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H. Amekura, N. Umeda, Y. Sakuma, O. A. Plaksin, Y. Takeda, N. Kishimoto, and Ch. Buchal

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Zn and ZnO nanoparticles fabricated by ion implantation combined with thermal oxidation, and the defect-free luminescence

H. Amekura,[a] N. Umeda, Y. Sakuma, O. A. Plaksin, Y. Takeda, and N. Kishimoto
Nanomaterials Laboratory, National Institute for Materials Science (NIMS), 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

Ch. Buchal
Institut fuer Schichten und Grenzflaechen (ISG1-IT), Forschungszentrum Juelich GmbH, D-52425, Juelich, Germany

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Silica glass implanted with Zn ions of 60 keV to 1.0×10^{17} ions/cm^2 was annealed in oxygen gas to form ZnO nanoparticles (NPs). In as-implanted state, the implanted Zn atoms form Zn metallic NPs inside of the silica. After annealing at 600 °C, ZnO NPs form on the surface, while Zn metallic NPs still remain in the deep region. At 700 °C, most of Zn atoms move to the surface to form the droplet-shaped ZnO NPs which show two photoluminescence bands, i.e., an exciton band at 375 nm and a defect band at ~500 nm. The defect band almost disappears in the samples annealed at 600 °C, which include both ZnO NPs and Zn NPs. © *2006 American Institute of Physics*.
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Since the discovery of stimulated emission from zinc-oxide (ZnO) nano-crystallite films at room temperature,[1] nanostructures of ZnO have received much attention because of possible applications in high-performance optoelectronic devices. Up to now, we have proposed[2] a method to fabricate oxide nanoparticles (NPs) in insulators, namely, the ion implantation combined with thermal oxidation (IICTO), and have fabricated NiO[3,4] and CuO[5] NPs in silica glasses (SiO_2). In this method metal NPs are formed inside of the insulators by ion implantation at first, then the metal NPs are oxidized by thermally activated migration of oxygen in the insulators, which is supplied from the annealing atmosphere. Independently, Liu *et al.*[6,7] have applied the IICTO method for the fabrication of ZnO NPs: They implanted Zn^+ ions of 160 keV to SiO_2 sample up to a very high fluence of 3×10^{17} ions/cm^2 and annealed the samples at 700 °C for 2 h in oxygen gas. They obtained ZnO phase. However, they insisted from their results of x-ray photoelectron spectroscopy that the products were ZnO film covering on the SiO_2 substrate, not ZnO NPs embedded in SiO_2 substrate. It is in contrast with NiO and CuO phases fabricated by the IICTO method, which are always obtained as NPs embedded in SiO_2 substrate.[3–5] Since Zn ions were implanted inside of the SiO_2 substrate, and since ZnO is formed on the surface of the SiO_2 substrate, drastic transportation of Zn element from inside of the SiO_2 substrate toward the surface is expected during the thermal oxidation. In this letter, cross-sectional transmission microscopy (XTEM) was applied at different annealing temperatures to confirm the drastic transportation of Zn atoms from inside of the SiO_2 substrate to the surface. Photoluminescence (PL) spectroscopy was carried out to characterize the quality of ZnO nanostructures formed at different annealing temperatures. Almost defect-band-free PL was observed from a sample in which metallic Zn and ZnO coexist. The mechanisms are also discussed in this letter.

Optical-graded silica glasses of KU-1 type (OH^- 820 ppm) of 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 ion flux was limited to less than 2 μA/cm^2 in order to maintain the sample temperature below 100 °C during the implantation. The implanted samples were annealed for 1 h in a tube furnace at a temperature between 600 and 900 °C under flowing oxygen gas of ~100 sccm at a pressure of ~1 atm.

A dual-beam spectrometer with a resolution of 1 nm was used for the transmittance and reflectance measurements in the wavelength range of 190–1700 nm at room temperature. The absorption was determined from the transmittance and the reflectance, applying the correction for multiple reflections in the sample.[8] XTEM was conducted at an acceleration voltage of 200 kV. PL was excited by the 325 nm line (3.81 eV) from a continuous wave mode He–Cd laser with an excitation power density of ~2 W/cm^2. The spectra were detected by charge coupled device arrays through a 30 cm monochromator with a single grating. Wavelength-dependent sensitivity of the PL detection system was corrected using a standard Xe lamp.

