Proceeding of ICNM - 2009

1st International Conference on Nanostructured Materials and Nanocomposites (6 – 8 April 2009, Kottayam, India)

Published by : Applied Science Innovations Private Limited, India.
http://www.applied-science-innovations.com

****

ZnO nanoparticles in SiO_2 fabricated by Ion Implantation and Thermal Oxidation

Hiroshi Amekura* and N. Kishimoto

Quantum Beam Center, National Institute for Materials Science (NIMS),
3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
**Corresponding author email: amekura.hiroshi@nims.go.jp*

1. Introduction :

Various kinds of new methods are explored to form nano-materials with more excellent properties, and soon some of the most excellent nano-materials will be used in industry. However, what does "the excellence" mean for industry? Nano-materials which have good compatibility with the present technology can be one of "the excellent materials". In near-future some excellent nano-materials / nano-devices can be introduced in semiconductor integrated circuit technology. However, because the semiconductors are very weak against contamination, nano-materials / nano-devices which are made by low-purity methods, e.g., some kinds of wet chemical processes, cannot be used. Contrary nano-materials / nano-devices made by high-purity processes, such as ion implantation, are greatly hopeful. Consequently we have studied nanoparticle (NP) formation by ion implantation.

For these years, we have proposed a new method to fabricate oxide NPs using Ion Implantation and Thermal Oxidation (II&TO) [1-3]. In this method, metal ions, e.g., Zn^+ ions, of 60 keV are implanted to SiO_2 substrate up to a concentration much higher than the solubility limit, forming a super-saturated solid solution of Zn atoms in SiO_2. Spontaneously the secondary phases of nano-meter sizes, i.e., the metal NPs, are formed inside the SiO_2 substrate as a consequence of phase separation. After the implantation, the samples are annealed in an oxidizing atmosphere in order to enhance the migration of oxygen inside the SiO_2 substrate and to oxidize the metal NPs embedded in the substrate to oxide NPs.

2. Experimental :

Optical-grade silica glasses of KU-1 type (OH^- 820 ppm) were implanted with Zn^+ ions of 60 keV up to a fluence of 1.0×10^{17} ions/cm^2. Isochronal annealing was carried out from 400 to 900°C with 100°C steps for 1 h each, in a tube furnace under O_2 gas flow of 100 sccm. The samples were evaluated at room temperature (RT) by optical absorption spectroscopy (OAS), Grazing incident X-ray diffraction (GIXRD), cross-sectional transmission electron micropscop (XTEM), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and photoluminescence (PL) spectroscopy.

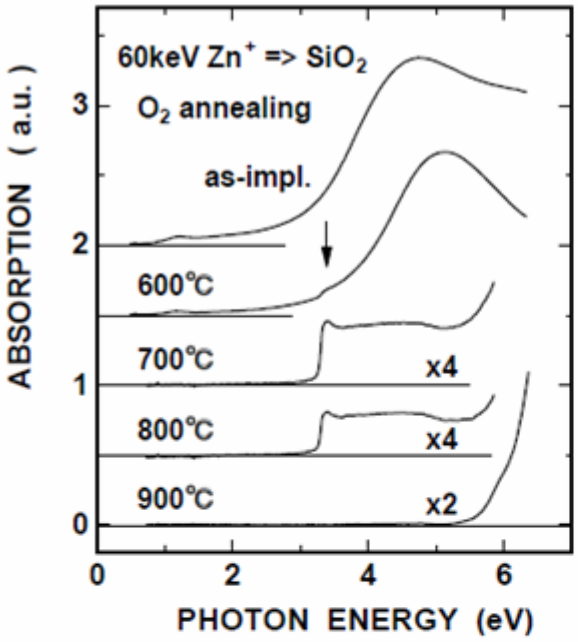

Fig. 1. Optical density spectra of silica glass implanted with Zn+ ions of 60 keV up to 1.0×1017 ions/cm2, in as-implanted state and annealed in oxygen gas flow at 600, 700, 800 and 900°C for 1 hour each, respectively. The spectra at 700°C and higher temperatures are magnified by factors written.

