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Effects of irradiation defects on the nucleation of silver nanoparticles in spinel

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ABSTRACT

Composites with embedded metal nanoparticles attract much interest due to their unique physical properties, which considerably depend on size and shape of the nanoparticles, and on interparticle distance and dispersity of these parameters. Crystal defects can have an effect on the nucleation of nanoparticles. In this paper, the effect of defects on the nucleation and growth of silver nanoparticles was investigated. Argon ions with kinetic energy of 110 keV were implanted into spinel crystals, to produce defects in the surface-near region, and silver ions were then implanted into the region rich in defects. UV–VIS spectroscopy and TEM were used to analyze the samples. It is found that the introduction of defects can enhance the nucleation of silver nanoparticles and mediate their size distribution, and that the size of these nanoparticles for the sample with argon pre-implantation is larger than that in the sample without argon pre-implantation. During an annealing process, defects can improve the growth efficiency of nanoparticles.

1. Introduction

Composites with embedded nanoparticles have attracted much interest due to their unique physical properties, which enable promising application in novel electronic or photonic devices, such as non-linear optical devices and non-volatile memory devices [1]. Currently, the ion implantation is the widely used method of synthesis of metal nanoparticles in materials, due to its versatility and flexibility in control on ion concentration and depth distribution [2,3]. The properties of composites with embedded nanoparticles considerably depend on size and shape of the nanoparticles, and on interparticle distance and dispersity of these parameters [4]. Therefore, a variety of methods have been developed to try to control on these parameters.

One promising method is the use of irradiation defects to mediate the nucleation of nanoparticles. These defects are usually introduced by pre-implantation or irradiation. Defects have strong capacity of trapping impurities in substrate, which can act as pre-nucleation centers of nanoparticles. Some parameters of nanoparticles (size, distribution and size dispersion) can be mediated indirectly by control on defects via adjusting the parameters of incident ions (energy, flux, fluence and implantation temperature) [5–8]. Fedorov et al. investigated the effects of nanocavities formed by helium ion implantation and annealing on trapping of Au atoms in MgO substrate [5]. Patel et al. studied the influence of defects produced by ion pre-implantation on the size of Cu nanoparticles synthesized by ion beam mixing in silica glass [6]. It revealed that the average size of Cu nanoparticles can be controlled by the pre-implantation dose. Zhou et al. also used a similar method to investigate the effects of irradiation defects on nucleation and distribution of Au nanoparticles in sapphire substrates [7]. Recently, Giulian et al. presented a typical result of almost mono-dispersed Pt nanoparticles synthesized by ions implantation in silica glass [8]. In this study, Pt-ions were implanted into the region rich in defects produced by ion irradiation, the difference in size among Pt nanoparticles (average size ~ 3.0 nm) in the projected range is less than 1 nm in diameter.

In this paper, the ultraviolet–visible spectrometry (UV–VIS) and transmission electron microscopy (TEM) are used to study the influence of defects on the nucleation of silver nanoparticles in spinel. The annealing behavior of silver nanoparticle under condition with defects is also investigated.

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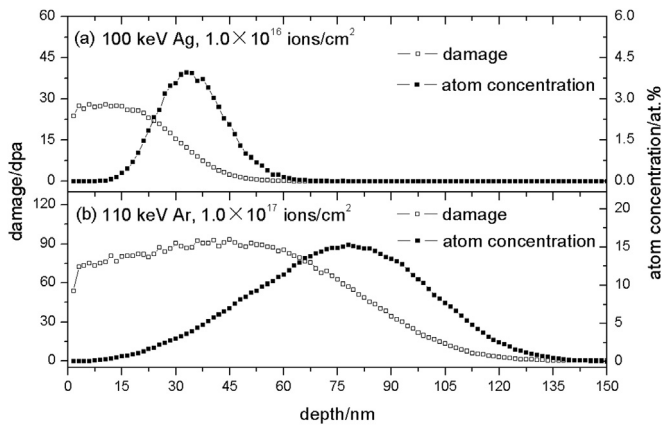

Fig. 1. The distribution of damage (dpa) and atom concentration (at. %) with depth simulated by SRIM 2006 for (a) silver and (b) argon ion implantation.

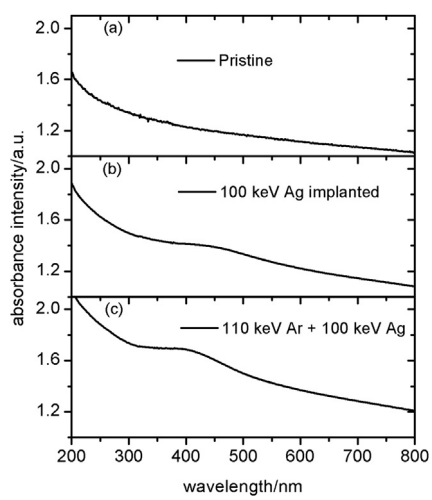

Fig. 2. The UV–VIS spectra for the (a) pristine sample, (b) sample implanted only with silver ions and (c) sample with argon ion pre-implantation implanted with silver ions.

