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RAPID ANNEALING OF BLACK ZnO THIN FILMS PREPARED BY PULSED LASER DEPOSITION

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ZnO thin films were deposited by pulsed laser deposition (fluence 2.2 J/cm^2) in vacuum on different substrates kept at room temperature. This temperature allowed for fast film growing, however the as-prepared films had low transparency. To improve this optical property, keeping up at the same time the high electric conductivity of the films, post-annealing procedures in vacuum and in air were carried out. The influence of these procedures on the optical absorption, photoluminescence and electrical properties has been investigated. It is shown that the annealing in air improves only the transparency of such a film, however its conductivity decreases markedly. In turn, vacuum annealing for 3 min. at 600° C results in better transparency of the films, with their electric conductivity kept high.

1. INTRODUCTION

Transparent conductive coatings are important in the solar cell manufacturing. Zink oxide is one of the most suitable materials for such applications, being cheap, inert and non-toxic. A conductive and transparent ZnO coating can easily be obtained using the pulsed laser deposition (PLD) technique [1]. Pure ZnO films produced by PLD have the n-type conductivity due to zinc excess or oxygen vacancies [2, 3]. The conductivity of such a film gradually decreases with the oxygen pressure increasing during ZnO deposition [2]. Consequently, a ZnO film deposited in vacuum is oxygen-deficient, has a high electron concentration and, therefore, high electrical conductivity.

The optimal substrate temperature for deposition of highly transparent ZnO thin films with low resistivity is known to be 350–400 °C [2, 4]. However, at higher substrate temperature the growth of films slows down owing to a high desorption rate of deposited atoms; in this case, for the growth at high substrate temperature a longer time is needed, besides, more targets are consumed. We deposited ZnO films in vacuum on a substrate kept at room temperature (RT), after which a post-annealing procedure was used to improve the optical properties of the deposited films.

2. EXPERIMENTAL

Ablation of a ZnO ceramic target was performed in a vacuum of 10^{-5} Torr, using the third harmonic (355 nm) of an Nd:YAG (SL-312, *Expla*) 135 ps laser with a 10 Hz repetition rate. A laser beam was focused by a spherical lens into a spot of 1 mm in diameter, with the resultant fluence of ~2.2 J/cm^2. The target –

sample distance was 30 mm. Several substrates were chosen: CaF_2 and quartz for the optical measurements, glass and highest-quality mica for the AFM and conductivity measurements. The deposition time was 30 min. After deposition, some of the samples were annealed in the same vacuum chamber at 600 °C for 3 min.

The optical absorption was measured on a UV-VIS SPECORD spectrophotometer (M40, *Carl Zeiss*). The photoluminescence was exited by a variable wavelength laser (NT-342/3UV, *Expla*) at 275 nm and measured by a spectrometer (SR-303i-B, *Andor Technologies*). The surface topography was scanned by a CP-II AFM (*Veeco*), with tapping tips DP15 (*Mikromasch*) used. For measuring the electrical properties of the films, Al contacts were deposited by thermal evaporation. The current-voltage curves were obtained using a function generator (33220A, *Agilent*), a multimeter (2000, *Kethley*), and a picoampermeter (6485, *Kethley*).

The thickness of films was measured by the AFM after material deposition when a height step formed by a shadow mask. The mask (TEM copper grid, *Agar Scientific*) was placed on the substrate before the deposition process. After that the mask was removed, and rectangular islands of deposited material were scanned by the AFM to measure the resulting film thickness. Its values were obtained to be ~200 nm in the central region and ~30 nm in the peripheral part of the sample (15 mm apart from the centre) after 30 min deposition at the laser fluence of 2.2 J/cm^2.

3. RESULTS

The middle part of a ZnO film obtained by PLD in vacuum at RT had dark-brown colour at the centre, while the peripheral part was transparent (Fig. 1*a,c*). The brown coloration was attributed to the defect electronic states, such as oxygen vacancy, interstitial zinc atoms and low-valence ZnO [5]. Probably, at a high deposition rate the Zn and O atoms are lacking time or energy to form a defect-free crystal. The AFM topography measurements (Fig. 2) show that the film surface is quite smooth, with small-sized grains in the peripheral part (roughness average R_a = = 2.7 nm and ten-point height R_z = 25 nm), and more rough surface in the central (dark) region (R_a = 13 nm and R_z = 105 nm).

