A benzene-thermal metathesis route to pure metastable rocksalt GaN

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Here, pure metastable rocksalt GaN was first prepared *via* a benzene-thermal metathesis route through the reaction of GaI_3 and $NaNH_2$ at 210 °C and under 3 MPa pressure, in which I_2 acted as the transporting agent. The as-prepared product was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). X-Ray photoelectron spectra (XPS) were used to determine the average composition ratio, which is Ga:N = 1.14:1. The photoluminescence spectrum shows that the rocksalt GaN emits two PL peaks positioned at 330 and 348 nm.

Introduction

GaN has recently attracted much attention because of its wide use in optical devices operating at blue and ultraviolet wavelengths and in high-temperature electronic devices.[1,2] At ambient pressure, GaN usually crystallizes in the wurtzite structure, whereas there are another two cubic structures of GaN: zincblende and rocksalt. Zincblende GaN was formed during a film preparation process,[3,4] while rocksalt GaN only appeared under ultrahigh pressures of at least 37 GPa and was observed with *in situ* energy-dispersive X-ray diffraction, using diamond anvil techniques. In such a diamond anvil cell, during unloading, the wurtzite structure began reappearing at about 25 GPa and the rocksalt structure disappeared completely after the pressure was completely released.[5] From the crystal structural point of view, high pressure can result in a series of III–V and II–VI transformations from a fourfold-coordinated wurtzite crystal structure to a sixfold-coordinated rocksalt crystal structure. Rocksalt GaN is an intriguing metastable phase with many of its characteristics being quite different from those of its wurtzite and zincblende counterparts. For example, the rocksalt structure is typical of an ionic bond while wurtzite and zincblende structures possess partially covalent and ionic properties, with the former being somewhat more prominent. Although various calculations have done to predict the properties of rocksalt GaN, such as optical and dielectric, it is difficult to study these properties in the diamond anvil cells under megabar pressure, and furthermore, till now pure metastable rocksalt GaN was not available under ambient pressure. Thus, it is an enormous challenge to obtain such pure metastable high-pressure phases under mild conditions. One successful example includes the MOVCD synthesis of diamond thin films, which is well-known to be synthesized at pressure as high as 2000 bar.[6]

Since Johnson *et al.* first described the conversion of metallic Ga in a NH_3 stream into wurtzite GaN above 900 °C, a number of notable advances have been reported in the past decade in the synthesis of wurtzite GaN or GaN with mixed wurtzite and zincblende structures.[7–18] Recently, Hu *et al.* synthesized 30 nm GaN particles with a wurtzite structure *via* the reaction of GaI_3 and NaN_3 at 380 °C, employing iodine as the heat sink and diluents. In this case, the formation of wurtzite GaN was essentially due to the reaction of metallic Ga and N_3 radicals, which formed from the decomposition of GaI_3 and NaN_3, respectively.[19] We even developed a benzene-thermal process to synthesize 30 nm GaN by utilizing the metathesis reaction of Li_3N with $GaCl_3$ in superheated benzene solvent at 280 °C.[20] Surprisingly, the product was a mixture of wurtzite GaN and rocksalt GaN, which could be clearly confirmed by X-ray powder diffraction (XRD) and high-resolution transmission electronic microscope (HRTEM). Since the synthetic conditions were far below the region of rocksalt thermodynamic stability, the appearance of rocksalt GaN at ambient pressure is regarded as a size effect since a wider range of materials may be metastable in nanocrystals than in extended solids.[21] Although rocksalt GaN accounted for only about 10% of the sample, it gave us the idea that pure metastable rocksalt GaN might possibly be obtained by using a suitable synthetic strategy and could exist under ambient conditions. Applying the strategy that turning down the heat may favor a possible route to metastable compositions and structures as well as to thermodynamically stable low-temperature phases that would decompose at higher temperatures,[22] we have been searching for a milder route to metastable rocksalt GaN. Here, we report the latest result on the formation of rocksalt GaN, with the entire process being described by the following equation:

$$GaI_3 + 3NaNH_2 + 3I_2 \xrightarrow{\text{benzene, 483 K}} GaN + 3NaI_3 + 2NH_3$$

Experimental

Typically, 5 mmol GaI_3, which was synthesized according to the literature,[23] was dissolved in benzene solution. This solution with 30 mmol $NaNH_2$ powder and 30 mmol I_2 was put into a Teflon-lined stainless steel autoclave of 50 mL capacity, which was filled with benzene up to 95% of the total volume. Argon gas was passed through the solution to purge the solution. The autoclave was maintained at 210 °C for 24 h and then allowed to cool to room temperature naturally. A tan precipitate was collected, which was washed with dilute hydrochloride acid and methanol to remove any reagents and byproducts. The final product was dried in vacuum at 60 °C for 3 h, and then annealed at 400 °C in vacuum for 3 h.

