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Enhanced nanoparticle formation by indentation and annealing on 2 MeV Cu ion-implanted SiO_2

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Enhancement of surface plasmon resonance (SPR) in optical absorption has been found on Cu ion-implanted SiO_2 substrate modified by micro-indentation and post-annealing. Micro-indentation effects on surface plasmon resonance (SPR) in optical absorption have been studied to control nanoparticle formation in Cu ion-implanted SiO_2 substrate. The SiO_2 was firstly implanted with 2 MeV Cu^{2+} ions at an ion flux of 4 $\mu A/cm^2$, up to a fluence of 6×10^{16} ions/cm^2. After the ion implantation, dot-array patterns of micro-indents were made by a micro-Vickers hardness tester, and followed by annealing at 600 °C in vacuum for 1 h. The optical absorption spectra of the indented region and the non-indented flat region were measured and compared with each other. After post-annealing at 600 °C, the indented area showed higher absorbance of SPR at 2.2 eV than that of the flat region annealed under the same annealing conditions. The TEM study shows larger and denser Cu precipitates inside the indentation than those in the flat area. The results indicate that the defects produced by indentation enhance the atomic migration in the plastic zone during thermal relaxation process, resulting in promoting the enhanced precipitation of Cu nanoparticles.

1. Introduction

High-fluence ion implantation is a promising method to generate metal nanoparticles embedded in insulators. The merits of this method are high efficiency in nanoparticle formation and good controllability of a depth profile of the nanoparticles by changing the incident ion energy. The nanoparticle composites are one of the most promising candidates for photonic materials, due to large optical nonlinearity and ultra-fast response associated with the surface plasmon resonance. Self-assembled metal nanoparticle composites have been fabricated by high-flux negative ion implantation [1]. A 2D distribution of nanoparticles was attained by injecting high-energy ions under an optimal condition. The in-beam nanoparticle formation is caused by ion energy deposition, enhanced diffusion and precipitation of immiscible metal atoms.

By the aid of the self-assembling mechanism, the depth profile of nanoparticles can be controlled to a 2D-like structure [2], but the lateral control of nanoparticle distribution has not been fully achieved, except for tedious methods such as micro-beam drawing or masked implantation. Consequently, position-control methods for nanoparticle are desired. To develop the quantum effects of metal nanoparticles, it is also demanded to achieve a regularly spaced and monosized nanoparticle-array structure. To synthesize a 3D-ordered nanoparticle array by ion implantation, a few techniques may so far be available, e.g. focused ion beam implantation (FIB) [3], and masked implantation with nanotemplates [4]. The FIB is one of the best methods for nanofabrication but a time-consuming process. The masking methods are limited to low energy implantation, since most of the nanotemplates cannot withstand the high-energy ion implantation. More recently, laser-assisted precipitation of nanoparticles as an alternative method was reported [5]. Compared to the conventional masking methods, the laser irradiation has the advantages of its simplicity [6]. However, the spot size of laser manipulation usually cannot be downsized to a nanometer level.

In this work, a micro-indentation method combined with post-annealing is presented to explore controllability of nanoparticle precipitation via interaction of the stress/strain fields with solutes/precipitates. Early work showed a significant effect of mechanical strain on the atomic diffusion [7,8]. The micro-indentation has advantages of good controllability in position, easiness of the processing, applicability to insulating substrates and low-cost processing.

2. Experimental

Optical-grade silica glasses KU-1 (OH^- 820 ppm) of 15 mm in diameter and 0.5 mm in thickness were implanted with Cu^{2+} ions

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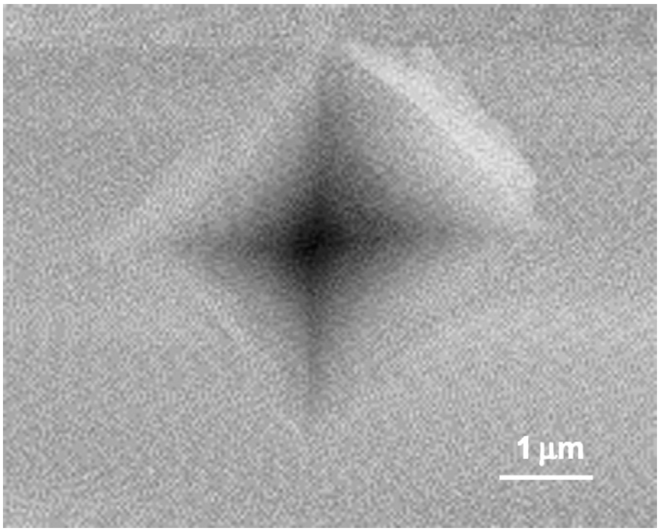

Fig. 1. SEM image of an indent made on 2 MeV Cu^{2+}-implanted SiO_2.

of 2 MeV from a Cs-assisted plasma-sputter-type ion source [9]. The ion flux and the fluence are 4 $\mu A/cm^2$ and 8×10^{16} ions/cm^2, respectively. The simulation code SRIM2003 was used to predict the depth profile of Cu implants. The projected range of Cu ions of 2 MeV was estimated to be 1.53 μm. Indentation patterns were made on the implanted substrates by a micro-Vickers hardness tester at a load of 100 mN. During the micro-Vickers indentation, a pyramid-shaped diamond tip with apex of 136° is forced into the substrate surface, holding time is 15 s. The pattern consists of arrays of 40×50 micro-indentations, with a 10 μm spacing. Surface morphology of the indented surface was examined by scanning electron microscopy (SEM JEOL JSM-6700). The average diagonal length and maximum displacement in depth of indent on SiO_2 samples are 4.15 μm and 250 nm, respectively.