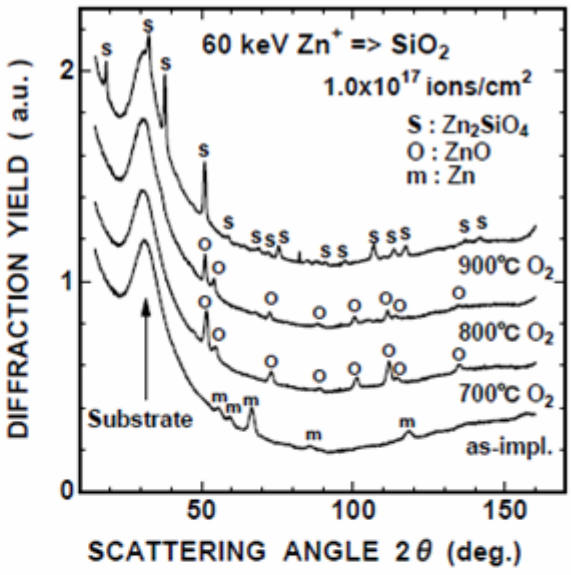

Fig. 2. Grazing incidence x-ray diffraction (GIXRD) patterns of SiO_2 implanted with Zn^+ ions of 60 keV up to 1.0×10^{17} ions/cm^2, in as-implanted state and annealed in oxygen gas flow at 700, 800 and 900°C for 1 hour each, respectively. Diffraction peaks labeled by "m", "O"and "S" are ascribed to Zn-NPs, ZnO-NPs and Zn_2SiO_4-NPs, respectively.

3. Results and Discussion :

Figure 1 shows isochronal annealing effects on the optical density spectra of SiO_2 sample implanted with Zn^+ ions to 1.0×10^{17} ions/cm^2 [4]. In as-implanted state, a strong absorption peak was observed around 4.8 eV. GIXRD pattern of the as-implanted sample is shown in Fig. 2. All the diffraction peaks except a broad one from amorphous SiO_2 substrate are ascribed to diffraction peaks of Zn metal. These observations indicate that Zn NPs are formed in SiO_2 even in the as-implanted state. to 600°C, the spectrum shows little change. After 700°C annealing, drastic changes are induced. The absorption in the visible region disappears and an absorption-edge appears at ~3.25 eV. The GIXRD clearly shows a transformation in the diffraction patterns from Zn metal to ZnO at 700°C, as shown in Fig. 2. As the absorption in the visible region is almost zero, most of Zn NPs transform to ZnO NPs. It should be noted that a small kink appears at ~3.3 eV even after 600°C annealing. A small portion of Zn NPs starts the transformation to ZnO NPs even at 600°C. After the transformation to ZnO NPs, the optical density decreases to ~1/4 of that of Zn NPs. However, RBS results show that Zn content is almost constant up to 900°C, although the depth profile changes. The decrease of optical density after the transformation to ZnO NPs is primarily due to decrease of the oscillator strength in the observed energy region, not due to decrease of Zn content in the sample.

After 800°C annealing, the absorption due to ZnO NPs slightly decreases. After 900°C annealing, the absorption edge at ~3.25 eV completely disappears, and the edge shifts to ~5.3 eV. The new absorption edge of ~5.3 eV is close to a literature value of the bandgap energy of Zn_2SiO_4. The GIXRD measurements confirm the transformation of the diffraction patterns from ZnO to Zn_2SiO_4 at 900°C, as shown in Fig. 2.

The formation of Zn metallic NPs in the as-implanted state was confirmed by XTEM as shown in Fig. 3(a) [5]. 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 appearance of a small kink around 370 nm. The color of the sample is still brownish. However, XTEM shows formation of ZnO NPs of droplet shape on the surface (Fig. 3(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 disappears, and a steep absorption edge appeared around 370 nm. The color of the sample changes to transparent. As shown in Fig. 3(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 decreases. After annealing at 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. XTEM shows the transformation from the droplet-like ZnO NPs on the surface to a continuous-layer-like Zn_2SiO_4 phase.

