STRUCTURE AND OPTICAL PROPERTIES OF ZnO THIN FILMS GROWN BY MAGNETRON SPUTTERING

I. Parkhomenko[1)], L. Vlasukova[1)], I. Romanov[1)], D. Caffrey[2)], A. Zhussupbekova[2)], D. Korolev[3)]
[1)]*Belarusian State University, 4 Nezavisimosti Ave., 220030 Minsk, Belarus, parkhomenko@bsu.by, vlasukova@bsu.by, romivan@bsu.by*
[2)]*School of Physics, Trinity College, The University of Dublin, Dublin 2, Ireland, dcaffrey@tcd.ie, zhussuppa@tcd.ie*
[3)]*Lobachevsky State University of Nizhny Novgorod, 4 Ashgabad Str., 603105 Nizhny Novgorod, Russia, dmkorolev@phys.unn.ru*

ZnO films of different thicknesses have been formed on quartz and oxidized Si substrates using a magnetron sputtering technique. RS and PL spectroscopy as well as measurements of absorption and reflectance spectra were used in order to investigate a phase composition and optical properties of deposited films. RS data confirmed the wurtzite structure of ZnO as well as the presence of Zn_i, V_O, or defect complexes containing Zn_i and V_O in ZnO. Thin ZnO films (14 and 40 nm) revealed an optical reflectance lower than that of bare SiO_2/Si substrates in the visible and IR range. Annealed ZnO films exhibit strong emission in blue and red spectral range. It indicates a potential application of them as antireflection coatings for silicon based solar cells and light-emitting structure.

Keywords: SiO_2/Si wafers; magnetron sputtering; ZnO thin films; structure and optical properties; oxide electronics.

Introduction

Zinc oxide (ZnO) has received widespread attention due to its remarkable properties in several fields that extend from optoelectronic devices up to pharmaceutical applications. ZnO is characterized by good transparency and such interesting properties as high electrical conductivity [1, 2], diluted ferromagnetism, multiferroic properties above room temperature [3, 4] and resistive switching behavior [5-7]. These properties make ZnO a promising candidate for applications as non-volatile resistive memory [8], spintronic devices with high energy efficiency and integrated photonic devices [9, 10]. Semiconducting metal oxides with large bandgap (thus transparent to the visible range of radiation, such as ZnO with a bandgap of ~3.37 eV) can be used to fabricate thin-film transistors with high channel mobility [11]. In view of possible technological applications, it is interesting to explore the growth of thin ZnO films on Si wafers.

Here we present an investigation of structural and optical properties of thin ZnO films formed on Si and quartz wafers by magnetron sputtering.

Experiment

There were two sets of samples. For the first set, the initial samples of 1×1 cm^2 were cut from the thermally oxidized n-type Si wafer with SiO_2 thickness of 40 nm. The second set included the samples of quartz glass. All samples were ultrasonically cleaned in isopropanol for ten min prior to deposition. The ZnO deposition was carried out at 300 °C using magnetron sputtering of 2.00’’ ZnO target with 50 W applied power in an Ar atmosphere at pressure of 10^{-3} mbar. The thicknesses of deposited ZnO films (*d*) were 14, 40 and 100 nm. After deposition a part of samples was annealed at 500 °C for 1 hour in oxygen.

To investigate ZnO phase composition Raman measurements were performed in backscattering geometry with Nanofinder High End micro-Raman spectrometers (LOTIS TII) using a 532-nm (2.3 eV) laser beam, far from the resonance condition of ZnO. Optical spectra (transmission (*T*) and reflectance (*R*)) were studied at room temperature in the spectral range of 190–2500 nm by means of Lambda 1050 spectrometer (Perkin Elmer). Absorption coefficients (α) were calculated by the formula:

$$\alpha = -\frac{1}{d}\ln\frac{T}{1-R}.$$

A room-temperature photoluminescence was studied using the He-Cd laser beam at the wavelength λ = 325 nm as excitation source.

Results and discussion

Fig. 1 shows the Raman spectra of ZnO films on quartz and Si substrate.

