Temperature-controlled growth and photoluminescence of AlN nanowires

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A B S T R A C T

By varying the substrate temperature in the range of 800–1000 °C, the conditions for the synthesis of AlN nanowires were optimized. Al powders were heated under flowing ammonia gas. The samples were characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy, and photoluminescence (PL) spectroscopy. Based on the absence of tip particles, the growth mechanism of AlN nanowires was considered to follow a vapor–solid process. The overall intensity of the PL spectra was increased by increasing the synthesis temperature, whereas their shapes were changed by varying the synthesis temperature. The associated emission mechanisms are discussed.

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1. Introduction

One-dimensional (1D) nanostructures, including nanowires, nanobelts, and nanotubes, not only have promising applications in electronics, optoelectronics, and biological areas, but also have great potential to assist with the understanding of how size factors into physical and chemical properties [1,2]. Aluminium nitride (AlN), which is a III-nitrides semiconductor material with a band gap of 6.2 eV [3], is a promising material for application in electronics and optoelectronics, such as light emitting devices [4]. In addition, it has extraordinary and useful properties including high thermal conductivity, a low thermal expansion coefficient, a low dielectric loss, a high piezoelectric response, good mechanical strength, and chemical and thermal stability [5]. Accordingly, 1D nanostructures of AlN have been the focus of widespread attention due to their prospective applications in optoelectronic and field-emission nanodevices [6–8]. Thus far, AlN nanowires have been fabricated using a variety of techniques, including the arc discharge method [6], chloride-assisted chemical vapor deposition [9], and in carbon nanotube confined reactions [10]. In the present study, a simple and effective technique in which AlN structures are successfully fabricated via the direct reaction of Al and NH₃ at sufficiently high temperatures is used. It is anticipated that the effects of the processing conditions on the growth and characteristics of nanowires need to be intensively studied to achieve investigations of novel physical properties and preferred designs of nanodevices. Accordingly, this study represents a novel investigation of the effects of the synthesis temperature on the morphology and optical properties of AlN nanowires.

2. Experimental details

AlN nanowires were grown on gold (Au: approx. 3 nm)-coated Si substrates in a horizontal tube furnace. Al powder and NH_3 gas served as the aluminum and nitrogen sources, respectively. With argon (Ar) being used as a carrier gas, the flow rates of Ar and NH_3 were 100 and 20 sccm, respectively. An alumina boat holding both the substrate and the Al powders was placed inside a quartz tube. In order to investigate the effect of the temperature, different substrate temperatures were set at 800, 900, and 1000 °C with a reaction time of 1 h.

The products were characterized by glancing-angle X-ray powder diffraction (XRD, Philips X'pert MRD), scanning electron microscopy (SEM, Hitachi S-4200), transmission electron microscopy (TEM, Philips CM-200), and energy-dispersive X-ray (EDX) spectroscopy attached to the TEM. Photoluminescence (PL) studies were carried out at room temperature with a luminescence spectrophotometer using a He–Cd laser with 325 nm excitation.

3. Results and discussion

Fig. 1a–c shows SEM images of the samples grown at 800, 900, and 1000 °C, respectively. While the sample grown at 800 °C exhibits cluster-like structures on the substrate, both the samples grown at 900 and 1000 °C comprise 1D structures in a large quantity. From enlarged micrograph shown on the upper-right

