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Electron irradiation effects in GaSb compound nanoparticles have been studied by transmission electron microscopy, in order to examine structural stability under electron irradiation in a nanometer-sized system. It is revealed that when 75 keV electron irradiation was carried out in approximately (10–25)-nm-sized GaSb particles kept at 423 K, a phase separation of the GaSb compound was induced to form a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell. The phase separation was induced neither by 75 keV electron irradiation in GaSb nanoparticles kept at more than 443 K or less than 363 K nor by 200 keV electron irradiation in particles kept from 363 to 443 K. It is suggested that the phase separation in GaSb nanoparticles may be induced by electronic excitations rather than knock-on displacements.

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Semiconductor compound materials which have ionic, covalent, or mixed bonding exhibit a wide variation in damage response to electron irradiation. Atom displacements in these materials may be produced either by direct momentum transfer from the irradiating electron to an atom nucleus or as a response to alteration of atomic electronic states by ionizing radiation. Electronic effects will be expected to become much more important in semiconductor compound materials.

In our previous studies on knock-on displacement events in III-V compound materials such as GaAs, GaSb, and so on, it was evident that MeV electron irradiation induces chemical disordering or amorphization at low temperatures.[1,2] From the viewpoint of alteration of electronic states, several criteria for efficient coupling of the electronic stopping power of matter to atom displacement phenomena have to be satisfied in bulk solids: for example, (1) the electronic excitation must be localized to a few atom sites; (2) the excitation must have a lifetime comparable with the phonon period in order to couple into a mechanical response of the nuclear masses; (3) the available excitation energy must be comparable to the atom displacement energy in its excited state; (4) an energy to momentum conservation mechanism must exist.[3] In materials with both ionic and covalent bonding such as semiconductor compounds, it was shown that electronic excitations enhance the formation and migration of defects in bulk solids.[4] On the other hand, in isolated molecules it was found that electronic excitations generated by interaction with ionizing radiation tend to induce atom displacements and the resulting structural changes because it is easy to satisfy the criteria mentioned above. However, to the authors' knowledge, there is no example of studies from either the viewpoint of knock-on displacement events or of electronic excitations in mesoscopic solids such as nanoparticles.

Thus, in the present work, electron irradiation effects in GaSb compound nanoparticles have been studied by transmission electron microscopy, in order to see whether irradiation-induced atom displacements and the resulting structural changes occur in a nanometer-sized system or not.

Preparation of size-controlled GaSb (Ga–50 at. % Sb) particles was carried out with the use of a double-source evaporator installed in the specimen chamber of an electron microscope. The evaporator consists of two spiral-shaped tungsten filaments. An amorphous carbon film was used as a supporting film and it was mounted on a molybdenum grid. It was annealed at approximately 1000 K for about 30 s in the electron microscope prior to the experiments. Using the evaporator, gallium was first evaporated from one filament to produce nanometer-sized gallium particles on the supporting film. Antimony was then evaporated from the other filament onto the same film. The supporting film was kept at ambient temperature during the deposition. Vapor-deposited antimony atoms quickly dissolved into the gallium particles to form GaSb 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. This annealing treatment was done in an attempt to allow high atomic mobility in the particles which would homogenize the solute concentration. The chemical compositions of the particles on the film were checked from the intensity ratio of the Ga $L\alpha 1$ to the Sb $L\alpha 1$ peak by energy-dispersive x-ray spectroscopy. The specimens with chemical compositions controlled within approximately ±3 at. % Sb of the stoichiometric composition of 50 at. % Sb were used for the electron irradiation experiments.

The electron irradiation experiments and observations were carried out using the same microscope. The microscope used was a Hitachi H-800 TEM operating at accelerating voltages of 75 and 200 kV. The electron microscope was equipped with a turbomolecular pumping system and a liquid-nitrogen-cooled anticontamination device to achieve a base pressure below 2×10^{-5} Pa. The contamination was kept quite low. The maximum value of electron flux used for irradiation was approximately 1.5×10^{21} m^{-2} s^{-1}. The temperatures of the supporting films were kept from 363 to 443 K during irradiation. Structural changes associated with irradiation were observed *in situ.*

A typical example of structural changes in GaSb nanoparticles associated with 75 keV electron irradiation at 423 K is shown in Fig. 1. Figures 1(a) and 1(a′) show a bright-field image (BFI) of particles with diameter of approximately