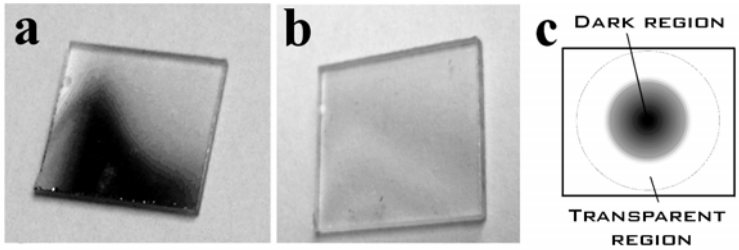

Fig. 1. Photos of a quartz sample taken before (*a*) and after (*b*) vacuum annealing; a schematic picture of a ZnO film obtained by PLD with a dark central and a transparent peripheral regions (*c*).

To improve the optical transparency we used the vacuum annealing of ZnO coated samples at 600 °C for ~3 min. The annealing procedure turned out to be quite effective: dark coloration of the as-prepared ZnO film rather quickly disappeared, and the annealed film became transparent (Fig. 1*b*).

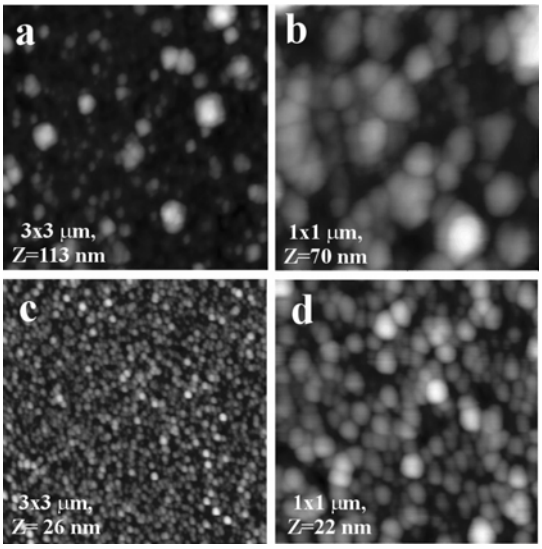

Fig. 2. Surface topography of the ZnO film: central (dark) region (*a, b*), peripheral region (*c, d*).

The optical absorption spectra of the ZnO film before and after vacuum annealing measured in dark and transparent regions are presented in Fig. 3*a*. No distinctive absorption edge can be seen on the spectra measured in the dark region of ZnO film before annealing. Obviously, optically active defect states are abundant and hide the band edge absorption. However, after annealing this edge becomes clearly visible; changes in the transparency of the peripheral (transparent) region after this procedure are not much pronounced.

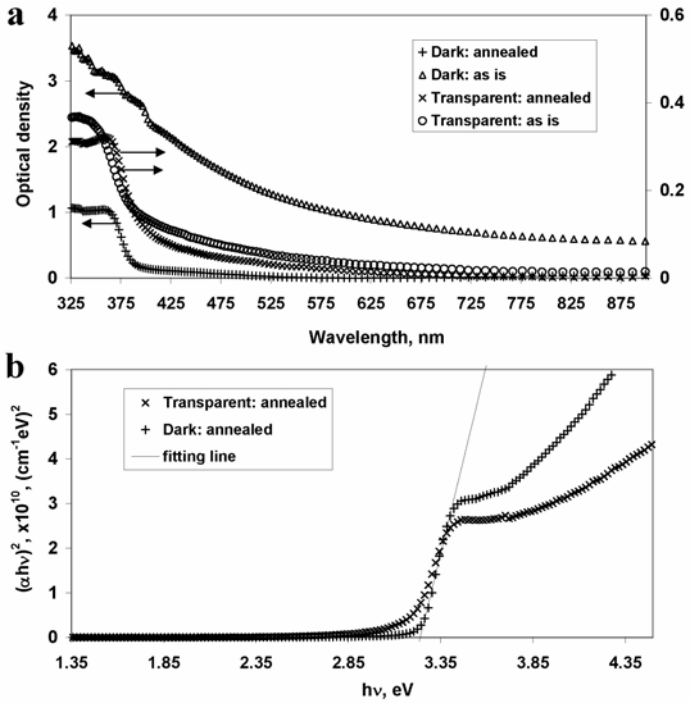

Fig. 3. Optical absorption of the ZnO film before and after vacuum annealing; optical density is plotted *vs* wavelength (*a*) and $(\alpha h\nu)^2$ *vs.* the photon energy $h\nu$ (*b*).

