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Embedment of ZnO nanoparticles in SiO_2 by ion implantation and low-temperature oxidation

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Samples of silica glass (SiO_2) implanted with 60 keV Zn ions to a fluence of 1.0×10^{17} ions/cm^2 were annealed in oxygen gas to form ZnO nanoparticles (NPs). Although the ZnO NPs were formed mainly *on the* SiO_2 *surface* after oxidation at 700 °C for 1 h, they were formed *inside the* SiO_2 *substrate* after lower temperature and long-duration oxidation at 500 °C for ~70 h, i.e., the embedment of ZnO NPs in SiO_2 was attained. The embedded NPs show a slightly stronger exciton peak and much weaker defect luminescence than the NPs formed on the surface. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2709509]

Zinc oxide (ZnO) is receiving considerable attention because this material is a wide-gap semiconductor with a large exciton binding energy of 60 meV, which stabilizes the excitons even at room temperature.[1] Because of the concentrated oscillator strength with respect to exciton transitions, laser action is easily attainable even in nanostructures. Moreover, new lasing phenomena characteristics of nanostructures have been observed including random laser[2] and self-formed cavity laser.[3] Nanostructures of ZnO are highly attractive for light-emitting/laser applications, and various attempts have been made to fabricate ZnO nanostructures of high quality.

A successful process is ion implantation combined with thermal oxidation.[4–6] In this method, Zn metal nanoparticles (NPs) are formed in transparent insulators such as silica glass (SiO_2) by Zn ion implantation of several tens to a few hundred keV. The implanted samples are then annealed in an oxidizing atmosphere so that the Zn NPs are oxidized to ZnO NPs. Using this method, Liu *et al.* formed ZnO NPs after annealing at 700 °C for 1 h.[4]

However, as proposed by Liu *et al.* in their early work,[4] and confirmed later by cross-sectional transmission microscopy (XTEM),[7,8] depth profiling by x-ray photoelectron spectroscopy (XPS),[8] and Rutherford backscattering spectrometry (RBS),[8] most of the ZnO NPs are formed on the surface of the SiO_2 substrate in this method. This result provides a striking contrast to NiO and CuO NPs fabricated by the same method, where the NPs are formed inside the SiO_2 substrate.[9,10] It is speculated that the dissolution of Zn atoms from Zn NPs is enhanced at elevated temperatures around 700 °C. The dissolved Zn atoms migrate toward the surface of the SiO_2 substrate, and oxidation occurs close to the surface with oxygen supplied from the atmosphere. The formation of oxide NPs close to the surface has also been observed in Fe-implanted Al_2O_3 (Ref. 11) and Co-implanted SiO_2.[12] In the cases of Ni and Cu, which form oxide NPs embedded in SiO_2, the diffusion constants in SiO_2 and/or the dissolution efficiencies are probably much less than those of Zn, Fe, and Co.

By contrast, metal NPs produced by ion implantation are in the embedded form because each implanted ion requires a certain depth for its deceleration in solids. Embedded NPs have some advantages against NPs formed on the surface: the embedded NPs are protected by matrix from attacks from outside, e.g., chemicals, force, etc. The matrix inhibits, to some extent, the aggregations between NPs. It is a challenging task to form *embedded* ZnO NPs in a SiO_2 matrix using ion implantation and thermal annealing/oxidation.

Our strategy is as follows. The formation of ZnO NPs on the surface is probably due to a much larger diffusion constant of Zn atoms than that of oxygen in SiO_2. While the diffusion constant of oxygen in SiO_2 has been reported as

$$D^{\mathrm{ox}}(T) = D_0^{\mathrm{ox}} \exp(-E_{\mathrm{ox}}/kT), \quad (1)$$

where $D_0^{\mathrm{ox}} = 2 \times 10^{-9}$ cm^2/s and $E_{\mathrm{ox}} = 1.3$ eV,[13] the diffusion constant of Zn in SiO_2 has not been elucidated but is probably given by the Arrhenius form,

$$D^{\mathrm{Zn}}(T) = D_0^{\mathrm{Zn}} \exp(-E_{\mathrm{Zn}}/kT). \quad (2)$$

Even when $D^{\mathrm{Zn}}(700\ ^\circ\mathrm{C}) \gg D^{\mathrm{ox}}(700\ ^\circ\mathrm{C})$, annealing at a much lower (higher) temperature than 700 °C comparatively reduces the Zn diffusion and enhances the oxygen diffusion, if the activation energy E_{Zn} is larger (smaller) than E_{ox}. In fact, our present study has shown that the reduced formation of surface NPs and enrichment of embedded NPs are attainable by low-temperature oxidation at 500 °C for ~70 h, indicating $D^{\mathrm{Zn}}(500\ ^\circ\mathrm{C}) \sim D^{\mathrm{ox}}(500\ ^\circ\mathrm{C})$.

