

# Photoluminescence Studies of Aluminum Nitride Nanowires

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We report the production of AlN nanowires by the thermal heating method, for exploring their photoluminescence properties. The room-temperature photoluminescence properties were investigated with different annealing environment. While broad emissions with peaks at around 2.45 and 2.95 eV were obtained from both unannealed and annealed samples, the additional 2.1 eV peak was found from the annealed samples. We have suggested the possible emission mechanisms based on the assumption that both 2.45 eV peak and 2.1 eV peak are ascribed to the nitrogen vacancies. Annealing in N<sub>2</sub> environment exhibited lower intensities of 2.45 eV peak and 2.1 eV peak in comparison to those in Ar environment, presumably due to the suppression of nitrogen vacancies.

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## 1. Introduction

Aluminium nitride (AlN) is a promising material for application in electronics and optoelectronics [1]. In recent years, several researchers have reported the photoluminescence (PL) properties of nanocrystalline AlN and suggested that the efficient visible luminescence of nanocrystalline wurtzite AlN in the 2–4 eV region makes it promising materials for light-emitting applications [2, 3]. However, there has been rare report on the properties and associated mechanisms of PL emission. Along with its high surface/volume ratio and high crystallinity which is favorable for light-emitting devices, 1D nanostructures of AlN have been the focus of widespread attention due to their prospective applications in optoelectronic and field-emission nanodevices [4–6]. In the present study, a simple and effective technique was introduced, in which AlN structures are successfully fabricated via the direct reaction of Al and NH<sub>3</sub>. Since the study on the effects of the processing conditions on the optical properties contributes not only to revealing the PL mechanism but also to achieving preferred designs of optoelectronic devices, we investigated the effects of the annealing ambience on the PL of AlN nanowires.

## 2. Experimental

For preparing the AlN nanowires, Al powders were heated under flowing ammonia reactive gas (20 sccm) and argon carrier gas (100 sccm). The samples were grown on gold (Au: approximately 3 nm)-coated Si substrates in a horizontal tube furnace. Al powder and NH<sub>3</sub>

gas served as the aluminum and nitrogen sources, respectively. An alumina boat holding both the substrate and the Al powders was placed inside a quartz tube. The substrate temperatures were set to 1000 °C for 1 h. Subsequently, thermal annealing was carried out.

The samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). PL measurement was conducted at room temperature in a SPEC-1403 PL spectrometer with the 325 nm line from a He–Cd laser (55 mW).

## 3. Results and discussion

Figure 1a displays the top-view SEM image, revealing that the substrate surface is covered with a large quantity of curved 1D nanostructures. Figures 1b and c show the elemental maps of Al and N elements for a typical nanowire in inset of Fig. 1a. We reveal that nanowire is comprised of Al and N elements throughout the entire volume. Also, our previous results indicated that the nanowire is crystalline in a hexagonal AlN phase [7].

So as to study the effect of thermal annealing on the PL of AlN samples, the AlN nanowires prepared at temperature of 1000 °C are considered. In order to investigate the characteristics of the origin of the emission bands, we annealed the samples of the as-synthesized AlN nanowires in alumina tube for 1 h in N<sub>2</sub> (flow rate: 500 standard cm<sup>3</sup>/min (sccm)) and Ar (flow rate: 500 sccm) atmosphere at a temperatures of 900 °C. Figure 2a shows the PL emission spectra of the as-synthesized, Ar-annealed, and N<sub>2</sub>-annealed AlN nanowires, upon photoexcitation at 3.82 eV. Fitting the spectral feature with Gaussian functions, the best fit of the emission of Fig. 2b was obtained with two Gaussian functions, of which peaks are centered at 2.45 eV in the green region and 2.95 eV

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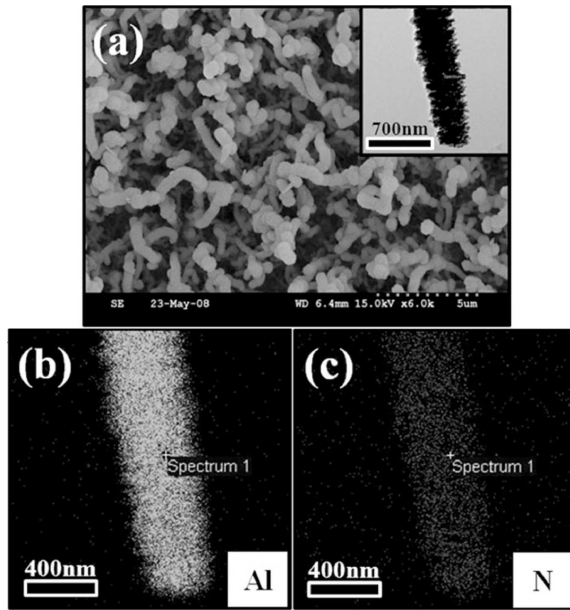


Fig. 1. (a) SEM image (inset: low magnification TEM image) and corresponding elemental maps of (b) Al and (c) N elements.

