V-C Nano-Structure in Metal Oxides Prepared by Synchrotron Radiation and Swift Heavy Ions

In the project, micro-nano fabrication technique for metal oxide has been examined. The first one is the deep x-ray lithography and the liquid phase deposition method. Periodic arrangements of titanium dioxide (TiO_2) micro structure projections were fabricated in a supersaturated aqueous solution using ordered microcavities of poly(methylmethacrylate) as a template. The shape and periodicity of the TiO_2 projections were strictly controlled with the depth and arrangement of the cavities because crystalline TiO_2 was uniformly grown on the organic surface through heterogeneous nucleation. This biomimetic route is applicable to designed synthesis of three-dimensional architectures for photonic structures of various metal oxides. The other method is by using of the latent tracks introduced by the swift heavy ion. Micro structure having nano-order flatness was achieved after chemical etching. This method can be applied to create photonic crystal structure of titanium dioxide.

V-C-1 Nano/Micro-Structure in Metal Oxides Prepared by MeV Ions, Laser and Synchrotron Radiation

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As semiconductor device dimensions are scale down, there is also a parallel trend to minimized mechanical components and integrate these micro-mechanical components. Microelectronic devices to form micro-electro-mechanical systems (MEMS) and photonic crystals are typical examples. Especially, there has been increasing interest in photonic crystals in which the refractive index changes periodically. Various important scientific and engineering applications, such as control of spontaneous emission, sharp bending of light, trapping of photons, *etc.*, may be realized by creating photonic band-gap. Recently, a few semiconductors like Si, InP, GaAs, and GaP have been shown to exhibit micrometer-size pores. However, it might be too difficult to use photonic crystals of semiconductors in the photonic network. Firstly, it is impossible to connect regular optical waveguide to semiconductor with low optical transmission loss because of the difference of refractive index. Reflection between photonic crystal of semiconductor and regular optical waveguide will cause the loss of light power. One of the most attractive application for photonic crystal is the super-prism effect. This is the reason why photonic crystal draws our attention as the substitute of arrayed wavelength grating (AWG). However, thermal expansion coefficient of semiconductor is too large to use in a conventional atmosphere. In contrast, thermal expansion coefficient in some ceramics is known as almost zero. For example, thermal expansion coefficient values of silicon, TiO_2 and $94SiO_2{:}6TiO_2$ are 7×10^{-6} /K, 7×10^{-7} /K, $\sim 0 \times 10^{-7}$ /K, respectively. In other words, photonic crystals of semiconductor must be used under constant temperature precisely controlled. Photonic crystal as well as AWG would lose the reliability when they must be used at a constant temperature. This is the second reason for why photonic crystals of semiconductor are hard to use as a photonic network device. A material having very low thermal expansion coefficient as well as a refractive index in the vicinity of 1.45 must be the best material for photonic crystal. We know that photonic crystal made of $SiO_2{:}GeO_2$ or $SiO_2{:}TiO_2$ materials would be satisfied such aspects, yet we do know little about micro (nano) fabrication technique for ceramics.

In the present review, periodic arrangements of titanium dioxide (TiO_2) micro projections were fabricated in a supersaturated aqueous solution using ordered microcavities of poly(methylmethacrylate) as a template. The shape and periodicity of the TiO_2 projections were strictly controlled with the depth and arrangement of the cavities because crystalline TiO_2 was uniformly grown on the organic surface through heterogeneous nucleation. This biomimetic route is applicable to designed synthesis of three-dimensional architectures for photonic structures of various metal oxides.