Samples of optical-grade silica glass of the KU-1 type (OH^- 820 ppm), 15 mm in diameter and 0.5 mm in thickness, were implanted with $^{64}Zn^+$ ions of 60 keV up to a fluence of 1.0×10^{17} ions/cm^2. The projected ranges of 46 and 27 nm were calculated for Zn ions of 60 keV in SiO_2 by the SRIM2003 (Ref. 14) and TRIDYN codes,[15] respectively. The large difference between the calculated ranges is due to the sputtering removal of the surface layer. In fact, a result of the depth profiling by XPS shown in a previous paper[8] confirms that the TRIDYN result is better. The implanted samples were annealed in a tube furnace at 500 °C under flowing oxygen gas of ~100 SCCM (SCCM denotes cubic centimeter per minute at STP) at a pressure of $\sim 1.0 \times 10^5$ Pa. A dual-beam

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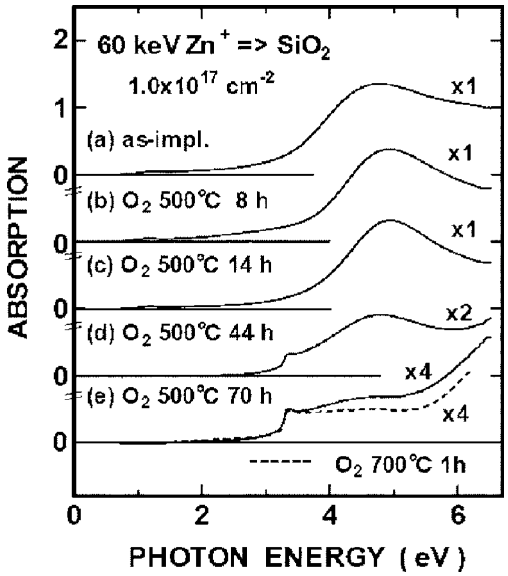

FIG. 1. Optical absorption spectra of SiO_2 samples implanted with 60 keV Zn^+ ions to a fluence of 1.0×10^{17} ions/cm^2 measured at room temperature, in the as-implanted state (a) and after annealing in oxygen gas at 500 °C for various durations [(b)–(e)]. The dotted line shows the absorption spectrum after annealing at 700 °C for 1 h. The spectra are shifted vertically for clarity and the horizontal lines indicate the base lines.

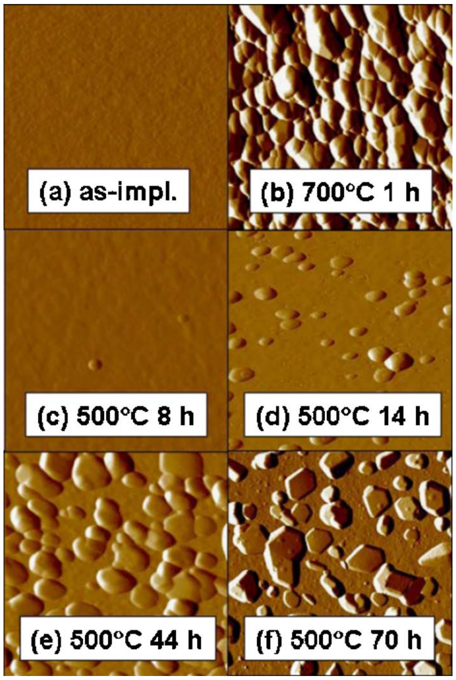

FIG. 2. (Color online) AFM images of SiO_2 sample surfaces implanted with 60 keV Zn^+ ions to a fluence of 1.0×10^{17} ions/cm^2, in the as-implanted state (a) and after annealing in oxygen gas at 700 °C for 1 h (b) and at 500 °C for various durations ranging from 8 to 70 h [(c)–(f)]. The size of each image was 1×1 μm^2.

