مجلة جامعة تشرين للبحوث والدراسات العلمية - سلسلة العلوم الأساسية المجلد (35) العدد (4) 2013
Tishreen University Journal for Research and Scientific Studies - Basic Sciences Series Vol. (35) No. (4) 2013

Structural Characterizations, Optical and Electrical Properties of Zinc Oxide Thin Films Grown by Atomic Layer Deposition Method

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(Received 29 / 7 / 2013. Accepted 23 / 9 /2013)

□ ABSTRACT □

In this paper we present the structural, optical and electrical characteristics of ZnO thin films grown for different parameters by the atomic layer deposition (ALD) method. The films were grown on glass and silicon substrates at low temperatures. We used diethyl-zinc (DEZn) and deionized water as zinc and an oxygen sources, respectively. Measurements of surface morphology, photoluminescence at room temperature (RT PL) and Hall Effect were made for ZnO layers. The films obtained at 130°C show the highest carrier concentration (1.1×10^{19} cm^{-3}) and the lowest resistivity (2.84×10^{-2} Ωcm). The films exhibit mobility up to 19.98 cm^2/Vs that we associate to the technological process used.

Keywords: atomic layer deposition, electrical properties, optical properties, structure of zinc oxide.

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المميزات البنيوية والخصائص الضوئية والكهربائية لأفلام رقيقة من أكسيد الزنك منماة بطريقة الترسيب الذري الطبقي

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(تاريخ الإيداع 29 / 7 / 2013. قُبِل للنشر في 23 / 9 /2013)

ملخّص

نقدم في هذه الورقة الخصائص البنيوية والضوئية والكهربائية لأفلام رقيقة من أكسيد الزنك تمت تنميتها من أجل بارامترات مختلفة بوساطة طريقة الترسيب الذري الطبقي (ALD) . وقد نميت هذه الأفلام على ركائز من الزجاج والسيلكون عند درجات حرارة منخفضة. استخدمنا ثنائي إيتيل الزنك (diethyl-zinc) والماء منزوع الأيونات كمصادر للزنك والأكسجين، على التوالي. أجريت قياسات مورفولوجيا السطح، والتألق الضوئي في درجة حرارة الغرفة ومفعول هول لطبقات من أكسيد الزنك. وقد بينت الدراسة أن الأفلام التي تم الحصول عليها عند درجة حرارة 130°C تظهر أعلى تركيز للحاملات (1.1×10^{19} cm^{-3}) وأقل مقاومة (2.84×10^{-2} Ωcm). كما أظهرت الأفلام حركية تصل إلى 19.98 cm^2/Vs وأنها ترتبط مع عملية التكنولوجيا المستخدمة.

الكلمات المفتاحية: الترسيب الذري الطبقي، الخصائص الكهربائية، الخصائص الضوئية، بنية أكسيد الزنك.

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INTRODUCTION:

Zinc oxide (ZnO) is nowadays extensively studied as a very attractive material for optoelectronic applications. The main advantages of some crucial features of this material, such as its wide direct band gap (3.37eV at T=300K) or high exciton binding energy (60 meV at T = 300K) have already been widely discussed in numerous papers and reviews [1-3]. The main requirement for transparent electrode application is low resistivity which should be on the order of 10^{-3} Ω cm or even less. This goal can be achieved in two ways, i.e. by formation of intrinsic donors due to lattice point defects or by intentional doping with extrinsic atoms [4].

Atomic Layer Deposition (ALD) technique has large potential to be widely used in production of photovoltaic (PV) devices, for deposition materials used in active parts of solar cells or for deposition of transparent conductive oxides (TCOs) for upper, transparent contacts of solar cells [5]. One of the most important properties of ALD method is possibility of low temperature growth. ZnO films with attractive electrical properties can be deposited at below 200°C, at conditions suitable for construction of semiconductor/organic material hybrid structures. This opens possibilities of construction of novel PV panels based on very cheap organic materials forming PV devices of third generation. Moreover, ZnO is considered at the moment to be one of the most promising TCO materials and as partner of CdTe in a second generation of PV devices [6].