in the blue region, respectively. The green emission in AlN is known to be attributed to the N deficiency or vacancy [8], in which the radiative recombination of a photon-generated hole with an electron occupying the N deficiency is involved in the process. Also, the blue emission in AlN can be ascribed to the transition from the shallow level of  $V_N$  to the ground state of the deep level of the  $V_{Al}^{3-}-3xO_N^+$  defect complexes, while transition to the excited states of the deep level can result in the phonon structure [2]. It was revealed that  $V_{Al}^{3-}$  and  $O_N^+$  are the most favorable oppositely charged defects to be generated when the Fermi level is somewhat above the midgap, and Mattila et al. indicated the possibility of the formation of  $V_{Al}^{3-}-3xO_N^+$  defect complexes [2]. By comparing Fig. 2c with Fig. 2b, it is observed that the intensity of 2.45 eV peak is noticeably increased. We surmise that the nitrogen has been evaporated from the surface of the AlN nanowires by means of the high-temperature annealing, generating the nitrogen vacancies. On the other hand, it appears that the 2.1 eV peak in yellow region has been generated by the Ar annealing. It is generally known that the low-energy emission is related to crystal defects or defect levels associated with nitrogen vacancy, aluminium interstitials, or oxygen-related defects ( $O_N^+$ ) [8]. In particular, the yellow emission in AlN is ascribed to oxygen point defects ( $O_N^+$ ) [8]. We suppose that the oxygen in ambience can be incorporated into the N vacancy sites during the thermal annealing. The oxygen point defects in AlN could easily take the place of N to generate deep level.

Figure 2d shows the PL spectrum of  $N_2$ -annealed sample, which was convoluted with three Gaussian func-

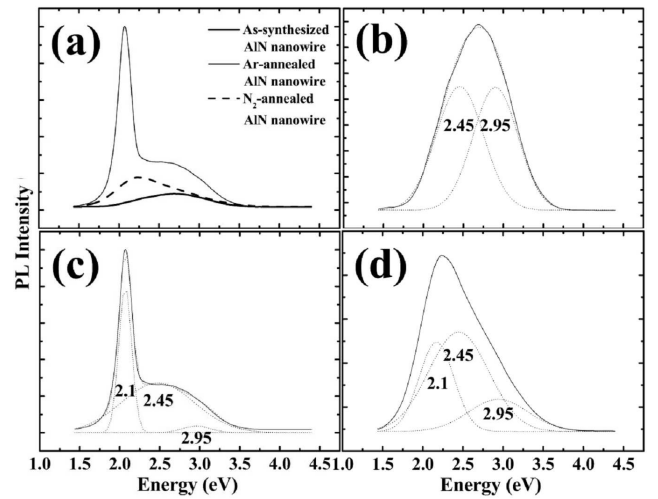


Fig. 2. (a) Room-temperature PL spectra of AlN nanowires. Gaussian convolution analysis for (b) as-synthesized, (c) Ar-annealed, and (d)  $N_2$ -annealed samples.

tions. Also, Fig. 3 shows the integrated PL intensities of 2.1 eV, 2.45 eV, and 2.95 eV peaks for as-synthesized, Ar-annealed, and  $N_2$ -annealed samples. By comparing  $N_2$ -annealed sample with Ar-annealed one, we observe that the PL intensities of 2.45 eV peak and 2.1 eV peak have been significantly reduced by changing the ambience from Ar to  $N_2$ . The  $N_2$  ambience reduced the amount of the N vacancies in AlN nanowire, suppressing the 2.1 eV peak as well as the 2.45 eV.

By the way, Fig. 3 indicates that the 2.95 eV peak is almost invariant by the thermal annealing, presumably due to the complicated nature of the emission mechanism. Further systematic study is underway.

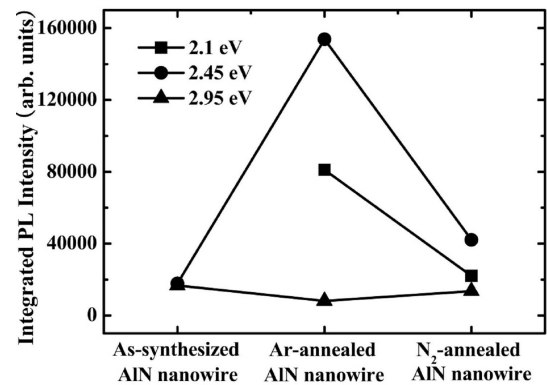


Fig. 3. Integrated PL intensities of 2.1 eV, 2.45 eV, and 2.95 eV peaks for as-synthesized, Ar-annealed, and  $N_2$ -annealed samples.

In conclusion, we have synthesized AlN nanowires by the thermal heating method, for investigating the PL properties. We have studied the PL properties by the thermal annealing in both Ar and  $N_2$  ambience and by

conducting PL measurements at room temperature with the photoexcitation at 3.82 eV. Gaussian fitting analysis on as-synthesized sample reveals the existence of 2.45 and 2.95 eV centered bands. By annealing in Ar ambience, not only the 2.45 eV peak was intensified but also the 2.1 eV peak was newly generated. Also, changing the annealing ambience from Ar to N<sub>2</sub> reduced the intensities of 2.45 eV and 2.1 eV peaks. We have explained the involved PL mechanisms in terms of the nitrogen vacancies in AlN nanowires.

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