Eur. Phys. J. D **37**, 231–235 (2006)
DOI: 10.1140/epjd/e2005-00272-8

The European Physical Journal D

Effect of electron flux on electronic-excitation-induced phase separation in GaSb nanoparticles

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Received 26 April 2005 / Received in final form 4 July 2005

Abstract. We studied the effect of electron flux on phase separation induced by electronic excitation in GaSb nanoparticles, in order to see whether the phase separation is characterized as a cooperative phenomenon, in which a nonlinear relation may be found between density of excited states introduced and the efficiency of the phase separation or not. The phase separation to two phases consisting of an antimony core and a gallium shell proceeds abruptly after incubation time with increasing electron dose and does only at the flux above a threshold value. It is suggested that such nonlinear behaviors take place as a cooperative phenomenon among electronic-excitation effect, nano-size effect and temperature.

PACS. 61.80.-x Physical radiation effects, radiation damage – 81.30.-t Phase diagrams and microstructures developed by solidification and solid-solid phase transformations – 64.75.+g Solubility, segregation, and mixing; phase separation

1 Introduction

In isolated molecules, electronic excitations by photon beam induce the dissociation and isomerization of molecules easily [1,2]. It is known that a formation and migration of lattice defects often take place also on bulk semiconductor solid surfaces excited electronically [3–5]. It is required to induce such electronic-excitation-induced atomic displacements that dense excited states localize in a molecule or in a part of solids. 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 [6]. This result suggests that long-range atomic diffusion was induced by electronic excitation to separate deferent two phases, because in an isolated compound nanoparticle which has a high ratio of the surface to the volume, the excited states which cause instability of the hetero-bond tend to localize and atomic mobility is higher than that in the corresponding bulk materials. In such case that the phase separation in III-V compound nanoparticles is induced by electronic excitation, it is expected that the phase separation will be characterized as a cooperative phenomenon, in which a nonlinear relation may be found between density of excited states introduced and the efficiency of the phase separation. From these viewpoints, in the present work we have studied the effect of electron flux on the phase separation induced by electronic excitation in GaSb nanoparticles.

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 nanoparticles 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. 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 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-800 transmission electron microscope operating at an accelerating voltage of 75 kV. The electron fluxes used for excitations were from 5.0×10^{20} to 5.0×10^{21} e m^{-2}s^{-1}. The temperature of particles on the supporting films was kept at 423 K during the experiments. Phase separation associated with electronic excitations was observed in situ by bright-field images (BFIs) and selected-area electron diffraction patterns (SAEDs).

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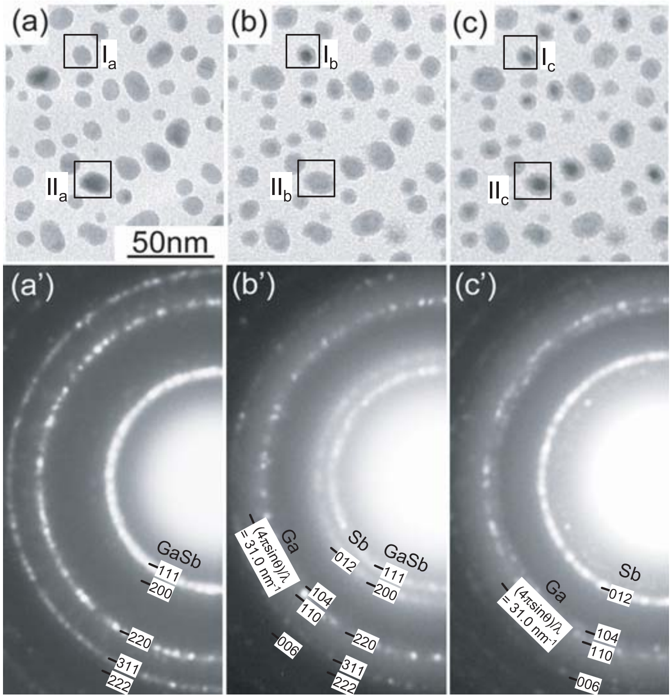

Fig. 1. An example of the structural change in GaSb particles by electronic excitation with 75 keV incident electrons at the flux of 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$. (a) A BFI of particles with the diameter of 10–20 nm, and (a') the corresponding SAED before excitation. (b) The same area after excitation for 90 s (the dose of 4.5×10^{23} e m^{-2}), and (b') the corresponding SAED. (b) The same area after excitation for 180 s (dose of 9.0×10^{23} e m^{-2}), and (c') the corresponding SAED.