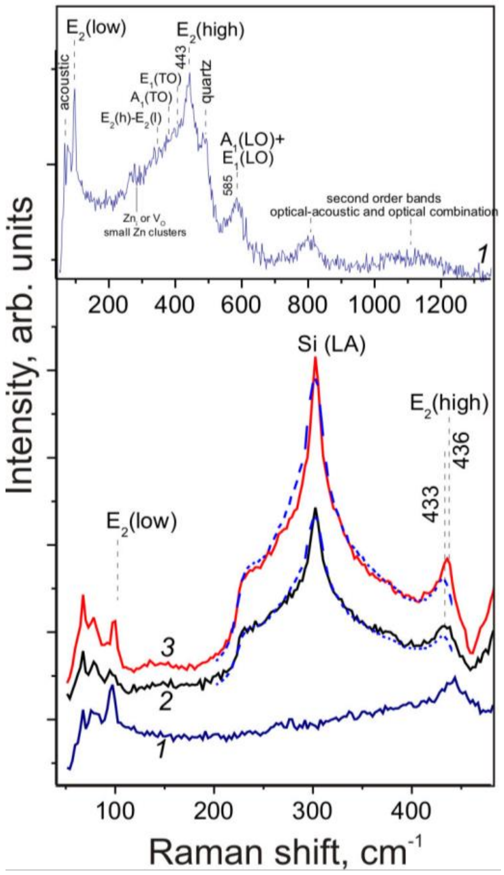

Fig.1. Raman spectra of ZnO (100 nm) films formed on quartz substrate (*1*) and on SiO_2/Si substrate before (*2*) and after annealing (*3*). The dashed lines are corresponding normalized spectra of SiO_2/Si substrate

Raman spectra of ZnO films deposited on SiO_2/Si as well as on quartz substrate exhibit band at 99 cm^{-1}. The presence of E_2 (high) peak at 443 cm^{-1} confirms the wurtzite structure of ZnO. The shift this peak from tabular value (437 cm^{-1}) is possibly caused by the compressive strain in the film. The presence of band at 585 cm^{-1} in ZnO is commonly assigned to zinc interstitials (Zn_i), oxygen vacancies (V_O), or defect complexes containing Zn_i and V_O. The band at 584 cm^{-1} (LO-quasi-mode) related to Zn_i and V_O defects exhibits only for the samples on quartz substrate. One can conclude, the film deposited on SiO_2/Si substrate contains lesser defects in comparison with film on quartz substrate. Unfortunately, the ZnO characteristic band at ~437cm^{-1} overlaps with signal from Si (at 432 cm^{-1}). However, on closer inspection, one can see weak increase and shift of this band after annealing. Besides, annealing results in an increase of ZnO band at 90 cm^{-1}. Thus, annealing improves crystalline quality of ZnO films deposited on SiO_2/Si substrate. It should be noted that the position of E_2 (high) band for films on SiO_2/Si substrate is closer to standard one at 437cm^{-1}. So, the ZnO film on SiO_2/Si substrate is not stressed, unlike the film on quartz substrate.

Fig. 2 depicts optical spectra of ZnO films on quartz substrates.

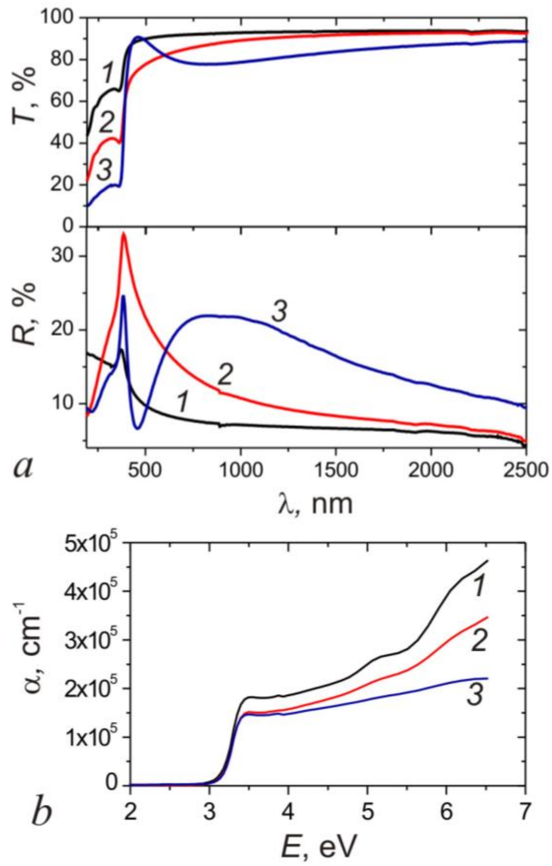

Fig.2. Transmittance, reflectance (*a*) and absorption (*b*) spectra of ZnO films with thicknesses 14 (1), 40(2) and 100 nm (3) deposited on quartz substrates

One can see from Fig. 2 that ZnO films are characterised with high transmission in the range of 400-2500 nm. The thicker ZnO films exhibit higher reflectance than the thinner ones in the IR wavelength range. The thinner films exhibit higher absorption in UV range maybe due to more free charge carriers.

