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Field emission from honeycomblike network of vertically aligned AlN nanoplatelets

Y. B. Tang, H. T. Cong,[a] and H.-M. Cheng
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

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Honeycomblike network of vertically aligned AlN nanoplatelets was synthesized on etched Si substrate via a simple vapor phase method without catalyst. The nanoplatelets are hexagonal wurtzite AlN and their thickness is 10–100 nm. Field emission (FE) measurements showed that this nanostructure has a low turn-on field of 3.2–5.0 V/μm and a threshold field of 7.8–12.1 V/μm at sample-anode distances of 50–100 μm. The fluctuation of FE current with density of 10 mA/cm^2 over 5 h is lower than 3%. The low turn-on and threshold fields and the small fluctuation of current demonstrate that this two-dimensional AlN nanostructure is a promising FE material. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2337277]

Owing to its low electron affinity, good mechanical properties, and excellent thermal and chemical stabilities, aluminum nitride (AlN) is a good material for field emission (FE) applications.[1–3] 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.[4,5] Recently, AlN nanostructures were found to have better FE performances than conventional AlN materials.[6–10] In recent years, many kinds of AlN nanostructures have been synthesized, mainly one-dimensional (1D) ones such nanotubes,[6,11,12] nanowires,[13–15] nanotips,[7–10] etc. However, the report of two-dimensional (2D) AlN nanostructures such as nanowalls, nanoplatelets, and nanosheets is relatively rare. The nanoscale size and large surface area of 2D nanostructures may provide opportunities for several potential applications such as field emitters, gas sensors, and electrodes for fuel cells. Field emission properties of nanobelts of some materials MnO_3,[16] CuO,[17,18] SnO_2,[19] and so on, have been extensively investigated in recent years. In this work, we synthesized a honeycomblike network of vertically aligned AlN nanoplatelets on Si substrate via a simple vapor phase route without catalyst, and then studied its FE properties. The good FE performance showed that this 2D nanostructure is a promising candidate for FE application.

AlN nanoplatelets were synthesized in a horizontal tube furnace by heating the mixture of Al and $AlCl_3$ powders in the flow of N_2. Briefly, a Si wafer (2×3 cm) was used as the substrate, which was etched using 2% hydrofluoric acid for ~5 min and ultrasonically cleaned by acetone and deionized water several times to remove silicon oxide from its surface. An alumina boat containing a mixture of Al (1.0 g) and $AlCl_3$ (0.5 g) powders was placed at the center of a small quartz tube which then was transferred to the center of the tube furnace, and the Si substrate was placed in a ceramic boat and deposed downstream of the gas flow with a distance of ~15 cm from the reactants. The furnace was then pumped to 2.0×10^{-2} Torr and purged with a constant Ar flow of 100 SCCM (standard cubic centimeter per minute at STP). The Ar gas was substituted by N_2 (50 SCCM) as the furnace was heated to 1200 °C at a rate of 30 °C/min. The reaction was maintained for 1 h at a pressure of 3 Torr. After the furnace was naturally cooled down to room temperature under the flow of Ar, a layer of white product was observed on the surface of the Si substrate. However, when the nonetched Si wafer was used as the substrate and other conditions were kept the same, we did not get a similar result. The phase purity, morphology, structural characterization, and elemental composition analysis of the as-prepared product were investigated using x-ray diffraction (XRD, Regaku D/max-2400), a field emission scanning electron microscope (SEM, JEOL JSM-6301F), and a high-resolution transmission electron microscope (HRTEM, JEOL2010) equipped with an energy dispersive x-ray spectroscopy (EDS, Inca).

Figure 1(a) shows the SEM image of an as-grown sample deposited on the Si substrate. It reveals that a large quantity of nanoplatelets vertically grew on the Si substrate and connected with each other to form a honeycomblike network. The edges of the nanoplatelets are irregular and the side surfaces of some of the nanoplatelets are not smooth. The high-magnification SEM image is shown in Fig. 1(b). It can be seen that the thickness of the nanoplatelets is not uniform but decreased gradually from the bottom to the top

