Process of phase separation induced by low energy electronic excitation in GaSb nanoparticles

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Abstract. The process of electronic-excitation-induced phase separation in GaSb nanoparticles has been studied by transmission electron microscopy from the viewpoint of the relationship between the atomic diffusion and the behaviour of the defects introduced by electronic excitation. When approximately 20 nm-sized GaSb particles kept at 430 K are excited by 25 keV electrons, gallium atoms on the lattice points are displaced to form vacancies and gallium interstitials in the crystal. Two-phase separation takes place via the void formation and an increase in lattice constant of GaSb. It is suggested that the vacancy supersaturation near the particle core brings about the void formation and the diffusion of gallium interstitials to the particle surface causes the phase separation.

1. Introduction

Compound semiconductor materials which have covalent bonding exhibit a wide variation in damage response by electron irradiation. Atom displacements in these materials are produced either by direct momentum transfer from the irradiating electron to an atom nucleus or as a response to alteration of electronic states by ionizing radiation [1-3]. In low energy electron irradiation, electronic excitation effects will be expected to become much more important in the compound semiconductor materials. Recently, it was found that GaSb nanoparticles excited by 75 keV electrons transform to two phases consisting of an antimony core and a gallium shell [4-7]. This result suggests that long-range atomic diffusion was induced by electronic excitation to separate into two deferent phases, since the excited states which make the hetero-bond unstable tend to localize in an isolated compound particle which has high surface to volume ratio and atomic mobility in nanoparticles is higher than that in the corresponding bulk materials. However, details on the process of such an atomic diffusion are not clear. It is generally well-known that atomic diffusion is closely related to the mobility of defects such as vacancies and interstitials. In the present work, we have studied the process of electronic-excitation-induced phase separation in GaSb nanoparticles based on the behaviors of the defects introduced efficiently by 25 keV electron excitation.

2. Experimental procedures

Preparation of size-controlled GaSb particles was carried out with the use of a double-source evaporator installed in the specimen chamber of an electron microscope. An amorphous carbon film was used as a supporting film and was mounted on a molybdenum grid. Using the evaporator, gallium...
was first evaporated from one filament to produce gallium particles on the supporting film, and then antimony was 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 gallium particles to form GaSb (Ga-50at%Sb) compound particles [8-10]. The particles were then annealed in the microscope at 573 K for 3600 s and were slowly cooled from the annealing temperature to room temperature in 2700 s, in an attempt to allow high atomic mobility in the particles which would homogenize the solute concentration. Electronic excitation experiments and observations were carried out using the same microscope. The microscope used was Hitachi H-7000 transmission electron microscope operating at an accelerating voltage of 25 kV. The electron flux used for excitations was 1.0x10^{20} e m^{-2}s^{-1}. The temperature of particles on the supporting films was kept at 397-430 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). Changes in the lattice constant of nanoparticles were evaluated from the SAEDs measured at least 4 times.

3. Results and discussion

An example of the structural changes in GaSb particles kept at 430 K by electronic excitation with 25 keV incident electrons is shown in Fig. 1. Figures 1(a) and (a') show a BFI of particles with the diameter of approximately 20 nm before excitation and the corresponding SAED, respectively. As indexed in the figure (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 (i.e., up to the dose of 6.0x10^{21} e m^{-2}) is shown in Fig. 1(b). In the interior of the particles after the excitation, there appears a void with bright contrast due to the disappearance of diffraction contrast, as seen from a comparison of the parts in insets Ia and IIa in (a) with those in Ib and IIb in (b). The SAED taken after the excitation is shown in Fig. 1(b'). In the SAED, Debye-Scherrer rings of the zincblende structure are recognized again. Changes in the lattice constant in GaSb particles are shown as a function of total electron dose in Fig. 2. In approximately 20 nm-sized GaSb particles kept at 430 K after excitation of the dose of 6.0x10^{21} e m^{-2}, the lattice constant increased up to 1.8 % compared with that before excitation. The lattice constant of GaSb particles under the same excitation condition increased up to about 2.6 % with increasing dose.

![Figure 1](image-url)

**Figure 1.** An example of the structural changes in approximately 20 nm-sized GaSb particles kept at 430 K by electronic excitation with 25 keV incident electrons at the flux of 1.0x10^{20} e m^{-2}s^{-1}.

