Microsecond-temporal and pocometer-spatial resolution in situ observation of fast dynamic process in nanoparticles by cryo-ultrahigh voltage electron microscopy

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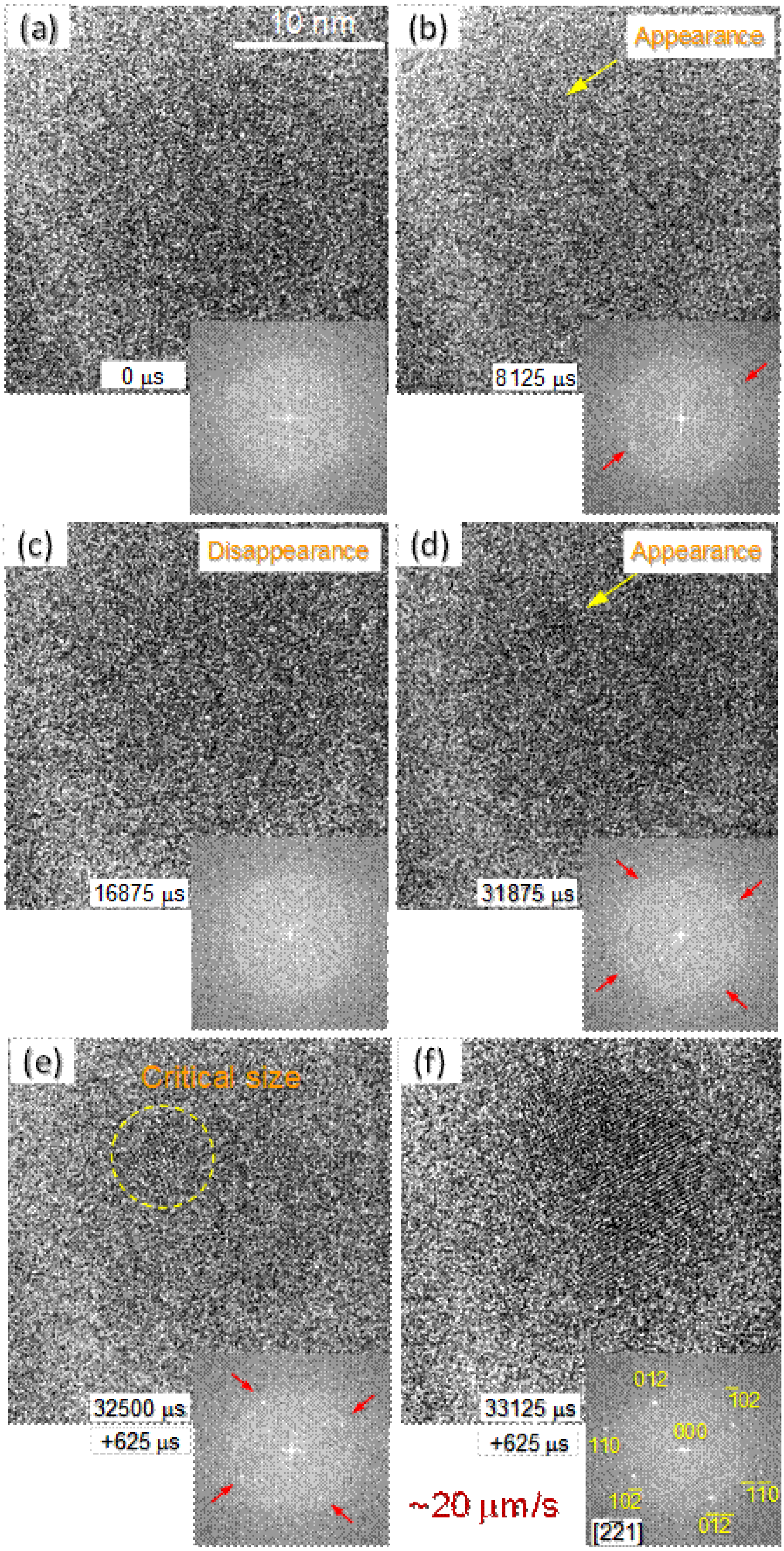
Fast in situ observation by TEM is one of useful techniques in researches on phase transitions of nanoparticles. It was evident that amorphous antimony nanoparticles can be crystallized with ease by stimulation from the outside. Knock-on displacements by high energy electron irradiation also become one of the stimulations for the crystallization of the amorphous nanoparticles. In the present study, electron-irradiation-induced crystallization processes of amorphous antimony nanoparticles have been studied by ms-temporal and pm-spatial resolution in situ observations by the cryo-ultrahigh voltage electron microscope developed collaboratively by Osaka University and JEOL.

Amorphous Sb nanoparticles supported on thin amorphous C substrates were prepared by a vapor-deposition method. Electron irradiation experiments and the simultaneous in situ observations were carried out by JEM-1000EES ultra-high voltage electron microscope operating at an accelerating voltage of 1 MV. The time for one frame was 625 μs.

Fig. 1 shows one of typical examples of high resolution observations during a crystallization in an about 20 nm-sized amorphous Sb nanoparticle. The (a) ~ (f) show snapshots during crystal growth in about 20 nm sized nanoparticle. In Fig. 1(b), a 2 nm-sized crystalline nucleus appears on the surface of the nanoparticle, and the FFT pattern from the particle is in set. Week 2 spots are recognized as indicated by red arrows in the FFT pattern, and correspond to nucleation of the small crystal. From Fig. 1(c) to (d), the nucleus repeats an appearance and disappearance. When the nucleus grows up to about 5 nm in diameter in Fig. 1(e), the amorphous Sb nanoparticle is crystallized in the whole nanoparticle as shown in Fig. 1(f). In the FFT pattern, the week four spots in Fig. 1(e) change to an obvious net pattern in Fig. 1(f), which is indexed as the [2-21] zone axis pattern of Sb crystal. In this case of a 20 nm-sized nanoparticle, the interface migration rate is estimated to be approximately 20 mm s^{-1}. The interface migration rate depends on the particle size, and it was confirmed that the smaller the particle size is, the faster the velocity is. From this observation, the critical nucleus size for crystallization is estimated to be approximately 5 nm.

An elastic interaction in the interface between this crystalline nucleus and the amorphous nanoparticle may induce the crystallization all over the nanoparticle. The amorphous nanoparticle has to jump beyond the activation energy for the crystallization. At the early stage of the crystallization, small nucleus fluctuates between a formation and an annihilation. However, when the size of the nucleus is larger than the critical size for crystallization, the elastic interaction energy of an interface between this crystalline nucleus and the amorphous matrix will be larger than the activation energy. It is suggested that the elastic interaction energy is a trigger for crystallization in amorphous Sb nanoparticles.



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