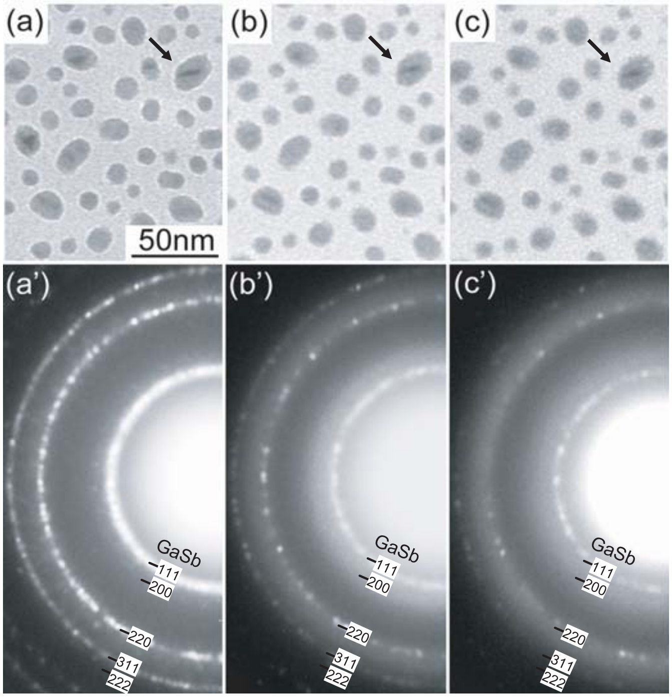

Fig. 2. An example of the behavior in particles by electronic excitation at lower flux of 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$. (a) A BFI of particles with the diameter of 10–20 nm, and (a') the corresponding SAED before excitation. (b) The same area after excitation for 900 s (the dose of 4.5×10^{23} e m^{-2}), and (b') the corresponding SAED. (b) The same area after excitation for 1800 s (dose of 9.0×10^{23} e m^{-2}), and (c') the corresponding SAED.

3 Results

An example of the structural change in GaSb particles by electronic excitation with 75 keV incident electrons at the flux of 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$ is shown in Figure 1. Figures 1a and 1a' show a BFI of particles with the diameter of 10–20 nm before excitation and the corresponding SAED, respectively. As indexed in Figure 1a', the Debye-Scherrer rings can be consistently indexed as those of GaSb which has the zincblende structure with a lattice constant of $a_0 = 0.61$ nm. The same area after excitation for 90 s (i.e., up to the dose of 4.5×10^{23} e m^{-2}) is shown in Figure 1b. In the interior of approximately 10 nm-sized particles after the excitation, there appears a structure consisting of a core with dark contrast and a shell with bright contrast, as seen from a comparison of the part framed squarely by $\mathrm{I_a}$ in (a) with that framed by $\mathrm{I_b}$ in (b). The SAED taken after the excitation is shown in Figure 1b'. 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 with lattice constants of $a_0 = 0.43$ nm and $c_0 = 1.13$ nm, and of GaSb. The value of the scattering vector ($K = (4\pi \sin\theta)/\lambda$) for the halo ring is approximately 31.0 nm^{-1} which is corresponding to the first halo of liquid gallium. The same area after excitation for 180 s (i.e., up to the dose of 9.0×10^{23} e m^{-2}) is shown in Figure 1c. Also in the interior of approximately 20 nm-sized particles after the excitation, 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 by $\mathrm{II_a}$ in Figure 1a and $\mathrm{II_b}$ in Figure 1b with the part framed by $\mathrm{II_c}$ in Figure 1c. In the SAED shown in Figure 1c', Debye-Scherrer rings of crystalline antimony are recognized, superimposed on a halo ring of liquid gallium. It was confirmed by dark-field electron microscopy that nanoparticles after the electronic excitation have the two-phase structure consisting of a crystalline antimony core and a liquid gallium shell. From these results, it is evident that two-phase separation takes place in GaSb particles excited at the flux of 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$. After the phase separation, the two-phase structure consisting of a crystalline antimony core and a liquid gallium shell is kept during the observation at a lower flux. The temperature 423 K is too low to react sufficiently for a short time of the observation, though the constituent atoms tend to diffuse to form GaSb compound rather than to separate two phases under irradiation at the low flux.

