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OPTICAL AND TEM CHARACTERIZATION OF PHASE TRANSFORMATION IN Zn ION IMPLANTED AND THERMAL OXIDIZED QUARTZ

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1. INTRODUCTION

Metal and metal oxide nanoparticles (NPs) embedded in various matrices have been the object of increasing interest due to their peculiar physical properties significantly different from the corresponding ones of bulk material. Metallic Zn NPs can be used in UV photo-detectors. Zinc oxide NPs play an important role too, since ZnO has direct band gap of 3.37 eV, large exiton binding energy of 60 meV. So they can be used in UV light-sources, electroluminescence displays and according to other ZnO properties such as sorption effect, room temperature ferromagnetism, and others, they may be applied in modern devices [1]. Previously, metallic Zn and ZnO NPs have been produced in Zn implanted silica, because ion

implantation is one of the most clean and flexible techniques [2-3]. In this paper the optical characterization parameters of Zn implanted quartz during NP formation at annealing are reported.

2. EXPERIMENTAL

Optical-grade high-pure (OH^-: 50 ppb) amorphous quartz slides were implanted by $^{64}Zn^+$ ions with fluence of $5\times10^{16}/cm^2$ and energy of 50 keV. During implantation the ion current density was less than 0.5 $\mu A/cm^2$ to avoid the magnificent substrate heating. Then the samples were subjected to isochronally oxidation during 1h in temperature ranges from 400 up to 800°C. The Zn contained phase creation and its thermal evolution were investigated by recording the optical transmission (OT) spectra at room temperature in a spectral range 200–800 nm using Specord-M40 UV-Vis spectrophotometer and by photoluminescence (PL) at temperatures of 10 and 300 K in a spectral range 350–800 nm with 325 nm wavelength illumination of He-Cd laser. Visualization and identification of NPs was made by study of the cross section samples using Tecnai G2 20 S-Twin (FEI) transmission electron microscope (TEM) at accelerative voltage of 200 kV fitted with electron diffraction, an EDAX detector attachment for X-ray energy dispersive spectroscopy (EDS) microanalysis, and with a high angle annular dark field detector (HAADF) for scanning operation. The EDS maps of the element distribution and the NP sizes were determined in the STEM regime.

3. RESULTS AND DISCUSSION

3.1. OPTICAL TRANSMISSION

Figure 1a shows the optical transmission (OT) spectra in UV-Vis range of as implanted and annealed samples. As a result of Zn implantation a broad absorption band appears in the spectrum which extends to near-infrared region according to Fig.1b. This structure less spectrum can be attributing to Zn metallic phase. An annealing at 600ºC strongly reduces this absorption but a new band arises in a range 330–380 nm. This band can be attributed to an exciton absorption peak connected with ZnO phase germination. An annealing in oxygen at 800°C further increases this absorption (Fig.1a), absorption edge appeared due to complete ZnO phase formation. Since the absorption in the visible region due to metallic Zn phase fully disappears the metallic Zn phase has transformed to the transparent ZnO and Zn_2SiO_4 phases in the implanted layers.

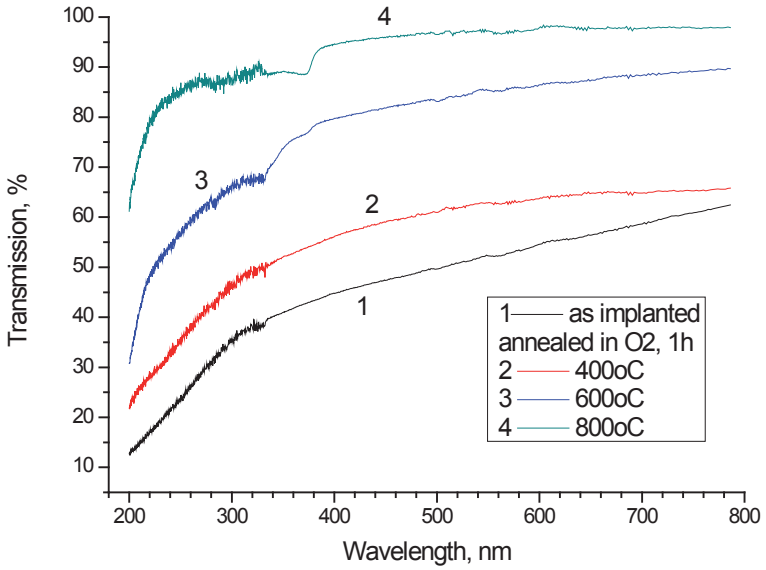


Figure 1: OT spectra of implanted and annealed samples.