There are a few papers which report on low temperature ZnO films fabricated by ALD [7-9]. These papers deal mainly with the growth window and structural properties of ALD - ZnO thin films fabricated with diethylzinc (DEZn) and water precursors and are focused on growth temperature above the limit defined by low thermal budget of organic electronics.

AIM OF STUDY:

This paper deals with structural, optical and electrical characteristics of ZnO grown by ALD at extremely low temperature (120°C and 130°C). We analyze the influence of growth conditions on the behavior of photoluminescence and strongly affecting electrical properties of ZnO layers obtained. Also, we show that both surface roughness as well as the preferred orientation can be controlled by the growth temperature and ALD cycle parameters.

MATERIALS AND RESEARCH METHODS:

Zinc oxide films were deposited by the ALD method on glass and Si substrates. We used diethyl-zinc (DEZn) and deionized water vapour as zinc and oxygen precursors, respectively. The pressure in the growth chamber was a few mbar; (about ~10^2 mbar). The films were grown at two different temperatures, i.e. at 120, and 130°C. In the ALD process, reactants (precursors) are sequentially introduced to the growth chamber where they reach a surface of the growing film. Each cycle of precursor's dose is separated by purging the chamber with the neutral gas (e.g. nitrogen) [10].

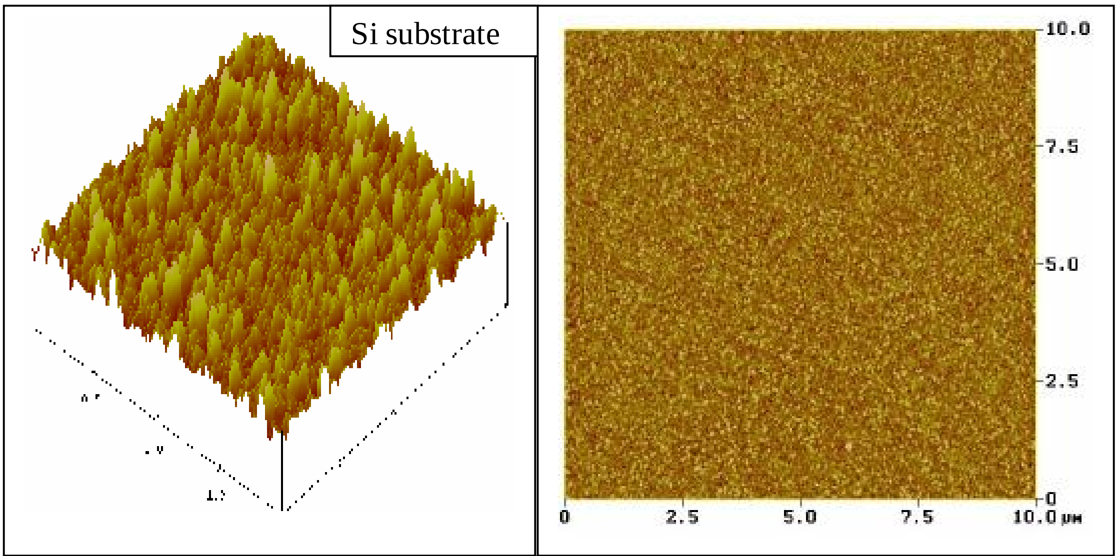
Following growth parameters were used by us in the ALD process: pulsing times (time of introducing of a given precursor): for H_2O -15 ms, for DEZn – between 15 ms and 60 ms. To achieve low free electron concentration relatively long purging times: for H_2O - 8 s or 20 s, for DEZn - 4 s or 8 s were necessary [11, 12]. The thickness of obtained films was measured by Mikropack Nanocalc 2000 reflectometer for ZnO on Si substrates (97 nm at 120°C and 249 nm at 130°C). The atomic force microscope (AFM; Veeco, Digital Instruments) in tapping mode was used to investigate the surface morphology of the films.

