

Qualitative investigation of the surface electrical potential in ZnO thin films by scanning surface potential microscopy

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Zinc oxide (ZnO) is an n-type semiconductor that has large industrial applications as a transparent conductive electrode in photovoltaic devices. In spite of these extensive applications, the source of conductivity in ZnO is still in debate. A reliable means to study the surface electrical properties of this material in thin films form is necessary for better understanding. As a result, a varied number of techniques for the ZnO thin films surface electric charge characterization have been reported in recent years. Among these techniques, scanning surface potential microscopy (SSPM) has emerged as an alternative, efficient tool for the characterization of dielectric and semiconductor thin films. The SSPM technique uses the standard non-contact atomic force microscope setup, making it possible to map simultaneously the sample's topography and surface electric potential distribution. The results of the characterization of ZnO and Al-doped zinc oxide (ZnO:Al) thin films by SSPM have been crucial to quantify the surface electric potential variations present in this samples.

Keywords SSPM; ZnO; ZnO:Al; thin film

1. Introduction

In the last few years, the extensive investigation, continuous miniaturization of the photovoltaics devices and increase of new concepts on the studies of transparent conducting oxide thin films for solar energy have placed more emphasis on the third-generation photovoltaic [1]. Generally, one of the most commonly used materials as transparent electrodes is indium tin oxide, but as its principal component, the indium, is scarce, toxic and expensive material researchers are looking for viable alternatives[2]. The most important candidate is ZnO due to its non-toxicity, low cost, and abundance. When not doped, this ZnO presents high resistivity due to its low carrier concentration. Therefore, doped ZnO transparent conducting thin films are being prepared with elements of the groups III and IV by several deposition techniques [3, 4]. However, the thin film deposition process is quite complex. There is much interest in understanding how the deposition parameters and dopant content affect local electrical surface potential of ZnO thin films and their functionalities on the microscale when applied on photovoltaic devices [5]. In fact, the surface electric potential is a complicated function that depends on the dopant concentration in semiconductors, both surface and bulk properties, and has been a critical parameter that influences the device's efficiency. Therefore, the qualitative and quantitative analysis of electrical transport and local surface electric charge distribution in nanoscale transparent conducting thin film has become a great challenge [6, 7]. SSPM is an atomic force microscopy (AFM)-based technique that senses electrostatic forces with a conductive probe and can thus in principle be used to obtain images of localized charges on surfaces and to measure the surface potential on semiconducting materials. Here, we show that the morphology and the surface electric charge distribution of ZnO and ZnO:Al can be studied at the nanoscale by SSPM.

2. Materials and methods

The ZnO and ZnO:Al thin films were grown on glass substrate by RF magnetron sputtering from ZnO (4 in. diameter) and ZnO:Al (Al₂O₃ 2 wt.%, 4 in. diameter) ceramic targets, respectively. Glass substrates were ultrasonically cleaned in acetone and deionized water and dried with N₂. Prior to each deposition film deposition, the chamber was evacuated to a base pressure of 8.0 x 10⁻⁴ Pa and the target was sputter-cleaned for 10 min at RF. Sputtering power was maintained at 200 W, and all the films were deposited at 3.0 Pa. The target-substrate distance was 50 mm for all films deposited, and no external heat treatment was applied during the time of the deposition. The films' thickness was nearly 300 nm, which was measured in-situ by using the quartz crystal thickness monitor. The electrical behaviors of the films were characterized by the four-point probe method (Ectopia HMS-300) at room temperature. The morphology and surface electrical potential of the films were investigated in detail by atomic force microscopy and SSPM techniques, respectively.

The SSPM is a technique based on standard non-contact AFM system that provides information on the electrostatic potential variations on the sample surface by mapping the difference of potential, $\Delta\Phi$, between the conductive tip and sample. The potential difference is given by [8]:

$$\Delta\Phi = \frac{\Phi_{tip} - \Phi_{sample}}{e} \quad (1)$$

where Φ_{sample} and Φ_{tip} are the work functions of the tip and sample, respectively, and e is the magnitude of the electron charge. The principle used to measure the electrostatic potential of sample in this technique is similar to the Kelvin method [9]. However, the major difference between both is that SSPM analyzes the attractive electrostatic force, F , instead of AC currents for each point of the sample area scanned. Therefore, this force takes the form:

$$F = \frac{1}{2}(\Delta\Phi)^2 \frac{\partial C}{\partial z} \quad (2)$$

where z is the tip-sample distance, and C is the separation-dependent capacitance between the tip and sample. However, conductive tips are used as a Kelvin electrode, and a positive bias voltage is applied to sample through the electronic of the AFM. Simultaneously, an AC voltage, $V_{AC} \sin \omega t$, is applied with a value below than the normal AFM oscillator frequency, which matches the natural frequency of mechanical oscillation of the cantilever-tip system (40-70 kHz). The potential from the fixed charges on the samples is different from that in the tip. Therefore, the interaction between tip and sample may be zeroed by applying an external DC voltage, V_{DC} , to the tip and adjusting until it matches the electric potential from the surface measured. Consequently, an alternating force component is introduced in the cantilever, which depends on the potential deriving from fixed charges of the samples, and becomes [8, 10]:

$$F = \frac{1}{2} \frac{\partial C}{\partial z} (V_{DC} + \Delta\Phi + V_{AC} \sin \omega t)^2 \quad (3)$$

Thus, to acquire electrical potential images, the probe scans 10 nm above the sample surface, experiencing electrostatic interactions changes with the surface and finally, the electric potential at each pixel is recorded by the computer to convert the gray-level or color-coded scale to build the electric potential image [11].

A scanning probe microscope (Quadrex Multimode, Veeco Instruments), operated under ambient conditions, was used to obtain non-contact mode AFM and SSPM side-by-side images for the investigation of surface topography and the corresponding local electrostatic potential of the ZnO and ZnO:Al thin films. All topographic measurements were obtained using a Micromasch conductive Pt-Ti cantilever with nominal spring constant of 5.0 N/m and resonance frequency of 160 kHz. SSPM was calibrated with standard surface structures gold/SiO₂.

3. Results and discussion

The surface topography and local distribution of surface electric potential of ZnO and ZnO:Al thin films were analyzed. Images of a small part of the poled area by AFM and SSPM are shown in Fig. 1. The AFM images show that both ZnO (Fig. 1a) and ZnO:Al (Fig. 1(c)) thin films in all cases were characterized by a granular structure with a grain size of about 190 nm (see Table 1).

Table 1 Grain size, Hall and superficial resistivity for the ZnO and ZnO:Al thin films.

Sample	Grain size (nm)	Hall resistivity ($\Omega \cdot \text{cm}$)	Superficial resistivity (a. u.)
ZnO	190.5±0.8	7.63×10^{-1}	0.34±0.03
ZnO:Al	180.8±0.8	4.34×10^{-3}	1.02±0.03

The corresponding SSPM images were taken when a bias of - 0.2 V was applied to the sample before the scanning. The SEPM image of ZnO film showed in Fig. 2(b) reveal a heterogeneous surface potential distribution, with a well-defined surface potential variation. From the surface potential image, is observed regions of the sample with higher potential gradient characteristic of accumulated charges. In these regions, the higher potential gradient shows a degree of correlation with the more elevated point of the surface. The more elevated regions on the topographic image are characteristic of the presence of bigger grains due to an agglomeration process during the grain growth. Therefore, the electric potential is more negative on the elevated point of the surface when compared to the depressions in the films' surface mainly because O²⁻ is held at the boundary of grains. Consequently, the charge carrier concentration increases into the grain volume and cannot be easily released, slightly increasing the surface potential value in this region. However, it can also be seen clearly that the SSPM image for the ZnO:Al films (Fig. 1(d)) shows that adjacent grains presented very similar surface potential. At the same time, one can see a non-uniformity of the surface potential resulting of regions of high and low surface potentials characterized by bright and dark areas on the image. This phenomenon may be the result of the easy mechanism of electric charge transport across the interface of each grain and the electrical properties of the grain boundary [12, 13].

