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The mechanism of nanoparticle precipitation induced by electron irradiation in transmission electron microscopy☆

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1. Introduction

Nanoparticle (NP) precipitation triggered by electron irradiation is a phenomenon often observed in (scanning) transmission electron microscopy ((S)TEM) studies [1–6]. Although this is a type of unwanted specimen damages in pristine materials [4,5], sometimes this may serve as a synthetic tool to produce nanostructure in desired materials [6]. Either to avoid or to use it, one needs to understand mechanisms to optimize experimental conditions as required. Previously, both knock-on and radiolysis have been overwhelmingly considered as the main causes of NP precipitation or beam damage [4,6]. The former is due to kinetic energy and momentum transfer from a beam electron to an atom, resulting in displacement of the affected atom. The latter is originated from ionizing atom electrons by beam electrons, and decays of the excited electrons may result in displacement of an atom (specifically an anion) [for a review see 5]. Apparently, these two mechanisms can easily scramble an ordered structure into a disordered state by randomly displacing atoms, but it is not obvious why they can also drive the randomly displaced atoms into a new and ordered structure (or phase). Temperature rise due to the energy deposit may be a possibility [7], but most experimental evidences strongly suggest that the precipitation be a result of an athermal crystallization process [3,8–10]. Thermodynamically, the precipitation (or phase transformation) is driven by lowering the Gibbs free energy of system. However, in (S)TEM, electron irradiation continuously injects energy into the specimen. To overcome this dilemma, a two-energy-levels model was suggested [11]. A part of energy input may be dissipated into the environment as the irradiated specimen's atoms rearrange to relax the atomic structure. During the rearrangement process the specimen is driven to a stimulated higher-energy state (E_2), which is thermodynamically unstable and quickly decays releasing some energy. After the rearrangement is complete the internal energy of the specimen (E_3) drops below the original internal energy (E_1), i.e. $E_2 > E_1 > E_3$ [11].

In recent studies, the induced electric field by electron irradiation has been identified as the main cause for beam damage in a variety of materials, in which the formation of NPs triggered by electron irradiation is categorized as phase separation [5,12,13]. There are several types of NP formations. From the mass-conservative point of view, one type involves drastic mass loss from the beam-irradiated region. In these materials, some species are more volatile than others under electron beam; the induced electric field may liberate them into vacuum or to adjacent region [6]. The species left in the irradiated region and/or ejected to the adjacent region may form particles [14–17]. Usually, these particles are formed on surfaces of specimen or supporting thin films.

Besides, there is another type of precipitation, in which the mass in the irradiated region does not have noticeable change or the mass loss is not directly associated with the NP precipitation [1–3]. In this study we only focus on this type of precipitation and demonstrate experimentally the nucleation process in Ru doped SiO_2 amorphous films. Several characteristics can be easily recognized, which include random distribution of NPs, and their small sizes. Most importantly, the precipitation can be identified as a nucleation dominated process, of which the usual coalescence and aging stages do not occur. These characters are common in the electron-beam triggered precipitation and have also been often observed in other materials [1]. Furthermore, we provide a detailed explanation why and how electron beam irradiation can produce the NPs in these materials based on the convention nucleation and growth theory under electric field. All experimental observations can be well interpreted by the proposed mechanism of the induced electric field.

2. Experimental

Amorphous Ru-Si-O films were deposited by reactive rf magnetron co-sputtering from a Ru20Si90 25 cm diameter, fine-grained composite target. The sputtering gas was a mixture of 11% oxygen in argon at a total pressure of 10 mTorr. According to previous work this mixture guaranteed that an oxygen-saturated film would be produced [18,19]. Substrates were 20 nm thick silicon monoxide (SiO) films suspended on

☆ Ru nanoparticles (NPs) can precipitate in Ru doped SiO_2 amorphous thin films, triggered by electron irradiation in (scanning) transmission electron microscope ((S)TEM). A new mechanism was introduced to interpret the formation of metal NPs in (S)TEM. The induced electric field by electron irradiation, which originates from charging due to ionizations and excitations of atom electrons, can reduce the Gibbs free energy barrier for nucleation of metal particles. Furthermore, the directional ion drifting driven by the electric forces may accelerate the kinetic process of metal particle precipitation.

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300 mesh copper grids (Ted Pella, Inc), which had been stripped of their formvar protective film by solvent washing. These substrates were kept near room temperature during deposition by mounting them on a massive copper holder. A deposition rate of 0.1 nm/s was achieved at an rf power of 30 W. The films produced for this study had a nominal thickness of 20 nm.

The Ru NPs were precipitated and analyzed using JOEL 2010F (S)TEM, equipped with Gatan electron energy loss spectrometer, operating at both TEM and STEM illumination mode at 200 kV. The precipitation of Ru NPs was observed by *in situ* imaging, electron diffraction and electron energy loss spectroscopy (EELS) techniques. The energy resolution of EELS was about 1.0 eV.

3. Results

The as-deposited Ru-Si-O thin films used in this study are uniform and no pre-existing particles can be observed. The thin films are also stable; there is no morphology change in the samples after being stored in air at atmospheric pressure for more than a year. However, Ru NPs can be easily precipitated after the thin films are exposed to electron beam in (S)TEM.

Fig. 1 shows a time series of phase contrast images of the Ru-Si-O thin film. The first image (initial) was taken right after the area was exposed to electron beam. Overall, the initial image is quite smooth and homogeneous. The fine grainy contrast is due to the high frequency noise of phase contrast. After 4 minutes of exposure to the same beam of electrons, very faint particle-like contrasts start to occur, and they were everywhere in the illuminated region. The contrasts become stronger and stronger thereafter. After 12 minutes of exposure, the crystal structure can be seen in these particles. The particle sizes do not increase significantly with further electron beam exposure. The average size is about 3.5 nm after 12 minutes of exposure, while it only increases slightly to about 4.0 nm after 23 minutes of exposure. Overall, the sizes of these nanoparticles are in the range of 3–5 nm. Fig. 2 is a higher magnification image recorded after the particles have been well precipitated by the electron beam. The crystalline lattices of nanoparticles can be easily seen.