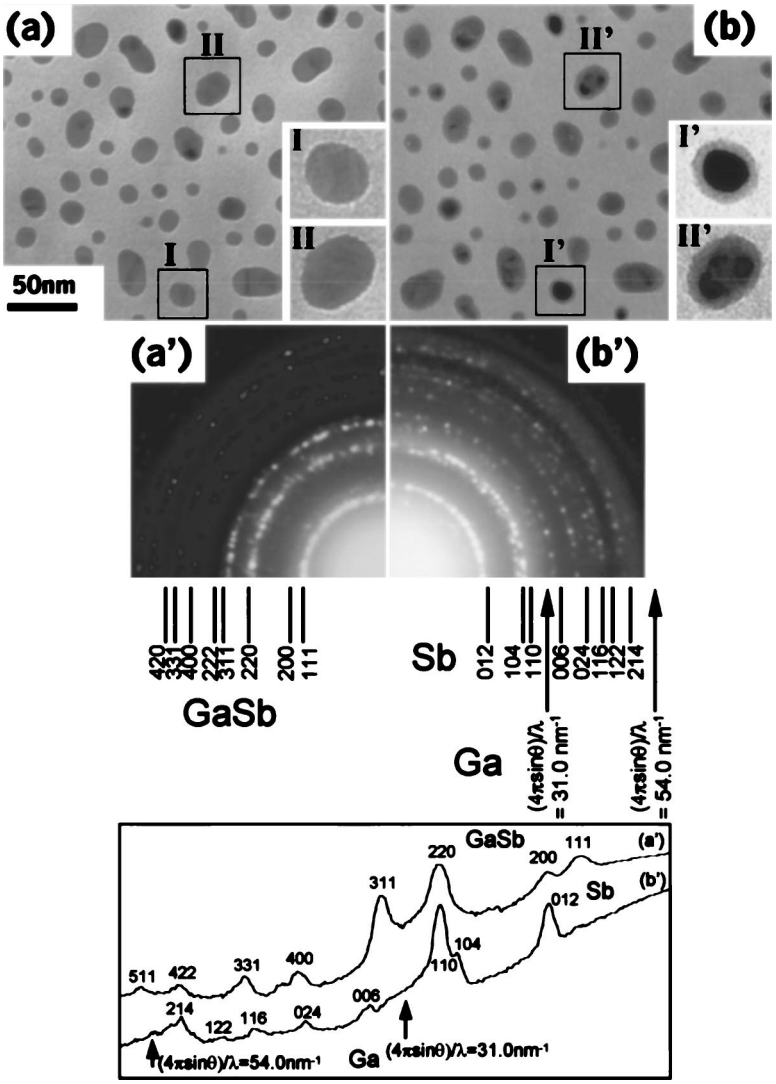

FIG. 1. A typical example of the structural change in GaSb nanoparticles associated with 75 keV electron irradiation at 423 K. (a) A BFI of particles of 10–25 nm in mean diameter, and (a′) the corresponding SAED before irradiation. (b) The same area after irradiation for 240 s, and (b′) the corresponding SAED. The line profiles of the SAEDs are indicated.

10–25 nm before irradiation and the corresponding selected-area electron diffraction pattern (SAED), respectively. The insets in the BFI show enlargements of the parts framed. The line profiles of the SAEDs are indicated. As noted in Fig. 1(a′), the Debye-Scherrer rings can be consistently indexed as those of GaSb (which has the zinc-blende structure with a lattice constant of $a_0=0.61$ nm). The same area after irradiation for 240 s is shown in Fig. 1(b). In the interior of particles after irradiation, there appears a definite structure consisting of a core with dark contrast and a shell with bright contrast, as seen from a comparison of the insets (I and II) in (a) with those (I′ and II′) in (b). The corresponding SAED taken from the irradiated region 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 $[K=(4\pi\sin\theta)/\lambda]$ for the halo rings are approximately 31.0 and 54.0 nm^{-1} which correspond 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 irradiation.

In an attempt to elucidate the spatial arrangement of the two phases (i.e., crystalline antimony and liquid gallium) induced by the electron irradiation, the microstructure in the individual particles was examined by dark-field electron microscopy. An example of the results is depicted in Fig. 2. Figures 2(a) and 2(b) are a BFI and a dark-field image (DFI) of the same sample shown in Fig. 1(b), respectively. The DFI was taken by setting the objective aperture on a part of the Sb 012 Debye-Scherrer ring. Particles A to D in Figs. 2(a) and 2(b) are encircled by dashed lines. From a comparison of particles A to D in Fig. 2(a) with those in 2(b), it is evident that crystalline antimony is present preferentially at the central portion of individual particles.