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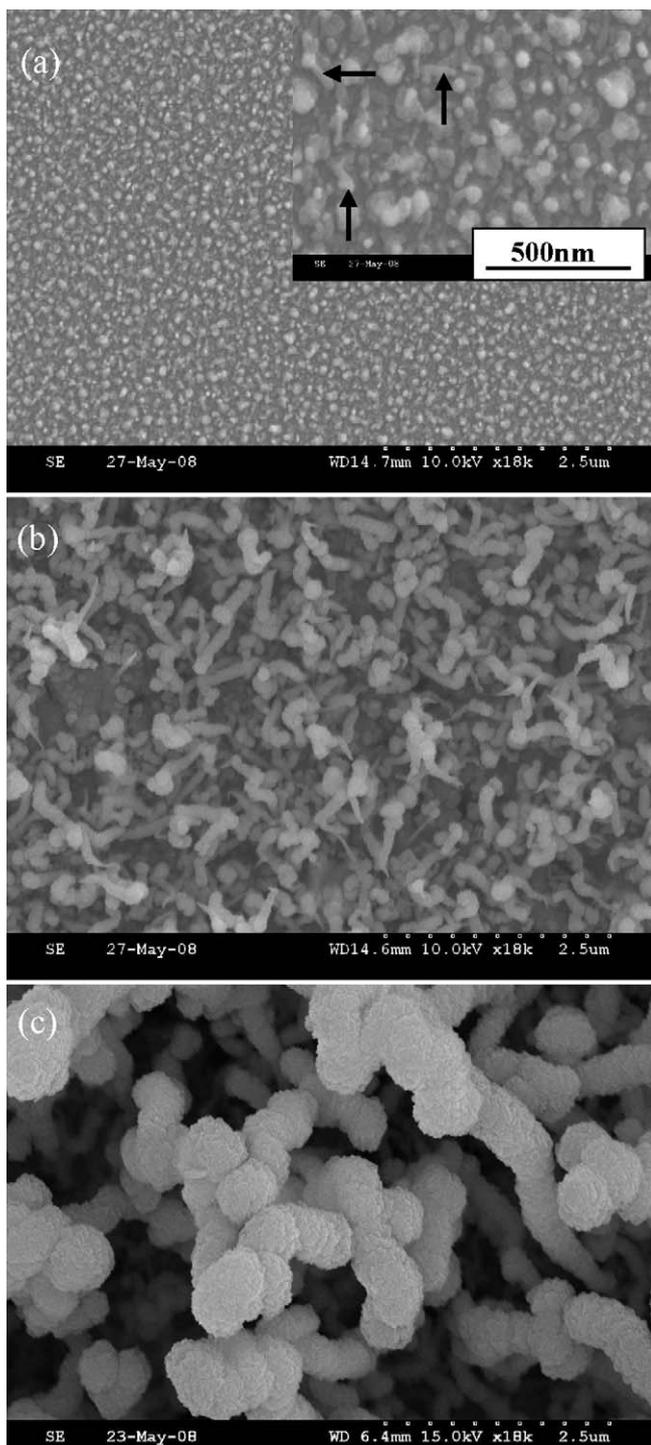 *E-mail address:* hwkim@inha.ac.kr (H.W. Kim).

Fig. 1. Top-view SEM micrographs of the products grown at: (a) 800 °C, (b) 900 °C, and (c) 1000 °C. The inset of (a) shows an enlarged image, in which arrowheads indicate the presence of relatively thin and short nanowires.

Fig. 2. XRD pattern of AlN nanowires grown at 900 °C.