In order to see the effect of the electron flux on structural changes in GaSb particles, an experiment by electronic excitation at lower flux of 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$ was carried out. An example of the behavior by electronic excitation in particles is shown in Figure 2. Figures 2a

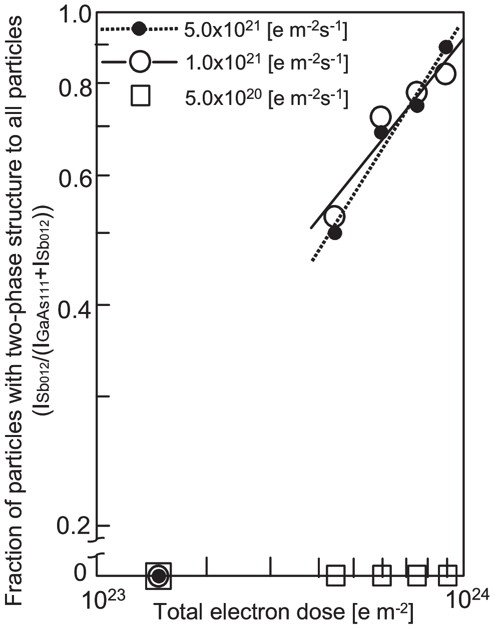

Fig. 3. Changes in fraction of particles with two-phase structure to all of the particles as a function of total electron dose irradiated for the electronic excitation. The marks of a black circle, a open circle and a square indicate fractions of particles transformed from the compound to the two-phase structure at the electron flux of 5.0×10^{21}, 1.0×10^{21} and 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, respectively.

and 2a' show a BFI of particles before excitation and the corresponding SAED, respectively. In the SAED, Debye-Scherrer rings can be consistently indexed as those of GaSb. Figures 2b and 2b' show a BFI from the same area after excitation for 900 s (i.e., up to the dose of 4.5×10^{23} e m^{-2}) and the corresponding SAED, respectively. As seen from the comparison of the bend extinction contour in the particle indicated by the arrow in Figure 2a with that in the same particle indicated by the arrow in Figure 2b, the particle remains unchanged in the microstructure. In the SAED, Debye-Scherrer rings can be consistently indexed as those of GaSb again. A BFI and the SAED from the same area after excitation for 1800 s (i.e., up to the dose of 9.0×10^{23} e m^{-2}) are shown in Figures 2c and 2c', respectively. The particle again remains unchanged in the microstructure as indicated with the arrow. The SAED (Fig. 2c') can be consistently indexed as Debye-Scherrer rings of GaSb again, though the intensity becomes somewhat diffuse. It is noted here that such a phase separation as observed after electronic excitation at the flux of 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$ is absent during the electronic excitation at lower flux of 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$.

Through the experiments, it has been evident that the phase separation induced by electronic excitation with 75 keV incident electrons in GaSb particles kept at 423 K becomes more difficult to occur with decreasing electron flux. The behaviors of the electronic-excitation-induced phase separation will be discussed as functions of the total electron dose and electron flux as follows.