This fact suggests that in GaSb nanoparticles kept at 423 K the 75 keV electron irradiation induces phase separation to form a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell.

A typical example of behavior in GaSb nanoparticles associated with 75 keV electron irradiation at 443 K is shown in Fig. 3. Figures 3(a) and 3(a′) show a BFI of particles before irradiation and the corresponding SAED, respectively. The diameter of the particles is again approximately 10–25 nm. In the SAED, Debye-Scherrer rings can be consistently indexed as those of GaSb. Figures 3(b) and 3(b′) show a BFI

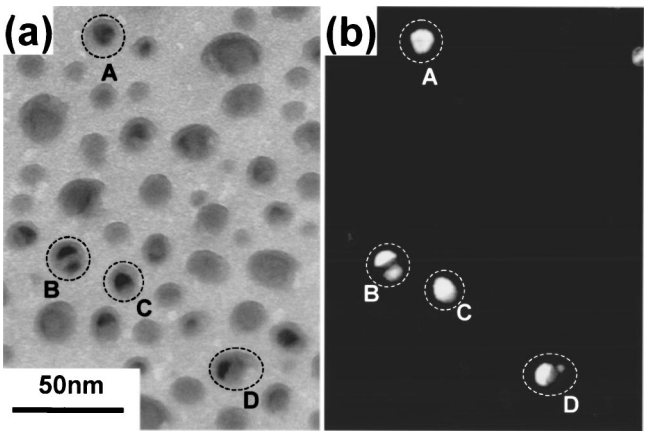

FIG. 2. (a) A BFI of the same sample shown in Fig. 1(b). (b) A DFI of the same area as in (a) taken by setting the objective aperture on a part of the Sb 012 Debye-Scherrer ring. In (b), regions of crystalline antimony appear bright.

of the same area after irradiation for 240 s and the corresponding SAED, respectively. The particles remain unchanged in both the microstructure and the SAED. This result indicates that such phase separation as observed during the irradiation in GaSb nanoparticles kept at 423 K is absent during the irradiation in the particles kept at 443 K.

An example of behavior in GaSb nanoparticles kept at 363 K during 75 keV electron irradiation is shown in Fig. 4. In the SAED taken from the region irradiated for 240 s [Fig. 4(b′)], the Debye-Scherrer rings from GaSb nanoparticles are not changed as compared with those before irradiation as shown in Fig. 4(a′). This result indicates that such phase separation as observed during irradiation in particles kept at

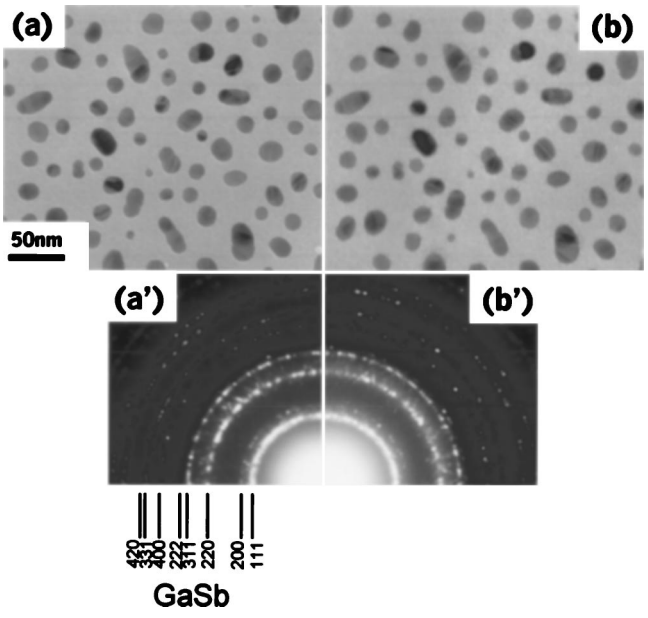

FIG. 3. A typical example of the behavior in GaSb nanoparticles associated with 75 keV electron irradiation at 443 K. (a) A BFI of particles of 10–25 nm in mean diameter, and (a′) the corresponding SAED before irradiation. (b) The same area after irradiation for 240 s, and (b′) the corresponding SAED.