V-C-2 Structure of Latent Tracks Created by Swift Heavy Ions in Amorphous SiO_2 and Zinc Phosphate Glass

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The structure of latent tracks introduced by swift-heavy-ion irradiation was examined on both amorphous SiO_2 and zinc phosphate glass ($68P_2O_5{:}25ZnO{:}4.5Al_2O_3{:}2.5Na_2O$). In amorphous SiO_2, the frequency of the infrared absorption assigned to the asymmetric stretching vibration of Si–O decreased with irradiation. This IR peak shift has been found to be related to the transition of normal six-membered rings of SiO_4 tetrahedra to planar three-membered rings. The high etching rate of the latent tracks is strongly related to planar three-membered rings. In the ion-irradiated zinc phosphate glass, two bridging oxygen atoms bound to a phosphorus atom turned into one bridging oxygen atom. Scission of the Zn–O bond was not observed. It was concluded that the high etching rate of the latent tracks in zinc-phosphate glass is related to P–O bond scission.

V-C-3 Structural Change Induced in TiO_2 by Swift Heavy Ions and Its Application to Three Dimensional Lithography

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Rutile TiO_2 single crystal was irradiated by heavy ions with a high energy of the order of several tens of MeV. A good etching selectivity that only the irradiated surface is well etched by hydrofluoric acid is induced by the irradiation. Through X-ray diffraction and high-resolution electron microscopy, it became clear that the irradiated region lost crystallization. It is considered that this amorphous region and the surrounding region are dissolved in hydrofluoric acid. Through calculation of ion energy, it was found that the etching always stopped at the depth where the electronic stopping power of the ion decayed to a critical value of 6.2 keV/nm, regardless of the ion species in the case of I, Br, Cu, and Ti ions. However, in the case of Ca ions with energies higher than about 72 MeV or Cl ions with energies higher than about 77 MeV, the irradiated top surface was not etched with the hydrofluoric acid, but the inside several μm deep from the irradiated surface was etched. A calculation shows that the critical factor which determines whether the irradiated surface can be etched or not is the lateral energy density on the surface deposited by ions. The etched surface observed by atomic force microscopy is very smooth with a roughness of the order of nm. Therefore, combination of ion irradiation and etching can be used as a novel fabrication method of nano-structures in rutile.

V-C-4 Strained Si–O–Si Bonds in Amorphous SiO_2 Materials

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Amorphous SiO_2 (a-SiO_2), such as bulk silica glasses and thin films has been one of the key materials in modern opto-electronic industries. These materials are currently used in communication technologies as optical fibers, thin films for electrical insulation in dynamic random access memories (DRAM), and optical lenses for excimer laser lithography, for example. The property essential for these applications is the wide band gap amounting to ~ 9 eV. However, bulk silica glasses commercially available and silica thin films show photo-responses to sub-band gap lights in the vicinity of 5 eV and unexpected trapping of charges, and the behavior has a strong dependency on the preparation history.

A number of studies were carried out to clarify the relationship between the properties and structural imperfections in the materials and the formation mechanisms of the defects. There are two categories of the imperfections: one is dopant- or impurity-related imperfections and the other is non-stoichiometry related defects. These defects constitute gap states in a-SiO_2. The structural identification was usually performed by absorption- and emission spectroscopy in the visible-ultraviolet region and electron spin resonance (ESR). The experimentally proposed models were compared with the predictions by theoretical calculations of energy levels.

Recent development of the excimer laser lithography technique led us to recognize that a latent member, which has been unnoticed because of no response to the optical absorption or emission in the visible-uv range and ESR absorption, exists in the family of active centers in a-SiO_2, that is a strained Si–O–Si bond originating from the planar three membered ring. In contrast, the puckered four membered ring is unstrained. Although it has been pointed out that there was a wide distribution in Si–O–Si bond angle from 90° to 180° by X-ray analysis or ^{29}Si solid state NMR, the physical and chemical responses of the Si–O–Si bonds with a particular bond angle could not be differentiated.

Very recently it was clarified that a strained Si–O–Si bond, in other words chemically excited bonds, has an optical absorption locating on the band edge. The chemically excited bond can be scavenged by fluorine doping, because it is chemically reactive. In the present review we show that the unresolved optical and electric responses of silica glasses can be comprehensively understood by taking the presence of the strained bonds into consideration.