(a) A BFI and (a') the corresponding SAED before excitation. (b) The same area after excitation for 60 s (i.e., up to the dose of 6.0x10^{21} e m^{-2}), and (b') the corresponding SAED. (c) The same area after excitation for 480 s (i.e., up to the dose of 4.8x10^{22} e m^{-2}), and (c') the corresponding SAED.
The same area after excitation for 480 s (i.e., up to the dose of \(4.8 \times 10^{22} \text{ e m}^{-2}\)) is shown in Fig. 1(c). In the interior of the particles after the excitation, the void in the individual particles changes in the shape and size due to vacancy migration from the void during the phase separation in order to decrease inner surface area of the particles that is the surface energy, as seen from a comparison of the inset in (b) with that in (c). The SAED taken after the excitation is shown in Fig. 1(c'). In the SAED, Debye-Scherrer rings are recognized, superimposed on a weak halo ring. The Debye-Scherrer rings can be indexed consistently as those of crystalline antimony, which has the hexagonal structure. The value of the scattering vector \((K = (4\pi \sin \theta) / \lambda)\) for the halo ring is approximately \(31.0 \text{ nm}^{-1}\) which corresponds to the first halo of liquid gallium. This result indicates that a two-phase mixture of crystalline antimony and liquid gallium was formed in the particles. It was confirmed by dark-field electron microscopy that nanoparticles after the electronic excitation have a two-phase structure consisting of a crystalline antimony core and a liquid gallium shell.

From the results, it was evident that when approximately 20 nm-sized GaSb particles kept at 430 K are excited by 25 keV electrons, two-phase separation takes place via void formation. Before phase separation, the lattice constants of GaSb increase with increasing electron dose.

A candidate for processes of electronic-excitation-induced phase separation predicted from the present experimental results will be discussed as follows. It is known that electronic excitations in III-V compounds which have covalent bonding bring about the formation of electron-hole pairs or final two-hole states by Auger transition [11, 12]. The interatomic potential changes at such electronic excited states and, consequently, an atom which was located on the site of minimum energy in the ground state becomes unstable. The atom displaces on the potential surface of the excited states to relax the energy and then to deexcite to the ground state again. When excess energy accumulated by the energy relaxation during the excitation is higher than the activation energy to displace from the atomic site immediately after the deexcitation, the atom can move to form point defects in the crystal. The introduction of high density of excitations is required for the initial step of atom displacements to convert directly the excess energy accumulated by the energy relaxation during the excitation into the atomic kinetic energy. A high density of excited states is enhanced by low energy excitation. The excited states tend to be pinned in nanoparticles in which the surface-to-volume ratio is high and the lattice is softened. A large number of pinning sites is effective for a long life time of the excited states and the resultant formation of high density of excited states.

Through the present experiments, it becomes evident that vacancies and interstitials introduced efficiently by electronic-excitation-induced atom displacements in nanoparticles act as a trigger for the void formation and phase separation. It was confirmed from previous experiments that optical excitation of the clean GaAs and GaP surfaces can lead to emission of neutral gallium atoms, since in the presence of electron-hole excitations the adiabatic potential energy surface for the gallium atoms becomes antibonding which causes their desorption [13-17]. On the other hand, it is possible to conclude that the radiation induced defects which are stable at room temperature in GaAs are most likely simple native defects, vacancies, interstitials or antisite defects [18]. It is speculated from these
previous results that gallium atoms on the lattice points are displaced by excitation to form gallium interstitials in the crystal. When vacancies and gallium interstitials generated by excitation become mobile and apart from annihilation by recombination, they contribute to the growth of dislocation loops. If dislocation loops act equally as a sink for a vacancy as for an interstitial, then no growth of dislocation loops will occur. The interstitials and interstitial dislocation loops have a strong compressive strain field and the compressive strain field interacts more strongly with a tensile strain field of the free surface layer of the particle than with strain fields of an individual interstitial or vacancy. The free surface layer of the particle will act as a preferential sink for interstitials and interstitial dislocation loops rather than for vacancies and their dislocation loops which have a tensile strain field. The result of this greater capture cross-section of the surface layer for interstitials and interstitial dislocation loops is to create a situation where the vacancies are the dominant species in the particle. Under these conditions of vacancy supersaturation, the vacancy dislocation loop will grow. The capture cross-section of the surface layer for vacancies and vacancy dislocation loops is smaller than that for interstitials and interstitial dislocation loops. The free surface layer of the particle will act as preferential sinks for only vacancies and the vacancy dislocation loops close to the surface. Consequently, the vacancies and the vacancy dislocation loops will disappear near the surface, and transform to a small void near the core. The void formation in the interior of particles induces swelling and the high concentration of interstitials increases the lattice constant of GaSb. Surface segregation of gallium interstitials to the particle surface will cause the phase separation in nanoparticles.

4. Conclusions
The process of electronic-excitation-induced phase separation in GaSb nanoparticles has been studied from the viewpoint of the relationship between the atomic diffusion and the behaviour of the defects introduced by electronic excitation. When approximately 20 nm-sized GaSb particles kept at 430 K are excited by 25keV electrons, gallium atoms on the lattice points are displaced to form vacancies and gallium interstitials in the crystal. Two-phase separation takes place via void formation and the increasing of lattice constant of GaSb. It is suggested that the vacancy supersaturation near the particle core brings about the void formation and the diffusion of gallium interstitials to the particle surface causes the phase separation.

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