Crystallization of GaN in Its Thermal Decomposition

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GaN powder, in carbon crucibles was heated at various temperatures in an induction furnace in a nitrogen atmosphere. Deposition of Ga$_2$O$_3$ was observed on a substrate that covered the crucible during heating at above 800°C. The recrystallization of GaN was detected in the deposit formed only at 850°C probably because Ga metal deposited on the substrate reacted with an active nitrogen released in the decomposition of GaN powder. GaN also recrystallized on the substrate at 1000°C in a reaction of the evaporated Ga metal with nitrogen atmosphere.

Such recrystallization was also observed when GaN powder was heated to above 850°C in an evacuated sealed quartz tube. Hexagonal thin platy crystals of about 4 μm diameter were obtained. Short duration heating at temperature close to 850°C was preferable to grow crystals because its decomposition simultaneously occurred with the recrystallization. It appears that GaN crystals do not grow in the sublimation process proposed previously but rather in the recrystallization.

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Introduction

Gallium nitride thin films have been used as blue light emitters. The demand for gallium nitride is expected to increase, as it is a blue laser. The use of such blue lasers, as opposed to the currently used red lasers e.g. GaAs, will increase the amount of data that can be stored on digital videodisks. However, the dislocation density is around 10$^6$ cm$^{-2}$ in the GaN thin films grown on sapphire substrates that are currently used as LED. It should be reduced to less than 10$^6$ cm$^{-2}$ for its laser application. Both the lattice dimentions and thermal expansion coefficient should be as close as possible between the substrate and GaN thin film. In this regard, GaN single crystals are the best substrate material to reduce the dislocation density.

GaN does not melt when heated in an ambient pressure of nitrogen. It decomposes to a mixture of molten gallium and nitrogen gas. High temperatures and pressures are required for GaN to melt. Karpiniski et al. reported a PT phase diagram of GaN.2 Platy single crystals (100 mm$^2$ x 300 μm)$^2$ were grown between 1400 and 1700°C and 1.2 to 2.0 GPa.3 Yaman et al. used sodium as a flux to grow single crystals of GaN.4,5 A Na and Ga mixture was heated in a pyrolytic BN crucible under a nitrogen pressure of 5 MPa in a temperature range of between 600 and 800°C for 300 hours. The maximum size of the platy crystals was 10 x 10 mm$^2$. Many colorless and transparent crystals of 1-2 mm also grew on the inner surface of the crucible.

Surnimoto Electric Industries Ltd. recently started to deliver GaN substrates of 2 inch in diameter.6) They were heteroepitaxially grown by vapor growth. Dislocations were concentrated in their pit area. This part, having many dislocations, was removed in order to produce a substrate with a dislocation density of less than 10$^6$ cm$^{-2}$. Bulk crystals still have the possibility of lower dislocation densities. Sublimation above 1000°C was used to grow GaN crystals in the late 1960s to 1970s.7,8) In an ambient nitrogen atmosphere GaN decomposes to a mixture of molten gallium and nitrogen gas as mentioned above. It is suspicious to assume the growth mechanism is sublimation. Very fast growth rates of several hundred μm/hour had been reported via this method.9 Kurai et al. grew homoepitaxial GaN film on bulk GaN prepared by sublimation.10) In this study GaN powder, contaminated with GaNH, Ga$_2$N$_2$H and GaN$_2$H impurities, was heated at 1100°C in mixed ammonia and nitrogen atmosphere. Many small bulk GaN crystals grew on the sapphire substrate placed above the powder. The volatile impurities were assumed to react with ammonia to form GaN crystals.

In the present study, pure GaN powder was heated either in nitrogen atmosphere by induction or in an evacuated sealed tube by conventional furnace heating. Deposition of GaN crystals on silica substrates was observed in the induction heating. Crystal growth also occurred during the heating of GaN powder in sealed tubes. The growth mechanism was discussed in these GaN powder heating.

Experimental

High frequency induction heating equipment (Sekisui Electron, Inc. U-1700) was used for the deposition of GaN crystals on silica glass substrates. Its induction coil was installed in nitrogen filled glove box. Either 0.1 g of 99.99% GaN powder or 0.5 g of pure Ga metal was placed in a carbon crucible (height 10 mm, inner diameter 10 mm). The crucible was covered with a quartz glass substrate (20 x 20 mm$^2$) and placed into a side-arm quartz sleeve, which was itself placed into the induction coil. It was heated to between 800°C and 1050°C for 1 hour in an atmosphere formed by flowing high purity nitrogen through the side-arm. The oxygen content in the nitrogen flow (below 0.01 ppm) was reduced to below 0.002 ppm with a gas-cleaning column (Nikka Seiko Co., Ltd., GC-RX).

Samples of 0.5 g of GaN powder were also sealed in evacuated quartz tubes (6 mm inner diameter, 150 mm in length). Each sample was heated, at 200°C/hour, in an electric furnace to a temperature of between 850°C and 1000°C for durations of between 1 hour and 1 week. The temperature gradient along the sealed tube was within 2°C. The effect of a 10°C/cm temperature gradient was also studied.

Products were characterized by powder X-ray diffractometry (Philips X’pert-MPD) with monochromatized Cu-Kα radiation and SEM-EDX (JEOL, JSM-5800LV).