Figure 1 shows annealing effects on the absorption spectra of SiO_2 implanted with Zn^+ ions to a fluence of 1.0×10^{17} ions/cm^2. In as-implanted state, the sample shows a strong and broad absorption band centered around 260 nm in the wavelength, which is ascribed to Zn metallic NPs.[9] The absorption extends toward the near-infrared (NIR) region through the whole visible region and then the sample shows brownish color. The formation of Zn metallic NPs in the as-implanted state was confirmed by XTEM as shown in Fig. 2(a). No NPs are observed on the surface or in the region shallower than ~10 nm. The depletion of NPs close to the surface is typical for metallic NPs formed by ion implantation, since the incident Zn ions of 60 keV are too energetic to stop close to the surface. After annealing in oxygen gas at 600 °C for 1 h, the absorption spectrum rarely changes except for the appearance of a small kink around 370 nm. The color of the sample is still brownish. However, XTEM shows

[a]Author to whom correspondence should be addressed; electronic mail: amekura.hiroshi@nims.go.jp

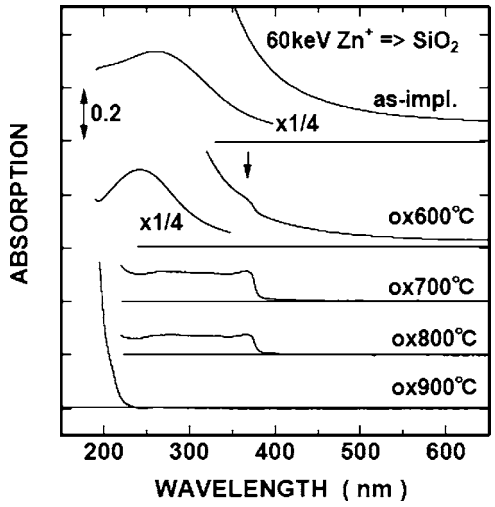

FIG. 1. Optical absorption spectra of SiO_2 samples implanted with Zn^+ ions of 60 keV to a fluence of 1.0×10^{17} ions/cm^2, in as-implanted state and after annealing in oxygen gas at various temperatures for 1 h. The spectra are shifted vertically for clarity and the vertical lines indicate the base lines.

formation of ZnO NPs of droplet shape on the surface [Fig. 2(b)]. Since ZnO NPs form on the surface of the SiO_2 substrate where no Zn NPs are observed in the as-implanted state, transport of Zn atoms from the deeper region to the surface is induced during the annealing at 600 °C in oxygen gas. The kink at 370 nm in the absorption spectrum is ascribed to the exciton peak of the ZnO NPs on the surface. After annealing in oxygen gas at 700 °C for 1 h, the absorption in the visible and NIR regions completely disappeared, and a steep absorption edge appeared around 370 nm. The color of the sample changes to transparent. As shown in Fig. 2(c), a lot of the droplet-like ZnO NPs and smaller NPs are observed on the surface and around 50 nm in depth, respectively. Since the absorption in the visible region due to Zn metal NPs completely disappears, not only the NPs on the surface but the NPs inside of SiO_2 have transformed to ZnO or other transparent phase. After annealing at 800 °C, the spectral shape of the absorption hardly changed, but the absorption intensity slightly decreased. After annealing at