It is known, the absorption coefficient is related to the photon energy (E) as given by Tauch's equation:

$$\alpha E = A(E - E_g)^{1/2}.$$

Fig. 3 presents photon energy (E) versus $(\alpha E)^2$ for ZnO thin films with different thicknesses. The optical band gap determined by extrapolating the straight portion to the energy axis is about of 3.23 eV for ZnO films on quartz substrates. For bulk crystalline ZnO this value is 3.8 eV. This suggests the existence of stress effect and/or shallow levels in band gap.

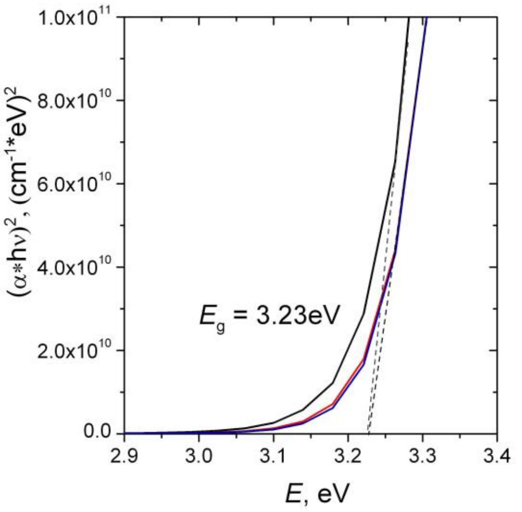

Fig. 3. Photon energy (E) versus $(\alpha E)^2$ for ZnO thin films with different thicknesses on quartz substrates

Fig. 4 depicts the reflectance spectra of as-deposited and annealed ZnO films on SiO_2/Si substrates which opaque in visible range. Thin ZnO films (14 nm) reveal an optical reflectance lower than that of bare SiO_2/Si substrates in the visible and IR range. It indicates a potential application of them as anti-reflection coatings for silicon based solar cells. By varying the thickness, a reflection minimum can be achieved at different spectral range: 600 and 1070 nm for 40 nm and 100 nm ZnO films, respectively.

Annealing doesn't result in notable change in reflectance spectra of ZnO films on SiO_2/Si substrate. However, it should be noted, that thick ZnO(100 nm) film exhibits the typical maximum of reflectance of ZnO at 365 nm. Annealing results in increase and blue shift of the maximum up to 370 nm. It can indicate increase of optical band gap via annealing.

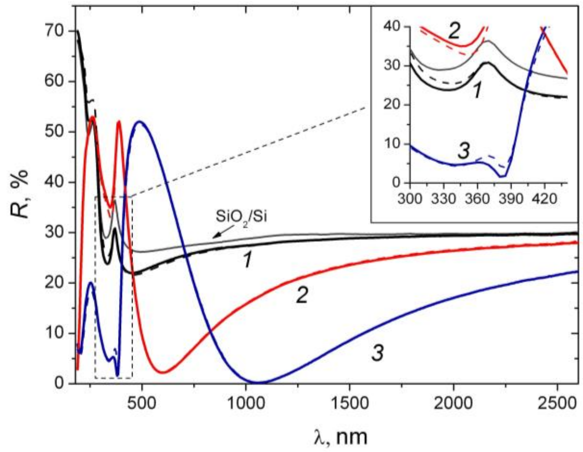

Fig. 4. Reflectance spectra of bare SiO_2/Si structure and ZnO films with thicknesses 14 (*1*), 40(*2*) and 100 nm (*3*) deposited on SiO_2/Si substrates before and after annealing (dashed lines)

Fig. 5 presents PL spectra of ZnO films (100 nm) on SiO_2/Si substrates as well as for bare SiO_2/Si structure. The band with maximum at 2.85 eV is registered for as-deposited ZnO film as well as for bare SiO_2/Si structure. Therefore, the emission at 2.85 eV can originate from the silica layer mainly by oxygen-deficiency centres. One can see UV emission peak at 3.24 eV in the PL spectra of as-deposited and annealed ZnO film. It is near band edge emission of ZnO attributed to free or bound exciton radiative recombination. It indicates a high crystalline quality of ZnO. Increasing UV emission after annealing indicates further crystal structure improvement. Increasing red emission (1.7 – 2.3eV) after annealing in oxygen can be explained via an increase of concentration of Zn vacancies or O interstitials due to increase of oxygen content in film.

