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Phase Separation Induced by Electron Irradiation in GaSb Compound Nanoparticles

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Electron irradiation effects in GaSb compound nanoparticles have been studied by transmission electron microscopy, in order to see both effects of irradiation-induced atom displacements and self-organization in atomic arrangements on structural stabilities in nanometer-sized system. It was revealed that when 75 keV electron irradiations were carried out in approximately 10-25 nm-sized GaSb particles kept at 423 K, the phase separation of GaSb compound is induced to form the two-phase structure consisting of crystalline antimony core and liquid gallium shell. No phase separation is induced by 75 keV electron irradiation in GaSb nanoparticles kept at more than 443 K or less than 363 K and, by 200 keV electron irradiation in the particles kept at 363-443 K. It is suggested that the phase separation may be induced as a synergistic response of electronic excitation-induced atomic displacements by electron irradiation and self-organization in atomic arrangements characteristic of semiconductor compound materials in nm-sized range.
Key words: nanoparticle, phase separation, III-V compound, irradiation effect, electronic excitation

1. INTRODUCTION

Semiconductor compound materials which have ionic, covalent or mixed bonding exhibit a wide variation in damage response by electron irradiation. Atomic 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. Electrical effects become much more important in the 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 mega-electronvolt (MeV) electron irradiation induces chemical and topological disordering at low temperatures [1,2]. From the viewpoint of alteration of electronic states, it was found that electronic excitations generated by interaction with ionizing radiation induce atom displacements with ease in molecular systems, but several criteria for efficient coupling of the electronic stopping power of matter to atomic displacement phenomena have to be satisfied in bulk solid state systems [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 even in the bulk system [4]. However, to the authors' knowledge, there is no example of studies on the system-size dependence of irradiation effects in semoconductor compounds, such as irradiation effects in the compound nanoparticles.

On the other hand, nanoparticles in the size range from a few to several nanometers often exhibit properties which are significantly different from those of the corresponding bulk materials. As an example of the previous studies, it was shown that when solute atoms are deposited onto nanoparticles kept at room temperature, a rapid spontaneous dissolution of solute atoms into particles takes place to form alloy or compound particles [5-8]. In this case, it was evident that atom mixing driven by the chemical free energy difference between the initial atomic structure and the final atomic structure could be induced with ease in nanoparticles [9-12]. It was confirmed from the previous studies that self-organization in atomic arrangements by chemical interactions among constituent atoms takes place in nanoparticles.

From the background mentioned above, in the present work, we have been studied on electron irradiation effects in GaSb compound nanoparticles by transmission electron microscopy (TEM), in order to see a synergistic effect of irradiation-induced atom displacements and self-organization in atomic arrangements

on structural stabilities in nm-sized system.

2. EXPERIMENTAL

Preparation of size-controlled GaSb (Ga-50at%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 baked 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 nm-sized liquid 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 liquid 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 determined by energy-dispersive x-ray spectroscopy (EDS). The analyses were carried out in TEM mode with an electron probe of approximately 1 μm in diameter. An ultra thin Be window x-ray detector at a high take-off angle of 68° was used. The chemical compositions of the particles were estimated from an intensity ratio of Ga Lα1 to Sb Lα1 peak. The error in composition of Ga-50at%Sb particles produced on the supporting film was controlled to be less than ±3 at%Sb.

3. RESULTS AND DISCUSSION

Electron irradiation experiments and observations were carried out using the same microscope. The microscope used was Hitachi H-800 TEM operating at accelerating voltages of 75 and 200 kV. The maximum value of electron flux used for irradiations was approximately 1.5×10^{21}e $m^{-2}s^{-1}$. Temperatures of the supporting films were kept at 363-443 K during the irradiations. Structural changes associated with irradiations were observed in situ.

A typical example of structural changes in GaSb nanoparticles associated with the 75 keV electron irradiation at 423 K is shown in Fig. 1. Figures 1(a) and (a') show a bright-field image (BFI) of particles with diameters of approximately 10-25 nm before irradiation and the corresponding selected-area electron diffraction pattern (SAED), respectively. Inset in the BFI shows an

