Nonlinear Responses of Electronic-Excitation-Induced Phase Transformations in GaSb Nanoparticles

H. Yasuda,[1,*] H. Mori,[2] and J. G. Lee[2]

[1]*Department of Mechanical Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan*

[2]*Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan*

(Received 22 September 2003; published 29 March 2004)

We studied electronic-excitation-induced phase transformations in nanoparticles using transmission electron microscopy. GaSb particles excited by 75 keV electrons transform to two phases consisting of an antimony core and a gallium shell or an amorphous phase, or remain in the original crystalline phase, depending on particle size and/or temperature. It is suggested that such nonlinear responses of the phase transformations may arise from synergistic effects of bond instability, localized excitations, enhanced diffusivity, or thermal equilibrium in reactions.

DOI: 10.1103/PhysRevLett.92.135501 PACS numbers: 61.80.–x, 81.30.–t

Phase transformations, as a result of relaxation after excitations by optical pumping, have been studied extensively in the field of photochemistry. It is well known as an exposure of photographic films that in crystals with ionic bonding, such as alkali halides, the electronic-excitation-induced atom displacements can be more efficient in forming metallic colloids in the crystals [1,2]. Also, in III-V compounds in which covalent bonding is more dominant than ionic bonding, it has been confirmed in previous studies [3–6] that atom displacements resulting from the formation and migration of lattice defects in the interior of the solids and desorption of atoms for the bulk surface takes place, but the yield of the atom displacements for each phenomenon is quite low. On the other hand, in isolated molecules electronic-excitation-induced structural changes are remarkably enhanced, since the excited states tend to localize in them. However, to the authors' knowledge, there is no example of studies on electronic-excitation-induced atom displacements and resulting structural changes in isolated mesoscopic material such as nanoparticles, in which the localized excitations are expected to be produced.

From the background mentioned above, in the present work, the structural changes induced by electronic excitations in III-V compound nanoparticles have been studied *in situ* by transmission electron microscopy. GaSb particles have been employed as specimens and investigated as functions of specimen temperature and particle size.

To prepare size-controlled GaSb particles and carry out the subsequent electronic excitation, a double-source evaporator was installed in the specimen chamber of a transmission electron microscope (TEM). An amorphous carbon film was used as a supporting film. Using the evaporator, gallium was first evaporated from one filament to produce gallium nanoparticles on the supporting film kept at ambient temperature, and then antimony was evaporated from the other filament onto the same film. Vapor-deposited antimony atoms quickly dissolved into gallium particles to form GaSb (Ga-50 at. % Sb) compound particles. The particles were then annealed in the microscope at 573 K for 3.6 ks and were slowly cooled from the annealing temperature to room temperature in 2.7 ks, in an attempt to homogenize the solute concentration. Electronic excitation experiments with an electron beam and observations were carried out using the same TEM. The electron energy and electron flux used for the excitations were 75 keV and $1.5 \times 10^{21} e\ \mathrm{m}^{-2}\,\mathrm{s}^{-1}$, respectively. The specimen temperature was kept at 293 to 573 K during the experiments. Structural changes associated with electronic excitations were observed *in situ* by bright-field images (BFIs) and selected-area electron diffraction patterns (SAEDs).

An example of structural changes by electronic excitation in GaSb particles kept at 423 K is shown in Fig. 1. Figures 1(a) and 1(a′) show a BFI of approximately 20 nm-sized particles before excitation and the corresponding SAED, respectively. As indexed in Fig. 1(a′), the Debye-Scherrer rings can be consistently indexed as those of the

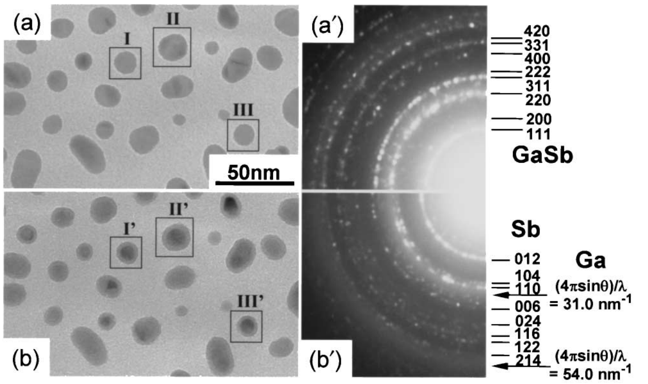

FIG. 1. An example of the structural change by excitation in approximately 20 nm-sized particles kept at 423 K. (a) A BFI of particles, and (a′) the corresponding SAED before excitation. (b) The same area after excitation for 240 s, and (b′) the corresponding SAED.

