Eur. Phys. J. D **43**, 177–180 (2007)
DOI: 10.1140/epjd/e2007-00094-8

THE EUROPEAN
PHYSICAL JOURNAL D

In situ TEM observation of synergistic electronic-excitation-effects of phase stability in III-V binary compound nanoparticles

H. Yasuda[1,a], A. Tanaka[1], H. Usui[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 24 July 2006

Abstract. Electronic-excitation-effects of phase stability in III-V binary compound nanoparticles have been studied by TEM. When GaSb particles were excited by 75 keV electrons, the compound transforms to a two-phase consisting of an antimony core and a gallium shell or an amorphous phase, or remains the original crystalline phase, depending on particle size and/or temperature. It is suggested that such nonlinear responses of the phase stability may arise from synergistic effects of bond instability under excited states, formation of high density of excited states, chemical equilibrium under excited states and temperature dependence of defects mobility.

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 covalent molecules, electronic excitations by photon induce the dissociation and isomerization of molecules easily [1,2]. On the other hand, in III-V compounds which have covalent bonding, electronic excitations induce atom displacements resulting from formation and migration of lattice defects in the interior of bulk solids and desorption of atoms from the surface, but the yield of the atom displacements for each phenomenon is quite low [3–6]. When the size of the III-V compound materials decreases to nanometer scale, structural changes as observed in the covalent molecules may be expected under electronic excitation [7–9].

In the present work, electronic-excitation-effects of phase stability in III-V binary compound nanoparticles have been studied by in situ transmission electron microscopy (TEM) using nanoparticles of GaSb compound, in order to see the effects of size and/or temperature on the phase stability in GaSb nanoparticles under electronic 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. The evaporator consists of two spiral-shaped tungsten filaments. The distance between the filaments and supporting film (substrate) for nanoparticles was approximately 100 mm. 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. The flux of depositing atoms was of the order of $10^{17}{\sim}10^{18}$ m^{-2}s^{-1}. Vapor-deposited antimony atoms quickly dissolved into gallium particles to form GaSb (Ga-50at%Sb) compound particles [10–12]. 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. This microscope used was equipped with a turbo-molecular pumping system and a liquid nitrogen-cooled anti-contamination device to achieve a base pressure below 2×10^{-5} Pa in the specimen chamber. The electron fluxes used for observations and excitations were $1.5 \times 10^{20} e$ m^{-2}s^{-1}

---

[a] e-mail: `yasuda@mech.kobe-u.ac.jp`

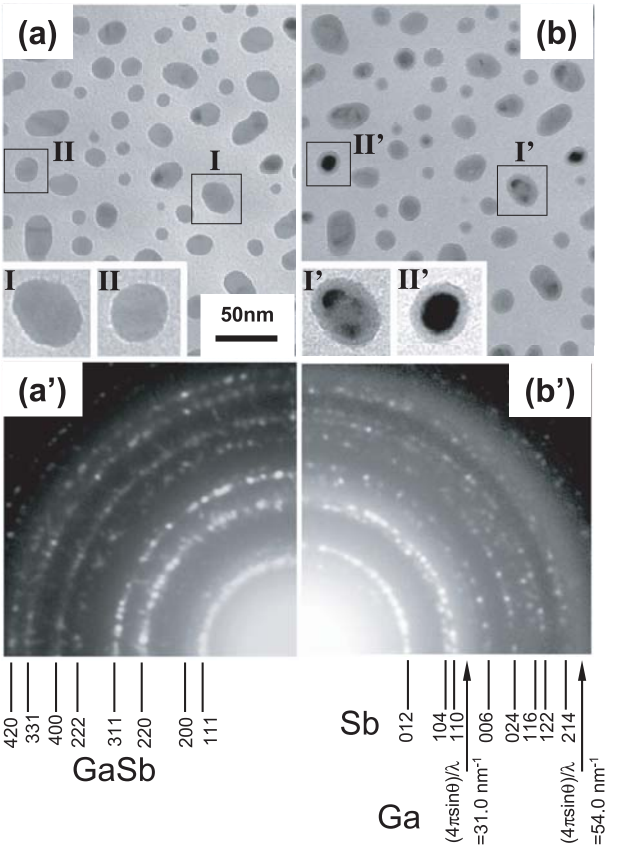

Fig. 1. An example of the structural change in GaSb particles kept at 423 K by electronic excitation. (a, a') A BFI of particles and the corresponding SAED before excitation, respectively. (b, b') The same area after excitation for 180 s (i.e., up to the dose of $2.7 \times 10^{23} e\ \mathrm{m}^{-2}$) and the corresponding SAED, respectively.

and $1.5 \times 10^{21} e\ \mathrm{m}^{-2}\mathrm{s}^{-1}$, respectively. The temperature of particles on the supporting films was kept from 293 to 573 K during the experiments. Structural changes associated with electronic excitation were observed in situ by bright-field images (BFIs) and selected-area electron diffraction patterns (SAEDs).