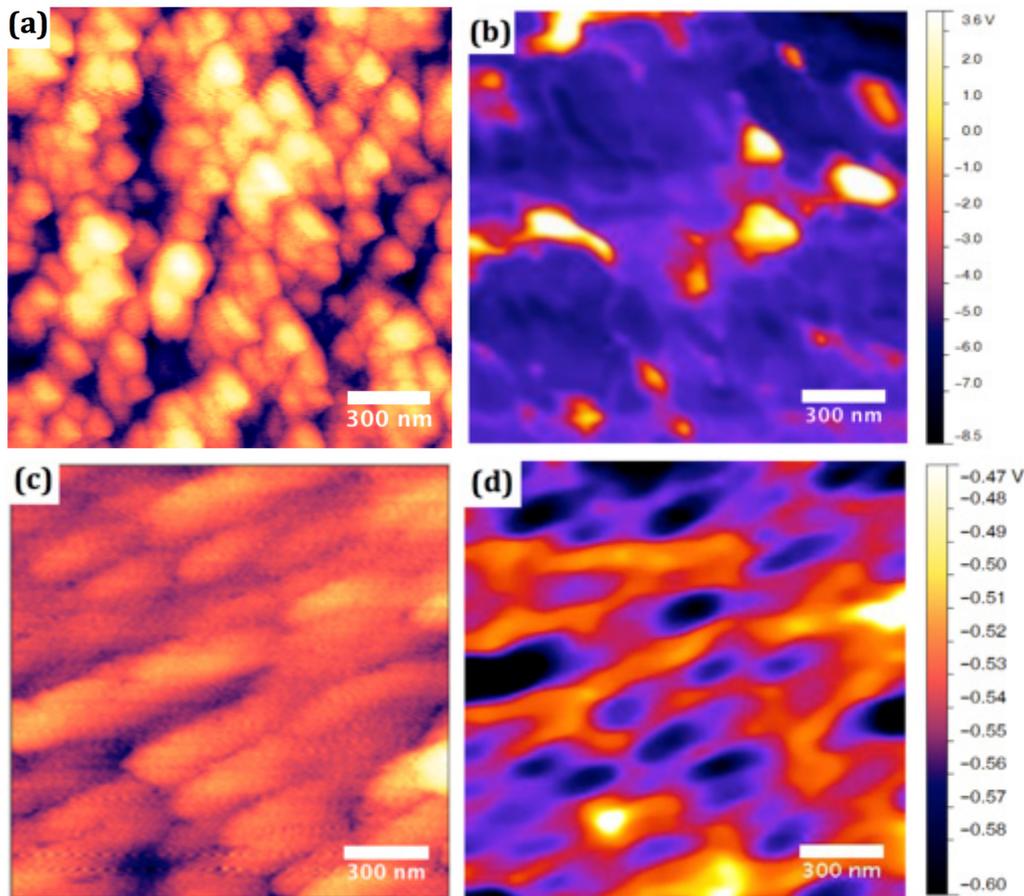


Fig. 1 Topography (left) and SSPM (right) images of the thin films: (a,b) ZnO and (c,d) ZnO:Al.

In fact, the different electrical properties of each grain boundary and the localized impurity state resulting from the Al^{3+} on the ZnO lattice make the grain boundary act as a conduction path for the electrical charges in ZnO:Al thin films [14-16]. This suggests that the mobility of the charge carriers through the grain boundary of the ZnO:Al thin film is due to the Coulomb repulsive interaction, diffusion process, or conduction process [15, 17-19]. In addition to this possible mechanism, the electric surface potential and the mechanism of charge transport on the surface of ZnO:Al depend on the surface roughness as well. Therefore, the value of the surface resistivity for the ZnO:Al film was calculated using the method proposed by Rakocevic et al. [20]. When compared to the surface resistivity value for the ZnO film, the ZnO:Al film surface resistivity decreased about 0.68 ± 0.03 in arbitrary units, which is in good agreement with the obtained decreasing value by four-point probe measurements, as shown in Table 1.

4. Conclusion

In summary, the surface electric potential in ZnO and ZnO:Al thin films was qualitatively studied by scanning surface potential microscopy. The SSPM images of the ZnO:Al film revealed that surface potential was much affected by the electrical properties of the grain boundary. The non-uniformity of the surface potential in this sample was discussed in terms of the easy mechanism of electric charge transport across the interface of each grain and the electrical properties of the grain boundary. As a result, this behavior, the easy mobility of the electrical charge carriers through the grain boundary of the ZnO:Al thin film, was attributed to the Coulomb repulsive interaction, diffusion process, or conduction process. The obtained surface potential images were useful for comparison of the surface resistivity with the values obtained by four-point probe measurements, which were in good agreement. Finally, these results can provide a good understanding of the electrical charge transport on ZnO and ZnO:Al thin film and its relevant improvements for application as a transparent electrode in photovoltaic devices.

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