. Moreover, this material can be easily prepared as a thin film without losing any of the attractive optical and electrical properties [1].

Several techniques can be used to obtain Ga:ZnO films, such as pulsed laser deposition [9,10], plasma-assisted molecular beam epitaxy [11], DC sputtering [12], RF magnetron sputtering [13,14], etc. Among them, the sputtering technique stands out due to its versatility, low cost and the possibility of scaling to large area substrates and high deposition rates for photovoltaic industrial applications. A large variety of substrates have been used, though the amorphous substrates are preferred by most authors. Since silicon is the basic material for commercial photovoltaic solar panels, we have chosen single crystalline Si (1 0 0) as the main substrate for our study. To the best of our knowledge no works devoted to Ga:ZnO films have been reported with such a substrate. Besides, we have prepared identical samples on amorphous silica substrates for the optical transmittance and Raman spectroscopy measurements.

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doi:10.1016/j.solmat.2011.04.001

Significant levels of doping are accompanied by changes in optical, electrical and/or structural properties. Beyond a certain threshold doping level a worsening of the properties and phase segregation can occur [15]. Problems to be addressed are the optimization of the deposition method and the determination of the influence of dopant concentration on its microstructure. Therefore, in this work we intend to study ZnO and Ga:ZnO films prepared on Si (1 0 0), relating the macroscopic, conductivity and optical properties with the microstructure, using a large variety of characterization techniques and very well-controlled deposition conditions.

2. Experimental

ZnO and Ga:ZnO films were deposited both on polished Si (1 0 0) and on amorphous silica substrates using a RF magnetron sputtering system. Two types of ceramic targets (AJA International, Inc.) were employed: pure ZnO (99.99%) and ZnO with a Ga_2O_3 content of 2 wt% (99.9%). The diameter of the targets was 5 cm and the substrate-to-target distance was 3 cm. The base pressure in the chamber was $<5\times10^{-4}$ Pa and the working pressure was maintained at 0.4 Pa with a high purity Ar gas regulated by a mass flow controller. The RF sputtering power was fixed at 150 W and the substrate temperature was maintained constant at 300 °C. ZnO and Ga:ZnO films with various thicknesses have been obtained by varying the deposition time (see Table 1). Thicker films on amorphous silica were specially grown for the Raman measurements because silicon substrates mask the spectrum from the films. X-ray diffraction data show similar patterns for the films, independent of the substrate and the film thickness.

The crystal structure of the films deposited on both substrates was determined by following the evolution of the 002 wurzite reflection from X-ray diffraction (XRD). The patterns were obtained on a Philips X'Pert Pro MPD automated diffractometer, equipped with a Ge (1 1 1) primary monochromator (strictly monochromatic $CuK_{\alpha1}$ radiation) and an X'Celerator detector. The overall measurement time was ~1/2 h per pattern to have very good statistics over the 2θ range of 10–80° with 0.017° step size.

The electrical resistivities were measured for the samples prepared onto Si substrates, using the conventional four-point probe method at room temperature, assuming homogenous conduction throughout the depth of the film. The optical transmittance measurements were made for the samples prepared onto an amorphous silica substrate, using a UV–vis spectrophotometer (Varian Cary 5000) in the wavelength range from 300 to 800 nm.

Table 1
Summary of the samples and their deposition and structural parameters. FWHM and grain size have been calculated from the XRD data. Film thicknesses were obtained from TEM and SEM images.

Samples		Deposition time (min)	Thickness (nm)	(0 0 2) Peak position (2Θ°)	FWHM (2Θ°)	Grain size (nm)
Composition	Substrate					
ZnO	Si	20	75	34.17	0.31	33
ZnO	Si	55	206	34.15	0.23	49
ZnO	Si	20	75	34.18	0.24	46
Ga:ZnO	Si	20	76	34.36	0.26	42
Ga:ZnO	Si	55	209	34.37	0.22	52
Ga:ZnO	Si	20	76	34.35	0.23	49
Ga:ZnO*	Si	240	900	–	–	–

* Prepared for Raman measurements and SEM.

X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Physical Electronic model PHI 5700 X-ray photoelectron spectrometer with MgK_α radiation (1253.6 eV) as an excitation source. Measurements were done on as-prepared samples on silicon and amorphous silica substrates and after 30″ of Ar^+ sputtering, in order to clean the contamination due to air exposure of the samples. The core level spectra were fitted using the XPSPeak software package [16].

Raman spectra were obtained for the films deposited on silica substrates, in backscattering geometry with a Renishaw Ramascope 2000 spectrometer equipped with an Olympus microscope (100× objective) and an ion argon laser (emission wavelength 514.5 nm). Laser power on the sample was about 3 mW. Spectra were collected at different points on the films. After checking the homogeneity of the films the spectra were stripped of the cosmic ray peaks and all the spectra for the same film were integrated to increase the signal to noise ratio. Although the system was operating in quasiconfocal mode and the thickest films were used, the probing depth was larger than the films thickness and the spectra contained an important contribution from the substrate. Thus, the scaled integrated spectrum of a bare substrate was removed from the spectrum of the films to obtain the spectrum of the ZnO and Ga:ZnO layers alone. This procedure worked best for films grown on an amorphous silica substrate, where the Raman spectrum of the latter is weak and broad.

Cross-sectional scanning electron microscopy (SEM) images using a JEOL SM-6490LV electron microscope combined with X-ray energy dispersive spectroscopy (XEDS) were used to analyze the chemical composition and Ga concentration of the 900 nm film, prepared on a silica substrate. Cross-sectional samples from the thinnest films of ZnO and Ga:ZnO deposited onto Si substrates were prepared for transmission electron microscopy (TEM), by dimple-grinding with a Gatan 656 dimpler and ion-milling with a Fischione 1010 model until an electron transparent area was obtained at the center of the sample. The procedure is fully described in reference [17]. Transmission electron microscopy studies were done using JEOL 3010 F TEM microscope with a field-emission gun, 300 kV acceleration voltage and 0.17 nm of structural resolution. Electron diffraction patterns were obtained by the selected area method (SAED), and image processing of the high-resolution images was carried out using Gatan Digital Micrograph and ImageJ software packages.

3. Results and discussion

The experimental parameters of the samples are gathered in Table 1 together with the results from XRD measurements for the ZnO and Ga:ZnO films deposited on amorphous silica and Si substrates. X-ray diffraction patterns are very similar for all samples showing only the wurtzite ZnO 002 reflection in the 10–80° 2θ range. This confirms that the films crystallize in the hexagonal wurtzite and are highly oriented with their crystallographic *c*-axis perpendicular to the substrate. This growth habit has been observed repeatedly for ZnO and Ga:ZnO films, irrespective of the preparation technique and substrate type [14,18]. The position of the peak does not depend appreciably on the film thickness nor the substrate and shifts slightly to higher angle only with doping, due to the smaller radius of Ga^{3+} ion compared to that of the Zn^{2+} ion, which promotes a very small diminution of the cation–oxygen bond length and consequently of the unit cell size. The evolution of the 002 reflection for the samples deposited during 20 min is shown in Fig. 1.

The variation of 002 ZnO peak position, the full width at half maximum (FWHM) and the grain size for the undoped ZnO and Ga:ZnO films are also shown in Table 1. The grain size was

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