3.2. PHOTOLUMINESCENCE

Figure 2 shows PL spectra of implanted samples and annealed in oxygen atmosphere at elevated temperatures. An insert shows the same spectra in an extended scale. After first thermal annealing at 400°C the PL signal slightly increases without any shift of its maximum due to formation of defect band luminescence. But oxidation at 600°C leads to appearance of a giant PL maximum at a wavelength of 370 nm, which is naturally related to the exciton recombination in the ZnO material. In other words, after annealing in oxygen at this temperature for 1h, we have the appearance of ZnO stable phase in silica glass matrix. After the next annealing in oxygen for 1h at temperature of 800°C the luminescence spectrum is slightly reduced in value, but we have peak at 384.245 nm is the second phonon replicas. In the long-wavelength region after this annealing step there appeared a weak maximum at 520 nm, which is usually associated with stoichiometry defects in ZnO NPs themselves: mainly, oxygen vacancies and interstitial zinc atom. The PL intensity ratio between the exciton line and the green defect band depends on the quality of ZnO, and usually they coexist with each other. After annealing at 800°C the green defect band becomes slightly larger, and the exiton peak becomes slightly smaller. The green band intensity increase corresponds to the degradation of the ZnO phase and its transformation to the Zn_2SiO_4 phase.

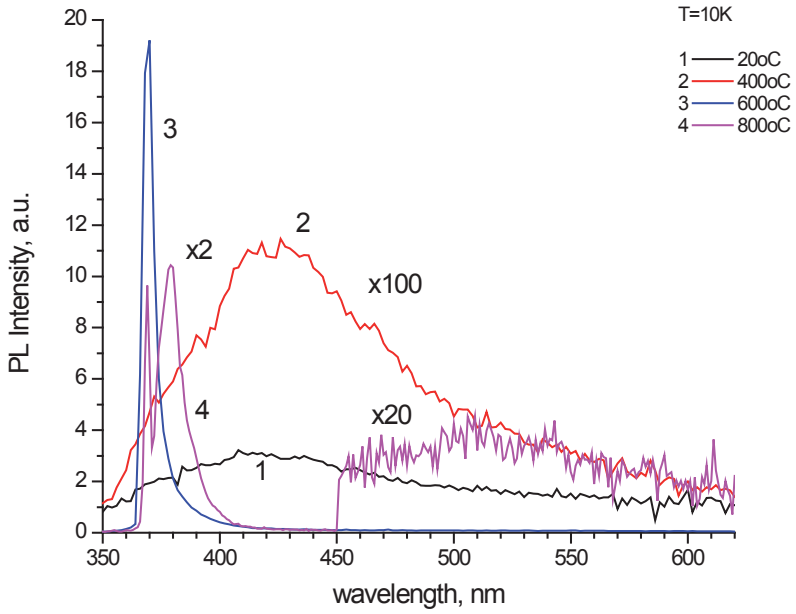
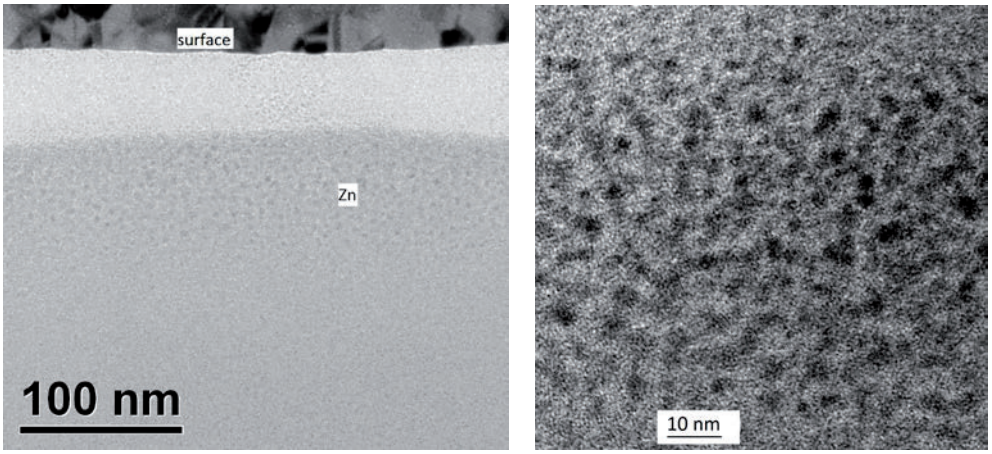


Figure 2: PL spectra of implanted and annealed samples.