3 Results

An example of the structural change by electronic excitation in GaSb particles kept at 423 K is shown in Figure 1. Figures 1a and 1a' show a BFI of particles with the diameter of approximately 20 nm before excitation and the corresponding SAED, respectively. 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 by the flux of $1.5 \times 10^{21} e\ \mathrm{m}^{-2}\mathrm{s}^{-1}$ for 180 s (i.e., up to the dose of $2.7 \times 10^{23} e\ \mathrm{m}^{-2}$) is shown in Figure 1b. Each of observations by BFIs and SAEDs was carried out within approximately 5 s by lower flux of $1.5 \times 10^{20} e\ \mathrm{m}^{-2}\mathrm{s}^{-1}$, therefore the excitation effect during BFI and SAED observations is negligibly small. In the interior of 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 squarely by $\mathrm{I_a}$ and $\mathrm{II_a}$ in Figure 1a with those framed by $\mathrm{I_b}$ and $\mathrm{II_b}$ in Figure 1b, respectively. 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. The values of the scattering vector ($K = (4\pi \sin\theta)/\lambda$) for the halo ring are approximately 31.0 and 54.0 nm^{-1} which are corresponding to the halos 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 was evident that two-phase separation took place in GaSb particles.

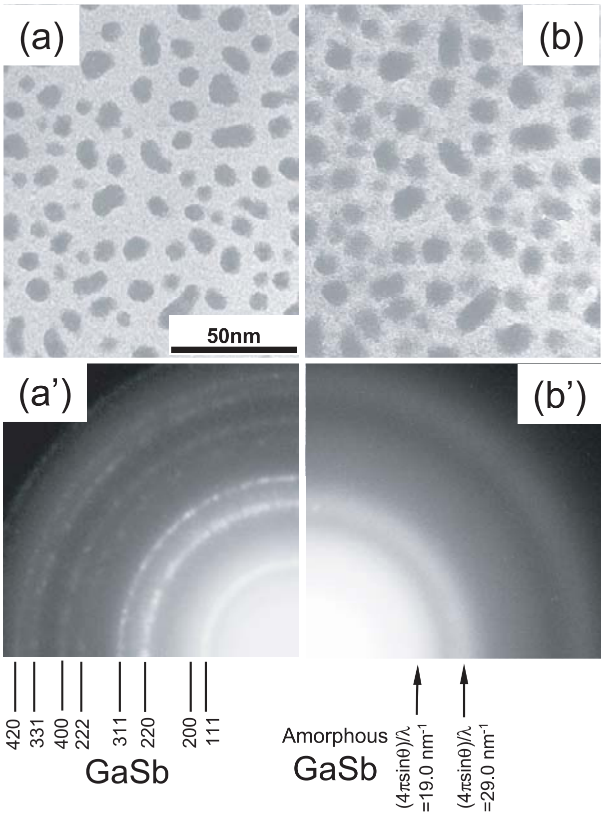

Fig. 2. An example of the structural change in GaSb particles kept at 293 K by electronic excitation. (a, a') A BFI of particles and the corresponding SAED before excitation, respectively. (b, b') The same area after excitation for 240 s and the corresponding SAED, respectively.

