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Structure Dependent Conductivity of Ultrathin ZnO Films

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Zinc oxide films dedicated for hybrid organic/inorganic devices have been studied. The films were grown at low temperature (100 °C, 130 °C and 200 °C) required for deposition on thermally unstable organic substrates. ZnO layers were obtained in atomic layer deposition processes with very short purging times in order to shift a structure of the films from polycrystalline towards amorphous one. The correlation between atomic layer deposition growth parameters, a structural quality and electrical properties of ZnO films was determined.

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1. Introduction

In recent years, the interest in thin films of wide-bandgap semiconductors has being increased rapidly. One of them is zinc oxide, which is currently widely investigated as a very promising II–VI semiconducting material for various electronic and optoelectronic purposes [1–3]. An important field of application of this material is organic electronics, in which ZnO deposited at a low temperature regime plays a role of an inorganic electrically active layer in devices [4, 5]. ZnO is a very promising material here because, opposite to most of organic semiconductors, it reveals the n-type conductivity with a level of a carrier concentration that can be substantially tuned by manipulating the growth parameters [6]. Moreover, such thin ZnO films can be deposited at temperatures below 200 °C which is the stability limit for most of organic semiconducting materials.

Most of organic semiconductors degrade under normal atmospheric conditions and require application of a surface protection layer. Zinc oxide deposited on the surface of an organic semiconductor is an active part of a junction, but also can play a role of a protection layer of such hybrid organic/inorganic device. For the latter purpose a perfect adhesion is needed, which is not easy to achieve because of surface porosity of organic semiconductors. In this case a polycrystalline or even an amorphous ZnO film structure is recommended provided relevant electrical parameters.

On the other hand, a ZnO sublayer with decreased structural quality is always observed in the interface region and it is important to investigate its electrical properties. Semiconductor films used in electronic devices are usually very thin (between 100 nm and 200 nm), so such an interface layer is expected to significantly influence the electrical characteristic.

In the present study we investigated electrical parameters of ultrathin (thickness about 100 nm) polycrystalline ZnO films deposited at the low temperature regime, i.e. a temperature adequate for application in hybrid organic/inorganic devices. In dedicated series of atomic layer deposition (ALD) processes very short purging times were applied in order to shift polycrystalline growth towards amorphous one. For these films we determined correlation between ALD growth parameters, reduced structural quality and electrical properties.

2. Experimental

The polycrystalline ZnO layers were grown by ALD in the Savannah-100 reactor using diethylzinc and deionized water as zinc and oxygen precursors, respectively. As substrate we used silicon which was uniformly covered with the ZnO film in a double exchange reaction between precursors. Nitrogen was used as purging gas. Before the ALD growth process the substrates were sequentially rinsed in acetone, 2-propanol and deionized water. The growth processes were performed for 500 ALD cycles, which resulted in the film thickness between 70 nm and 100 nm. The obtained thickness depends on the deposition temperature and is related to the ALD growth window [6].

In the present experiment we performed a series of deposition processes with a different ALD purging time that ranged from 0.1 s to 2 s, while the rest of the ALD parameters (pulsing times and pressures) remained fixed.

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The ALD growth process consists of many deposition cycles and each of them consists of four stages: two pulsing times of both precursors and two purging times after precursors. The latter parameters influence a lot the crystallographic quality of deposited films. It has been found that films with good crystallographic quality require quite long purging times, even above 10 s [7]. Therefore we expected that shortening of purging times would shift a structure of the films from polycrystalline towards amorphous one. The ALD growth processes were performed at 100 °C, 130 °C, and 200 °C.

3. Results and discussion

Atomic force microscopy (AFM) images show that the obtained films are atomically flat and the surface roughness, defined by the root mean square (RMS) value, is about 3 nm (see Fig. 1, down), so it is only slightly higher than in case of ZnO films grown with purging time of 8 s and 20 s [6, 7]. This level of the surface roughness is appropriate for electronic applications. Scanning electron microscopy (SEM) images (Fig. 1, top) show a granular microstructure with grain diameters from 25 nm to 75 nm depending on ALD process parameters. The grain size was approximately 50–75 nm for 130 °C growth temperature, while at the temperature of 200 °C it was slightly smaller, below 50 nm.

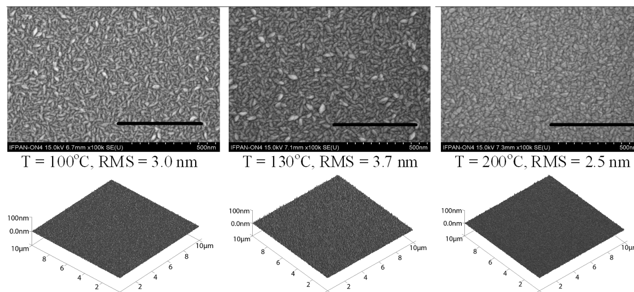

Fig. 1. SEM (top) and AFM (bottom) images of 100 nm thick ZnO films grown with purging time 2 s. The 500 nm scale is shown at SEM images. AFM images cover an area of 10×10 μm^2.