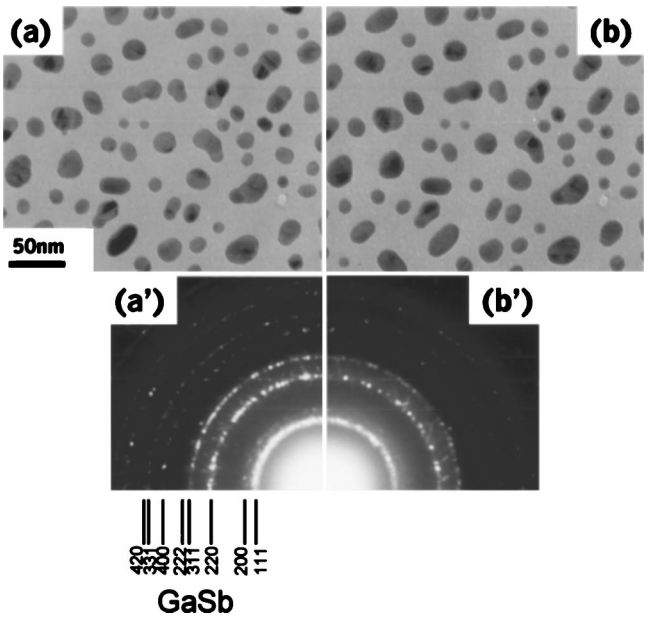

FIG. 4. A typical example of the behavior in GaSb nanoparticles associated with 75 keV electron irradiation at 363 K. (a) A BFI of particles of 10–25 nm in mean diameter, and (a′) the corresponding SAED before irradiation. (b) The same area after irradiation for 240 s, and (b′) the corresponding SAED.

423 K is also absent during irradiation in particles kept at 363 K.

In order to study the effect of electron energy on irradiation in GaSb nanoparticles, 200 keV electron irradiation was carried out. A typical example of GaSb nanoparticles associated with 200 keV electron irradiation at 423 K is shown in Fig. 5. The diameter of the particles is again approximately 10–25 nm. The structure in the particles remains unchanged as seen from a comparison of the SAED in Fig. 5(a′) with that in Fig. 5(b′). It is noted here that such a phase separation as observed during the 75 keV electron irradiation in particles kept at 423 K was not induced by 200 keV electron irradiation in particles kept at the same temperature. In our other experiments, it was confirmed that remarkable structural changes did not take place, when 200 keV electron irradiations were carried out in (10–25)-nm-sized GaSb particles in the temperature range from 363 to 443 K.

Through the present experiments, it becomes evident that when the 75 keV electron irradiation was carried out in approximately (10–25)-nm-sized GaSb particles kept at 423 K (in a limited temperature range of more than 363 K or less than 443 K), a phase separation of the GaSb compound is induced to form a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell. Here, it is considered that oxidation is not related to the phase separation phenomenon, as the fact that the phase separation of the GaSb compound is induced in a limited temperature range is not in agreement with the general rule that the higher the temperature, the faster the specimen oxidizes. It was also confirmed that hydrocarbon contamination cannot be deposited at the specimen temperature of more than approximately 400 K. These facts suggest that oxidation and contamination have no affect on the phase separation in GaSb nanoparticles.

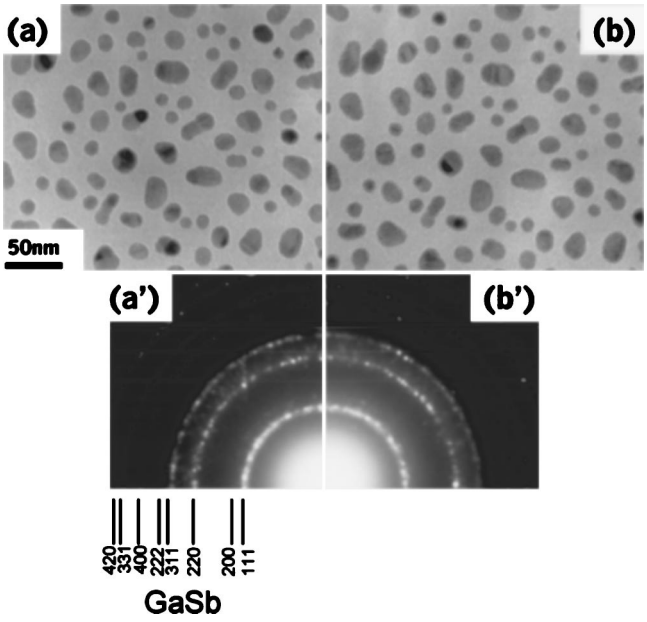

FIG. 5. A typical example of the behavior in GaSb nanoparticles associated with 200 keV electron irradiation at 423 K. (a) A BFI of particles of 10–25 nm in mean diameter, and (a′) the corresponding SAED before irradiation. (b) The same area after irradiation for 240 s, and (b′) the corresponding SAED.