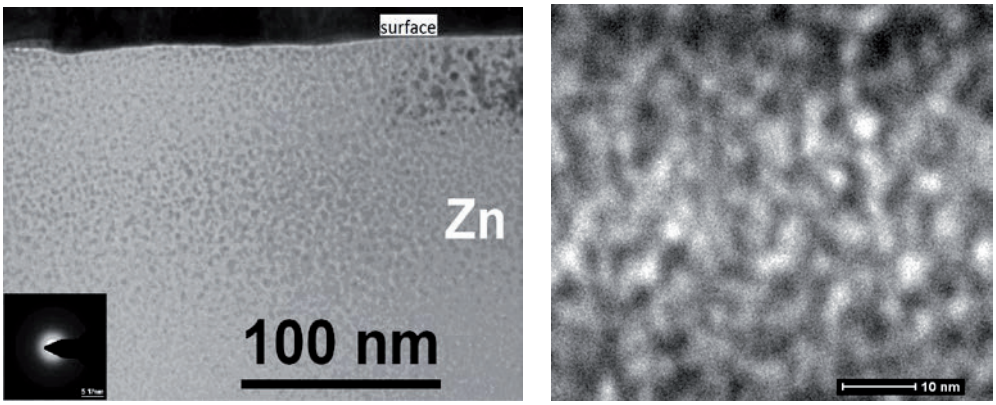


a) b)

Figure 3: TEM survey image (a) and HRTEM image (b) for implanted sample in a Zn layer.

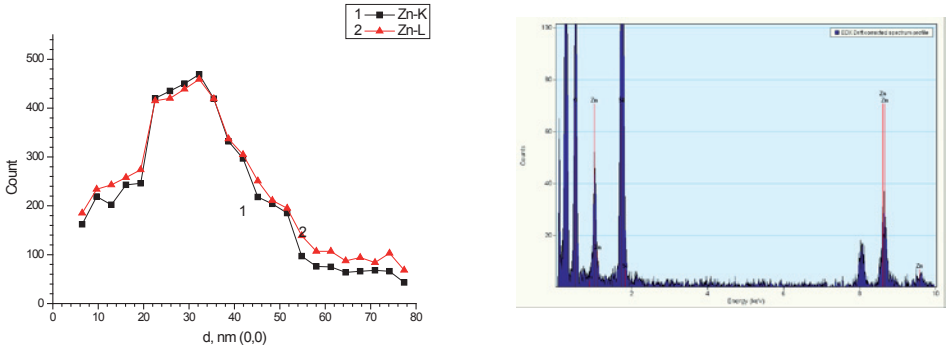
3.3. TRANSMISSION ELECTRON MICROSCOPY

Figure 3 shows panoramic TEM (a) and HRTEM in the middle of Zn NP layer (b) images of a near-surface quartz layer after the Zn ion implantation. The bright light band that corresponds to implanted zinc is clearly seen in the middle of pattern. According to the experimental data in Figure 3a, the Zn distribution has a maximum concentration at projective range Rp=40nm. This agreed with the SRIM calculations [5]. The areas of Zn NPs are easily seen in the middle of TEM pattern in Figure 3a and on a HRTEM in Figure 3b. The presence of Zn in the form of NPs was revealed by a change in the contrast on the TEM image. The distribution of Zn NP diameters has



a) b)

Figure 4: TEM survay image (a) and STEM image (b) for annealed sample of Zn NPs layer.



a) b)

Figure 5: Zn-L and Zn-K profiles (a), and EDS spectrum (b) of annealed sample.

a normal (Gaussian) line shape and an average diameter value is about 3 nm. Amorphous state of metallic Zn NPs is confirmed by HRTEM image (b) that does not show traces of Zn crystal planes.

In Figure 4 there are presented a TEM survay image (a) and STEM image in the middle of contained Zn NP layer (b) for the sample after annealing in oxygen at 800°C during 1h. In the insert of Figure 4a there is presented the electron diffraction pattern of annealed sample. In Figure 4a there are clearly visible NPs containing Zn. Their distribution is also normal (Gaussian) view. The average of NP size value is about 4.5 nm. They are amorphous too and their amorphous state is confirmed by electron diffraction pattern that represents halo in insert of Figure 4a. From the above studies optical data suggest that these NPs are a ZnO phase or other phases of these compounds, namely Zn_2SiO_4, and may be $ZnSiO_3$.

Figure 5 shows the EDS profiles of Zn-K and Zn-L (a) lines and entire EDS spectrum of annealed at 800°C sample in the middle of Zn layer at the depth of 30 nm (b). One can see that Zn-K and Zn-L lines profiles have a maximum at 30 nm, i.e. Zn atoms moved from their initial position towards the surface during annealing. In Figure 5b we can see the EDS peaks of Zn-La1 and Zn-Lb1 at 1.0117 and 1.0347 keV correspondently, Zn-Ka1 and Zn-Ka2 at 8.63886 and 8.61578 keV correspondently, and at last Zn-Kb1 line at 9.5720 keV.

4. CONCLUSIONS

1) After the quartz implantation by $^{64}Zn^{+}$ ions with fluence of $5\times10^{16}/cm^2$ and energy of 50 keV the amorphous metallic Zn NPs with an average radius of 3 nm were created.
2) Then the samples were subjected to sequentially isochronally furnace annealing in oxygen atmosphere during 1 h in temperature ranges from 400°C up to 800°C. During this process there was phase transformation from metallic Zn phase to its oxide form.
3) After annealing at 800°C the Zn NPs transform to the ZnO or/and Zn_2SiO_4 phase with average radius of 4.5 nm.

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