Room temperature photoluminescence (RT PL) spectra reveal that all the samples show a band-edge PL at 377 nm. For samples obtained at 100 °C and 130 °C a wide defect-related PL band between 500 nm and 700 nm was also seen, while it is absent in PL spectra of ZnO films deposited at 200 °C. The defect-related band is significantly stronger when purging time is very short (see Fig. 2) and it is more than twice weaker when purging time exceeds 1 s. Intensity of a band-edge PL increases slightly when purging time becomes longer. Both these effects demonstrate the influence of the purging time on the structural quality of the films. The peak observed at 540 nm is only a second harmonic of the $\alpha = 270$ nm excitation wavelength.

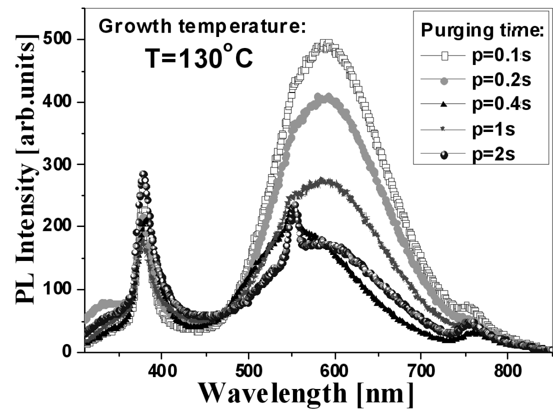

Fig. 2. Room temperature photoluminescence spectra of ZnO films about 100 nm thick deposited at 130 °C with different purging times (from 0.1 s to 2 s).

Interesting results are provided by the Hall measurements that were obtained in the van der Pauw geometry using the RH2035 PhysTech GmbH system equipped with a permanent magnet producing a magnetic field $B = 0.426$ T. As ohmic contacts to ZnO, the e-beam evaporated bi-layers of Ti(100 Å)/Au(400 Å) were used.

The Hall effect studies showed that the ZnO layers obtained at 200 °C are characterized by the n-type conductivity, with carrier mobility 20–22 cm^2/(V s) and a high electron concentration ($\approx 4 \times 10^{19}$ cm^{-3}) that only weakly depends on the purging time.

On the other hand, the ZnO layers obtained at 100 °C and 130 °C with very short purging times (0.1 s, 0.2 s, 0.4 s) behave differently. The Hall measurements reveal the p-type conductivity with a carrier concentration of about 1.5×10^{16} cm^{-3}. For ZnO films deposited at 130 °C with longer purging times we observed the n-type conductivity while films deposited at 100 °C still show p-type conductivity, even for purging time 2 s. We assume that these results can be slightly influenced by the electrical characteristic of the substrate. The ZnO films were deposited on a resistive p-type Si(001) substrate with carrier concentration of 1.2×10^{12} cm^{-3} and mobility 316 cm^2/(V s). Only samples deposited at temperatures 100 °C and 130 °C with very short purging time reveal an effect of the p-type conductivity.

Some light on the observed effect is shed by the X-ray diffraction (XRD) studies. They show that all investigated ZnO samples were polycrystalline, even these deposited with very short pulsing times (0.2 s). In XRD spectra one can observe (10.0), (00.2), (10.1) and (11.0) crystallographic orientations. Their relative intensity depends on deposition temperature. Higher deposition temperature privilege the (00.2) crystallographic orientation. When we compare XRD spectra of ZnO films deposited with purging time 0.4 s at 100 °C, 130 °C (both reveal the p-type conductivity) and 200 °C (with the n-type conductivity) we see that the intensities of (10.0), (10.1) and (11.0) diffraction peaks are similar. The only dif-

ference can be seen in both intensity and location of the (00.2) diffraction peak, which is much stronger for ZnO film deposited at 200 °C. Also its maximum is located at 2Θ angle 34.4°, while for films deposited at 100 °C and 130 °C it is observed slightly lower, at 2Θ angle 34.2°. This indicates that a change observed in the type of conductivity is related to the mechanical stress in the ZnO/Si interface layer.

4. Summary

To summarize, we investigated a few series of very thin (70 nm to 110 nm) ZnO films that were obtained in the ALD processes with very short purging times (from 0.1 s to 2 s). The films were grown at temperatures 100 °C, 130 °C, and 200 °C that are appropriate for deposition on organic substrates. The films show granular surface structure with the surface roughness about 3 nm. RT PL spectra show a band-edge PL line at 377 nm and defect-related band. The intensity of the latter one anti-correlates with a purging time. The films grown at 100 °C and 130 °C with purging time below 1 s show *p*-type conductivity when deposited on a resistive silicon substrate. Based on the XRD studies we tentatively ascribe this effect to the stress in the ZnO sublayer near the ZnO/interface.

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