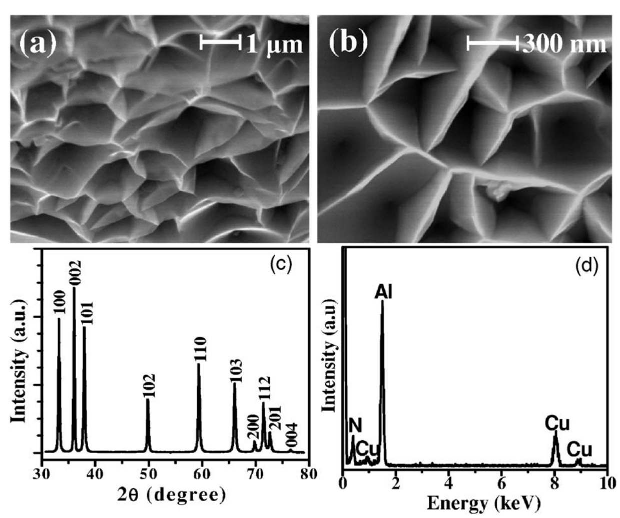

FIG. 1. SEM images of nanoplatelets: (a) tilted top view and (b) high magnification. (c) XRD diffraction spectrum and (d) EDS spectrum of AlN nanoplatelets.

[a]Author to whom correspondence should be addressed; electronic mail: htcong@imr.ac.cn

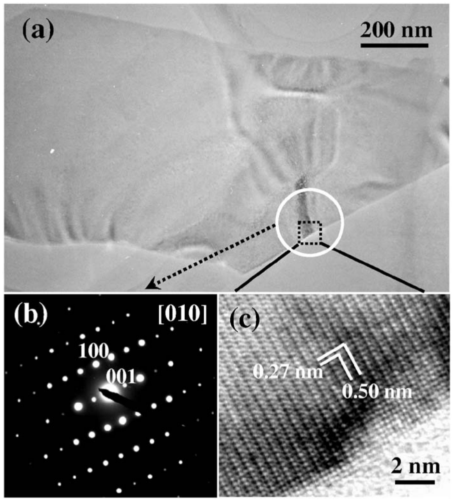

FIG. 2. (a) TEM image, (b) SAED pattern, and (c) the magnified HRTEM image of a single AlN nanoplatelet.

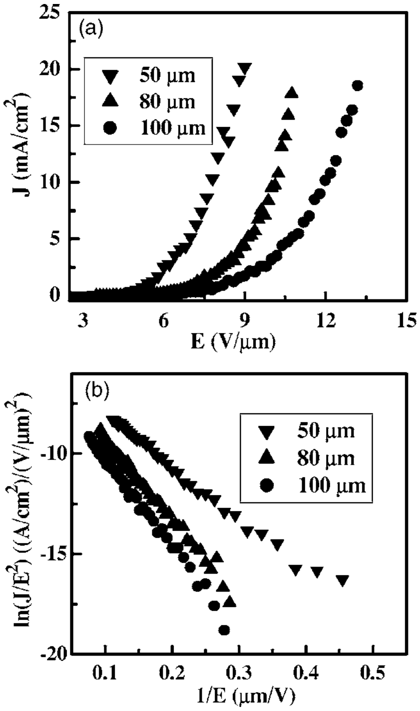

FIG. 3. (a) Field emission current density (J) as a function of the applied electric field strength (E) at three anode-sample distances of 50, 80, and 100 μm. (b) The corresponding FN plots of the $\ln(J/E^2)$ vs $1/E$.

to form a wedge shape, which is favorable for enhancing the mechanical stability of the nanostructures and acquiring higher emission current stability in field emission process. The thickness of the nanoplatelets varies from 10 to 100 nm, and their height varies from several hundred nanometers to several microns.

Some of the as-synthesized nanoplatelets were scratched from the Si substrate for XRD and EDS analyses, and the results are shown in Figs. 1(c) and 1(d), respectively. All the diffraction peaks in the XRD spectrum can be readily indexed to hexagonal wurtzite AlN with lattice constants of $a=3.114$ Å and $c=4.979$ Å (JCPDS Card No. 25-1133). The EDS spectrum [Fig. 1(d)] presents that these nanoplatelets are only composed of Al and N elements [the Cu peaks originated from the transmission electron microscope (TEM) Cu grid]. Quantitative analysis reveals that the Al/N atomic ratio in nanoplatelets is about 1.00:0.93 (thus being close to pure AlN within the experimental error).