In order to estimate whether the electron-irradiation-induced phase separation in GaSb nanoparticles observed in the present experiments is responsible for knock-on displacements or electronic excitations, the characteristics of the present experimental results are discussed as follows.

(1) The structural change by knock-on displacements is enhanced with increasing incident electron energy, because they are induced by the incident electron having energy higher than the threshold energy for atom displacements. However, this phase separation is induced by several tens of keV electron irradiation and is suppressed with increasing incident electron energy.

(2) Knock-on displacements will induce chemical disordering or amorphization, that is, disordering of atom arrangements, which were observed by 2 MeV electron irradiation in continuous thin films of GaSb in our previous studies.[1,2] However, this phase separation does not correspond to disordering.

(3) The structural change induced by knock-on displacements is able to occur only at low temperatures at which point defects (i.e., vacancies or interstitial atoms) introduced by irradiation are frozen in, and is suppressed by the enhancement of the mobility of the point defects with increasing temperature. However, this phase separation occurs only in the optimum temperature range. The fact that no phase separation is induced in particles kept at less than 363 K indicates that there is no relation between the occurrence of the phase separation and the mobility of point defects.

These facts suggest that this phase separation may be resulting from electronic-excitation-induced atom displacements rather than knock-on displacements. The phase separation observed in GaSb compound nanoparticles will be discussed qualitatively from the viewpoint of electronic-excitation-induced atom displacements.

It is known that in crystals with ionic bonding such as alkali-metal halides the electronic-excitation-induced atom displacements can be more efficient to form metallic colloids in the crystals.[5,6] A desorption of surface atoms by electronic excitation has been observed also at the surface of III-V semiconductor compounds.[7–9] It is proposed as a mechanism that the emission of atoms from the surface occurs due to breaking of the bond by local electronic transitions from the bonding states to the antibonding states, that is, the formation of excited states such as electron-hole pairs or pairs of holes (for example, produced by Auger transition process). Since the fundamental electronic excitation produces delocalized excited states in the solid, localization of the excitations is required for the initial step for the emission of atoms. Then, the interactions of the excited states with various kinds of defects on the surfaces are effective in those localizations. The energy accumulated by the localization of the excited states is directly converted into atomic energy, resulting in the atomic emission. However, the yield of the emission of atoms from the bulk surface in III-V compounds observed in the previous studies is quite small. A similar mechanism could play an important role also in the phase separation in GaSb compound nanoparticles. It is considered that atom displacements and the resulting phase separation could be remarkably enhanced, since the excited states tend to localize in isolated nanoparticles which have a high ratio of the surface to the volume.

It is noted from the present experiment that an optimum temperature range for the phase separation appears. From the optimum temperature range for the thermal activation of the reaction, changes in the free energy of formation under excitation is estimated on the basis of thermal equilibrium. In the reaction for GaSb compound formation, $Ga+Sb \rightarrow GaSb$, the heat of formation at 298 K, ΔH, is $-41.9\ \mathrm{kJ\,mol^{-1}}$.[10] The values of standard entropy at 293 K for GaSb, gallium, and antimony are 77.4, 41.0, and $45.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively.[10] The formation entropy at 293 K calculated using these values is $\Delta S = -9.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$. In the Ga-Sb binary system in which ΔH is negative ($-41.9\ \mathrm{kJ\,mol^{-1}}$), the chemical (covalent and ionic) bond between gallium and antimony is stabilized in the ground state. If phase separation from the compound to two pure substances (i.e., antimony and gallium) occurs, the free energy should increase. However, once such a hetero-bond is excited, it can be destabilized by the mechanisms mentioned above, and consequently the homo-bond (between gallium and gallium or between antimony and antimony), which is neither covalent nor ionic, may be more stabilized. In order to satisfy such a change in the free energy ΔH under excitations may have to become a positive value. If the difference between ΔH in the ground state and that in the excited states, that is, the increase of the potential energy of GaSb accompanied by the excitation, is supplied by the energy accumulated by some kinds of electronic transition, the phase separation could be induced. It is expected that the bond instability induced by the excitations changes the sign of the heat of formation positively. It is noted in the present experiments the temperature at which the phase separation successfully occurs is optimized in a limited range. From the result of a drastic suppression of the phase separation by the