X-ray diffraction (X'Pert MPD diffractometer) measurements were performed with monochromatic Cu K_{α}(l=1.54 Å) radiation. The Hall effect measurement setup consists of the current source (Keithley current/voltage source 238), the voltmeter (Keithley multimeter 2000), and the temperature controller (Lake Shore 331). The typical values of electrical current flown through the sample were I_{dc}=0.1-1 mA for samples with resistance about 1 kΩ (low resistance samples) and I_{dc}=0.1-1 μA for 1 MΩ and greater (high resistance samples). Photoluminescence (PL) spectra were measured in the range 340–820 nm with the excitation wavelength of 300 nm using SM2203 Spectrofluorimeter with built in two double monochromators, 150 W high pressure Xe lamp as the excitation source, and the R-928 Hamamatsu photomultiplier for the PL detection.

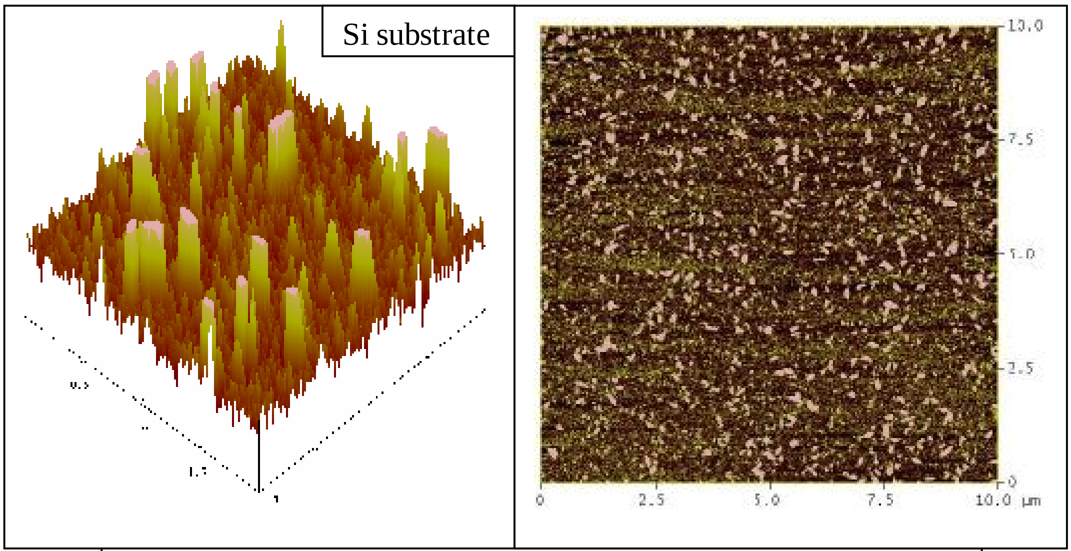
RESULTS AND DISCUSSION:

The root mean square (rms) of surface roughness obtained from the atomic force microscopy (AFM) images varied between 6.907 and 2.364 nm with an accuracy of 0.1 nm, so the films were atomically flat (Fig. 1). The rms values slightly depend on growth temperature and purging time and strongly decrease with the decreasing temperature.

Structural properties of ZnO layers were obtained from XRD in a full angular range. The investigated angular region (2θ) was 25°- 70° and included the ZnO related diffraction maxima corresponding to (10.0), (00.2), (10.1), and (11.0) crystallographic orientations. The XRD spectra show the polycrystalline structure of ZnO films grown at low temperatures (Fig. 2). We found that the relative intensities of the individual peaks depend on the deposition temperature and other growth process parameters such as pulsing and purging times [12]. The images in figure 2 show the highest reflection intensity for (00.2) orientation in the sample. Therefore, one can relate columnar crystal growth to the preference of c-axis orientation perpendicular to the substrate surface.