After the micro-indentation, thermal annealing was carried out in a quartz-tube furnace in vacuum ($<1.33 \times 10^{-3}$ Pa) for 1 h, at temperature of 600 °C. A dual beam spectrometer with resolution of 1 nm (scanning from 190 to 2100 nm) was used to measure the reflectance and transmittance on the indentation-patterned area and the non-indented flat surface. The micro-absorbance measurement area was conducted for the area of 100×100 μm^2, containing approximately 100 indents. The morphology of Cu precipitates beneath the indented and non-indented surfaces was investigated by transmission electron microscopy (TEM) of JEM-2000FX.

3. Results and discussion

3.1. Mechanical changes induced by micro-indentation

Fig. 1 shows an SEM image of a single indent, which was made on the 2 MeV Cu^{2+}-implanted SiO_2. The indentation was made by forcing a pyramid-shaped tip onto the substrate. After the indenter is retracted, the stressed substrate undergoes elastic recovery to release part of the stress, resulting in a residual plastic deformation.

The Vickers indenter causes an upside-down pyramid impression; the deformation zone is presumed to be a hemispherical plastic zone with the characteristic size, d (Fig. 2a). Around this plastic region, the material is permanently strained elastically. Some of the past work indicate creation of point defects of vacancies and interstitials [10], which give microscopic stress fields in their vicinity. The indentation mechanics developed for a semi-infinite half-space allows us to determine the plastic-zone radius c to be 2–3 times larger than a half of the diagonal: $c \approx (2\text{–}3)d/2$ [11,12].

The localized residual stress field intersects with the embedded layer of implanted Cu ions (projected range 1.53 μm). The implants inside the residual stress fields undergo compression stress, and those in-between the residual stress fields are under tensile stress. Therefore, an array of indents produces an array of localized stress zones, which can be regarded as potential wells for the implants.

3.2. Micro-indentation effects combined with thermal annealing

All the SiO_2 samples were pre-implanted with 2 MeV Cu^{2+} ions to a fluence of 8×10^{16} ions/cm^2, indented with the pattern, and then annealed at 600 °C. The behaviors of the plastic zone during annealing were reported by Kese et al. [13]. The plastic zone for as-indented state is a solid hemisphere, with a characteristic size d. As the annealing starts, transformation of plastic zone starts at its interface region with the indent. The relaxation of plastic zone starts from the indent and proceeds radically outwards towards its boundary with the substrate matrix. As annealing progresses, the solid hemisphere is transformed into a shell of plastically deformed material containing a mass of transformed material within its cavity; the thickness of this shell in the plastic zone remains unchanged (Fig. 2b). The relaxation in the plastic zone involves restoring of the substance from condensed to uncondensed state, via fast diffusion process. As the annealing time prolonged, the plastic zone is completely transformed and no plastically deformed material is left, as shown in Fig. 2(c).

Fig. 3 shows optical absorption spectra as measured for the indentation-patterned area and the flat surface area, for (a) after annealed at 600 °C and (b) as-implanted. For the as-implanted samples, Fig. 3(b), the shape of SPR in absorption spectra measured for the indentation-patterned area is similar to that for the flat surface area. Weak SPR peaks at 2.2 eV were observed for the both areas. The absorption spectrum of the micro-indented pattern is higher than that of the non-indented flat surface. The difference in the absorption intensity arises from a change in optical property caused by the presence of micro-indents, i.e., diffraction or refraction by the indents. It should be noted for the later discussion that the direct optical change caused by the indentation is as much as this difference in the absorption spectrum.

After 600 °C annealing for 1 h, Fig. 3(a), the spectrum of the flat surface remains almost the same as the one before annealing, but

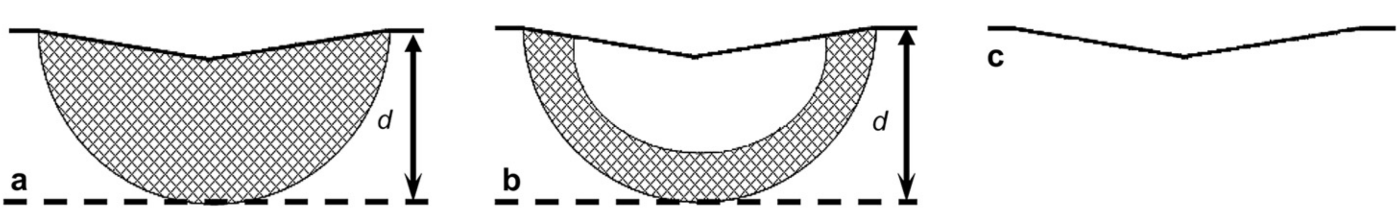

Fig. 2. Schematic diagram showing the transformation of the plastic zone beneath the Vickers indent during annealing. (a) The plastic zone is in the form of a solid hemisphere with a characteristic size, d. (b) The transformation of the plastic zone begins at its interface region with the indent. (c) With prolonged annealing at temperatures above T_g, the plastic zone is completely transformed and there is no plastically deformed material surrounding the indent [13].