Conclusions

Structure and optical properties of ZnO films deposited on quartz and oxidized Si by magnetron sputtering have been studied. RS data confirms the wurtzite structure of ZnO

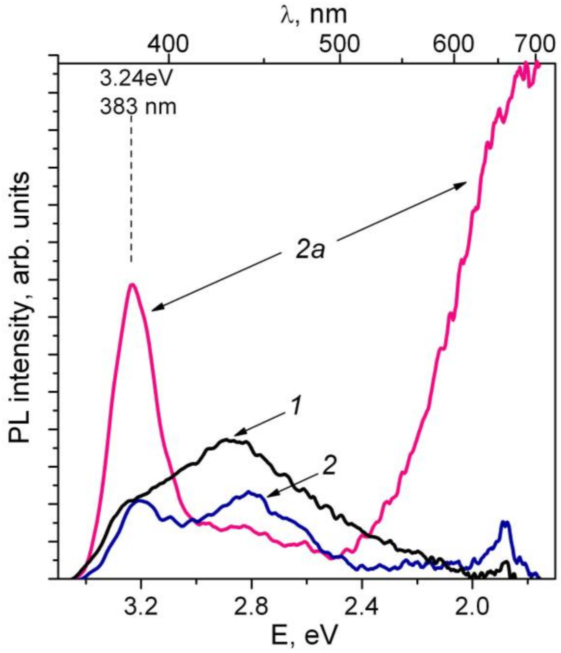

Fig. 5. PL spectra of annealed SiO_2/Si substrate (*1*) and ZnO (100 nm) film deposited on SiO_2/Si substrate before (*2*) and after annealing (*2a*)

as well as the presence of Zn_i, V_O, or defect complexes containing Zn_i and V_O in ZnO.

Analysis of RS data reveals, too, that the films deposited on SiO_2/Si substrates contain less defects in comparison with the films on quartz substrates.

ZnO films are characterized with high transmission in the range of 400 – 2500 nm. The optical band gap for ZnO films on quartz substrates is about of 3.23 eV. For bulk crystalline ZnO this value is 3.8 eV. A decrease of the band gap value in our experiment can be explained via an existence of stress effect or shallow levels in the band gap. Thin ZnO films (14 nm) on SiO_2/Si substrates reveal an optical reflectance lower than that of initial SiO_2/Si substrates in the visible and IR electromagnetic range. It indicates a potential application of ZnO films as antireflection coatings for silicon based solar cells. Change in reflectance spectra of thick ZnO film (100 nm) after annealing indicates improvement of its crystal quality.

PL data confirm a high crystalline quality of ZnO (100 nm) film annealed in oxygen at 500 °C for 1 hour. Increasing red emission (1.7 – 2.3eV) after annealing can be ascribed to an increase of concentration of Zn vacancies or O interstitials due to increase of oxygen content in film.

References

1. Chang J.F., Wang H.L., Hon M.H. Studying of transparent conductive ZnO:Al thin films formed by RF reactive magnetron sputtering. *Journal of Crystal Growth* 2000; 211: 93-97.
2. Mass J., Bhattacharya P., Katiyar R.S. Effect of high substrate temperature on Al-doped ZnO thin films grown by pulsed laser deposition. *Material Science and Engineering* 2003; B. B103: 9-15.
3. Liu H., Wang Y., Wu J., Ahang G., Yan Y. Oxygen vacancy assisted multiferroic property of Cu-doped ZnO films. *Physical Chemistry* 2015; 14: 9098-9105.
4. Yang Y.C., Zhong C.F., Wang X.H., He B., Wei S. Q. Room temperature multiferroic behavior of Cr-doped ZnO films. *Journal of Applied Physics* 2008; 104: 064102.
5. Chang W.Y., Lai Y.C., Wu T.B., Wang S.F., Chen F., Tsai M.J. Unipolar resistive switching characteristics of ZnO thin films for nonvolatile memory applications. *Applied Physics Letters* 2008; 92: 022110.
6. Karthik K.R.G., Prabnakar R.R., Hai L., Batabyal S.K., Huang Y.Z., Mhaisakar S. G. A ZnO nanowire resistive switch. *Applied Physics Letters* 2013; 103: 123114.
7. Yang Yu., Gao P., Gaba S., Chang T., Pan X., Lu W. Observation of conducting filament growth in nanoscale resistive memories. *Nature Communications* 2012; 3: 732.
8. Bibes M., Barthélémy A. Multyferroics: Towards a magnetoelectric memory. Nature Materials 2008; 7: 425-426.
9. Namoune A., Touam T., Chelouche A. Thickness, annealing and substrate effects on structural, morphological, optical and waveguiding properties RF sputtered ZnO thin films. *Journal of Materials Science -Materials in Electronics* 2017; 28: 2207-12219.
10. Meriche F., Touam T., Chelouche A., Dehimi M., Solard J., Fisher A., Boudriouna A. et al Post-annealing effects on the physical and optical waveguiding properties of RF sputtered ZnO thin films. *Electronics Materials Letters* 2015; 115: 826-870.
11. Divine Kh.N., Shashi P., Anjana D., Richard B.M. Cross Electrical Perfomance and Stability of ZnO Thin-Film Transistors Incorporating Gadolinium Oxide High-k Dielectrics. *Advances in Materials* 2018; 7: 137-143.