inset of Fig. 1a, it is noteworthy that the product grown at 800 °C includes a small number of 1D structures, which are relatively thin and short (indicated by arrowheads). Both the products grown at 900 °C and those grown at 1000 °C have a rough surface. Based on the SEM micrographs, it was estimated that the average diameter and length of the 1D structures increased as the growth temperature increased. It was also observed that 1D structures synthesized at 900–1000 °C do not have catalytic particles on their ends.
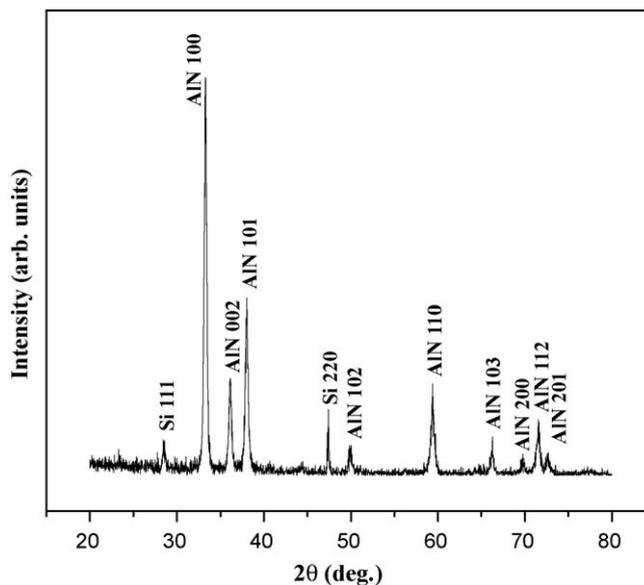
Fig. 2 shows a typical XRD pattern of AlN nanowires synthesized at 900 °C. Apart from the Si-associated peaks coming from the Si substrate, the XRD pattern coincides with the characteristic peaks of a hexagonal AlN structure with lattice parameters of a = 3.111 Å and c = 4.979 Å, which are in good agreement with previously reported data (JCPDS card: No. 25-1133). It was observed that the synthesis temperature did not significantly affect the XRD pattern.

Fig. 3a shows a low-magnification TEM image that reveals that the nanowire produced at 900 °C has a rough surface. This is in good agreement with the SEM image. Fig. 3b shows an enlarged TEM image. TEM investigations indicated that no metal catalyst was present at the tips of the nanowires. Fig. 3c shows an associated selected area electron diffraction (SAED) pattern in which the diffraction rings can be indexed as the (1 0 0), (1 0 1), (1 0 2), and (1 0 3) planes according to the hexagonal AlN structure. Fig. 3d is a lattice-resolved enlarged image of the dotted box in Fig. 3b. It shows a spacing of 0.269 nm between two neighboring layers, corresponding to the d_{100} spacing of hexagonal AlN. For comparison study, we have carried out a TEM investigation on the nanowires produced at 800 °C. Although Fig. 1a revealed that the 800 °C-grown product mainly consisted of film-like structures, there sporadically exist a few 1D structures. Fig. 4a shows a low-magnification TEM image of an 800 °C-grown 1D structure. Fig. 4b shows an enlarged TEM image, revealing that the nanowire is single-crystalline, whereas its surface region is amorphous. EDX spectrum (not shown here) indicated that not only the crystalline core region but also the amorphous surface region consisted of Al and N, suggesting that the surface region resulted from non-equilibrium growth conditions. Fig. 4c shows a corresponding SAED pattern, revealing that the nanowire exhibits diffraction spots due to its single-crystalline nature. In addition, the diffusive-natured ring pattern may correspond to the amorphous structure on the nanowire surface.