Thickness: 97 nm. Growth rate: 1.94 Å/cycle. RMS: 2.364 nm.
T_S=120 °C, 500 cycles. water 15ms/20s, DEZn 60ms/8s



Thickness: 249 nm. Growth rate: 2.49 Å / cycle. RMS: 6.907 nm

T_S=130°C, 1000 cycles, water 15 ms/8s, DEZn 15ms/1/4s

Fig. 1: (left side) The AFM image of a 2 ´ 2 mm^2 region of the ZnO/Si layers, and (right side) surface morphology of image 10 ´ 10 mm^2 at two different temperatures.

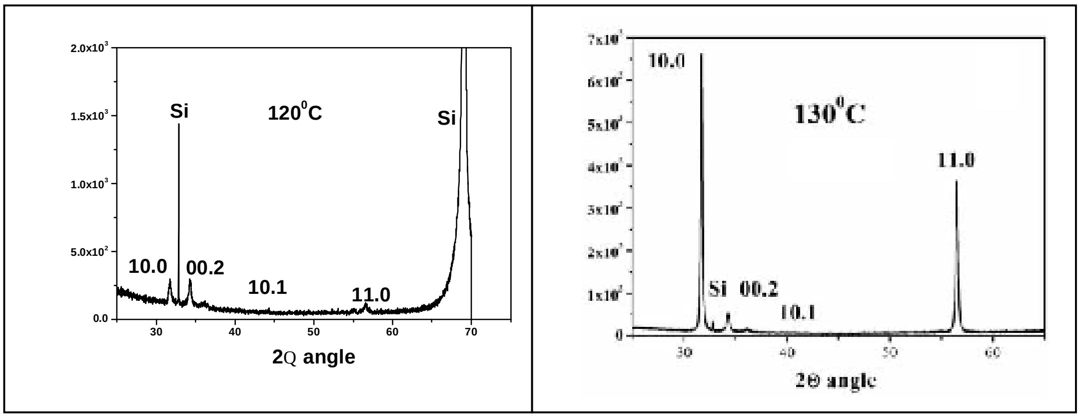
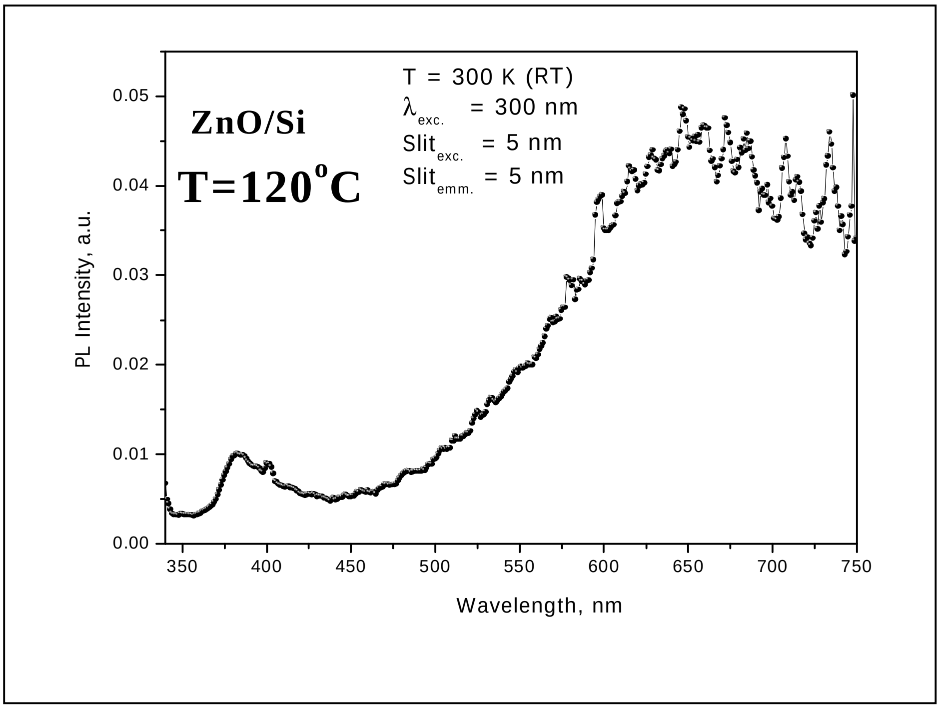
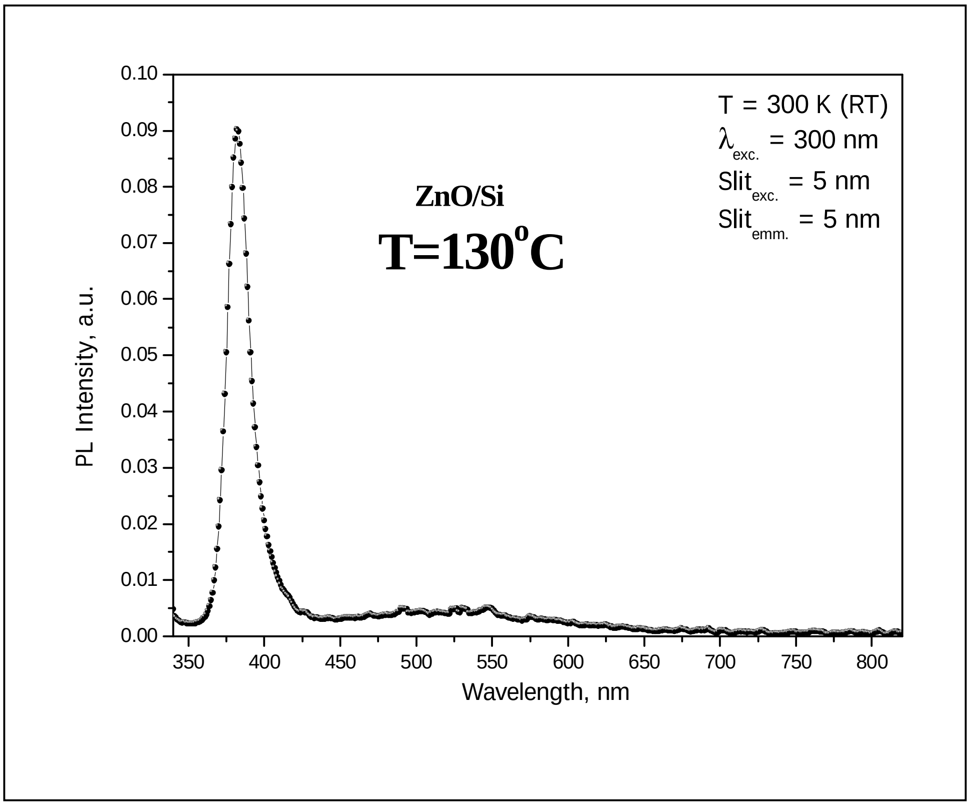