The structural changes induced by electronic excitation in approximately 10nm-sized particles kept at 293 K have been studied, as shown in Figure 2. In the SAED after excitation for 240 s (Fig. 2b'), only haloes are recognized. The values of the scattering vector of the halo rings are approximately 19.0 nm^{-1} and 29.0 nm^{-1} which

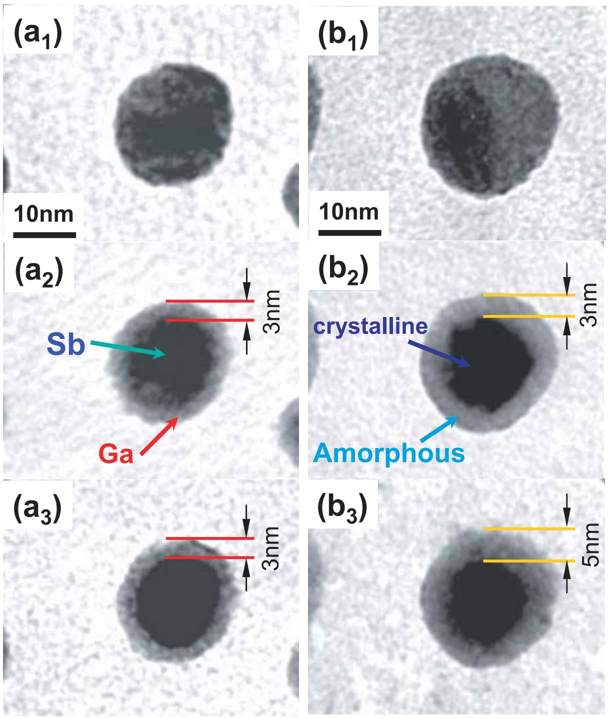

Fig. 3. Typical sequences of excitation process in an approximately 20 nm-sized GaSb particle. (a_1–a_3) Morphologies in the same particle kept at 423 K before excitation, after excitation for 60 s and after excitation for 240 s, respectively. (b_1–b_3) Changes in the same particle kept at 293 K before excitation, after excitation for 60 s and after excitation for 240 s, respectively.

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.

In order to see the process in the phase separation and amorphization in the particles, successive stages in morphological changes have been observed. Figures 3 are typical sequences of excitation process in an approximately 20 nm-sized GaSb particle. Figures 3a_1 to 3a_3 show changes in the same particle kept at 423 K during excitation. After excitation for 60 s, phase separation takes place to form a crystalline antimony core and a liquid gallium shell, as shown in Figure 3a_2. The shell thickness is approximately 3 nm. After excitation for 240 s, the shell thickness remains constant because no more compositional changes can be induced after the phase separation, as shown in Figure 3a_3. On the other hand, Figures 3b_1–3b_3 show changes in the same particle kept at 293 K during excitation. After excitation for 60 s, amorphization takes place on the surface in the particle, as shown in Figure 3b_2. After excitation for 240 s, the amorphous shell thickness increases from 3 to 5 nm as seen from a comparison of Figure 3b_2 with 3b_3. From the results, it was evident that the phase separation takes place abruptly after the compositional fluctuation in the particle, but the amorphization proceeds gradually from the surface of the particle.

Figure 4 summarizes the results on the phase transformations induced by electronic excitation as functions of particle size and temperature. Total electron dose is fixed at $3.6 \times 10^{23} e\ \mathrm{m}^{-2}$. In this figure, two-phase separation consisting of a crystalline antimony core and a liquid gallium shell, formation of an amorphous phase and original crystalline phase with the zincblende structure are schematically illustrated as three kinds of pictures, 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 transformations, that is, competitive formations of three kinds of phases with decreasing particle size and/or temperature were observed by the 75 keV electronic excitation.

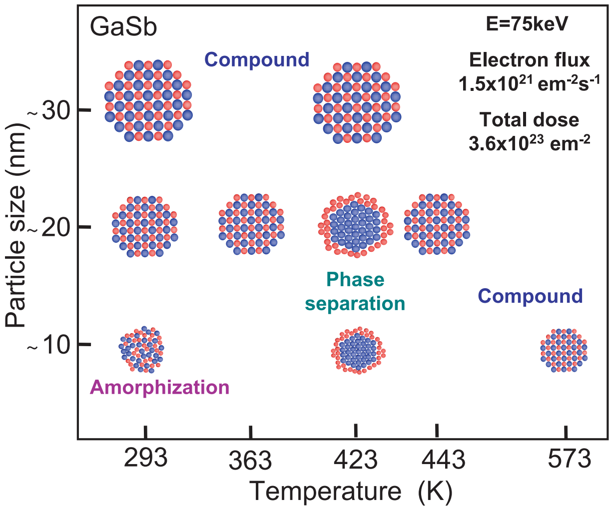

Fig. 4. Summary of the results on the phase transformations induced by electronic excitation as functions of particle size and temperature. Total electron dose is fixed at $3.6 \times 10^{23} e\ \mathrm{m}^{-2}$.

