Formation mechanism and photoluminescence of AlN nanowhiskers

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Abstract
Aluminium nitride (AlN) nanowhiskers were synthesized on Si substrate by an oxide-assisted vapour transport and condensation method at 900 °C. Electron scanning microscope observations reveal that the whisker-like nanostructured architectures are composed of nanotips growing out from the surfaces of central sphere-like cores. The stem diameter of the nanotip is ∼100 nm and decreases with increasing distance from the core. The formation mechanism of the nanowhiskers is discussed on the basis of structural characterization. It is inferred that Fe2O3 plays an important role in the relatively low temperature growth of the AlN nanowhiskers. The photoluminescence of the nanowhiskers shows a broad blue luminescence band which can be Gaussian divided into three subbands. Spectral examinations and analysis reveal that the three subbands are connected with nitrogen vacancy, oxygen impurity and surface luminescence, respectively. The successful growth of AlN nanowhiskers would provide significant applications in modern optoelectronic and luminescence nanodevices.

1. Introduction
As an important semiconductor with the largest band gap (6.2 eV) among group III nitrides, aluminium nitride (AlN) has attracted much attention due to its excellent properties, such as high thermal conductivity, low coefficient of thermal expansion which closely matches that of silicon, excellent mechanical strength and chemical stability [1]. Hence in the past several years, considerable efforts have been devoted to synthesis of AlN nanostructures including nanoparticles [2], nanorods [3, 4], nanobelts [5], nanotubes [6], oriented columns [7], straight and zigzag nanowires [8, 9] and nanoneedle arrays [10]. It is also known that AlN has a small electron affinity value ranging from negative to 0.6 eV [11, 12], which means that electrons can be easily extracted from the surface to vacuum when an electric field is applied, thereby giving rise to a large field emission current density which is most attractive for field emission applications [13]. As a result, significant effort is being devoted to reducing the tip size and increasing the density of the emitting sites by using hierarchical nanostructures [12]. As nanowhiskers are filamentary crystals, possessing a high emitter density, large aspect ratio and large contact proportion with the substrate, they have potential applications in field emission devices. In addition, due to the unique physical and chemical performance of AlN nanowhiskers, the strength and toughness of materials (ceramics, glass, polymer, etc) compounded with nanowhiskers will be greatly improved. Until now, there have been many methods of growing AlN whiskers and single crystals. The earliest report about the growth of AlN whiskers is Kohn’s experiment [14, 15]. Taylor and Lenie [16] synthesized AlN nanowhiskers through the sublimation method. Fu et al [15] fabricated AlN whiskers by the carbothermal reduction and nitridation (CRN) method using a mixture of Al2O3 with carbon. However, these methods require high temperature and long reaction time, which prevent them from being widely adopted. He et al [3] and Liu et al [17] have observed the intense luminescence of AlN nanostructures and attributed the emission band to defects. However, this assignment is apparently incomplete due to scarce knowledge about structural properties of nanostructural AlN, especially the nature of defects.

In this work, we report a convenient chemical vapour deposition (CVD) technique, using Al powders and N2/NH3
as the metal and nitrogen sources, together with additional Fe₂O₃ powder that plays a crucial role in lowering the synthesis temperature, to fabricate AlN nanowhiskers at a low temperature of 900 °C. Scanning electron microscope (SEM) observations reveal that the whisker-like nanostructured architectures consist of nanotips growing out from the surfaces of central sphere-like cores. The stem diameter of the nanotip is ~100 nm and decreases with increasing distance from the core. The photoluminescence (PL) measurement discloses that the AlN nanowhiskers have a broad blue emission band, which can be Gaussian divided into three subbands. On the basis of spectroscopic analysis, we assign the three subbands to defect-related emissions. The obtained results suggest the potential applications of the nanowhiskers in modern optoelectronic and luminescence nanodevices.