GaSb compound which has the zinc blende structure with a lattice constant of $a_0 = 0.61$ nm. The same area after excitation for 240 s is shown in Fig. 1(b). In the interior of particles, there appears a structure consisting of a core with dark contrast and a shell with bright contrast, as seen from a comparison of the parts framed squarely by I, II, and III in 1(a) with those framed by I′, II′, and III′ in 1(b), respectively, The SAED taken after the excitation is shown in Fig. 1(b′). In the SAED, Debye-Scherrer rings are recognized, superimposed on halo rings. The Debye-Scherrer rings can be indexed consistently as those of crystalline antimony which has the hexagonal structure with lattice constants of $a_0 = 0.43$ nm and $c_0 = 1.13$ nm. The values of the scattering vector $[K = (4\pi \sin\theta)/\lambda]$ of the halo rings are approximately 31.0 and 54.0 nm^{-1} which are corresponding to those from liquid gallium. This fact indicates that a two-phase mixture of crystalline antimony and liquid gallium is formed in the particles after the excitation. It was confirmed by dark-field electron microscopy that particles after the excitation have a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell. Contrasts of the core-shell structures in the BFI are distinguished obviously, when the crystals of antimony satisfy Bragg reflection conditions and, consequently, appear dark, as indicated by square frames. The phase separation should take place also in all of the smaller (approximately 10 nm-sized) particles in which the contrasts of the core-shell structures are not clear due to the insufficient Bragg reflection conditions of antimony crystals in Fig. 1(b′).

The temperature dependence of the behavior associated with electronic excitation in approximately 20 nm-sized particles has been examined. Examples of observations after electronic excitation for 240 s in particles kept at 443 and 293 K are shown in Figs. 2 and 3, respectively, In the SAEDs before excitation [i.e., Figs. 2(a′) and 3(a′)] and after that [i.e., Figs. 2(b′) and 3(b′)], Debye-Scherrer rings can be consistently indexed as those of the GaSb compound. The particles remain unchanged in both the microstructure and SAED after excitation. It has been noted here that such a phase separation as observed after excitation in particles kept at 423 K is absent in the particles kept at 443 and 293 K.

The particle-size dependence of the behavior associated with electronic excitation in particles kept at 423 K has been examined using both larger and smaller particles than those in Fig. 1. A typical example of the observations in approximately 30 nm-sized particles is shown in Fig. 4. The particles remain unchanged in both the microstructure and SAED after excitation for 240 s. It has been evident that phase separation is not induced with increasing particle size to approximately 30 nm. An example of the structural changes in approximately 10 nm-sized particles is shown in Fig. 5. Particles after excitation have a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell, as seen from a comparison of the BFI in Fig. 5(a) with that in Fig. 5(b). In the SAED taken after excitation for 240 s [Fig. 5(b′)], Debye-Scherrer rings of crystalline antimony are recognized, superimposed on halo rings from liquid gallium. These facts indicate that phase separation is induced by electronic excitation also in approximately 10 nm-sized particles kept at 423 K.

In order to see the temperature dependence of structural changes in approximately 10 nm-sized particles, the electronic excitation experiment in particles kept at 293 K was carried out, as shown in Fig. 6. In the SAED after excitation for 240 s [Fig. 6(b′)], only halos are recognized. The values of the scattering vector of the halo rings are approximately 19.0 and 29.0 nm^{-1} which correspond to those from amorphous GaSb. This result indicates that amorphization has been induced after the excitation in 10 nm-sized particles kept at 293 K.