spectrometer was used for transmittance and reflectance measurements in the wavelength range of 190–1700 nm at room temperature (RT). The absorption was determined from the transmittance and the reflectance, applying a correction for multiple reflections in the sample.[16] The surface morphology was observed by atomic force microscopy (AFM) in the tapping mode with a scanning area of 1×1 μm^2. XTEM was conducted at an acceleration voltage of 200 kV. Photoluminescence (PL) was excited by the 325 nm line (3.81 eV) from a cw-mode He–Cd laser with an excitation power density of ~2 W/cm^2. The spectra were detected at RT by cooled charge coupled device arrays through a 30 cm single monochromator.

Figure 1 shows the absorption spectra of a SiO_2 sample implanted with 60 keV Zn ions to 1.0×10^{17} ions/cm^2, in the as-implanted state, and after annealing at 500 °C in oxygen gas for various durations. In the as-implanted state, a broad band due to metallic Zn NPs[17] is observed around 4.8 eV. After 1 h annealing at 500 °C, the peak shifts to 4.9 eV. Since a similar high-energy shift was observed after annealing *in a vacuum* at 400 °C for 1 h,[18] the shift is ascribed to growth of Zn NPs and a partial recovery of damaged SiO_2 substrate. At 8 and 14 h, the spectra show almost no changes except that the peak shifts to 4.95 eV. After 44 h annealing, a sharp peak appears at 3.3 eV, indicating the partial formation of ZnO NPs. However, the broad band at 4.8 eV due to Zn metal NPs still coexists with the ZnO peak. An absorption spectrum of a sample oxidized at 700 °C for 1 h is plotted in Fig. 1 by a dotted line. After 70 h annealing at 500 °C, almost the same spectrum as that observed at 700 °C for 1 h was obtained. A period of ~70 h was required to oxidize most of the Zn NPs at 500 °C, while less than 1 h was required at 700 °C. From Eq. (1), the diffusion constants of oxygen in SiO_2 are given as 1×10^{-17} and 6×10^{-16}cm^2/s at 500 and 700 °C, respectively. To obtain the same diffusion length $L=(4Dt)^{1/2}$ at 700 °C for 1 h, 6×10 h is required at 500 °C. This shows good agreement with the experimental value of ~70 h, suggesting an oxygen-diffusion-limited reaction.

The formation of ZnO NPs on the surface of the SiO_2 substrate and the morphology changes by oxidation annealing were evaluated by AFM. In the as-implanted state [Fig. 2(a)], the surface was very flat as indicated by the R_q value of 0.39 nm,[19] where R_q is the surface roughness, i.e., the root-mean-square of the height deviation. After annealing at 700 °C for 1 h, numerous ZnO NPs with domelike shapes overlapped each other and covered the whole surface, as shown in Fig. 2(b). The R_q value increased to 13.0 nm. The corresponding cross-sectional view was observed by XTEM, and is shown in Fig. 3(a). The XTEM image also confirms that the ZnO NPs were mainly formed on the surface of the SiO_2, while some NPs remained inside the SiO_2.

In the case of annealing at 500 °C, the surface was as flat as in the as-implanted state up to ~5 h duration. Small hemispheres appeared on the surface at 8 h duration. After 14 h duration, many ZnO NPs whose shapes were not exactly domelike but rather flat island shapes appeared on the surface. After 70 h duration, when most of the Zn NPs had been transformed to ZnO as shown in Fig. 1, a large number of ZnO NPs having flat island shapes were formed on the surface. Some of the NPs showed facets. However, comparing Figs. 2(b) and 2(f), it is clear that ZnO NP formation on the surface was drastically reduced by low-temperature annealing at 500 °C. A XTEM image corresponding to Fig. 2(f) is shown in Fig. 3(b). Only a few ZnO NPs are observed on the surface, and most of the ZnO NPs are formed inside the SiO_2 substrate. These results are confirmed by RBS measurements, where the migration of Zn species toward the surface which was observed after annealing at 700 °C for 1 h is reduced to some extent. It should be noted that the observed surface was covered with glue even during