2. Experimental procedure

AlN nanowhiskers were synthesized in a conventional electric resistance furnace with a horizontal quartz tube. The mixture of Al and Fe₂O₃ powders (3 : 1 in weight) was used as raw material and placed in a ceramic boat which was set at the centre of the quartz tube. A Si substrate (1.5 x 2.5 cm²) was placed downstream of the gas flow at a distance of 4.5 cm from the boat in order to collect the growth product. After evacuation of the quartz tube to 1–2 Pa, argon gas was introduced into the alumina tube to remove the residual oxygen before the furnace was heated. The reaction was carried out at 900 °C and NH₃/N₂ was introduced at a rate of 150 sccm for 90 min. Then the furnace was naturally cooled down to room temperature under the flow of Ar, and a layer of white product was obtained on the surface of the Si substrate. The phase purity of the as-prepared product was examined using powder x-ray diffraction (XRD) with Cu Kα radiation from 30° to 80° (2θ) in steps of 0.03° (λ = 0.154 nm). A field emission SEM (JEOL JSM-7000F) was used to observe the morphology of the as-prepared product. In addition, we use ultrasonic vibration to detach nanowhiskers from the substrate and disperse them in alcohol. Then the suspension was dropped onto a copper grid covered with carbon film for further high resolution transmission electron microscope (HRTEM, JEOL JEM-4000EX) characterization. The PL spectrum was measured on a Fluoro Tau-3 fluorescence spectrophotometer (Jobin Yvon Company) with a 450 W Xe lamp as light source. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source of Mg Kα = 1253.6 eV. All the measurements were run at room temperature.

3. Experimental results and analysis

The structure of the as-grown product was determined by analysing the XRD pattern. As shown in figure 1, all the diffraction peaks can be identified to be connected with hexagonal wurtzite-structured AlN crystal with lattice constants a = 0.3114 nm and c = 0.4978 nm (Joint Committee Powder Diffraction Standard (JCPDS) data file Card (No 25-1133)). No characteristic peak associated with other crystalline forms was detected in the XRD pattern. This result suggests that the product obtained from the Si substrate contains only the crystalline phase of AlN and other phases should be below the detection limit of the XRD.

The low-magnification SEM image of the as-synthesized product is displayed in figure 2(a). One can see that the as-synthesized product consists of a large number of uniform nanostructures. These whisker-like nanostructured architectures are composed of nanotips growing out perpendicularly from the surface of central spheres. The enlarged SEM image in figure 2(b) presents more details on the morphology of the AlN nanowhiskers. It can be observed that the AlN nanowhiskers with an average stem diameter of ~100 nm gradually become thinner with increasing distance from the central sphere and finally form a sharp tip. The length of a typical nanowhisker is ~1 μm. In addition, many small crystallites exist on the surfaces of the nanowhiskers,
which makes the nanowhisker have a rough surface. Here we should mention that further SEM morphology characterization of these nanostructures was rather difficult due to complicated structures of these nanowhiskers. For the same sample, we also found different morphologies of the whisker-like architectures, as exhibited in figure 2(c). It shows many intact spheres, on which many nanowhiskers grow, just like those observed in figure 2(a). Figure 2(d) shows the enlarged view of a separate sphere. The diameter of the sphere is about 1 μm and the lengths of the nanowhiskers are shorter than those observed in figure 2(b). Considering that the product formation is sensitive to temperature in the CVD process, we attribute the differences in morphology between figures 2(a) and (b) to gradient temperature distribution on the same substrate.

A typical HRTEM image of a single nanowhisker is shown in figure 3(a), from which we can see that each whisker consists of a main trunk (nanowhisker core) and secondary branches (nanotips). The nanowhisker cores extend throughout the entire length, whereas the nanotips grow on the surfaces of the nanowhisker cores in the radial direction. Some reports have pointed out that the formation of these nanotips (parasitic nucleations) depends on the fabrication conditions. In our experiments, we found by preliminary experiments that increasing the growth temperature or/and the gradient temperature distribution on the same substrate.