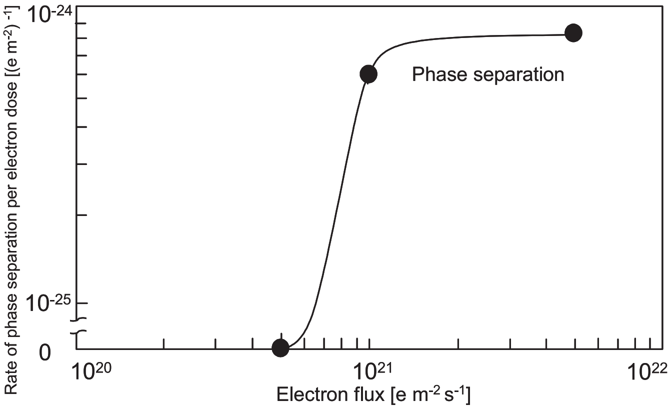

Fig. 4. The change in the rate of the phase separation per unit dose as a function of the flux.

Figure 3 shows changes in fraction of particles with two-phase structure to all of the particles as a function of total electron dose irradiated for the electronic excitation. The fraction of particles with two-phase structure to all of the particles has been evaluated by measurements of ratio of the intensity of Sb 012 reflection to the sum of the intensities of GaSb 111 reflection and Sb 012 reflection, based on the line profiles reproduced from the corresponding SAEDs. In this figure, marks of a black circle, a open circle and a square indicate fractions of nanoparticles transformed from the compound to the two-phase structure at the electron flux of 5.0×10^{21}, 1.0×10^{21} and 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, respectively. No phase separation is induced by the irradiation up to the dose of 9.0×10^{23} e m^{-2} at the flux of 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$. On the other hand, at the flux of both 1.0×10^{21} and 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, the phase separation starts in the dose range of 1.5×10^{23} to 4.5×10^{23} e m^{-2} and proceeds with increasing dose, though phase separation is not induced by the irradiation up to the dose of 1.5×10^{23} e m^{-2} at all. The rates of the phase separation per unit dose, which are estimated by the gradients of the solid and dotted lines obtained by the method of least squares in Figure 3, are 6.1×10^{-25} and 8.4×10^{-25} $(e\ \mathrm{m}^{-2})^{-1}$ at the flux of 1.0×10^{21} and 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, respectively, and are not so remarkable as dependent on the flux. Another point to be noted here is that the phase separation does not always start at the same time as the irradiation is carried out and proceeds abruptly after an incubation time (time corresponding to the dose of $(1.5\text{–}4.5) \times 10^{23}$ e m^{-2} in the case).

Figure 4 shows the change in the rate of the phase separation per unit dose as a function of the flux. At the flux of 5.0×10^{20} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, the phase separation does not take place at all, however at the fluxes of 1.0×10^{21} or 5.0×10^{21} e $\mathrm{m}^{-2}\mathrm{s}^{-1}$, the phase separation proceeds at the rate of the phase separation per unit dose of 6.1×10^{-25} and 8.4×10^{-25} $(e\ \mathrm{m}^{-2})^{-1}$, respectively. It is evident from the figure that a fixed and higher flux is required for the electronic-excitation-induced phase separation and the rate of the phase separation per unit dose becomes nearly constant at the flux above the threshold value (the range from 5.0×10^{20} to 1.0×10^{21} e $\mathrm{m^{-2}s^{-1}}$ in this case).

4 Discussion

Such a phase separation will be induced by stabilization of the homo-bonds between the same kinds of atoms (i.e., gallium–gallium or antimony–antimony) caused by the breaking of the hetero-bond between the different atoms (i.e., gallium–antimony) and enhancement of long-range atomic diffusion required for cohesion of the same kinds of atoms. The synergistic effect among electronic-excitation effect, nano-size effect and temperature plays an important role to achieve the breaking of the hetero-bond and the resulting stabilization of the homo-bonds and enhancement of long-range atomic diffusion.

The following mechanism will give an explanation for the change in bond stability induced by electronic excitation.