4 Discussion

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 III-V compounds which have covalent bonding occur through the process that an excess energy accumulated 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 [13–15]. The introduction of high density of excitations is 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 dense excitation. High density of excited states tends to introduce in nanoparticles which are isolated and have a high ratio of the surface to the volume. It is considered that the dense excitations and the resulting formation of primary point defects by atom displacements may act as a trigger for phase separation or amorphization in nanoparticles.

From the viewpoint of chemical equilibrium, in the Ga-Sb binary system in which the heat of formation ΔH is negative (–41.9 kJ mol^{-1}), the chemical 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, in which the cohesive energy is 271 kJ/mol and 265 kJ/mol, respectively) occurs, the free energy should increase. However, when the bonding (valence) electron is excited to the antibonding state to form carriers such as electron-hole pairs or pairs of holes, the increase of those carriers will bring about metallic character rather than semiconducting character in nanoparticles. The metallic character induced under the excited states forms metallic bonds (between gallium and gallium or between antimony and antimony) as a stable state. It is consequently considered that the free energy of the reaction for the phase separation GaSb → Ga+Sb becomes negative under the excited states.

The phase stability will be controlled by kinetic process under such a chemical equilibrium. At elevated temperatures, recombination of the primary defects (i.e., vacancy and interstitial) suppress phase transformations because of the high mobility of defects. On the other hand, at room temperature, the primary defects are frozen in the compound crystal because of the low mobility of defects and consequently the amorphization is induced by chemical disordering and short range atom displacements. However, in the range of the temperatures, at which vacancies are mobile but interstitials are immobile, long range diffusion can take place. According to the chemical equilibrium mentioned above, 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 mJm^{-2}) is slightly lower than that of solid antimony (i.e., 370 mJm^{-2}) [16]. 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 [17,18]. 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.

5 Conclusions

Electronic-excitation-effects of phase stability in III-V binary compound nanoparticles have been studied by TEM. When GaSb particles were excited by 75 keV electrons, the compound transforms to a two-phase consisting of an antimony core and a gallium shell or an amorphous phase, or remains the original crystalline phase, depending on particle size and/or temperature. It is suggested that such nonlinear responses of the phase stability may arise from synergistic effects of bond instability under excited states, formation of high density of excited states, chemical equilibrium under excited states and temperature dependence of defects mobility.

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".

References

1. S. Koshihara et al., J. Phys. Chem. B **103**, 2592 (1999)
2. S. Iwai et al., Phys. Rev. Lett. **88**, 057402 (2002)
3. A. Schmid, P. Braunlich, P.K. Rol, Phys. Rev. Lett. **35**, 1382 (1975)
4. A.D. Townsend et al., Rad. Effects **30**, 55 (1976)
5. J. Kanasaki et al., Phys. Rev. Lett. **89**, 257601 (2002)
6. J.W. Corbett, *Electron Radiation Damage in Semiconductors and Metals* (Academic Press, NY, 1966)
7. H. Yasuda, H. Mori, J.G. Lee, Phys. Rev. Lett. **92**, 135501 (2004)
8. H. Yasuda, H. Mori, J.G. Lee, Phys. Rev. B **70**, 214105-1 (2004)
9. H. Yasuda et al., Eur. Phys. J. D **37**, 231 (2006)
10. H. Yasuda, H. Mori, Phys. Rev. Lett. **69**, 3747 (1992)
11. H. Yasuda, H. Mori, Z. Phys. D **31**, 131 (1994)
12. H. Yasuda, K. Furuya, Eur. Phys. J. D **10**, 279 (2000)
13. J. Kanasaki et al., Phys. Rev. Lett. **70**, 2495 (1993)
14. J. Singh, N. Itoh, Y. Nakai, J. Kanasaki, A. Okano, Phys. Rev. B **50**, 11370 (1994)
15. O. Pankratov, M. Scheffler, Phys. Rev. Lett. **75**, 701 (1995)
16. E. Rabinowitz, *Friction and Wear of Materials* (John Wiley & Sons, 1965)
17. H. Yasuda, K. Furuya, Eur. Phys. J. D **10**, 279 (2000)
18. H. Yasuda, H. Mori, J. Cryst. Growth **237/239**, 234 (2002)