Figure 7 summarizes the results on the phase transformations induced by electronic excitation as functions of particle size and temperature. Total electron dose is fixed at $3.6 \times 10^{23} e\ \text{m}^{-2}$. In this figure, the double circle, circle, and square indicate the two-phase separation

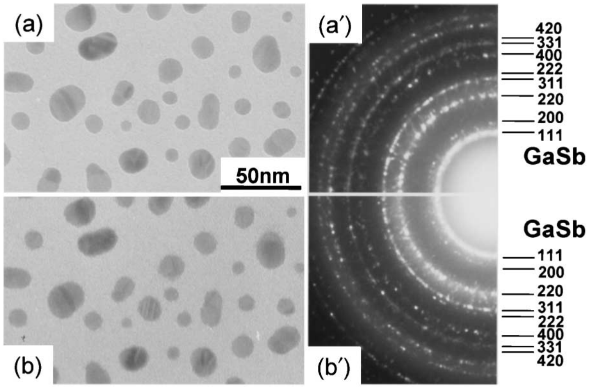

FIG. 2. The behavior by excitation in approximately 20 nm-sized particles kept at 443 K, (a) and (a′) before excitation, (b) and (b′) after excitation for 240 s.

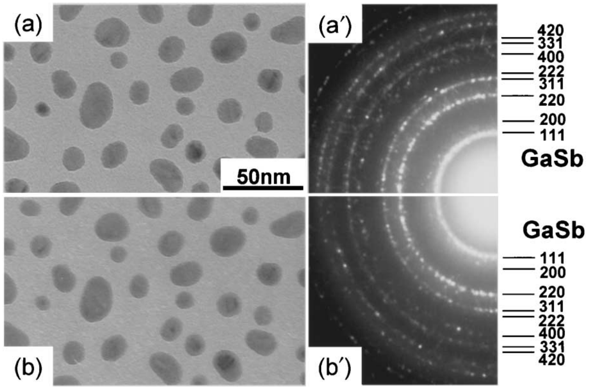

FIG. 3. A behavior by excitation in approximately 20 nm-sized particles at 293 K, (a) and (a′) before excitation, (b) and (b′) after excitation for 240 s.

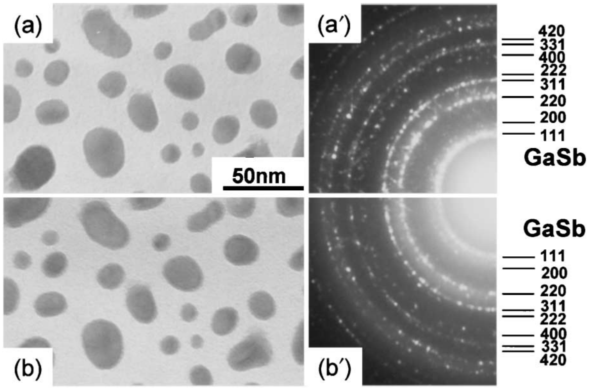

FIG. 4. A behavior by excitation in approximately 30 nm-sized particles at 423 K, (a) and (a′) before excitation, (b) and (b′) after excitation for 240 s.

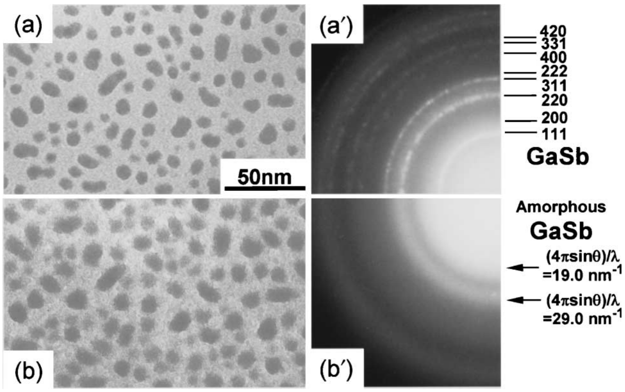

FIG. 6. An example of the structural change by excitation in approximately 10 nm-sized particles kept at 293 K, (a) and (a′) before excitation, (b) and (b′) after excitation for 240 s.

consisting of a crystalline antimony core and a liquid gallium shell, formation of an amorphous phase, and original crystalline phase with the zinc blende structure, respectively. From the results, it is evident that the phase transformations are suppressed with increasing particle size and temperature. The other points noted here are that in approximately 20 nm-sized particles the phase transformation is again suppressed with decreasing temperature, but, in approximately 10 nm-sized particles the phase transformation varies from phase separation to amorphization with decreasing temperature. Such nonlinear responses of phase transformation, that is, competitive formations of three kinds of phases with de creasing particle size and/or temperature, were observed by the 75 keV electron excitation.