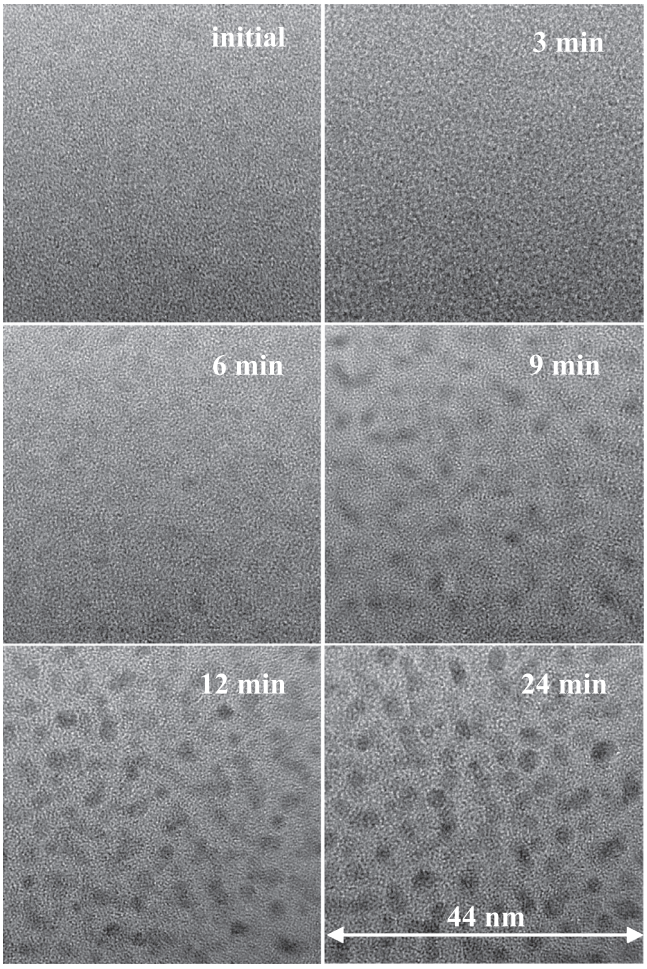

Fig. 1. Selected images in a time series of phase contrast imaging showing the evolution of nanoparticles in the Ru-Si-O thin films by high-energy electron irradiation. The current density of electron beam was 10.4 PA/cm^2, and the exposure time for each image was 1 s. The total irradiation times are given in each image. The "initial" indicates that the first image was taken right after the area was exposed to electron beam.

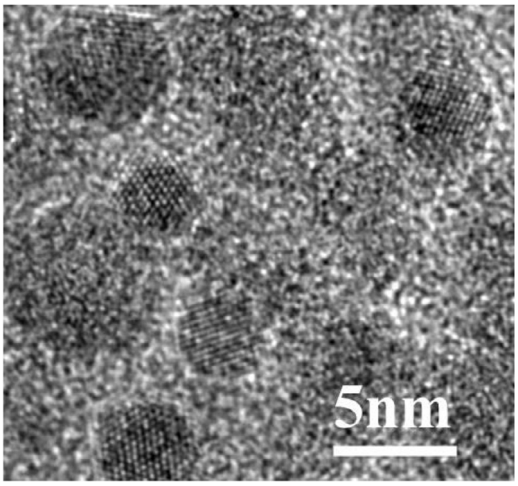

Fig. 2. High resolution TEM image showing lattice fringes in individual nanocrystals of Ru.

The electron diffraction patterns corresponding to different stages of exposure are given in Fig. 3. The initial diffraction shows that the thin film was amorphous (Fig. 3a): no sharp diffraction spots or rings can be seen. With the increase of exposure to electron beam, diffraction rings

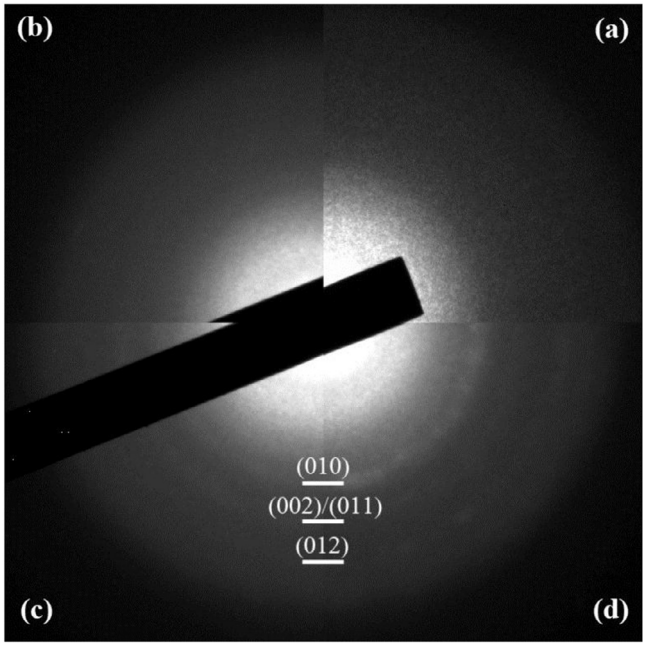

Fig. 3. Time series of electron diffraction patterns showing the crystallization of Ru nanoparticles in the Ru-Si-O thin films. The indices of diffraction rings are depicted.