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Asynchronous melting of embedded metal nanoparticles and silica matrix for shape elongation induced by swift heavy ion irradiation

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ABSTRACT

Although the mechanism of shape-elongation of nanoparticles (NPs) by swift-heavy-ion-irradiation is still under debate, melting and solidification of NPs for pico-second region by thermal spikes has been proposed as one of the processes involved. Elongation of high melting point (MP) NPs (vanadium, $T_{MP}^{bulk} = 1890\,^{\circ}C$) and of low MP NPs (zinc, $T_{MP}^{bulk} = 420\,^{\circ}C$) were compared under irradiation with 200 MeV Xe^{14+} ions. Irrespective of the large difference in their MPs, both the V and Zn NPs showed comparable elongation. The insensitivity of elongation to the MP can be explained by the asynchronicity of melting of the silica and the NPs.

1. Introduction

Metal nanoparticles (NPs) are a focus of attention due to their various attractive optical, electronic, and magnetic properties that are not observed in their bulk counterparts, including ultra-fast optical response [1] and strong electric field enhancement [2] of the surface plasmon resonance (SPR), single electron transport [3], super-paramagnetism [4], and the finite-size effect [5]. These properties can be tuned by controlling the size, size distribution, and shape of the NPs, as well as the matrix composition.

With regard to the shape control of metal NPs, a new approach was discovered in 2003 by D'Orleans et al., who irradiated Co NPs embedded in SiO_2 by swift heavy ions (SHIs) of 200 MeV iodine [6]. They observed elongation of NPs to nanorods under irradiation at high fluences. One of the attractive properties of these NPs is that the elongation is induced along the direction of the SHI beam; i.e., all major axes of the elongated NPs are parallel with each other and the direction is controlled by the SHI beam.

While this phenomenon has been extensively studied by many groups [7–25] since its discovery, its mechanism has not yet been clarified. Roorda et al. reported the elongation of Au cores of Au/silica core/shell particles by irradiation with 30 MeV Se ions and suggested that the SiO_2 matrix plays an important role in the elongation of metal NPs. They ascribed the elongation to in-plane stress induced by the ion-hammering effect of the SiO_2 matrix (and radiation-induced softening of the metal NPs) [7]. However, this mechanism was criticized because the energy threshold of the ion-hammering was different from that of the elongation [9]. Furthermore, Klaumuenzer pointed out that the observed elongation was too large to be explained by the ion-hammering model alone, even with additional radiation-induced softening of NPs via any known deformation mechanism [19]. Rather, the importance of the melting of NPs by the thermal spike effect has been speculated by many authors. One of the most widely accepted mechanisms, although still under debate, is the interplay of the ion-hammering effect of the SiO_2 matrix and the melting of NPs by the thermal spike effect, in which the molten NPs are elongated by the in-plane stress of the ion-hammering effect.

If melting of the NPs is essential, i.e., if the elongation is induced mainly during the molten phase of the NPs, larger elongation could be expected for NPs with a lower melting point (MP). To evaluate this proposition, we previously studied the elongation of zinc NPs embedded in SiO_2 under SHI irradiation of 200 MeV Xe^{14+} [25], since Zn has a low MP of $T_{MP}^{bulk} = 420\,^{\circ}C$, much lower than that of Au NPs ($T_{MP}^{bulk} = 1064\,^{\circ}C$), which have been extensively studied [9,11–13,15,18,20,22]. However, the elongation of Zn NPs was unexpectedly small [25]. As already mentioned, D'Orleans et al. [6] carried out SHI irradiation with iodine ions of 200 MeV, which have the same energy and almost the same ion mass as the 200 MeV Xe ions that we used. Furthermore, both our NPs (Zn) and the NPs used by D'Orleans et al. (Co) had an initial mean diameter of 10 nm. Even under almost the same conditions, the Zn NPs showed minimal elongation with an aspect ratio (AR) of 1.2–1.7 at a fluence of 5×10^{13} ions/cm^2, while the Co NPs showed larger elongation with an AR of 4–5 at the same fluence.

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However, the elongation strongly depends on many parameters such as the thickness of the SiO_2 covering layer [22] and the ion flux [24]. The result is less credible if we compare our data with those reported by other groups, because the experimental conditions are not completely identical. To answer this criticism, in this letter we report the elongation of vanadium NPs ($T_{MP}^{bulk} = 1890$ °C) under the same conditions as the Zn NPs ($T_{MP}^{bulk} = 420$ °C) reported in our previous paper [25].

2. Experimental

Vanadium NPs were formed and irradiated under the same conditions as applied to the Zn NPs reported in our previous paper [25]. Spherical V NPs were fabricated in silica glass of KU-1 type (OH ~820 ppm) by implantation with V ions at 60 keV to a fluence of 1.0×10^{17} ions/cm^2. Even in the as-implanted state, i.e., without post-implantation annealing, V NPs approximately spherical in shape with a mean diameter of 9.0 nm and a standard deviation of 2.9 nm were formed within the surface layer of ~70 nm in thickness. The silica samples containing V NPs were irradiated with 200 MeV Xe^{14+} ions using the tandem accelerator at the Japan Atomic Energy Agency's Tokai Research and Development Center (JAEA Tokai). The SHI fluence ranged from 1.0×10^{11} to 5.0×10^{13} Xe/cm^2. The samples were irradiated at an incident angle of 45° from the surface normal, since this configuration has been found to be appropriate for the detection of NP elongation using absorption spectroscopy with linearly polarized light [25]. A dual-beam spectrometer was used for optical transmission measurements in the wavelength region of 215–1700 nm at room temperature (RT) with an optical polarizer (extinction ratio < 5×10^{-5}). The results were obtained in the form of optical density ($-\log_{10} T$) without correction for reflection, where T denotes the transmittance. Cross-sectional transmission electron microscopy (XTEM) was carried out at an acceleration voltage of 200 kV.