A candidate for mechanisms of such nonlinear responses of electronic-excitation-induced phase transformations will be discussed as follows. It is known that atom displacements induced by electronic excitations in compounds which have ionic, covalent, or mixed bonding occur through the accumulation of excess energy by local electronic transitions from the ground state to excited states; that is, the formation of electron-hole pairs or pairs of holes (for example, produced by Auger transition) is directly converted into the atomic kinetic energy [4–7]. The localized excitations are required for the initial step for atom displacements. The interactions of excited states with various kinds of defects (such as surfaces) are effective in the localization. A breaking of the bonds among loosely bound atoms by the localized excitations enhances the atom displacements by electron-lattice interaction. Such excited states tend to localize in nanoparticles which are isolated and have a high ratio of surface to volume. We consider that the localized excitations and resulting atom displacements may act as a trigger for phase separation or amorphization in nanoparticles. In a Ga-Sb binary system in which the heat of formation ΔH is negative ($-41.9\ \mathrm{kJ\,mol^{-1}}$), the chemical (covalent and ionic) bond between gallium and antimony is stabilized at the ground state. If the phase separation from the compound to two pure substances (i.e., antimony and gallium)

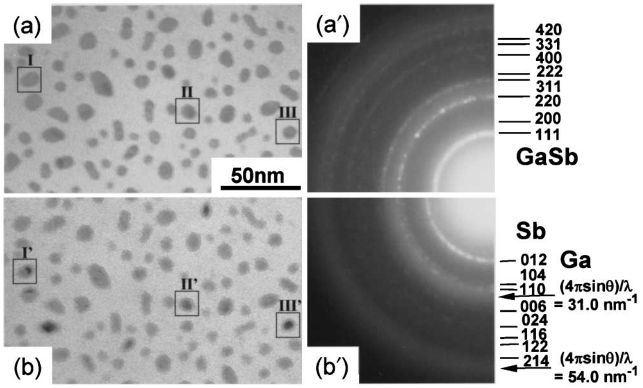

FIG. 5. An example of the structural change by excitation in approximately 10 nm-sized particles kept at 423 K, (a) and (a′) before excitation, (b) and (b′) after excitation for 240 s.

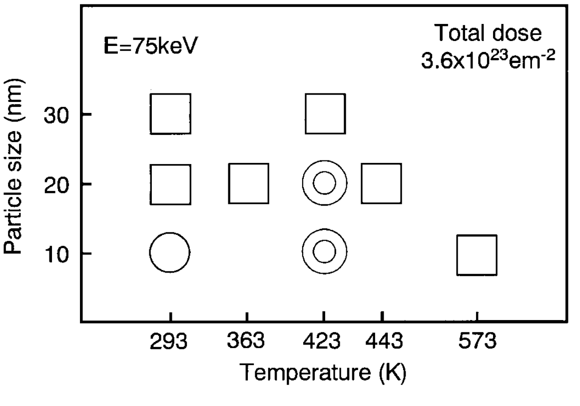

FIG. 7. Summary of the results on phase transformations induced by excitation as functions of temperature and size. The double circle, circle, and square indicate the two-phase separation consisting of a crystalline antimony core and a liquid gallium shell, the formation of an amorphous phase, and the original crystalline phase, respectively.