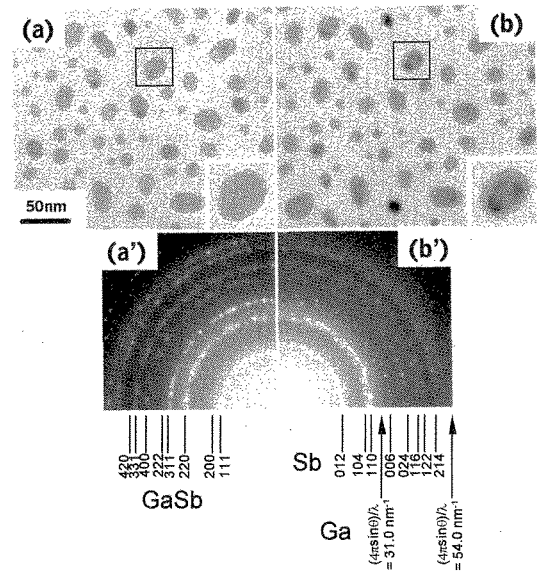

Fig. 1 A typical example of structural changes in GaSb nanoparticles associated with 75 keV electron irradiation at 423 K. (a)A BFI of particles of 10-25 nm in mean diameter, and (a') the corresponding SAED before irradiation. (b) The same area after irradiation for 240 ks, and (b') the corresponding SAED.

enlargement of a flamed part. As indexed in the figure (1(a')), the Debye-Scherrer rings can be consistently indexed as those of GaSb (which has the zincblende structure with lattice constant of a_0=0.61 nm). The same area after irradiation for 240 ks is shown in Fig. 1(b). In the interior of particles after the irradiation, there appear a structure consisting of the core with a dark contrast and the shell with a bright contrast, as seen from a comparison of inset in (a) with inset in (b). The corresponding SAED taken from the irradiated region are 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 nm^{-1} and 54.0 nm^{-1} which are corresponding to those from liquid gallium particles. This fact indicates that a two-phase mixture of crystalline antimony and liquid gallium is formed in the particles after the irradiation. The microstructure in the individual particles was examined by dark-field electron microscopy. It was confirmed that the 75 keV electron irradiation induces phase separation to form the two-phase structure consisting of crystalline antimony core and liquid gallium shell.

A typical example of behaviors in GaSb nanoparticles associated with the 75 keV electron irradiation at 443 K is shown in Fig. 2. Figures 2(a) and (a') show a BFI of particles before

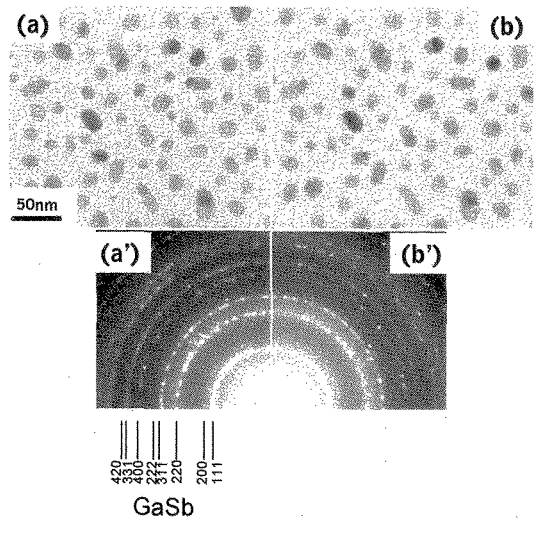

Fig.2 A typical example of behaviors in GaSb nanoparticles associated with 75 keV electron irradiation at 443 K. (a) A BFI of particles of 10-25 nm in mean diameter, and (a') the corresponding SAED before irradiation. (b) The same area after irradiation for 240 ks, and (b') the corresponding SAED.

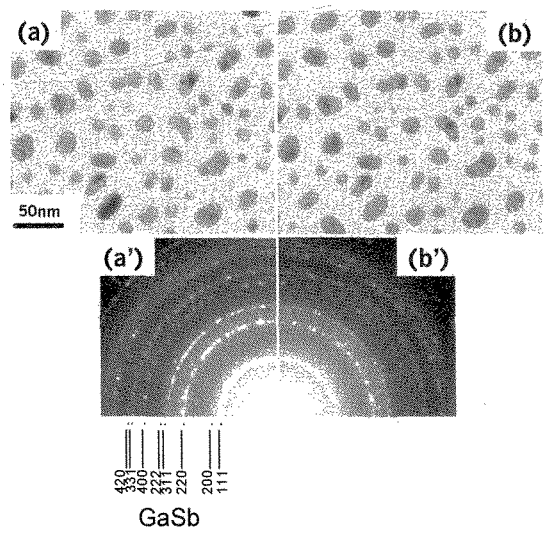

Fig.3 A typical example of behaviors in GaSb nanoparticles associated with 75 keV electron irradiation at 363 K. (a) A BFI of particles of 10-25 nm in mean diameter, and (a') the corresponding SAED before irradiation. (b) The same area after irradiation for 240 ks, and (b') the corresponding SAED.

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. A BFI of the same area after irradiation for 240 ks and the corresponding SAED are shown in Figs. 2(b) and (b'), respectively. The particles remain unchanged in both microstructures and SAED. This result indicates that such phase separation as observed on the irradiation in GaSb nanoparticles kept at 423 K is absent on irradiation in the particles kept at 443 K.