It was observed that no particle was attached to the tips of the nanowires grown at 900 °C (Figs. 1a and 3a and b), which were preferentially formed via a vapor–solid (VS) mechanism. In the present VS process, Al vapor are generated from Al powders [11]. According to the Gibbs–Thompson equation, the vapor pressure of Al particles would be elevated, which most likely permits the generation of Al vapors at the reaction temperature used in the present work [12]. In the next step, the Al vapor combines with
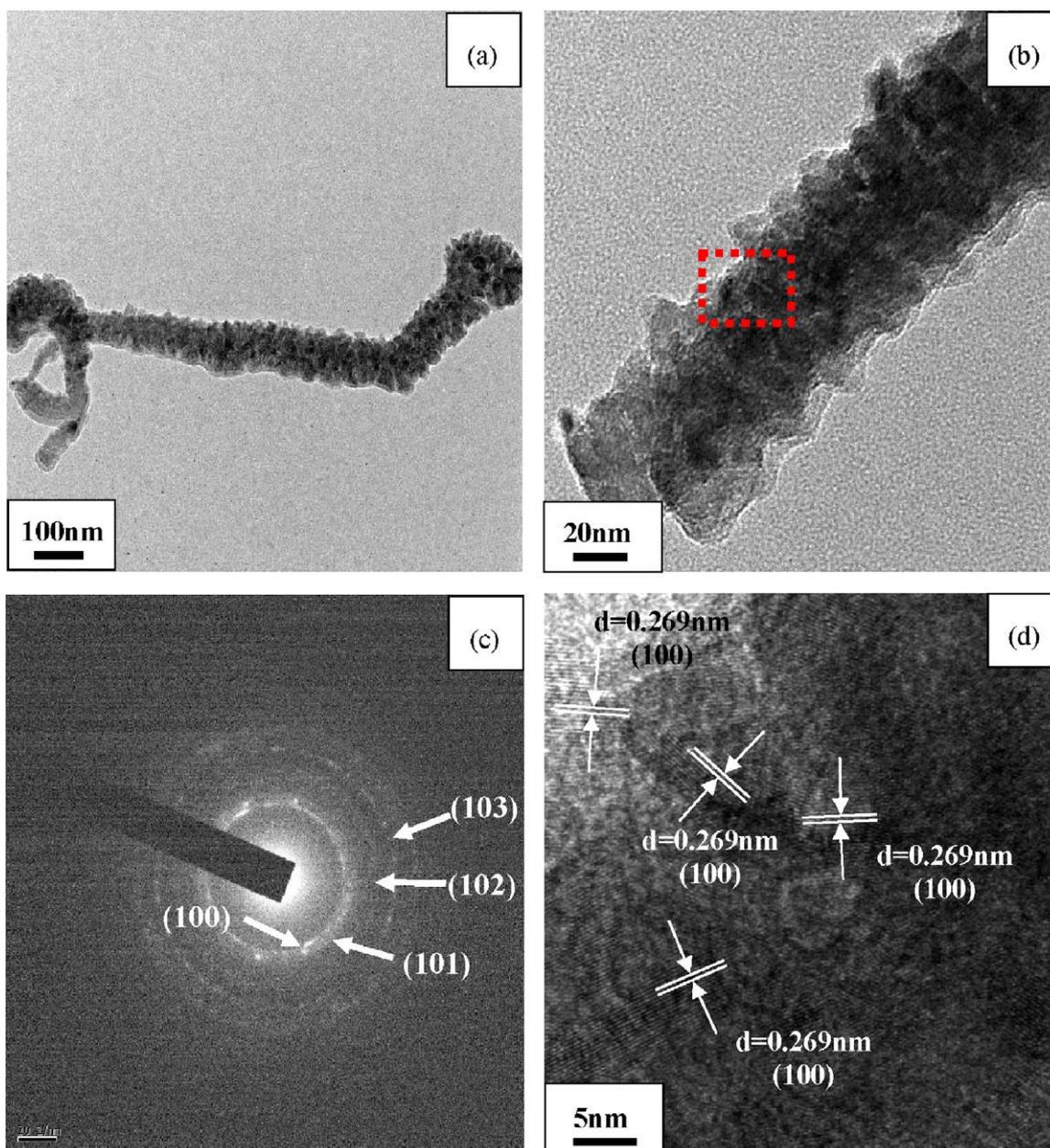
Fig. 3. (a) Low magnification TEM image of the product at 900 °C. (b) Enlarged TEM image. (c) Corresponding SAED pattern. (d) Lattice-resolved TEM image taken at the area enclosed by the dotted box in (b).

NH$_3$ gas [13], resulting in the formation of crystal seed for the growth of AlN nanowires. In addition, the experimental result reveals that the morphology of the AlN structures is dependent on the temperature, where the average diameter of the AlN 1D structures is increased as the growth temperature increases (Fig. 1). As the temperature increases, more Al vapor is produced. In this case, its partial pressure, and thus the degree of supersaturation, is increased over the substrate zone, which favors even nucleation on the structure surface. 2D or 3D growth will be facilitated and thus the diameter can be larger (Fig. 1c). On the other hand, at low temperatures, with the smaller partial pressure of Al corresponding to the small degree of super-saturation, 2D or 3D growth on the stem of the 1D structure will be suppressed, facilitating the growth of thin 1D structures (Fig. 1b). This result is in agreement with previous results in which the nanowire became thicker as the growth temperature increased [14,15].