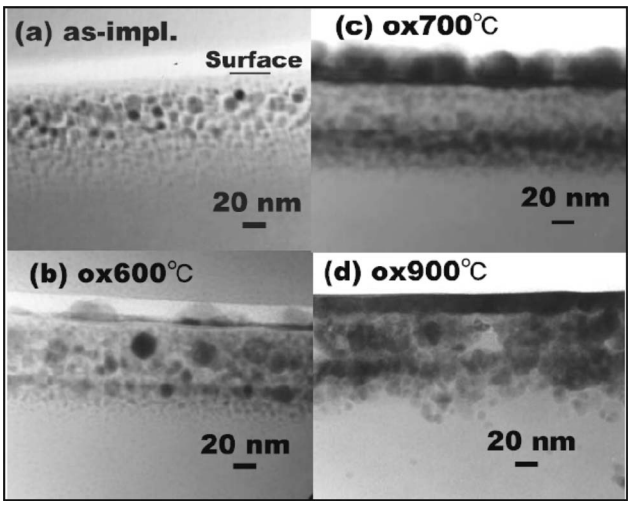

FIG. 2. Cross-sectional TEM images of SiO_2 samples implanted with Zn^+ ions of 60 keV to a fluence of 1.0×10^{17} ions/cm^2, (a) in as-implanted state and after annealing in oxygen gas for 1 h at (b) 600 °C, (c) 700 °C, and (d) 900 °C. In Fig. 2(a), the substrate surface is indicated by a line.

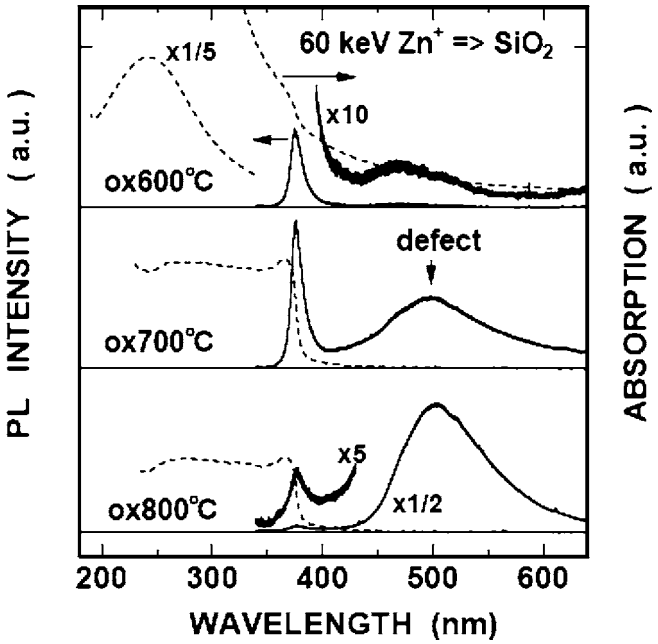

FIG. 3. Photoluminescence (solid lines) and optical absorption (dotted lines) spectra of SiO_2 samples implanted with Zn^+ ions of 60 keV to a fluence of 1.0×10^{17} ions/cm^2, and annealed in oxygen gas for 1 h at 600, 700, and 800 °C, respectively. The spectra are shifted vertically for clarity and the vertical lines indicate the base lines. A part of the spectrum at 600 °C is also shown with magnification of ten times.

900 °C for 1 h, the absorption edge again moves to ~5.3 eV, indicating the transformation of ZnO NPs to Zn_2SiO_4 phase whose band-gap energy is ~5.3 eV.[10] XTEM shows the transformation from the droplet-like ZnO NPs on the surface to a continuous-layer-like Zn_2SiO_4 phase.

Shallowing of the depth profile of metal NPs induced in oxidizing atmosphere has been also observed in Fe in Al_2O_3[11] and in Ge in SiO_2.[12] Here, we apply the model which has been proposed in Ge[12] to our Zn case: With increasing temperature, a lot of Zn atoms are detached from Zn NPs, and migrate in SiO_2 toward both directions of the surface side and deeper side. In the case of oxygen annealing, O_2 is supplied from the surface side only, and migrates into the SiO_2 substrate as the O_2 molecules form.[13] Once the migrating Zn atoms encounter and react with the oxygen molecules, ZnO is formed, which is immobile in SiO_2 at the annealing temperatures applied. Although the Zn atoms perform the nondirectional random walk, gradually the amount of immobile ZnO component increases at the shallower side, and eventually directional transportation of Zn atoms toward the surface side is attained.

Figure 3 shows PL spectra of SiO_2 implanted with Zn^+ ions of 60 keV. After annealing at 700 °C for 1 h where most of Zn NPs transform to ZnO NPs, a sharp peak and a broadband (so-called green band) were observed in PL spectrum at 375 and 500 nm, respectively. The sharp peak and the green band are, respectively, due to the free exciton and defects such as Zn interstitials or O vacancies.[14] While the PL intensity ratio between the exciton line and the green band depends on the quality of ZnO, the green band is a relatively common defect band and in many cases coexists with the exciton peak. Although the absorption spectrum does not change after annealing at 800 °C for 1 h, large changes are observed in PL spectra: the green band and the exciton peak become three times stronger and ~10 times

weaker, respectively. The increase of the green band intensity corresponds to degradation of the ZnO NPs.