The X-ray powder diffraction (XRD) pattern was acquired on a Japan MAC MXP18AHF diffractometer equipped with

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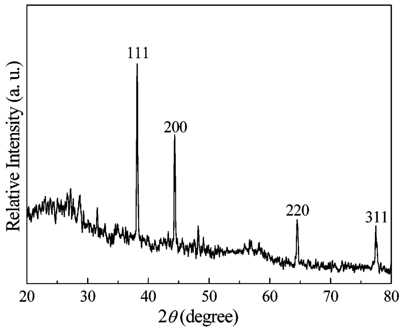

Fig. 1 X-Ray diffraction pattern of nanocrystalline GaN with rocksalt structure.

a graphite-monochromated Cu Kα radiation source (λ = 1.54056 Å), operating at 40 kV and 100 mA. XPS analysis was performed on an ESCALAB MKII with MgK_α ($h\nu$ = 1253.6 eV) as the exciting source. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C_{1s} peak to 284.5 eV. Transmission electron microscopy (TEM) was performed with a Hitachi H-800 transmission electron microscope, while selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were performed with a JEOL-2010 transmission electron microscope. The photoluminescence (PL) spectrum of rocksalt GaN was measured in a Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature, using an excitation wavelength of 236.6 nm and a filter wavelength of 290 nm.

Results and discussion

The phase of the final products was identified by X-ray diffraction; a typical XRD pattern is shown in Fig. 1. All the reflections can be indexed to (111), (200), (220) and (311) of the rocksalt GaN with lattice constant a = 4.082 Å, which is in good agreement with the calculated value[24] and our previous result.[20]

The composition and purity of the samples were investigated by X-ray photoelectron spectra (XPS) analysis, as shown in Fig. 2. In Fig. 2(A), the symmetrical gallium Ga_{3d} peak shows the existence of only one signal at 19.3 eV corresponding to GaN. From the nitrogen N_{1s} spectrum in Fig. 2(B), the peak at 397.5 eV corresponds to GaN, which is also close to that of bulk GaN. The content of Ga and N was quantified by the Ga_{3d} and N_{1s} peak areas and an average composition of Ga:N = 1.14:1 was obtained.

The morphology and microstructure of the sample was studied by using transmission electron microscopy, selected-area electron diffraction and high-resolution transmission electron microscopy. The TEM image [Fig. 3(A)] shows that the size of GaN nanocrystallites is 50 nm on average. In the HRTEM image [Fig. 3(B)], the obvious lattice fringes of rocksalt GaN indicate that the GaN is well crystalline. The plane intervals, measured as 2.3 Å, represent the stripe image of the (111) plane of rocksalt GaN. The SAED pattern [Fig. 3(C)] also confirmed its rocksalt structure.

The PL spectrum (Fig. 4) shows that the as-prepared sample emits two PL peaks positioned at 330 nm (3.76 eV) and 348 nm (3.56 eV), which are very close to the calculated gaps of L-K and Σ-K, respectively, under a pressure of 37 GPa. In addition, the energy difference between the two PL peaks is 0.2 eV, in perfect agreement with the calculated gaps between L-Σ in the calculated energy curve of rocksalt GaN.[25]

Our approach to rocksalt GaN is essentially based on the solvothermal metathesis reaction between gallium halides (GaX_3) and alkali metal nitrides (M_3N), in which two efficient strategies are put forward to favor the formation of metastable GaN: (1) carrying out the reaction under milder conditions for a longer time will be helpful to the formation of metastable phase and (2) the nitride source with stronger ionicity will favor the formation of metal nitride with stronger ionicity. Thus, several measures were taken. First, sodium amide ($NaNH_2$) was used as the nitrogen source, instead of lithium nitride (Li_3N). It is well-known that $NaNH_2$ transforms to Na_3N by loss of ammonia on heating,[26] and the re-nascent Na_3N can be regarded as a good nitrogen source due to its high reactivity:

$$3\,NaNH_2 \rightarrow Na_3N + NH_3$$

$$GaI_3 + Na_3N \rightarrow GaN + 3\,NaI$$

More important, Na_3N has a stronger ionicity than Li_3N, which will be propitious to the formation of ionic GaN with rocksalt structure. In addition, the release of NH_3 increases the pressure in the system rapidly, which may also be helpful to the formation of rocksalt GaN.

Second, the gallium halide salt (GaX_3) involved in the reaction was changed from $GaCl_3$ ($\Delta H_{rxn} = -645$ kJ mol^{-1}) to GaI_3($\Delta H_{rxn} = -515$ kJ mol^{-1}).[8] Among the GaX_3, GaI_3 is the best candidate as it has the weakest Ga–X bond, which can guarantee the metathesis reaction of GaX_3 and Na_3N. Besides, according to the reported results,[27] GaI_3 exists mostly as single molecules at 210 °C and under 3 MPa, perhaps due to the large steric hindrance effect of the I^- ion, while $GaCl_3$ exists as dimers due to the strong Lewis acidity of Ga(III), which makes $GaCl_3$ more difficult to decompose.

