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Ion beam shaping of Au nanoparticles prepared by micellar technique

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ABSTRACT

Irradiation-induced burrowing and ion-induced shaping effects of Au nanoparticles are investigated. Hexagonally arranged Au nanoparticles prepared by micellar technique with diameter ~10 nm and inter-particle distance of about 80 nm were sequentially irradiated with 200 keV Ar^+ ions to fluences of 5×10^{15} ions/cm^2. Irradiation with Argon ions causes sinking of the Au nanoparticles into the subjacent SiO_2 layer due to capillary driving forces related to specific wetting conditions while the spherical shape is conserved. Subsequent irradiation with 54 MeV Ag^{8+} swift heavy ions of these spherical Au nanoparticles confined within a silica matrix shapes them into prolate nanorods and nanowires whose principal axes are aligned along the beam direction. Above a threshold fluence two deformation regimes have been observed. For relatively low fluences Au nanoparticles elongate into nanorods depending on their volume. For high fluences, the formation of nanowires is observed provided that the inter-particle distance is short enough to allow for an efficient mass transport through the silica matrix.

1. Introduction

Aligned nanorods represent unique subsets of metallic nanostructures that are of particular interest because of their anisotropic shape resulting in improved or even novel optical properties [1]. In the literature, a number of studies on the fabrication of aligned metallic nanostructures (both nanorods and nanowires) have been reported during the past years, but the investigated methods yield randomly oriented structures (by chemical methods) [2], small areas (e.g. electron or focused ion-beam lithography) [3] or are limited to a specific class of materials (e.g. porous alumina templated growth) [4]. One of the interesting aspects that recently attracted the attention of the scientific community is the possibility to grow such nanostructures by ion irradiation of embedded metal nanoparticles (NPs). With respect to this, the ion beam shaping technique represents a ground-breaking and powerful tool to manipulate matter on the nanometer scale, allowing fabrication of composite systems with new and unique properties. The ion-induced shaping of metallic NPs was first reported by D'Orleans et al. [5–7] for Co NPs embedded in SiO_2 matrix exposed to a 200 MeV Iodine ion beam. At low irradiation fluence, the elongation into nanorods of some of the particles accompanied by fragmentation of some others is observed while at higher fluences nanorods continue to grow during irradiation, likely at the expense of smaller nanostructures. After this discovery various experiments were undertaken to study this new phenomenon in a larger class of metal NPs (Au, Ag, etc.) [8–15]. Nevertheless, the underlying mechanism driving it has not been completely elucidated yet, even though few theoretical studies have been attempted [5,12,16,17]. It emerged from these studies that a desired aspect ratio of the elongated NPs can be achieved by optimization of the ion beam parameters. In this paper, we report on investigation of the irradiation-induced embedding of hexagonally arranged Au NPs, prepared by micellar technique, and further on the application of the technique to the differently prepared Au NP/SiO_2 composite with an emphasis on reproducibility of the ion-shaping effects investigated recently [14]. By monitoring our experimental data, we demonstrate for the second time the existence of the presumably size-dependent threshold and saturation fluences for the shaping effects mentioned.

2. Experimental

Hexagonally arranged spherical gold NPs, with average diameter of 10 nm (size dispersion 10%) and areal densities of NPs of 2×10^{10} particles/cm^2 were deposited on top of Si/SiO_2 substrates by using micellar technique. This approach offers the possibility to control the particle size as well as the inter-particle distance over a rather broad range (diameters between 1 nm and 12 nm, distances between 30 nm and 140 nm). Furthermore, the finally obtained NP arrays exhibit a high degree of hexagonal order. For more details about the sample preparation we refer the reader to the literature [19–22]. In the present case, Au NPs are prepared with an average

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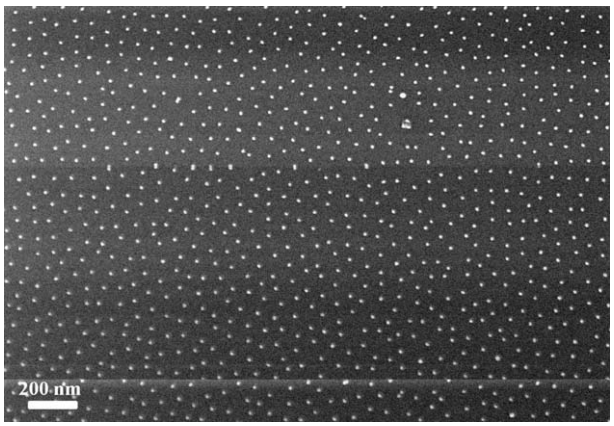

Fig. 1. Scanning electron microscopy (SEM) image of the hexagonally arranged Au NPs prepared by micellar technique (average diameter 10 nm, average inter-particle distance 80 nm).

inter-particle distance of about 80 nm. The thickness of the top silica film onto which Au NPs are grafted amounts to 200 nm. High-resolution scanning electron microscopy (SEM) at 30 keV is employed to image the surface of the sample after deposition of the Au NPs. The recorded corresponding image of the sample surface is shown in Fig. 1.