The ZnO is known to be a direct-band-gap semiconductor, and hence the absorption graph should be plotted as $(\alpha hv)^2$ versus the photon energy hv. The band gap E_g in the thin film is approx. 3.15–3.2 eV (according to the fitting of the absorption edge position, see Fig. 3*b*).

To gain additional information on the electronic states of the ZnO film before and after annealing, photoluminescence spectra were measured (Fig. 4). The as-prepared ZnO film exhibits a small exciton peak at 386 nm (3.21 eV) and broad unstructured emission from 430 to 900 nm, which agrees well with the absorption spectra of the ZnO film before annealing (Fig. 3*a*). After the vacuum annealing the exciton peak intensity grows up several times, while the low energy emission decreases, except the broad shoulder centred at approx. 500 nm (2.48 eV). This is associated with a singly-ionized oxygen vacancy [6]. After annealing in air the exciton peak grows about 3 times, and the 500 nm shoulder disappears.

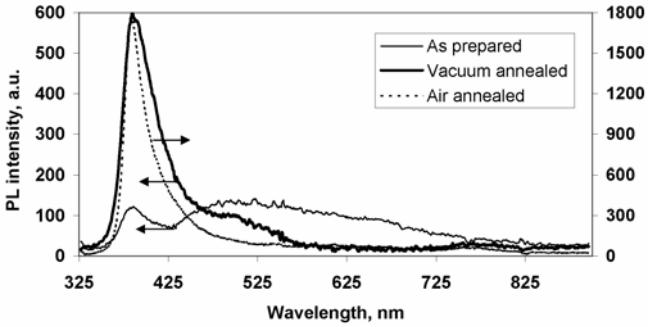

Fig. 4. Room temperature PL spectra of the ZnO film measured in a dark region of the sample before and after annealing in vacuum and in air.

To measure the current-voltage dependence and to find film resistivity, onto the ZnO samples Al contacts were deposited [1]. The obtained C–V dependence was linear, and the resistivity of as-prepared ZnO films was estimated to be $2–4 \cdot 10^{-2}$ Ωcm, which is close to the previously reported resistivity of $2 \cdot 10^{-2}$ Ωcm for undoped ZnO films deposited at 400 °C and a partial oxygen pressure of 350 mTorr [4]. The resistivity of films annealed in vacuum increased ~ 10 times, whereas that of films annealed in air – 10^4 times. This result agrees with the assumption that the conductivity of undoped ZnO films is provided by zinc excess or oxygen vacancies [2, 3]. The photoluminescence spectra of the vacuum-annealed film have a band corresponding to the ionized oxygen vacancy, which disappears in the spectra of the air-annealed film.

4. CONCLUSIONS

Conductive ZnO films were prepared by pulsed laser deposition in vacuum 10^{-5} Torr at RT. The low substrate temperature allows a higher growth rate of the films to be reached in comparison with that on a heated substrate, making however them highly opaque. Annealing of such a film in air significantly improves its transparency but sharply reduces its electric conductivity. In turn, annealing in vacuum for 3 min at 600 °C allows more transparent films to be obtained, keeping their conductivity at a high level.

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ZnO PLĀNO KĀRTIŅU, KAS IEGŪTAS AR LĀZERALBLĀCIJU, ĀTRĀ ATDEDZINĀŠANA

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K o p s a v i l k u m s

ZnO plānas kārtiņas tika iegūtas, izmantojot impulsu lāzerablāciju vakuumā uz pamatnes pie istabas temperatūras. Zema temperatūra nodrošina ātru kārtiņas augšanu, taču uzklātajām kārtiņām ir zema gaismas caurlaidība. Atdedzināšana gaisā padara kārtiņas caurspīdīgas, taču ievērojami samazina to elektrovadītspēju. Atdedzināšana vakuumā 3 minūtes pie 600 °C uzlabo kārtiņas gaismas caurlaidību, saglabājot labu elektrisko vadāmību.

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