occurs, the free energy should increase. However, once such a heterobond is excited, it can be unstabilized by the mechanism mentioned above, and consequently the homobond (between gallium and gallium or between antimony and antimony), which is neither covalent nor ionic, may be more stabilized. In order to reduce the free energy of reaction which proceeds toward the phase separation in this binary system, the reaction has to be driven by positive ΔH originating from alteration of the chemical bonds. Positive ΔH is expected to be brought about the bond instability induced by the excitation. It is noted in the present experiments that the temperature at which the phase separation successfully occurs (especially in 20 nm-sized particles) is optimized in a limited range. From the result on a drastic suppression of the phase separation by the temperature change from 423 to 443 K, the free energy of GaSb formation under the excitation is speculated to change from a positive to a negative value with increasing temperature from 423 to 443 K. In order to satisfy such a change in the free energy, ΔH under the excitations may have to become a positive value. If the difference between ΔH in the ground state and that in the excited state, that is, the increase of the potential energy of GaSb accompanied by the excitation, is supplied by an energy accumulated by some kinds of electronic transitions, the phase separation could be induced. The reason why composite particles consisting of a crystalline antimony core and a liquid gallium shell are formed may be due to the different surface energy between gallium and antimony. Pure antimony particles are in the crystalline state, but pure gallium particles which have a low melting point are in the liquid state. The surface energy of liquid gallium is lower than that of crystalline antimony. Consequently, crystalline antimony will be surrounded with liquid gallium.

It was confirmed in our previous studies that enhanced atomic diffusivity in nanoparticles is suppressed with increasing particle size [8–10]. With increasing particle size, such phase transformations will be difficult to occur due to both dissipation of the localized excitations and suppression of atomic diffusivity. On the other hand, at lower temperatures at which long-range atomic diffusion is not activated thermally (i.e., at less than 363 K), any phase transformations cannot be induced in approximately 20 nm-sized particles. However, the amorphization may occur in approximately 10 nm-sized particles in which the lattice distortion by short range atom displacements can be introduced [11].

Effects of different parameters such as electron energy and electron flux on the phase transformations also have been found in our preliminary experiments. When the particles kept at 423 K are excited by 200 keV electrons, the phase separation as observed by the 75 keV electronic excitation was not induced since the cross section for excitation by 200 keV electrons may be reduced considerably. The electronic-excitation-induced phase separation is also dependent on electron flux. When the flux becomes nearly half of $1.5 \times 10^{21} e\ \mathrm{m}^{-2}\,\mathrm{s}^{-1}$, no phase separation is induced after excitation by the same total dose. The details will be published in separate papers.

In conclusion, a synergistic effect of bond instability by electronic excitations, localized excitations, atomic diffusivity, or thermal equilibrium and kinetics in the reactions may play an important role in nonlinear responses of the phase transformations in nanoparticles. Studies to elucidate the mechanism of the phase transformations in detail are in progress in our laboratory.

This work was, in part, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, under "Grant-in-Aid for Scientific Research" and "Nanotechnology Support Project."

---

*Author to whom correspondence should be addressed. Electronic address: yasuda@mech.kobe-u.ac.jp

[1] A. Schmid, P. Braunlich, and P. K. Rol, Phys. Rev. Lett. **35**, 1382 (1975).

[2] A. D. Townsend *et al.*, Radiat. Eff. **30**, 55 (1976).

[3] J.W. Corbett, *Electron Radiation Damage in Semiconductors and Metals* (Academic, New York, 1966).

[4] J. Kanasaki *et al.*, Phys. Rev. Lett. **70**, 2495 (1993).

[5] J. Singh *et al.*, Phys. Rev. B **50**, 11 370 (1994).

[6] O. Pankratov and M. Scheffler, Phys. Rev. Lett. **75**, 701 (1995).

[7] L.W. Hobbs, *Analytic Electron Microscopy* (Plenum, New York, 1980), p. 437.

[8] H. Yasuda, H. Mori, and H. Furuya, Philos. Mag. Lett. **80**, 181 (2000).

[9] H. Yasuda and H. Mori, Z. Phys. D **31**, 131 (1994).

[10] H. Yasuda and H. Mori, Z. Phys. D **40**, 140 (1997).

[11] H. Yasuda, K. Mitsuishi, and H. Mori, Phys. Rev. B **64**, 094101 (2001).