The hexagonally arranged Au NPs are sequentially irradiated with 200 keV Ar^+ ions to the maximum fluence of 5×10^{15} ions/cm^2. SEM images in Fig. 2a–c show diminishing particle heights relative to substrate level with sequential increase of the irradiation fluence. This observation is, however, not due to standard sputtering. Rather, a detailed study of the present system applying atomic force microscopy (AFM) as well as high resolution transmission electron microscopy (HR-TEM) to cross-sections of identically ion bombarded NPs, revealed a complete burrowing of the spherical NPs up to a practically equal depth within the subjacent SiO_2 layer. Fig. 3a shows an AFM image of the as-prepared Au NPs with scanning size of 2 μm × 2 μm, showing the particle height of about 10 nm. In Fig. 3b a typical distributions of particle height as extracted from the AFM measurements, including Gaussian fits, for particles as prepared and irradiated with 2×10^{15} and 3×10^{15} Ar ions/cm^2. AFM measurements were analyzed using WsXM software [23]. A detailed analysis of this irradiation-induced burrowing effect has been reported recently [22].

After the Ar bombardment an additional SiO_2 film of approximately 150 nm is deposited onto samples irradiated with 2.5×10^{15} and 5×10^{15} ions/cm^2 by reactive sputtering resulting in a confinement of the Au NPs within a 350 nm thick silica matrix. After deposition and annealing to 900 °C for 15 min, the silica film containing the Au NPs is irradiated with 54 MeV Ag^{8+} ions to fluences between 1×10^{12} and 1×10^{15} ions/cm^2.

3. Results and discussion

Fig. 4a shows the evolution of the Au RBS peak for several fluence values of the 54 MeV Ag^{8+} ions. The relatively sharp peak of the unirradiated regions corresponds to 10 nm virgin particles which are embedded in a SiO_2 matrix. With increasing Ag ion fluence the Au RBS peak broadens, which indicates that the Au becomes distributed over a larger depth region, indicative of the elongation of the NPs forming nanorods. The FWHM of the Au RBS peak after the irradiation is determined simultaneously for scattering angles of 120° and 170° (with respect to the incident beam direction). The evolution of the FWHM with fluence from the 120° detector is shown in Fig. 4b. From inspection of the figure, one can infer that i) No elongation of Au NPs can be discerned for

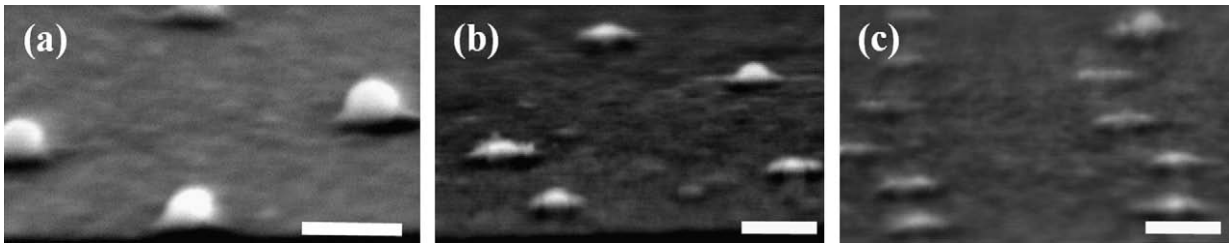

Fig. 2. SEM images of Au NPs on top of SiO_x/Si, as prepared (a) and after irradiation with 200 keV Ar^+ to fluences of 1.7×10^{15} ions/cm^2 (b) and 2.6×10^{15} ions/cm^2 (c) (80° titled view with respect to the surface normal). Scale bar is 25 nm.

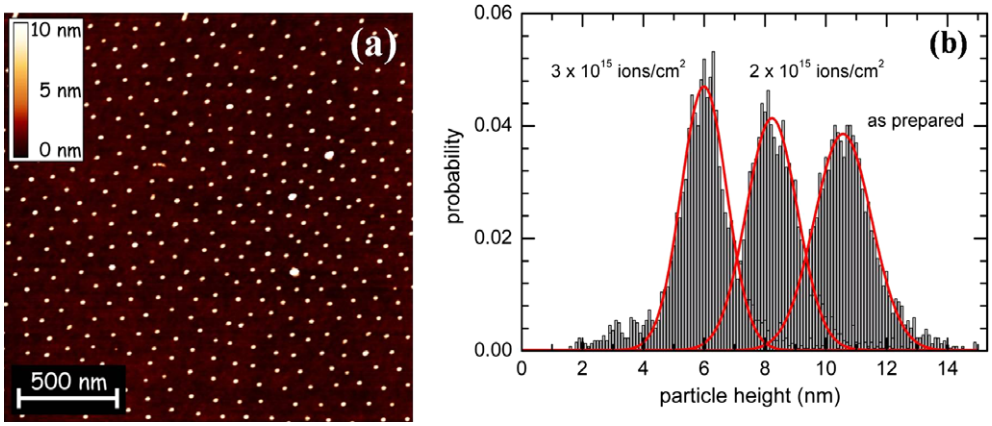

Fig. 3. (a) AFM image of Au nanoparticles (diameter 10.6 nm) on top of Si/SiO_2. (b) Size distributions of as-prepared and Ar^+-irradiated Au nanoparticles (200 keV, fluences as given in the inset). Solid curves are fits to Gaussians.