MORPHOLOGY, INTERNAL DEFECT AND GRAIN BOUNDARY OF ULTRA FINE GaP PARTICLES

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Abstract. GaP particles produced by the gas evaporation technique were studied by high resolution electron microscopy. The external shape of GaP particles less than 50 nm can be determined by lattice image of the particle. Crystals with the zinc blende structure grew in single crystal plate or octahedron or more complicated form composed of two or more plates. The intrinsic and extrinsic stacking faults, and growth faults were observed in a particle. These faults gave evidence of coalescence growth in GaP smoke. The boundaries between connected particles or twin particles were discussed as a problem of the stability of boundary energy due to the existence of the polarity of this crystal. It became evident that the coalescence phenomena in smoke can be explained by taking account of two processes with the temperature, i.e. liquid-like coalescence and surface melting coalescence.

1. Introduction

The properties of small clusters are nowadays the subject of increasing interest. Their atomic structure can be different from the usual bulk structure, for instance, they can have icosahedral instead of face centered cubic structure as found at the initial stage of vacuum deposition. 1) These icosahedral clusters have also been observed in smoke particles formed by a gas evaporation technique, 2) in which material is heated in an atmosphere of inert gas. Diamond crystals with the shape of icosahedral have been prepared by the method of chemical vapor deposition. 3) On the other hand, we showed that smoke particles of II–VI compounds such as ZnO, 4) CdS 5) and CdTe 6) smaller than 20 nm had zinc-blende structure. They grew the tetrapod crystals with wurtzite structure (ZnO, CdS, CdTe) and zinc-blende structure (CdTe). The icosahedral clusters were composed of tetrahedra, and each tetrahedron was composed of four (111) planes. It may be impossible to form the icosahedral cluster in II–VI compounds, because the tetrahedron with the surface only II
or VI elements must be formed, i.e. the stoichiometry or charge balance are lost. As the model to interpret the growth of tetrapod crystal, we proposed that zinc-blende clusters based on octahedron may be the building block in II–VI compounds. On the other hand, rhombic dodecahedron clusters have been proposed as “building blocks” for III–V compounds to account for {110} facets observed on growth, cleaved and etched surface. The growth of rhombic dodecahedron clusters on the (110) surface of III–V compounds seems to be natural, because there is no mismatching between the substrate and dodecahedron clusters, and the dodecahedron is composed of {110} surfaces without polarity. The crystallites attained by gas evaporation technique are grown in an atmosphere without any substrates, they show perfect three-dimensional shapes. Therefore the study of the crystallites by gas evaporation technique can elucidate the building block without the influence of the substrate.

Morphological studies are very important in crystal growth. Since most of the smoke particles were 10–100 nm in size, determination of crystal habits was done by the method of thickness fringe appearing electron microscopic image. For small particles less than 30 nm in size, this method was difficult because of ambiguity of deflection effects. The purpose of the present paper is to elucidate the external shape of GaP smoke particles by high resolution electron microscopy (HREM). The internal defects and the grain boundaries between the particles are elucidated by HREM, and the coalescence growth mechanism in smoke particles is discussed. The present method of the analysis can be applied to the characterization of fine ceramics, because most of the lattice constants of ceramic material have similar values to II–VI or III–V compounds.

2. Experimental

The chamber used for the sample preparation was a glass cylinder with a 17 cm inner diameter and 33 cm in height. GaP smoke was prepared by evaporating GaP powder (99.99%) from a tungsten V-boat (50 mm in length, 2 mm in width and 1 mm in depth) heated at 1200°C in He gas. The GaP powder had zinc-blende structure with lattice parameter a = 0.5446 nm. Particles in the produced smoke were collected on thin carbon films supported by standard electron microscope grids, and observed with a JEM-200CX electron microscope.

3. Results and Discussion

Typical smoke particles and corresponding electron diffraction patterns are shown in Fig. 1. The particles were composed of round shapes and rod shapes. Analysis of electron diffraction pattern shows that the particles are
Fig. 1. Electron microscopic image and electron diffraction pattern of GaP smoke particles. The particles were composed of mixture of zinc-blende and wurtzite structures.

composed of zinc-blende \((a=0.548 \text{ nm})\) and wurtzite crystals \((a=0.628, c=0.385 \text{ nm})\). Since crystallographic data for wurtzite crystals are not seen in literature, the lattice constants shown above are derived from cubic phase. The results are in good agreement as shown in the right side of Fig. 1. Appearance of both structures in smoke is similar to the results as found and discussed in some II–VI compounds.\(^{4-6}\)