2. Experimental

Single-crystal spinel samples with (110) orientation ($MgO \cdot 1.2(Al_2O_3)$) were pre-implanted with 110 keV argon ions to the fluence of 1.0×10^{17} ions/cm^2 with ion flux $\sim 2.0 \times 10^{13}$ ions/cm^2/s. Subsequently, the samples with or without argon ion pre-implantation were implanted with 100 keV silver ions to fluence of 1.0×10^{16} ions/cm^2 with ion flux $\sim 6.0 \times 10^{11}$ ions/cm^2/s. All implantations experiments were carried out at 350 °C. According to SRIM 2006 simulation [9], the damage produced by argon ion pre-implantation reaches a maximum at the depth of 40 nm (~92 dpa), and the concentration of argon atoms reaches a maximum around the depth of 80 nm (~15 at.%), as shown in Fig. 1a. The damage produced by silver ion implantation reaches a maximum at the depth of 10 nm (~28 dpa), the concentration of silver atoms has a maximum at the depth of 33 nm (~4 at.%), which is close to the region where the concentration of vacancies reaches a maximum, as shown in Fig. 1b. After implantation, the samples with or without argon ion pre-implantation were annealed at 900 °C for 1 h to investigate the effect of defects on nanoparticle growth.

The surface plasmon resonance (SPR) of metal nanoparticles occurs in the visible range of electromagnetic spectrum [10]. Therefore, the formation of silver nanoparticles in sample can be examined by the measurement of UV–VIS spectrometry, and the SPR absorbance intensity provides the information on nanoparticles concentration. In experiment, samples were characterized by optical absorption spectrometry (UV–VIS, PerkinElmer lambda900) and transmission electron microscope (TEM, JEOL JEM-2010).

3. Results and discussion

After silver ion implantation, an absorbance peak around 446 nm is observed (Fig. 2b). This peak is from the surface plasmon resonance (SPR) absorbance of silver nanoparticles. The appearance of this peak indicates the formation of silver nanoparticles. The absorbance intensity of SPR peak increases for the sample with argon ion pre-implantation (Fig. 2c) [11], which implies more silver nanoparticles formed in the sample. Therefore, the introduction of defects enhances the nucleation of silver nanoparticles. Positron annihilation spectroscopy (PAS) results indicated that the defects enhanced the nucleation of silver nanoparticles mainly are vacancy-type defects [11].

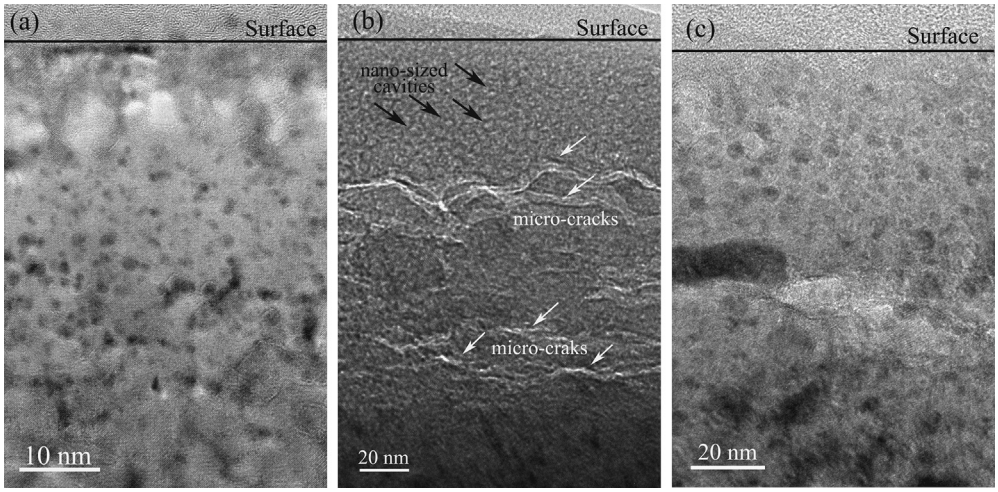

Fig. 3. Cross-section TEM micrographs for (a) sample implanted only with silver ions, (b) sample implanted only with argon ions and (c) sample with argon ion pre-implantation implanted with silver ions.