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An array of Eiffel-tower-shape AlN nanotips and its field emission properties

Yongbing Tang, Hongtao Cong, a) Zhigang Chen, and Huiming Cheng
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People’s Republic China

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An array of Eiffel-tower-shape AlN nanotips has been synthesized and assembled vertically with Si substrate by a chemical vapor deposition method at 700 °C. The single-crystalline AlN nanotips along [001] direction, including sharp tips with 10–100 nm in diameter and submicron-sized bases, are distributed uniformly with density of $10^8$–$10^9$ tips/cm$^2$. Field emission (FE) measurements show that its turn on field is 4.7 V/µm, which is comparable to that of carbon nanotubes, and the fluctuation of FE current is as small as 0.74% for 4 h. It is revealed this nanostructure is available to optimize the FE properties and make the array a promising field emitter. © 2005 American Institute of Physics. [DOI: 10.1063/1.1941462]

The promise that nanostructures may dramatically improve some desired properties of materials for many applications has stimulated great enthusiasm in synthesizing nanostructures of different shapes. 1–3 Owing to their unique geometries of small curvature radius, nanotips have attracted significant interests for various potential applications, such as probes for atomic force microscopy (AFM), tips for nanoinducers, and field emission sources. Practically, using these nanostructures demands that nanotip has excellent mechanical properties (strength, hardness, and toughness), thermal, and chemical stability. Meanwhile, aligning these nanostructures in a certain direction is vital to both fundamental investigations and practical applications.

As a III-V group wide-band-gap semiconductor, aluminum nitride (AlN) has found applications as electrical materials due to its high thermal conductivity, low coefficient of thermal expansion which closely matches that of silicon, excellent mechanical strength and chemical stability. 4 In addition, with very low values of electron affinity ranging from negative to 0.25 eV, 5–7 AlN is a promising candidate for field emission device applications because electrons in the materials with small electron affinity can be easily extracted from the surface to vacuum when an electric field is applied. It has also been reported that field electron emission could be enhanced when sharp emitters were coated with an AlN film. 5 It should be noted that AlN nanostructures (nanotubes or nanowires) were fabricated above 1000 °C by various methods such as arc-discharge, 9,10 carbon nanotubes confined reaction, 11,12 template-directed method, 13 and direct nitridation of Al powders. 14,15 However, there are few reports about synthesis in lower temperature and field emission (FE) properties of AlN nanotip arrays, and the reported AlN nanostructures have to be further assembled with other components to form useful devices.

Here, we report that an array of Eiffel-tower-shape single-crystalline AlN nanotips has been synthesized and assembled vertically with Si substrate by a simple chemical vapor deposition (CVD) method at 700 °C. This special nanostructure can effectively optimize FE properties. Compared with the other AlN nanostructures in previous reports, 10,11 the nanotip array is expected to be more suitable to serve as devices such as field emitter, probes of AFM, etc.

The synthesis was carried out in a conventional electric resistance furnace with a horizontal alumina tube. The mixture of Al and Fe$_2$O$_3$ nanoparticles (less than 100 nm in size and 3:1 in weight) was used as the raw material and placed in a ceramic boat which was set at the center of the alumina tube. A Si substrate (1.5 × 4 cm) was deposited downstream of the gas flow with a distance of 4.5 cm from the boat in order to collect growth product. Argon gas was introduced into the alumina tube to minimize any other side reaction before the furnace was heated to the reaction temperature. The temperature of Al source was maintained at 700 °C and NH$_3$ was introduced at a rate of 125 scm for 80 min. After the furnace was cooled down to room temperature, a layer of light-yellow product was found on the surface of the Si substrate and it was collected for later characterization. The phase purity and crystal structure of the product were detected by x-ray diffraction (XRD, Regaku D/max-2400). A field emission scanning electron microscopy (SEM, JEOL JSM-6301F) equipped with an energy dispersive spectroscopy (EDS, Link ISIS, Oxford) was used to observe the morphology and to analyze the elemental composition of the as-prepared product. Further detailed structural characterization was performed on a high resolution transmission electron microscopy (HRTEM, JEOL JSM-2010).

![FIG. 1. XRD spectrum of the product detached from the Si substrate.](https://example.com/xrd_spectrum.png)
Figure 1 shows XRD spectrum of the product detached from the Si substrate after reaction at 700 °C for 80 min. All the strong reflection peaks of the XRD pattern can be readily indexed to hexagonal wurtzite-structured AlN with lattice constants of $a=3.114\,\text{Å}$ and $c=4.979\,\text{Å}$ (JCPDS: No. 25-1133). No characteristic peak associated with other crystal-line forms was detected in the XRD pattern. These results suggest that the product obtained from the Si substrate contains indeed only one crystalline phase of AlN and the other crystalline phases are below the detection limit of the XRD.

Some typical SEM images of the as-synthesized product are shown in Figs. 2(a)–2(d). It is very interesting that the morphology of the product shows an Eiffel-tower-shape nanostructure, that is, nanotip, as shown in Fig. 2(a). Most of the deposited AlN nanotips are oriented vertically with respect to the Si substrate [Fig. 2(b)]. Independent of their size, AlN nanotips are always composed of two parts, a submicron-sized base and a sharp tip. As shown in Fig. 2(c), the base is a polygonal pyramid with a few hundred nanometers in size, and the sharp tip is 10–100 nm in diameter and ~1.0 µm in length. The EDS spectrum [Fig. 2(d)] indicated that these nanostructures only consisted of Al and N elements.