Our experimental results suggest that the use of Fe2O3 may play a key role in the relatively low temperature growth of the nanowhiskers. In the previous report, Balkas and Davis [18] obtained GaN powder through an intermediate product of Ga2O, which can be formed from a mixture of Ga (I) and Ga2O3 (s) via the reaction

\[ 4\text{Ga}(l) + \text{Ga}_2\text{O}_3(s) \rightarrow 3\text{Ga}_2\text{O}(g). \]  

(1)

However in the synthesis of AlN, Al2O vapour is difficult to obtain at low temperature because Al2O3 is hard to be reduced by Al or carbon due to its very low Gibbs free energy (1777 kJ mol\(^{-1}\) at 1000 K) [19]. According to the thermal mechanic calculation, the change of Gibbs free energy (\(\Delta G\)) in the reaction [20]

\[ 6\text{Al}(l) + \text{Fe}_2\text{O}_3(s) \rightarrow 3\text{Al}_2\text{O}(g) + 2\text{Fe}(s). \]  

(2)

can be determined to be -106.69 kJ mol\(^{-1}\) (1000 K), indicating that it is easy to reduce Fe2O3 by Al at 1000 K. Therefore, Fe2O3 instead of Al2O3 was engaged in our experiment as the oxidizer and thus can significantly facilitate the reaction. We discuss the formation mechanism of the nanowhiskers below. During the temperature-rising stage, Al2O was synthesized and carried by Ar from the alumina boat onto the Si substrate to form lots of small Al2O droplets (figure 4 (I, a)), which become bigger with increasing reaction temperature (figure 4(I, b)). This is similar to the formation of Mg or Ga droplets on a Si substrate [21–23]. When Ar is switched to reactive NH3/N2 at 900 °C, atomic nitrogen from decomposed ammonia became dissolved into these Al2O droplets via the following reaction:

\[ \text{Al}_2\text{O} + 2\text{NH}_3 \rightarrow 2\text{AlN} + \text{H}_2\text{O} + 2\text{H}_2. \]  

(3)

Due to the low solubility of nitrogen in Al2O droplets at the reaction temperature, the direct nitridation and supersaturation led to multiple nucleation of AlN crystals on the surfaces of the Al2O droplets (figure 4(I, c)). AlN nanocrystals were thus formed but did not propagate laterally probably due to its low solubility and low wetting characteristics with respect to the molten Al2O droplet, ensuring the 1D growth perpendicular to the droplet surface [21]. It is seen that Al2O droplets served as the nucleation sites for the growth of AlN nanowhiskers. For AlN with a wurtzite structure, the (0 0 1) plane is the closest-packed plane in the crystal, and stacking along the [0 0 1] direction therefore becomes energetically favourable. Under these conditions, the growth of the nanowhiskers along the [0 0 1] direction was favoured. Meanwhile, the molten Al in the ceramic boat would react with NH3:

\[ 2\text{Al}(l) + 2\text{NH}_3(g) \rightarrow 2\text{AlN}(s) + 3\text{H}_2(g). \]  

(4)

So, after the basal growth of the 1D AlN nanostructures, the vapour–solid epitaxy growth at the top sites along the whiskers also happened through the condensation of AlN species from...
the reaction of gaseous Al with NH$_3$, which formed a lot of nanocrystallites on the surface of the tips (figure 4(I, d)). With the prolongation of the reaction process, the vapour pressure of gaseous Al and Al$_2$O was gradually decreased due to the surface nitridation of the Al precursor in the boat. This resulted in gradual attenuation of the 1D nanostructures and thus the formation of AlN nanowhiskers consisting of nanocrystallites (figure 4(I, e)). We should stress here that the temperature is an important factor influencing the morphology, size and crystallinity of the synthesized product in the CVD process. In the lower temperature region, the reaction is slower and forms a small number of separate droplets (figures 4(II, a and b)). As Ar gas was switched to NH$_3$/N$_2$ at 900 °C, the AlN crystals nucleated from the Al$_2$O droplets and the Al$_2$O/Al vapours (figure 4(II, c)). These small nanocrystallites also provided the further nucleation sites (figure 4(II, d)). As the process evolves, the Al$_2$O and Al vapours decreased and formed intact but separate spheres with nanowhiskers on the surfaces for nitridation of the Al precursor in the boat (figure 4(II, e)).