temperature change from 423 to 443 K, the free energy of GaSb formation under excitations is speculated to change from a positive to negative value with increasing temperature from 423 to 443 K. In order to suppress the phase separation with increasing temperature, the value of $-T\Delta S$ has to be negative, that is, the value of ΔS has to be positive. Positive formation entropy ΔS could be brought about with increasing entropy of GaSb in the excited states. It is considered that the increase of entropy of GaSb in the excited states could be induced by the increase of the internal energy of constituent atoms, variety of atomic characteristics in different excited states, and so on. The suppression of the phase separation with increasing temperature may be speculated to be driven by the negative $-T\Delta S$ under excitations. On the other hand, at lower temperature at which long-range atomic diffusion is not activated thermally (i.e., at less than 363 K), no phase transformations can be induced. Generally, thermal equilibrium is discussed in the electronic ground state, but atom displacements induced by relaxation process of electronic defects produced in an electronic excited state under electron irradiation are dealt with in the present paper. The interpretation of thermal equilibrium is given for the phase separation at 423 K, because it is considered that this phase separation process is an equilibrium process in the excited state, at which the formation of a stable phase is driven by long-range diffusion. The process is diffusion controlled at less than 363 K at which phase separation cannot be induced. In this case, kinetic effects may play an important role.

In this phase transformation process, compositional fluctuation in the interior of particles which have the zinc-blende structure is required as a prestage of the phase separation. Chemical disordering takes place by destabilization of the chemical bond between foreign atoms by electronic excitation. Both the effects that the same kind of atoms cluster with decreasing degree of chemical order and that the surface energy of solid gallium (360 mJ m^{-2}) is slightly lower than that of solid antimony (370 mJ m^{-2}) bring about compositional fluctuation, which is induced by the diffusion of gallium toward the surface and the enrichment near the surface.[11] Compound nanoparticles with the zinc-blende structure consisting of a gallium-enriched crystalline GaSb shell and an antimony-enriched crystalline GaSb core remain because of the remarkable enhancement of solubility in nanoparticles. When the deviation from stoichiometric composition is increased above a threshold value, the abrupt increase of lattice strain energy will induce instabilization of the zinc-blende structure. Consequently, it is considered that the phase separation proceeds abruptly, when the lattice strain energy in the off-stoichiometric zinc-blende structure becomes higher than the interfacial energy in the two-phase structure consisting of a gallium shell and an antimony core. Composite nanoparticles consisting of a crystalline antimony core and a liquid gallium shell will be formed because the gallium shell separated near the surface transforms to the liquid phase because of the melting temperature depression with decreasing size.

On the other hand, the effect of incident electron energy on the electronic-excitation-induced phase separation will be discussed as follows. The cross section for the formation of the excited states introduced by electronic excitation in nanoparticles is quite sensitive to the incident electron energy. Inelastic scattering takes place in the nanoparticle transmitted by the incident electron. The cross section for the formation of the excited states may be approximately equivalent with that for inelastic scattering in nanoparticles. The mean free path length of an electron for the inelastic scattering λ is proportional to the incident electron energy E.[12] When the incident electrons pass the thickness D, the cross section for the inelastic scattering is estimated to be approximately proportional to D/λ. Consequently, in case of a fixed particle size, the cross section for the formation of excited states is proportional to $1/E$. It is suggested in the present experiments that the cross section for the formation of the excited states by the 200 keV electron irradiation may be reduced by approximately 38% of that by 75 keV electron irradiation. It is considered that the phase separation is remarkably suppressed by the 200 keV electron irradiation, by which the density of the excited states introduced is lower than that introduced by the 75 keV electron irradiation, when the total electron dose was fixed. In order to see details of the cross section for the formation of the excited states, effects of a different parameter, such as electron flux, on the phase transformations have also been found in our preliminary experiments. The electronic-excitation-induced phase separation is also dependent on electron flux. When the flux becomes nearly half of 1.5×10^{21} $e\,m^{-2}\,s^{-1}$, no phase separation is induced after excitations by the same total dose. Further details will be published in separate papers.

In conclusion, the electron-irradiation-induced phase separation in GaSb nanoparticles may be responsible for electronic excitations rather than knock-on displacements. Atom displacements and resulting structural changes driven by changes in bond stability induced by electronic excitation could take place with ease in nanoparticles. Studies to elucidate the mechanisms of electronic-excitation-induced atom displacements in nanoparticles in detail are in progress in our laboratory.

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