Fig. 5a–c shows the normalized PL spectra of samples synthesized at 800, 900, and 1000 °C, respectively, exhibiting a very broad emission band. As it is known that pure defect-free AlN cannot emit visible light at room temperature [16], the emission bands are attributed to several separated defect states inside the AlN band gap [17]. A Gaussian deconvolution analysis was carried out. Regardless of the growth temperature, the PL spectra exhibit a strong emission band centered around 3.0 eV as well as a relatively weak emission shoulder around 2.4 eV.

A strong peak at 3.0 eV in the violet region was previously reported from AlN nanobelts [16], AlN nanowhiskers [18] and AlN nanocrystalline solids [13], which have been attributed to deep level defects such as nitrogen vacancies [18,19], oxygen impurities [8,20–22], and antisite defects. In more detail, the wide blue emission bands (centered at 3.0 eV) from the AlN nanopowders were ascribed to the transition from the shallow level of nitrogen vacancies (V$_N$) to the ground state of the deep level of the defect
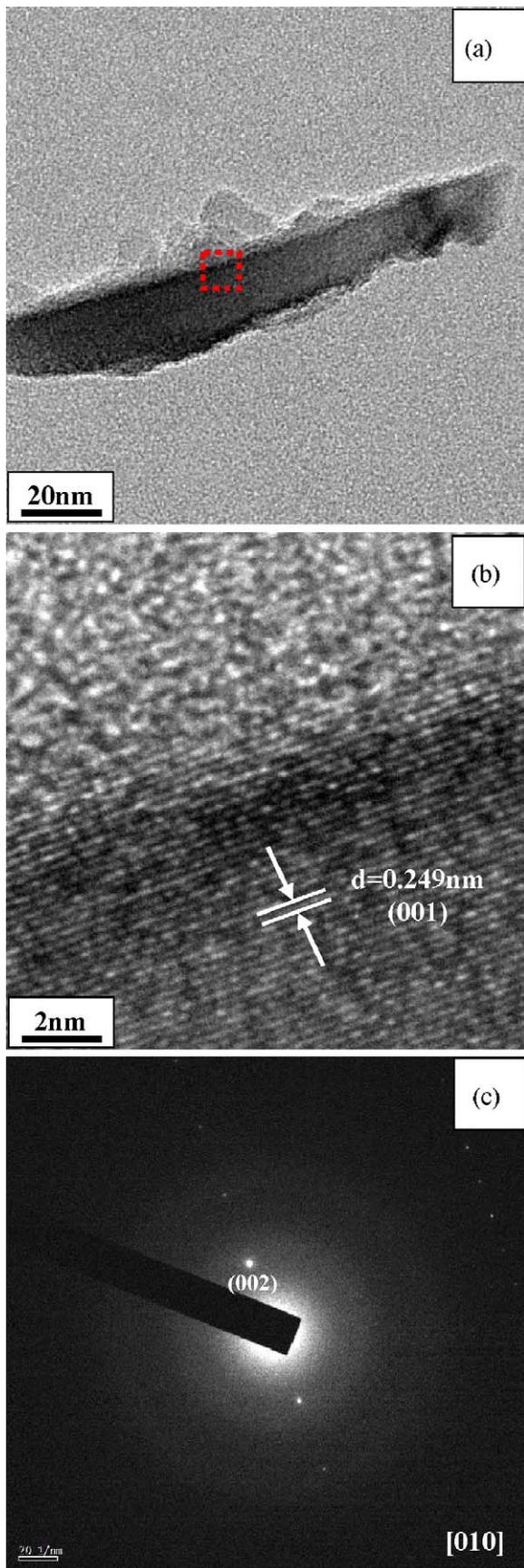
Fig. 4. (a) Low magnification TEM image of the product at 800 °C. (b) Enlarged TEM image taken at the area enclosed by the dotted box in (a). (c) Associated SAED pattern.
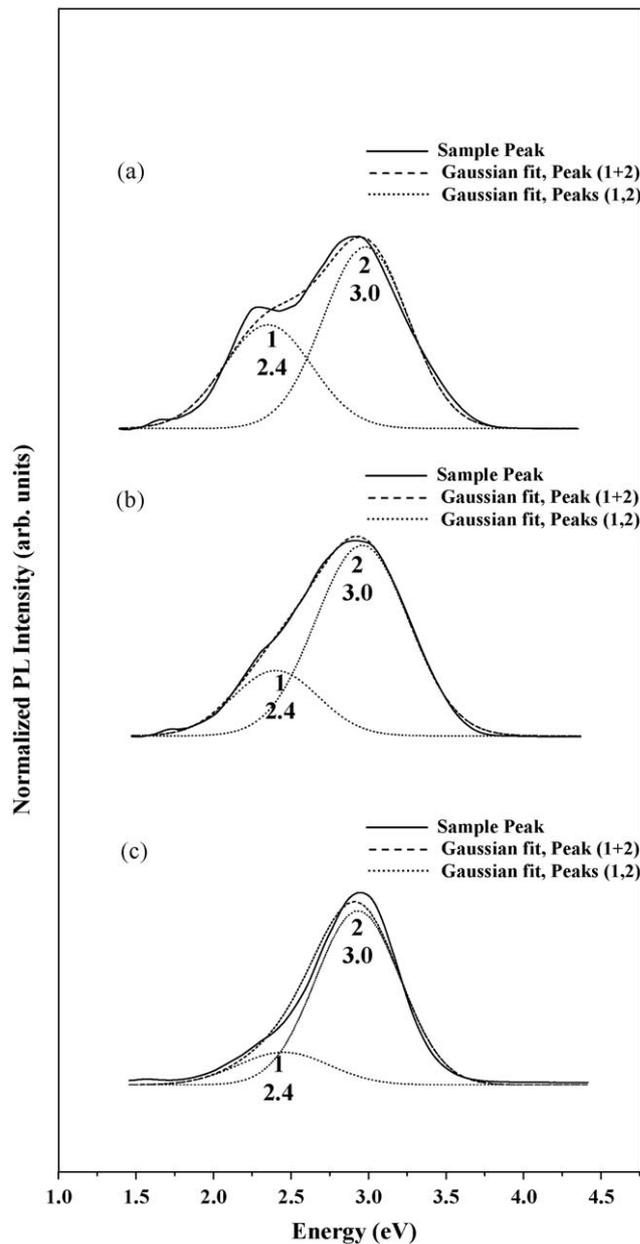