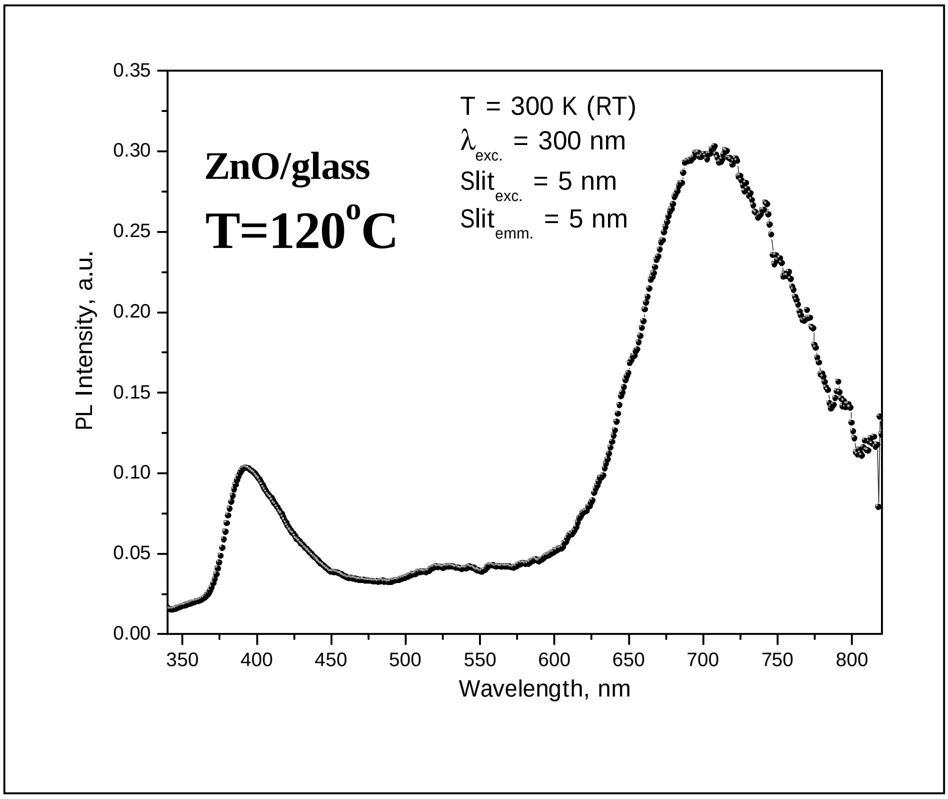
Fig. 2: XRD spectra for two ZnO films grown by ALD on silicon substrate at 120°C and 130°C.