One of the interesting observations is that the green (defect) band is drastically reduced by annealing at 600 °C for 1 h. In Fig. 3, the spectrum around the defect band is shown with magnification of ten times. Comparing with the sample annealed at 700 °C, the intensity of the defect band decreases to ~1/20 and the peak shifts to ~470 nm. As for the exciton peak, the intensity is slightly weaker than that of the sample annealed at 700 °C, i.e., the strongest exciton PL intensity case, but roughly comparable. It should be noted again that the absorption spectrum of the sample annealed at 600 °C is dominated by strong absorption due to Zn metallic NPs covering whole the visible region (see dotted lines in Fig. 3). The sample shows brownish color. It could be contrary to common sense if a homogenous semiconductor has absorption in the visible region but emits PL in the UV region only. In fact, the sample after annealing at 600 °C is no longer homogenous. While the surface is covered by the droplet-like ZnO NPs, the Zn metallic NPs survive in the SiO_2 substrate as shown in Fig. 2(b). The absorption in the visible region and the PL in the UV region are due to Zn NPs in deep region and ZnO NPs on the surface, respectively. One might consider that the disappearance of the green band was due to the absorption by the remaining Zn metallic NPs. However, it cannot happen because the absorption by Zn metallic NPs is weaker in the visible region than in the UV region.

According to thermodynamics data,[15] Zn_2SiO_4 phase is more stable than mixture phase of ZnO and SiO_2. ZnO NPs in SiO_2 exist as a metastable state. It should be noted that it does not mean that ZnO NPs in SiO_2 are not suitable for realistic applications: If the ZnO NPs are kept around room temperature, they are stable at least for years. While all the ZnO NPs in SiO_2 transform to Zn_2SiO_4 phase after annealing in oxygen gas at 900 °C for 1 h as shown in Fig. 1, even slightly lower temperature annealing at 800 °C for 1 h converts some portions of ZnO NPs to Zn_2SiO_4 phase. It is pointed out[16] that an increase of the PL intensity ratio of the green band to the exciton peak occurs during the transformation from ZnO to Zn_2SiO_4 because a lot of Zn interstitials and O vacancies are produced during the bond rearrangements between ZnO and Zn_2SiO_4 phases. Consequently, larger intensity ratio of the green band to the exciton peak is observed after annealing at 800 °C. With decreasing the annealing temperature, the transformation to Zn_2SiO_4 phase is reduced. The sample annealed at 700 °C shows weaker green band than the sample annealed at 800 °C. The defect-band-free PL at 600 °C may be due to the reduction of the transformation to Zn_2SiO_4 because of the low temperature.

Another possible origin of the defect-band-free PL is the remaining metallic Zn NPs in the deeper region at 600 °C. When ZnO NPs form at the surface of SiO_2 substrate, the metallic Zn NPs may act as reservoirs to supply Zn atoms continuously to the surface. Then the formation of stoichiometric ZnO NPs is attained. However, more studies are necessary for identification of the mechanisms of the defect-band-free PL at 600 °C.

Silica glass (SiO_2) was implanted with Zn^+ ions of 60 keV to a fluence of 1.0×10^{17} ions/cm^2, annealed in oxygen gas, and evaluated with XTEM, absorption and PL spectroscopies. After annealing at 600 °C for 1 h, some Zn atoms move to the surface of the SiO_2 substrate and form ZnO NPs of droplet shape, while other Zn atoms still form metallic NPs in the deep region. After annealing at 700 °C for 1 h, most of Zn NPs transform to ZnO NPs. After annealing at 900 °C for 1 h, ZnO NPs transform continuous-film-like Zn_2SiO_4 phase. Defect-band-free PL is observed in the samples annealed at 600 °C for 1 h, which contain ZnO NPs on the surface and metallic Zn NPs in the deep region.

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