A typical transmission electron microscopy (TEM) image of a nanotip is shown in Fig. 3(a), which was taken along one of its side surface perpendicular to the electron beam. Selected area electron diffraction (SAED) pattern [Fig. 3(b)] taken from the region marked by a dot circle in Fig. 3(a) can be indexed as that of single-crystalline wurtzite AlN recorded along the [010] zone axis. Figure 3(c) presents the corresponding HRTEM image which was taken near the edge and along the length of this tip. The spacing between any two adjacent lattice fringes (0.25 nm) corresponds to that of the (002) lattice planes of the hexagonal AlN. The axis of the tip is also perpendicular to the lattice plane (002), that is to say, the axis direction of AlN nanotips is generally along [001]. Both the HRTEM and SAED results demonstrate that the as-grown nanotips are single-crystalline growing along [001] direction of AlN hexagonal wurtzite structure.

The FE measurements were carried out inside a ball-type chamber which was pumped down to $5.0\times10^{-9}\,\text{Torr}$ by an ultrahigh vacuum system. The anode was a cylinder-shaped platinum probe (1 mm in diameter) and the cathode was AlN nanotip array, with a distance of 100 µm. High voltage was supplied by a power source (Keithley 248) and the current under increasing applied voltage which varied with a step of 10 V was recorded by a sensitive electrometer (Keithley 6514) with an accuracy of $10^{-11}\,\text{A}$. Figure 4(a) shows the measured FE current as a function of the applied voltage and the corresponding Fowler–Nordheim (FN) plot (the inset) of
AIN nanotip array. It can be seen that the emission started at 320 V, and the anode current reached 81 nA as the voltage was increased to 470 V. Here, we define the turn-on field ($E_{\text{to}}$) and the threshold field ($E_{\text{th}}$) as the electric fields required to produce a current density of 10 µA/cm² and 10 mA/cm², respectively. Since the emission area was 0.78 mm², the $E_{\text{to}}$ and the $E_{\text{th}}$ for the AIN nanotip array were 4.7 and 10.6 V/µm, respectively. Taniyasu et al.⁷ obtained a field of 23 V/µm at 9.5 µA/cm² for Si-doped AlN film, which is about five times higher than our result. The $E_{\text{th}}$ of AIN nanotip array is comparable to the reported values of carbon nanotubes.¹⁶,¹⁷ The reason for the low turn-on electric field and high FE current density are probably due to single-crystalline structure and nanosize of the emitter. Many researchers reported that in order to avoid a field screening effect, aligned nanostructures with low density was favored.¹⁸ The density of our AIN nanotip array was relatively low, ~10⁶–10⁷ tips/cm². Therefore, low value of $E_{\text{to}}$ and high value of FE current were obtained.

The FE current–voltage characteristics were analyzed by using the FN equation:¹⁹
\[
I = (1.54 \times 10^{-10})\beta V^2A/d^2\phi \times \exp(-6.83 \times 10^3 \phi^{3/2}d/\beta V),
\]
where $I$ is current, $V$ is applied voltage, $\phi$ is work function of the emitting material, $\beta$ is field enhancement factor, $A$ and $d$ are the area of emission and the distance between the anode and the cathode, respectively. The inset in Fig. 4(a) shows the FN plot of $\ln(I/V^2)$ vs $1/V$. The plot has an approximately linear relation within the measurement range, which confirms that the current indeed results from field emission. The field enhancement factor $\beta$ can be calculated from the slope of the FN plot if the work function of the emitter is known. Based on the reported value of work function of AlN (3.9–5.35 eV),²⁰ the estimated $\beta$ value varies from 1175.5 to 1888.7, which is enough for various applications of field emission. The $\beta$ factor is highly dependent on the geometrical shape of the emitter.²¹ Such high $\beta$ value is attributed to geometrical features of the front end of AlN nanotip, including high aspect ratio and nanosized sharp tip.

Figure 4(b) shows the result of FE current versus time for a period over 240 min at a pressure of 5.0 × 10⁻⁹ Torr under the fixed applied voltage of 1060 V for an initial current 77.89 µA. The average current and the standard deviation were calculated to be 77.53 and 0.57 µA, respectively. The ratio of them was as low as 0.74%, which proves the high current stability of AIN nanotip. Such low fluctuation has not been reported for AlN material. Yin et al.¹⁴ reported a fluctuation of 7% for hierarchical AlN comb-like nanostructures. A fluctuation of 5.5% for heavily Si-doped AlN has been reported by Taniyasu et al.⁷ When an electric field is applied to an emitter, much heat is generated at the sharp end of it because of high current density.²² Therefore, the FE device will exhibit poor stability if the emitter has not good thermal stability. The submicron-sized bases of our nanostructures have such a large connection area that they can quickly transfer the heat from the tip to the Si substrate, so the tip can be effectively protected from being destroyed due to the superheat. Furthermore, the observed high stability of the FE current is also attributed to the little change of the emission site which is the effect of the strong combination between the bases of AlN nanotips and the Si substrate.

In summary, an array of Eiffel-tower-shape AIN nanotips has been successfully synthesized and aligned vertically on Si substrate at 700 °C. The single-crystalline AIN nanotips along [001] direction, including sharp tips with 10–100 nm in diameter and submicron-sized bases, are distributed uniformly with density of 10⁶–10⁷ tips/cm². Its turn-on field is 4.7 V/µm for driving a current density of 10 µA/cm², which is comparable to that of carbon nanotube. Moreover, the fluctuation of field emission current with density of 10 mA/cm² for 4 h is within 1%. The low turn-on field and the small fluctuation of field emission current indicate Eiffel-tower-shape AIN nanotips assembled well with Si substrate would suitable to serve as devices such as field emitters, probes of AFM, etc.

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