Photoluminescence is a commonly used characterization method of layers grown by different techniques. Generally, the most important observation is the detection or not of the PL at the spectral region close to the band gap value (called “edge” PL) [1]. This PL is only seen in films of good structural quality and also at relatively low free carrier concentration. As already mentioned, ZnO has an atypically large value of free exciton binding energy, which is more than two times larger than the *kT* value at room temperature. As a consequence free excitonic PL can be seen in ZnO up to room temperature [11]. At low temperature excitons are usually localized by trapped at impurities (in ZnO predominantly donor impurities). On the other hand, observation of edge PL leads to the statements on the high quality of the obtained films. For the purpose of the present work we also looked for deep defect related bands, the intensity of which correlates with a high doping level with unintentional impurities.

PL experiments presented in this study were performed on a set of as grown ALD - ZnO samples deposited at two temperatures 120°C and 130°C. The PL spectra consist of two bands: a sharp band related to near band edge UV emission i.e., in the vicinity of 384 nm. Whereas a broad green luminescence band related to radiative recombination via deep defect / impurity levels i.e., in the spectral regions (550 -750 nm). First of all, this PL is stronger and narrower (for lower temperatures of the growth) in thicker films and increases with increasing temperature, reaching optimum growth (Fig. 3), but also for the selected growth conditions and for the Si substrate. In the present study we also found that the relative intensity of the edge PL emissions depends on the purging time after supplying the water precursor.







