



In-situ TEM observation of electronic-excitation-induced structural changes in III-V compound nanoparticles

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Abstract –Electronic-excitation-induced structural changes in nanoparticles have been studied by in-situ transmission electron microscopy. When GaSb particles were excited by 25 keV electrons at a fixed temperature, the porous structures are formed. With increasing the total dose, the porous compound transforms to a two-phase consisting of an antimony core and a gallium shell, or remains the original compound phase depending on the temperature. It is suggested that such nonlinear responses of the structural changes may arise from the behaviors of point defects introduced by the excitation.

Structural stability in materials under electronic excitation is different from that at the ground state. It is expected that electronic excitation effects on the structural stability will be enhanced in nanoparticles which have high surface to volume ratio and high atomic mobility. Recently, it was found by that when GaSb particles were excited by low energy electrons, the compound transforms to a two-phase consisting of an antimony core and a gallium shell or an amorphous phase, or remains the original compound phase, depending on particle size and/or temperature [1-4]. In the present paper, we studied structural changes induced by lower energy electronic excitation in GaSb particles by in situ transmission electron microscopy.

An example of structural changes in GaSb particles by 25 keV electronic excitation at 430 K is shown in Fig. 1. Figures 1(a) and (a') show a BFI of particles with the mean diameter of approximately 20 nm before excitation and the corresponding SAED, respectively. As indexed in Fig. 1(a'), the Debye-Scherrer rings can be consistently indexed as those of GaSb which has the zincblende structure. The same area after excitation for 60 s is shown in Fig. 1(b). In the interior of the particles after the excitation, there appear voids with bright contrast. As seen from a comparison of the magnified images I_a and II_a in (a) with I_b and II_b in (b), the diameter of nanoparticles after the excitation increased up to 15 % compared with those before excitation. In the SAED taken after the excitation as shown in Fig. 1(b'), Debye-Scherrer rings of the zincblende structure are recognized again, but the lattice constant increased up to 1.8 % compared with that before excitation. The same area after excitation for 480 s is shown in Fig. 1(c). The voids in the individual particles change in the shape and size, as seen from a comparison of the magnified images I_b and II_b in (b) with I_c and II_c in (c). In the SAED taken after the excitation as shown in Fig. 1(c'), Debye-Scherrer rings of crystalline antimony are recognized, superimposed on a weak halo ring with the value of the scattering vector ($K = (4\pi \sin \theta)/\lambda$) of approximately 31.0 nm^{-1} which is corresponding to the first halo of liquid gallium. This result indicates that a two-phase mixture consisting of a crystalline antimony core and a liquid gallium shell was formed in the particles. From these results, it has been evident that when GaSb particles kept at 430 K were excited by 25 keV electrons, two-phase separation takes place via void formation.

In this case, it is considered that gallium atoms on the lattice points are displaced by the electronic excitation to form vacancies and gallium interstitials in the crystal. The vacancy concentration in the particle core is higher than that in the surface layer, but interstitial concentration increases toward the surface. Consequently, under the condition of vacancy supersaturation in the particle core the vacancy clusters will grow to form a void, and the subsequent surface segregation of interstitial clusters will bring about the separation to the two-phase structure.

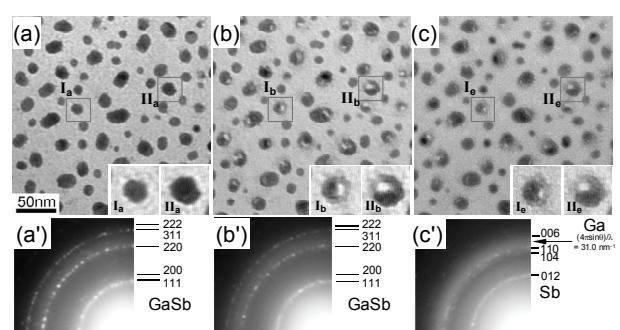


Figure 1: An example of the structural changes in approximately 20 nm-sized GaSb particles kept at 430 K by electronic excitation. (a) A BFI and (a') the corresponding SAED before excitation. (b) The same area after excitation for 60 s and (b') the corresponding SAED. (c) The same area after excitation for 480 s and (c') the corresponding SAED. The parts framed squarely are enlarged in the figures.

References

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