3. Results

Fig. 1 shows optical density spectra of the V NPs in silica detected by linearly polarized light. The spectra were recorded at polarization angles of 0°, 45°, and 90°, where the polarization plane of 0° was defined as the plane containing the SHI beam trajectory. The configuration is schematically shown in Fig. 1 of Ref. [25]. The V NP spectra monotonically increased with increasing energy. Before SHI irradiation, the spectra measured at different polarization angles coincided with each other. Even after irradiation of 1.0×10^{11} Xe/cm^2, the spectra at the different angles still coincided with each other, indicating little elongation. While a peak grew at ~5 eV with increasing fluence, the peak was ascribed to radiation-induced defects. In fact, the same peak was observed after SHI irradiation of silica without NPs [25]. Deviation between the different polarizations, i.e., linear dichroism, was observed at 1.0×10^{13} Xe/cm^2, and became clearer at 5.0×10^{13} Xe/cm^2, indicating progressive elongation of the NPs.

The elongation was also confirmed by XTEM. Fig. 2 shows XTEM images before and after SHI irradiation. Before SHI irradiation, the V NPs are approximately spherical in shape with a mean diameter of 9.0 ± 2.9 nm. After irradiation of 5.0×10^{13} Xe/cm^2, elongation of the NPs is clearly observed. It should again be noted that the irradiation was performed with an incident angle of ~45°. Consequently, the NPs were elongated at the same angle from the surface normal. To the best of our knowledge, the MP of vanadium ($T_{MP}^{bulk} = 1890$ °C) is the highest among those of the metal species in which elongation of NPs has been reported to date.

Changes in the major and minor dimensions (d_{major} and d_{minor}) of the V NPs before and after irradiation of 5.0×10^{13} Xe/cm^2 were

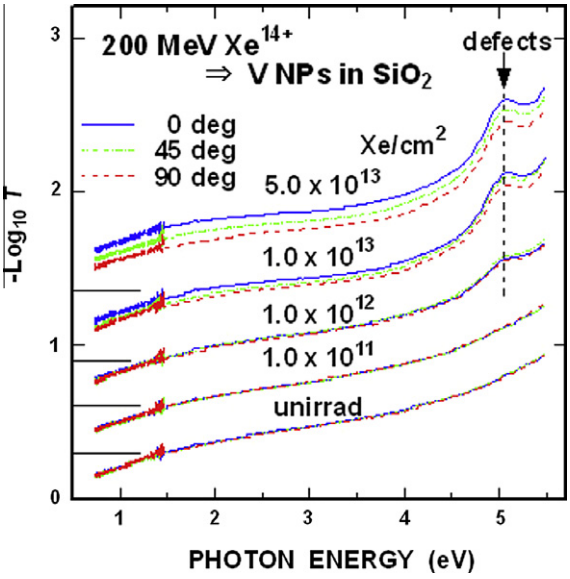

Fig. 1. Optical density spectra of V NPs embedded in silica, in the unirradiated state and after irradiation with 200 MeV Xe^{14+} ions at four different fluences. Linearly polarized light with polarization planes of 0°, 45°, and 90° (solid, dashed-dotted, and broken lines) from the plane of the SHI beam trajectory was used. The spectra taken at different fluences are vertically shifted from each other for clarity and the horizontal lines indicate the baselines. The arrow indicates absorption of radiation-induced defects of the silica matrix.

plotted, together with the corresponding data for Zn NPs irradiated under the same conditions, as shown in Fig. 3. Before irradiation, both types of NPs were approximately spherical in shape, as seen by the distribution of the data points on the diagonal lines indicating the relationship $d_{major} = d_{minor}$. After irradiation, the larger NPs deviated from this relationship, becoming elongated, while the smaller NPs maintained the existing relationship, remaining approximately spherical in shape. This behavior, i.e., the existence of a minimum size threshold for elongation, was first suggested by D'Orleans et al. [6] but clearly established by Ridgway's group [11,14,18,23]. With increasing fluence, d_{minor} finally becomes saturated to the threshold value. In our case, neither the V nor the Zn NPs reached the saturation state, as shown in Fig. 3, because the fluence of 5.0×10^{13} Xe/cm^2 was insufficiently high. Since neither type of NP reached the saturation state, we conclude that *V NPs show roughly comparable elongation to that of Zn NPs.*

In addition to plotting d_{major} and d_{minor}, as shown in Fig. 3, the AR of each NP was evaluated, where AR = d_{major}/d_{minor}. From this analysis, it was found that the ratio of NPs having an AR larger than 2 was 14% for V NPs and 7% for Zn NPs, indicating that Zn NPs exhibit less efficiency in elongation.

Fig. 3 shows a surprising result in that both the V and Zn NPs show roughly similar sizes and degrees of elongation, despite the large difference in their MPs (1890 °C for V and 420 °C for Zn). Furthermore, judging from the AR values, the Zn NPs were less elongated compared with the V NPs under the same fluences, while the MP of Zn is much lower than that of V. How can we explain the observation from the thermal spike model? Because the energy income from the SHIs to the systems consisting of metal NPs and silica is the same, metal NPs with a lower MP would be expected to remain in the molten phase for a longer time, and consequently show larger elongation.

4. Discussion

It has, of course, been pointed out by many authors [6,15,18,20] that the (initial) size of NPs strongly affects the degree of elongation. However, in our study the initial size distribution was