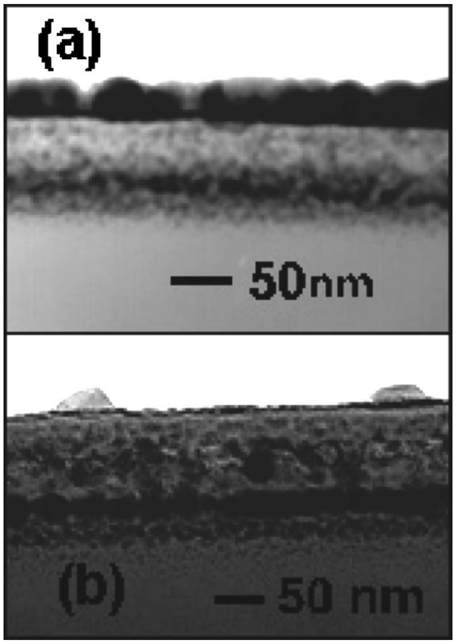

FIG. 3. Cross-sectional TEM images of SiO_2 samples implanted with 60 keV Zn^+ ions to a fluence of 1.0×10^{17} ions/cm^2 and annealed in oxygen gas at 700 °C for 1 h (a) and at 500 °C for 7×10 h (b).

the TEM observation, which excluded the possible loss of ZnO NPs on the surface during preparation of the TEM samples. The loss of surface NPs during annealing due to vaporization or other factors can also be excluded because the RBS results confirmed that more than 90% of the implanted Zn atoms remained inside or on the surface of the SiO_2 even after 500 °C annealing for ~70 h.

Figure 4 shows the PL spectra of samples oxidized at 700 °C for 1 h and at 500 °C for 70 h. While the sample oxidized at 700 °C for 1 h shows a sharp exciton peak at 376 nm and a defect band around 500 nm, the sample oxidized at 500 °C for 70 h shows a slightly stronger exciton peak at 376 nm and much weaker defect luminescence. Comparing with Figs. 2(b) and 2(f), following speculations are given: For the sample annealed at 700 °C for 1 h, ZnO NPs are formed for very short time, indicating that the NPs contain a lot of defects. However, the samples annealed at 500 °C for 70 h show flat and island-shape ZnO on the surface, indicating that there are much time for migration of Zn and O atoms on the surface and for compensation of defect sites. Consequently, the samples annealed at 500 °C for 70 h show less defect luminescence.

For comparison, the PL spectrum from a bulk ZnO single crystal was also measured by the same PL detection system. The exciton peak appeared at 380 nm. Although both the samples containing ZnO NPs show exciton peaks at ~376 nm, i.e., slightly blueshifted from the bulk value of 380 nm, it is not easy to attribute the blueshifts to the quantum size effect. From Figs. 2 and 3, it can be seen that the sizes of the ZnO NPs are too large to induce the large quantum size effect of the excitons. The blueshift is probably ascribable to the stress effect in ZnO NPs or to the self-absorption effect of the thick ZnO single crystal.

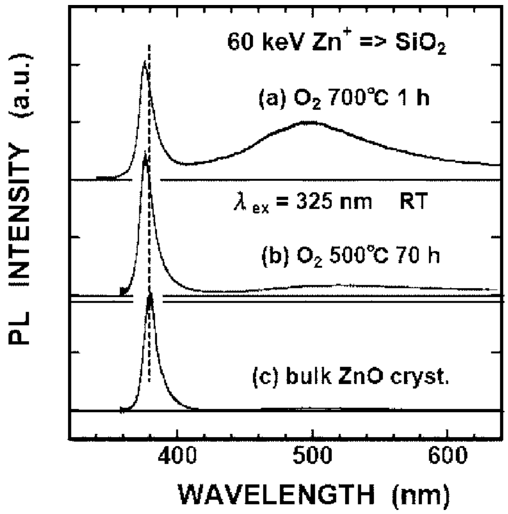

FIG. 4. Photoluminescence (PL) spectra of SiO_2 samples implanted with 60 keV Zn^+ ions to a fluence of 1.0×10^{17} ions/cm^2 and annealed in oxygen gas at 700 °C for 1 h (a) and at 500 °C for 70 h (b). The PL spectrum of a bulk ZnO single crystal (c) measured by the same PL detection system with a much shorter exposure time is also shown as a reference. The spectra are shifted vertically for clarity and the horizontal lines indicate the base lines. PL was excited by a He–Cd laser (325 nm), and measured at room temperature.

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