An example of behaviors during the 75 keV electron irradiation in GaSb nanoparticles kept at 363 K is shown in Fig. 3. In the SAED taken from the region irradiated for 240 ks (Fig. 3(b')), the Debye-Scherrer rings from GaSb nanoparticles are not changed as compared with those before irradiation as shown in Fig. 3(a'). This result indicates that such phase separation as observed upon irradiation in the particles kept at 423 K is also absent upon irradiation in the particles kept at 363 K.

Through the present experiments, it becomes evident that when the 75 keV electron irradiations were 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), phase separation of GaSb compound is induced to form the two-phase structure consisting of crystalline antimony core and liquid gallium shell.

In order to study effects of electron energy on behaviors with irradiation in GaSb nanoparticles, the 200keV electron irradiation was carried out. It was confirmed that remarkable structural changes did not take place, when the 200 keV electron irradiations were carried out in 10-25 nm-sized GaSb particles in temperature range from 363 to 443 K.

The structural change observed in GaSb compound nanoparticles will be discussed from viewpoints of a response to alteration of atomic electronic states by ionizing or near-ionizing radiation (a process called electronic excitation-induced atomic displacements) rather than knock-on displacements. In the previous studies, it was confirmed that chemical and topological disordering is induced by knock-on displacements with MeV electron irradiation in continuous thin films of GaSb kept at low temperatures of less than approximately 200 K and is suppressed with increasing temperature to room temperature [2]. The electron-irradiation-induced phase separation in GaSb nanoparticles observed at elevated temperatures in the present experiments is characterized as follows; (1) the structural change is induced by several tens of keV electron irradiation, and is remarkably enhanced with decreasing electron energy, (2) the structural change is not always attended by random atomic arrangements and by the resultant increase in configurational entropy, and (3) the influence of temperature on the structural change is independent of that on mobility of point defects introduced by knock-on displacements. These facts are consistent with the structural change resulted from electronic excitation-induced atomic displacements rather than from knock-on displacements.

It is well-known that the electronic excitation-induced atomic displacements can be more efficient in the crystal with the ionic bonding such as alkali halides [14,15]. A similar emission of atoms are observed also at the surface of III-V semiconductor compounds [16-18]. The emission of atoms from the surface by electronic transitions from the bonding states to the antibonding states, that is the formation of electron-hole (e-h) pairs, occurs due to breaking of the bond by local electronic excitation. Since the fundamental electronic excitation produces delocalized e-h pairs in the solid, localization of the excitation energy is required for the initial step for the emission of atoms. Here, the interactions of the e-h pairs with various kinds of defects on the surfaces are effective in the localization of e-h pairs. The energy accumulated by the localized electronic excited states is directly converted into the atomic energy resulting in the atomic emission. A breaking of the bonds of loosely bound atoms near defects on surfaces by multiple e-h pairs localization leads to the enhancements of the emission of atoms by electron-lattice interaction. Particularly, the localization of a pair of holes on a bond means the removal of its bonding electrons, and then such a bond is broken with ease. The excess energy may provide the thus freed atom with the kinetic energy to move it away from surface. The emission of atoms from the bulk surface in the III-V compounds observed in the previous studies is quite small in amounts. The similar mechanisms could play an important role also in the nanoparticles. It is considered that atomic displacements and the resultant the phase separation in nanoparticles could be remarkably enhanced by both effects (i.e., synergistic response) of the localization of multiple e-h pairs and pairs of holes produced by the electronic excitations in the GaSb compound nanoparticles, and of the self-organization in atomic arrangements driven easily by the free energy difference [11,12] in comparison with those on the surface of the bulk materials. Pure antimony nanoparticles are in crystalline or amorphous solid states, but pure gallium nanoparticles are in the liquid state. The surface energy of liquid gallium is lower than that of crystalline antimony. Consequently, the composite nanoparticles consisting of crystalline antimony core and liquid gallium shell will be formed.

Such a phase separation is thermodynamically interpreted in terms of the inversion from negative to positive mixing enthalpy induced by the electronic excitation. The positively-changed mixing enthalpy brings about the increase of the free energy in the system. The phase separation is observed only at optimum temperatures limited by a range. At the lower temperature than the optimum temperature range, which is insufficient to activate atomic mobility thermally, the phase separation is suppressed. With increasing higher temperature, the total free energy will decrease negatively because of the contribution to the negative free energy of entropy, and consequently the phase separation is suppressed again.

4. CONCLUSION

The phase separation may be induced as a synergistic response of electronic excitation-induced atomic displacements by electron irradiation and self-organization in atomic arrangements characteristic of semiconductor compound materials in nm-sized range. It is suggested that atom migration driven by the change in the free energy originating from electronic excited states could take place with ease in nanoparticles.

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