It is known that nanostructure AlN are promising for light-emitting applications due to their efficient visible luminescence in the 2–4 eV region [24, 25]. The room temperature PL spectrum of the AlN nanowhiskers taken under excitation with the 300 nm line of a Xe lamp is displayed in figure 5. The PL spectrum has a broad emission band ranging from ultraviolet (416 nm, 2.98 eV) to yellow (564 nm, 2.20 eV). It is generally believed that the low-energy emission is related to crystal defects or defect levels associated with nitrogen vacancy, oxygen-related centres (O$_N$)$^-$, or aluminium interstitials that have formed during growth. One may enquire how these emission bands radiatively recombine for photoexcited carriers because the excitation energy is less than the band gap of AlN. In fact, this is understandable because the presence of various defects/impurities could cause drastic defect/impurity excitations. These excitations do not need larger energy than the band gap. The broadband is obviously asymmetric indicating that the PL band should have more than one origin. To clarify its origin, the broad PL band is Gaussian divided into three subbands in the green and violet regions. Furthermore, no obvious position shifts but the intensities of the three subbands can be observed with changing the excitation wavelength, which reflects their defect-related origins. Jenkins and Dow [26] calculated the band structure of AlN and predicted that the energy of the nitrogen vacancy lies deep within the band gap. According to the calculation result, the subband at 416 nm is supposed to be likely associated with the vacancies of N in the AlN nanowhiskers. In our experiments, the nanowhiskers are formed at a relatively low temperature, and hence more nitrogen vacancies exist in the sample. We found that if the surface of the sample was changed, the 416 nm band follows a slight change in intensity, indicating that the vacancy defects are mainly local in the nanowhisker/nanotip cores. Youngman et al [27] reported that AlN single crystals grown under nitrogen-deficient conditions show a broad band in the blue region, consistent with our assignment. For our samples, we clearly observed the existence of oxygen by measuring the XPS spectrum. The inset of figure 5 shows the O 1s XPS spectrum. (This figure is in colour only in the electronic version)
existence of oxygen impurities in the sample. Notably, a green emission subband at around 564 nm is observable, which is most reasonably attributed to the surface luminescence of AlN nanowhiskers, because the positions and the intensities of this band trace well with the change of the sample surface. From the growth feature of our samples, we infer that the surface luminescence centres should be Al-rich surface defect states. Obviously, this band is morphologically related. A similar situation also occurs in the PL spectrum centred at around 533 nm which was observed in the AlN nanospheres [24].

According to the above defect features, we may easily seek a method to enhance the currently observed PL intensity. Xu et al [30] have recently studied the PL of F-passivated ZnO nanocrystalline films. They found that the presence of residual F ions in ZnO nanocrystalline film can dramatically decrease the visible emission and increase the ultraviolet emission. A possible mechanism is that some of the F ions passivate the surface defect states of ZnO nanocrystal, which prevents the holes in the valence band from being trapped in surface states and then tunnelling back into nanocrystals to combine with another source of visible emission. To date we have not conducted such work. However, this idea gives us some enlightenment, that is, enhancement of the emissions can be achieved by passivating the surface states. This will make more electrons and holes excited from the cores to radiatively recombine in the defect states of the cores.

4. Conclusions

AlN nanowhiskers have been successfully prepared by a simple oxide-assisted vapour transport and condensation method. The presence of Fe2O3 lowers the growth temperature of AlN nanowhiskers, and a five-stage growth mechanism is thereby deduced on the basis of detailed structural characterization. A blue emission band centred at 480 nm is observed, and assigned to optical transition from the level of $V_\text{N}^+$ to the ground state of the deep level of [V$_\text{Al}$]$^-$ $3 \times O_\text{N}$] defect complex. The subbands at 416 nm and 564 nm may be connected with nitrogen deficiencies and surface defect, respectively. The unique structure and light emission properties of the nanowhiskers suggest their potential applications in field emission and luminescence nanodevices.

Acknowledgments

This work was jointly supported by the Grants (Nos 60576061, 60476038, and BK2006715) from the National and Jiangsu Natural Science Foundations. Partial support was also from the State Key Program for Basic Research of China under Grant No 2006CB921803 and the City University of Hong Kong Strategic Research Grant No 7002138.

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