Third, the active additive I_2 was added to the metathesis reaction, acting as transporting agent. Here, iodine helps the NaI product to dissolve in the benzene in the form of NaI_3

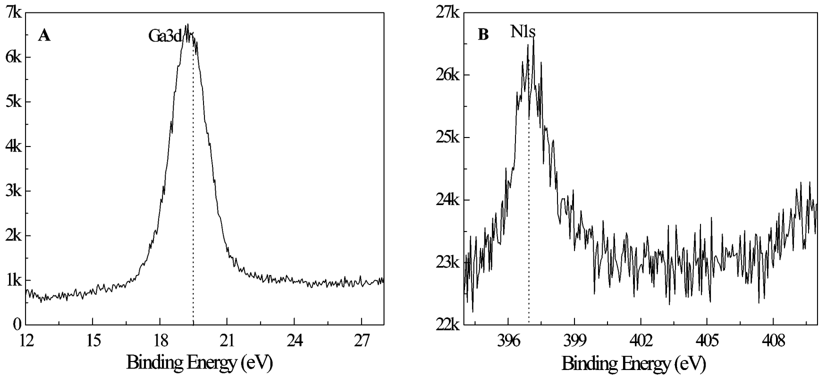

Fig. 2 XPS spectra of rocksalt GaN: (A) Ga 3d spectrum and (B) N 1s spectrum.

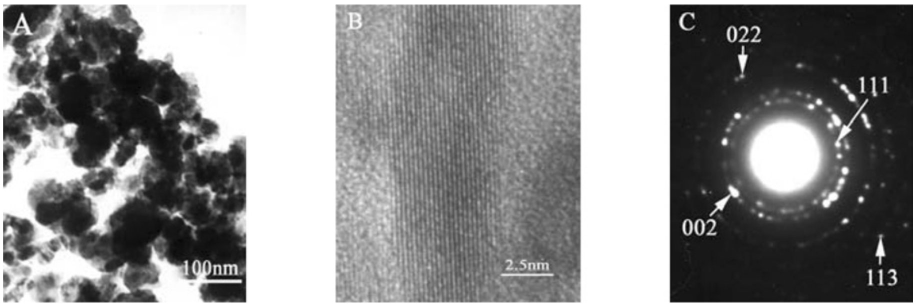

Fig. 3 (A) TEM image of nanocrystalline rocksalt GaN; (B) HRTEM image of nanocrystalline rocksalt GaN showing the lattice fringes of the (111) plane in rocksalt GaN; (C) SAED of rocksalt GaN.

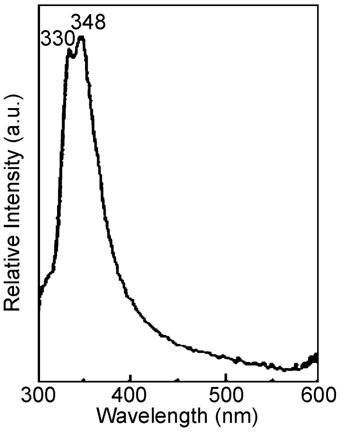

Fig. 4 Photoluminescence spectrum of rocksalt GaN at room temperature.

based on the following reaction, which can ensure the completion of the metathesis reaction of GaI_3 and Na_3N:

$$I_2 + NaI \rightarrow NaI_3$$

Fourth, the reaction temperature, time and the molar ratio between the reactants were carefully adjusted. The optimal mole ratio of the raw materials is GaI_3:$NaNH_2$:I_2 = 1:6:6. The annealing temperature is maintained at 400 °C for 3 h, as the as-prepared product would transform to wurtzite GaN if the annealing temperature was increased to 600 °C. These systematic optimizations have led to significant progress in preparing high-purity and high-quality nanocrystalline GaN with rocksalt structure.

Conclusions

In summary, we have developed a benzene-thermal metathesis process to prepare 50 nm rocksalt GaN through the reaction of GaI_3 and $NaNH_2$ at 210 °C, which utilized I_2 as the transporting agent. The product was pure GaN (with a yield above 50%) with a rocksalt structure, which was first appeared under 3 MPa. This rational benzene-thermal metathesis reaction at such a low temperature is a kinetically controlled process and favors the preparation of rocksalt GaN nanocrystallines with a low activiation barrier. This work suggests that it may be possible to synthesize a wide variety of semiconductor nanocrystals in high pressure phases, and to further study their properties under ambient conditions.

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