In III-V compound such as GaSb which has a mixed covalent and ionic character, when the bonding (valence) electron is excited to the antibonding state, the bonding electron is removed to form electron-hole pairs or pairs of holes. As a result, the gallium and antimony atoms may find themselves in a repulsive adiabatic potential, which causes the bond breaking. In the Ga–Sb binary system in which the heat of formation ΔH is negative (-41.9 kJ $\mathrm{mol^{-1}}$), the chemical (mixed covalent and ionic) bond between gallium and antimony is stabilized at the ground state. Since the fundamental electronic excitation firstly produces delocalized excited states in the solid, the localization of the excitations is required for the next step for the bond breaking. The energy accumulated by the localization of the excited states is directly converted into the atomic kinetic energy resulting in the atomic displacements [7–11]. If the phase separation from the compound to two pure substances (i.e., antimony and gallium, in which the cohesive energy is 271 kJ/mol and 265 kJ/mol, respectively) occurs, the free energy should increase. However, once such a hetero-bond is excited, it is broken by the mechanisms mentioned above, and consequently homo-bond (between gallium and gallium or between antimony and antimony), which is neither covalent nor ionic and is excitation-insensitive, may be formed as a stable state.

The higher quantum efficiency for the change in bond stability induced by electronic excitation is required for the phase separation. The quantum efficiency of electronic excitation is dependent on the life time of excitation and excitation probability. Higher density of excitation brought about by localized excitations plays an important role to make longer the apparent life time of excitation. Here, nano-sizing becomes remarkably effective for localized excitations, because excited states which have a strong interaction with various kinds of defects tend to localize in isolated nanoparticles which have a high ratio of the surface to the volume. The optimization of the incident electron energy is important to make higher the excitation probability. It has been found in our preliminary experiments that in the particles 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 20 keV electrons may be reduced considerably. The synergistic effect of electronic excitation effect and nano-size effect which will induce change in atomic interaction may act as a trigger for the phase separation. On the other hand, atomic diffusion is dependent on temperature and size. It was confirmed in our previous studies that atomic diffusion is enhanced with decreasing size in nanoparticles [12,13]. Both temperature and/or nano-size effect will enhance long-range atomic diffusion.

As mentioned above, from the results that the electronic-excitation-induced phase separation proceeds abruptly after an incubation time with increasing electron dose and does only at the flux above the threshold value, it is suggested that the phase separation observed in the present experiment is a nonlinear behavior. At the flux above the threshold value, the breaking of the hetero-bond and local cohesion of the same kinds of atoms take place in the interior of individual nanoparticles with increasing dose. The compositional fluctuation in the interior of the particles which have the zincblende structure occurs as a pre-stage of the phase separation. The gallium atoms diffuse toward the surface and are enriched near the surface, because the surface energy of solid gallium (i.e., 360 $\mathrm{mJm^{-2}}$) is slightly lower than that of solid antimony (i.e., 370 $\mathrm{mJm^{-2}}$) [14]. The lattice strain introduced by the deviation from the stoichiometric composition in the gallium-enriched GaSb shell and the antimony-enriched GaSb core may induce the structural instability at the next stage [15,16]. Consequently, it is considered that the phase separation from the zincblende structure to the two-phase structure consisting of a gallium shell and an antimony core proceeds abruptly after an incubation time and the gallium shell separated near the surface transforms to liquid phase because of the melting temperature depression in nanoparticles. On the other hand, at the flux below the threshold value, the breaking of the hetero-bond will be recombined because of lower density of excitation. The rate of the phase separation per unit dose becomes constant at the flux above the threshold value, because the diffusion of the atoms broken the hetero-bond by electronic excitation is becomes the rate-determining step in the phase separation. It is suggested that such nonlinear behaviors take place as a cooperative phenomenon among electronic-excitation effect, nano-size effect and temperature.

5 Conclusions

GaSb particles excited by 75 keV electrons separate two phases consisting of an antimony core and a gallium shell. The phase separation proceeds abruptly after an incubation time with increasing electron dose and does only at the flux above a threshold value. Such nonlinear behaviors suggest that the synergistic effect among electronic-excitation effect, nano-size effect and temperature plays an important role to achieve stabilization of the homo-bonds and enhancement of long-range atomic diffusion required for the electronic-excitation-induced phase separation. Studies to elucidate the mechanisms of the electronic-excitation-induced phase transformation 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".

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