Fig. 5. Normalized PL spectra of the products synthesized at (a) 800 °C, (b) 900 °C, and (c) 1000 °C with a photoexcitation energy of 3.82 eV.

complexes $(V_{Al}^{3-}-3 \times O_N^+)$ [13,19]. In addition, a weak peak shoulder around 2.4 eV in the green region was observed. Previously, a green PL band has been observed from AlN nanoparticles [23] and AlN whiskers [18], being related to the surface defect states.

Fig. 6a exhibits the variation in the PL spectra as synthesis temperature changes, indicating that the peak intensity increases with an increase in the synthesis temperature. It was surmised that an annealing process at a relatively high temperature tends to increase the number of defects, including vacancies, which are crucial for both emissions around 3.0 and 2.4 eV. Furthermore, based on Fig. 6b, the relative intensity of the 2.4 eV peak to the 3.0 eV peak for samples synthesized at 800, 900, and 1000 °C are approximately 0.57, 0.34 and 0.19, respectively, becoming suppressed with an increase in the synthesis temperature. In this study, the relative surface-to-volume ratio of the products decreases as the synthesis temperature increases. Accordingly,
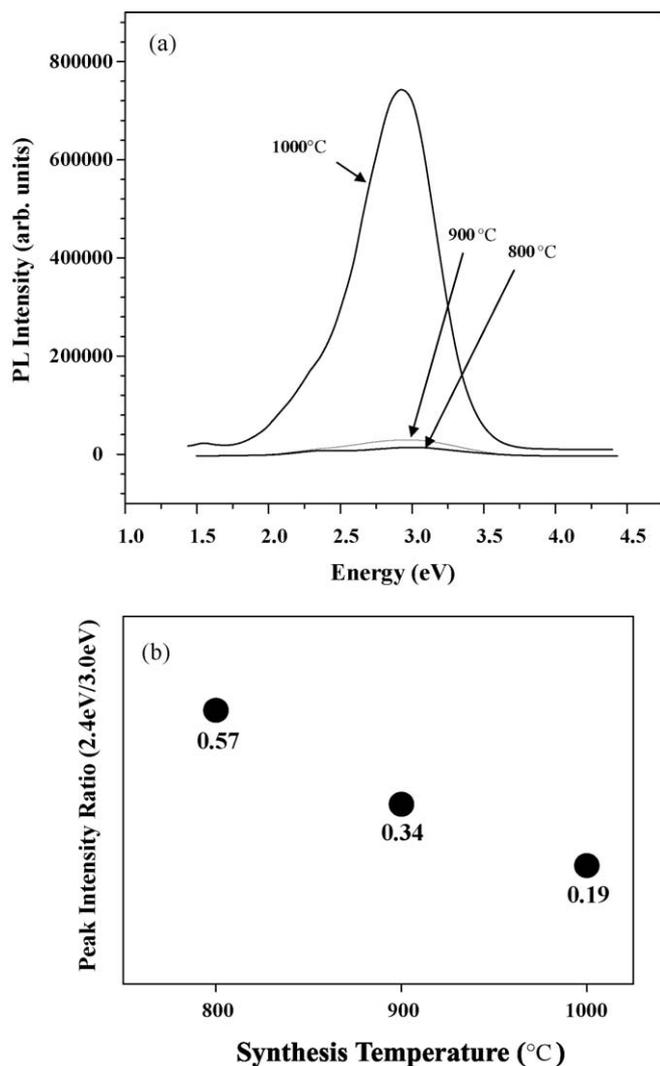
Fig. 6. (a) PL spectra depending on the synthesis temperature in the range of 800–1000 °C. (b) Variation of the peak intensity ratio (2.4/3.0 eV) while varying the synthesis temperature in the range of 800–1000 °C.

the contribution from the AlN surface to the overall PL emission will be decreased as the synthesis temperature increases, which agrees with Fig. 6b. Further systematic study will be conducted to reveal the nature of the surface-associated luminescence of AlN nanowires.

4. Conclusions

In summary, AlN nanowires were fabricated by heating Al powders under NH$_3$ ambient. SEM images indicate that the sample morphology changes as the synthesis temperature is varied and that thin nanowires form favorably at a lower temperature. XRD investigations reveal that the product consists of a hexagonal AlN structure. Lattice-resolved TEM images and SAED patterns reveal that the nanowires grown at 900 °C are comprised of a polycrystalline hexagonal wurtzite GaN structure. Due to the absence of tip nanoparticles, the growth mechanism of the AlN nanowires is mainly governed by a VS process. PL measurements with a Gaussian deconvolution process reveal that the emission spectra consist of both a 3.0 eV peak and a 2.4 eV peak regardless of the synthesis temperature. The shape of the PL emission spectra is changed as the synthesis temperature is varied. In this process, the relative intensity of 3.0 eV peak and the overall intensity increase as the synthesis temperature increases. Possible emission mechanisms were discussed.

Acknowledgement

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