Figure 2 shows HREM image of a particle with the size of about 15 nm having zinc-blende structure. The identification of the structure has been done by measuring lattice spacing and angle between lattice planes. Since the surface of the particle is a (110) plane, the external shape of the particle constructed from lattice images becomes as shown in Fig. 2(b). The thickness of the particle was estimated from particles corresponding to the side view.
Fig. 2. HREM image of GaP particle (a) and the corresponding external shape of the particle (b).
Fig. 3. HREM image of GaP particle (a) and the corresponding external shape of the particle (b).
Figure 3 shows HREM image of the wurtzite particle. It can be seen from the lattice image that the particle is a perfect single crystal. The external shape of the particle was that of an octahedral plate with the side surfaces of two \{1120\} planes. Figure 4(a) shows a HREM image of a particle and Fig. 4(b) is a highly magnified image of one part. The closed fringes of (111) planes with the distance of 0.31 nm are clearly seen. Although the Ga and P column are not completely resolved by the present microscope, the stacking sequence of the fcc structure along the \langle 111 \rangle direction can be elucidated. Figure 5 shows the model of zinc-blende crystal viewed along the [110] direction. Black and white circles shows Ga and P atoms. The symbol A, B and C in Fig. 4 shows the pair of Ga and P atoms. Since this crystal has a polarity along the direction [111], the emergence atoms at (111) and (\overline{111}) are different. Since the black spot in Fig. 4 corresponds to the projection of Ga and P column pair along [110] direction, the stacking sequence can be analysed by measuring the arrangements of black spots along (111) direction as shown in Fig. 4. The region of ABCABC...... sequences shows that the particle has zinc blende structure. As indicated by I, the sequences CBACBA changed to CBAC/ACBA. Therefore the boundary I can be identified as an intrinsic stacking fault. At the boundary indicated by E, the sequences ABCABC changed to

![HREM image of GaP particle containing the faults. I, E and T show intrinsic stacking faults, extrinsic stacking faults and growth faults.](image-url)
ABCA/CBCABC. Therefore the boundary E can be identified as an extrinsic stacking fault. At the boundaries indicated by T, the sequences ABCABC changed to ABCABC/BACBA. Therefore, the boundary T can be identified as a growth fault.

The intrinsic and extrinsic stacking faults may also be introduced during the mechanical deformation of crystal. But the growth fault was formed during the growth of the crystal. Therefore, it can be concluded that the faults seen in the picture are due to the growth process of fine particles. The size of GaP particles, which were collected at the height 5 mm from the evaporation source was about 8 mm, and the vapor of GaP was hardly seen above this place. Since the size of the crystal in Fig. 4 is about 45 nm, it can be concluded that liquid-like coalescence took place in GaP smoke. A similar coalescence could be observed in vacuum deposited films where multiple twinned particles (MTP) are formed after coalescence of MTP with other epitaxial particles or MTPs. Though an MTP particle can be formed after coalescence, which indicated its formation and growth involve a rearrangement of a considerable number of atoms, the particles containing the MTP grew larger by coalescence. Since the faults are running in one direction without disappearing in the particle as seen in Fig. 4, the faults may grow by coalescence with another particle even in the smoke.

Figure 6 shows HREM image of two particles. The configuration of two particles was determined by lattice image. The schematic presentation of two particles is shown in Fig. 7. Two particles based on {111} cubic octahedron contact at (111) twin planes as shown in Fig. 7(a). The particle in
Fig. 6 is viewed along to the arrows in Fig. 7(a) and presented in Fig. 7(b) indicating the lattice image in Fig. 6. The particles in Fig. 6 are truncated at (110) and (112) planes of the octahedral model, as is generally seen in smoke particles. This connection with twin relation shows that there is an octahedron clusters in smoke as is found in II–VI compounds. The round and rod shape particles in Fig. 1 are composed of truncated octahedron and thin plates shown in Figs. 1, 2 and 8.

The formation of twinned particles may be due to the coalescence between particles with definite orientations as to minimize their interface energy in a convection stream of inert gas. The coalescence discussed in Fig. 6 and Fig. 8 is different, i.e. the coalescence in Fig. 6 is liquid-like coalescence,
Fig. 7. Model of the twinned particle. The view in (b) corresponds to the image in Fig. 6.

Fig. 8. (a) HREM image of GaP particle. (b) Enlarged image of a part indicated by the circle in (a). The boundary connected with the particle containing growth faults is clearly different as indicated by arrows A and B.
and that in Fig. 8 is coalescence due to surface melting of the particles at lower temperature as found and discussed by using Ag smoke particle.\textsuperscript{14} Figure 8(a) shows an HREM image of the connected particles and an enlarged image of the region indicated by a circle is shown in Fig. 8(b). Since the central particle contains the growth faults, the boundary of two connected particles is clearly divided into two different area, as indicated by arrows A and B. The boundary indicated by arrow A connects smoothly and those indicated by arrow B connect like small angle grain boundaries. Since the present crystals have a polarity along the direction of $\langle 111 \rangle$ as shown in Fig. 5, the polarity changes by introducing the growth fault as indicated by arrows in Fig. 8, i.e. for example, Ge atom (or P atom) directions are shown. The boundary indicated by arrow A is connected to conserve the polarity, but the boundary indicated by arrow B is connected with polarity reversal, i.e. inversion took place. The boundary B corresponds to the inversion boundary.\textsuperscript{15} The feature of this boundary are different from the model proposed for BN crystal by X-ray topography\textsuperscript{16} and direct imaging of ZnSe crystal by HREM.\textsuperscript{9} Since the boundary energy connected at the region by arrow A is lower than the boundary shown B, the connection of these particles took place by the surface melting in the region shown by a double arrow. In order to contain the growth fault in a particle, boundary B may be formed. Therefore the coalescence of the crystal having the polarity took place so as to maintain the polarity of the crystal, and the growth of tetrapod crystals elucidated in II–IV compounds\textsuperscript{4,5–6} is reasonable. It can be concluded that the coalescence of the particles can be divided into two processes i.e. surface melting coalescence and liquid-like coalescence. It also turns out the HREM image method for these small particles can be used as a powerful characterization method for the fine ceramic industry.

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REFERENCES