Results and discussion

Some deposit on the quartz substrate was observed following induction heating above 800°C. It was gray although the GaN raw powder was vivid yellow. Its amount increased with the temperature. Although the GaN powder still remained in the crucible after heating below 800°C, only Ga metal particles

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with a spherical shape were present after heating above 850°C. 
X-ray diffraction showed only the presence of Ga$_2$O$_3$ with an amorphous Ga metal in the deposit formed at 800°C as shown in Fig. 1(a). A small amount of the Ga metal deposited onto the substrate was oxidized by the very small amount of residual oxygen in the high purity nitrogen atmosphere. The active Ga worked as an oxygen getter. Two broad diffraction halos were observed. One at 2θ = 21° and another at 2θ = 36° corresponding to the silica glass substrate and amorphous gallium respectively.

The deposit at 850°C was GaN with a small amount of Ga$_2$O$_3$ as shown in Fig. 1(b). Extrapolation of the GaN vapor pressure against temperature curve leads to it crossing the ambient pressure line at around 870°C. GaN was deposited on the substrate in a very rapid decomposition of the GaN powder in the crucible. Ga metal recombined on the substrate with active nitrogen generated in the thermal decomposition. Both the deposits at 900°C and at 950°C were mostly Ga$_2$O$_3$, as shown in Figs. 1(c) and (d). GaN in the crucible rapidly decomposed. The amount of the deposit was larger than that at 850°C. At this temperature most of the active nitrogen could not contribute to form GaN on the substrate. The evaporated Ga metal on the substrate was oxidized by the low concentrations of residual oxygen in the atmosphere. GaN was again observed on the deposit at 1000°C as shown in Fig. 1(e). The nitrogen atmosphere was thermally activated at this temperature and was therefore able to recombine with the Ga metal deposited on the substrate. The deposit at 1050°C was only amorphous GaN because the substrate itself was heated above the decomposition temperature.

A series of experiment were performed in which GaN powder was substituted with Ga metal in the carbon crucible. Only a halo corresponding to the silica glass substrate was observed in the XRD of the deposit at 850°C. Amorphous GaN was apparent in the deposit formed at 1000°C. This result supports the hypothesis that evaporated Ga can react with a nitrogen atmosphere to form GaN at 1000°C. Active nitrogen released in the GaN powder decomposition was effective in forming GaN in the deposit.

SEM observation of the deposit on the substrate formed from heating at 1000°C for 1 hour showed that spherical particles of less than 10 μm in diameter coexisted with fine platy crystals, as shown in Fig. 2. Oxygen was observed on the gallium spheres in the EDX measurements. Only gallium was detected on the platy crystals. The spheres can be assumed to be evaporated Ga metal particles covered with Ga$_2$O$_3$. The crystals were sintered hexagonal platelets of GaN crystals measuring 200~700 nm across the diagonal.

The GaN crystals on the substrate were formed by the nitridation of the evaporated Ga metal either by the active nitrogen released from GaN in its thermal decomposition at 850°C or with the nitrogen atmosphere at 1000°C. The situation is different from the recent sublimation growth using GaN powder with GaNH, Ga$_2$N$_2$H and Ga$_3$N$_2$H impurities.

The recrystallization of GaN was also confirmed in the following series of experiments involving the heating of GaN powder in evacuated sealed tubes. Color of the GaN powder changed from vivid to grayish yellow after being heated for 1 hour at temperatures of either 850°C, 900°C, 950°C or 1000°C. These temperatures are above the expected decomposition temperature. At 850°C some crystals of hexagonal platy form were grown as shown in the SEM photographs in Fig. 3. There were no spherical particles observed in these products in contrast to the results from the induction heating. The size of the crystals grown was larger in the powder heated at lower temperatures. Their surface texture became less sharp with increasing temperature because of the simultaneous decomposition and growth. The sealed tubes were also heated in a temperature gradient along their length of about 150°C. GaN powder in the high temperature region was heated above

![Fig. 1 XRD patterns of the deposit on silica glass substrate heated at (a) 800°C, (b) 850°C, (c) 900°C, (d) 950°C, (e) 1000°C, (f) 1050°C for 1 hour.](image1)

![Fig. 2 SEM photographs of the deposit on silica glass substrate heated at 1000°C for 1 hour.](image2)
850°C, but there was no deposition in the low temperature region of the sealed tube. This result shows that GaN crystals do not grow via a sublimation mechanism.

GaN crystals were grown in sealed tube without a temperature gradient at 850°C. Crystal growth was enhanced when the starting GaN powder was dispersed in the sealed tube. The size of the platy crystals became larger with the heating duration; 1 x 1.8 μm² for 10 hours, 3 x 2 μm² for 1 day and 3 x 8 μm² for 1 week. The surface of the longest crystal grown by heating for 1 week was not smooth, as shown in Fig. 4, because the crystals grew in repeated cycles of recrystallization and decomposition.

In summary, GaN powder was heated either by induction in a nitrogen atmosphere or in an evacuated sealed quartz tube. It thermally decomposed above 800°C to a mixture of Ga metal and active nitrogen gas. Recrystallization of GaN using this active nitrogen was observed in induction heating at 850°C. Crystals were grown most effectively in the furnace heating in evacuated sealed tubes at 850°C. GaN crystals do not grow in the sublimation but via the decomposition-recrystallization mechanism.

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