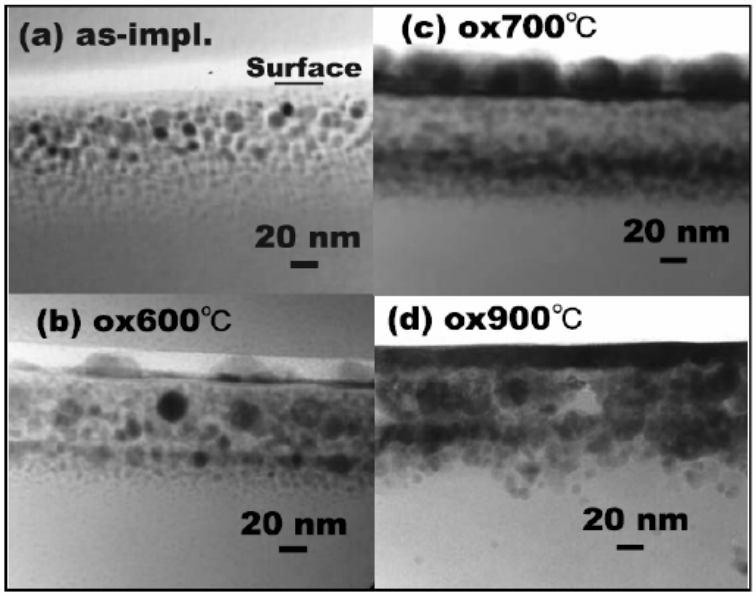

Fig. 3. Coss-sectional TEM images of SiO_2 samples implanted with Zn^+ ions of 60 keV to a fluence of 1.0×10^{17} ions/cm^2, (a) in as-implanted state and after annealing in oxygen gas for 1 h at (b) 600°C, (c) 700°C and (d) 900°C. In Fig. 3(a), the substrate surface is indicated by a line.

4. Conclusions :

The fabrication of ZnO NPs by ion implantation and thermal oxidation has been succeeded. However, in spite of the expectation, the ZnO NPs were mainly formed on the surface of the SiO_2 substrate, while Zn NPs were formed inside the substrate as embedded NPs. A lot of further new results are obtained so far. See Refs [1,6-10] .

References :

[1] H. Amekura and N. Kishimoto,*Fabrication of oxide nanoparticles by ion implantation and thermal oxidation*, in *Toward Functional Nanomaterials*, edited by Z. Wang (Springer, 2009).
[2] H. Amekura, Y. Takeda, K. Kono, H. Kitazawa, and N. Kishimoto, Rev. Adv. Mater. Sci. **5,** 178 (2003).

[3] H. Amekura, N. Umeda, Y. Sakuma, N. Kishimoto, and C. Buchal, Appl. Phys. Lett. **87,** 013109 (2005).
[4] H. Amekura, K. Kono, N. Kishimoto, and C. Buchal, Nucl. Instrum. Methods Phys. Res. B **242,** 96 (2006).
[5] H. Amekura, N. Umeda, Y. Sakuma, O.A. Plaksin, Y. Takeda, N. Kishimoto, and C. Buchal, Appl. Phys. Lett. **88,** 153119 (2006).
[6] H. Amekura, N. Umeda, H. Boldyryeva, N. Kishimoto, C. Buchal, and S. Mantl, Appl. Phys. Lett. **90,** 083102 (2007).
[7] H. Amekura, M. Yoshitake, O.A. Plaksin, N. Kishimoto, C. Buchal, and S. Mantl, Appl. Phys. Lett. **91,** 063113 (2007).
[8] H. Amekura, M. Ohnuma, N. Kishimoto, C. Buchal, and S. Mantl, J. Appl. Phys. **104,** 114309 (2008).
[9] H. Amekura, H.S. Wang, S. Hishita, J. Pan, N. Kishimoto, C. Buchal, and S. Mantl, Nanotechnology **20,** 065303 (2009).
[10] H. Amekura, N. Umeda, K. Kono, Y. Takeda, N. Kishimoto, C. Buchal, and S. Mantl, Nanotechnology **18,** 395707 (2007).