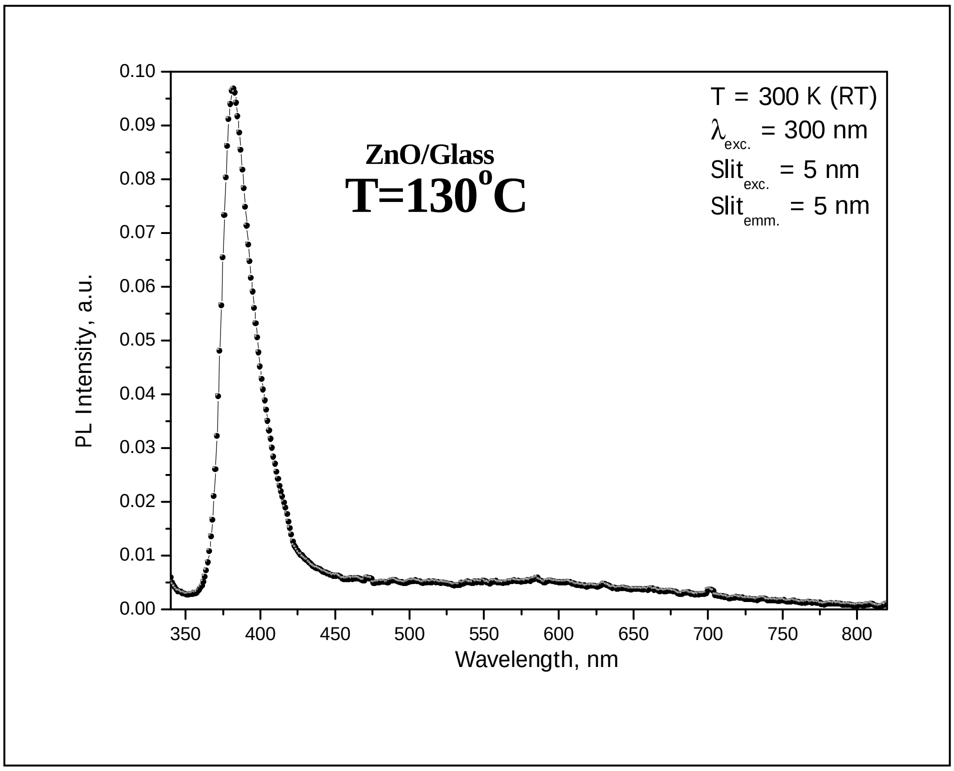


FIG. 3: PL observed at room temperature (RT) for the ZnO layer grown at 120°C and 130°C on silicon and glass substrates.

Electrical parameters of low temperature ZnO films were obtained from the Hall Effect measurements. The good ohmic contact was ensured by indium soldering the thin gold wires to the sample surface. It is observed the linear current-voltage characteristics of these contacts in the wide range of the current values. The results of Hall measurements for samples with a long purging time are gathered in Table.

TABLE. The results of Hall measurements for ZnO layers grown with the following growth parameters: pulsing time (H_2O)=15 ms, purging time=20s or 8s, pulsing time (DEZn) = 60ms or 15ms, and purging time=8s or 4s.

Mobility [cm^2/Vs]	Concentration [cm^{-3}]	Conductivity [$\Omega^{-1}cm^{-1}$]	Resistivity [Ω cm]	Carrier	T(°C)
14	9×10^{18}	2.01×10^{1}	4.95×10^{-2}	n	120
19.98	1.1×10^{19}	3.52×10^{1}	2.84×10^{-2}	n	130

For investigated ZnO samples free carrier concentration varied between 10^{19} and $10^{18}cm^{-3}$ and strongly correlated with deposition temperature, i.e., low free carrier concentration and low conductivity were observed for samples grown at lower temperature. The lowest observed free carrier concentration (measured for as grown samples) was achieved for sample at the level of $9\times10^{18}cm^{-3}$.

The best electrical parameters, i.e., the lowest free carrier concentration we obtained for ZnO films grown with a longer purging time (20 s) after water precursor. We assign this effect to the better purifying of the surface, which are referred to be abundant in ZnO films grown with a water precursor. One can notice that the highest carrier mobility is observed for the layer grown at 130°C. This probably influenced by the high crystallographic quality of grains and cannot due to the lower grain boundary scattering.

CONCLUSIONS AND RECOMMENDATIONS

The present results show that optical properties, electrical properties and surface morphology of ZnO thin films, grown at low temperature using DEZn precursor, vary with the thickness of the sample. We correlate PL with carrier concentration; when defects PL decreases, electron concentration increases, which suggests that in the thicker sample we have a lower concentration of some deep defects. Furthermore, for ZnO layers grown at temperature 130°C we did not observe defect related bands in the PL spectra. This is evidence that extremely low temperature growth by ALD can result in the high quality ZnO thin films with inefficient nonradiative decay channels. By comparison of structural, optical, and electrical properties of our LT ZnO films we noticed that LT ZnO growth correlates with good structural and optical properties.

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