Figure 2(a) presents a representative TEM image of an AlN nanoplatelet. The electron beam's transparent and ripplelike contrast characteristics demonstrate that the formed nanoplatelets are thin. Selected area electron diffraction (SAED) patterns [Fig. 2(b)] taken from the region marked by a circle in Fig. 2(a) can be indexed as that of single-crystalline hexagonal wurtzite AlN recorded along the [010] zone axis. Figure 2(c) is a magnified HRTEM image taken near the edge of this AlN nanoplatelet [highlighted by the square in Fig. 2(a)]. The adjacent lattice distances in directions parallel and perpendicular to the edge are 0.27 and 0.50 nm, respectively, corresponding to the d spacing of (100) and (001) crystal planes of hexagonal AlN. Both the SAED pattern and HRTEM image clearly show that this nanoplatelet is single crystalline, and TEM investigations on other AlN nanoplatelets also gave a similar result.

The FE measurements were performed by a two-parallel-plate configuration in a ball-type vacuum chamber which was pumped down to $\sim 7.0\times 10^{-6}$ Pa by an ultrahigh vacuum system. A cylinder-shaped platinum probe (with 0.785 mm^2 cross-sectional area) was used as the anode. The Si substrate with AlN nanoplatelets was stuck onto a copper stage using a conducting glue to act as the cathode, which can be moved by a linear-motion step controller to adjust the cathode-anode distance and to select positions of the FE measurements. High voltage was supplied by a power source (Keithley 248) and the current under increasing applied voltage was recorded by an electrometer (Keithley 6514) with picoampere sensitivity. The FE properties at three cathode-anode distances were measured. At each distance, five positions of AlN nanoplatelets were tested to verify the reproducibility, and the average FE current data were reported.

Figure 3(a) depicts the measured FE current density (J) as a function of the applied electric field (E) at three sample-anode distances of 50, 80, and 100 μm, respectively. The turn-on field (E_{to}) and the threshold field (E_{thr}) are defined as the electric fields at which a current density of 10 μA/cm^2 and 10 mA/cm^2, respectively, were obtained. E_{to}'s were measured to be $\sim$3.2, 4.3, and 5.0 V/μm for the three distances, respectively, and E_{thr}'s were found to be $\sim$7.8, 10.1, and 12.1 V/μm, respectively. It can also be seen that the maximum FE current density higher than 15 mA/cm^2 was achieved at all the three distances. Such high emission current density can produce sufficient brightness for FE displays (FEDs). The E_{to} value of AlN nanoplatelets is lower than that of similar nanostructures of other materials, such as MnO_3 nanobelts[16] (8.7–13.2 V/μm), and CuO nanobelt films[17] (6–11 V/μm) and arrays ($\sim$20 V/μm),[18] and close to that of SnO_2 nanobelt arrays (2.3–4.5 V/μm).[19] The low turn-on field and threshold field are probably due to the nanosized thin edges and perfect crystal structure of the AlN nanoplatelets. Moreover, the nanoplatelets vertically aligned in the direction of the applied electric field, which might result in a higher local electric field at their edges. In addition, the large interspaces of the AlN nanoplatelets in the honeycomblike network can effectively avoid the field-screening effect and lead to a higher FE current. It was found that the E_{to} and E_{thr} of the AlN nanoplatelets were increased with the increase of sample-anode distance, which is consistent with the results in some previous reports.[10] However, there are also contrary

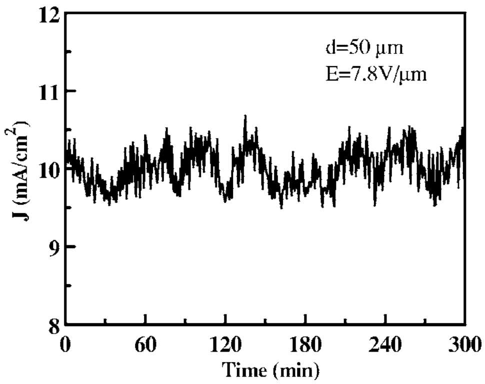

FIG. 4. Field emission current stability of the AlN nanoplatelets under an applied field of 7.8 V/μm at $\sim 7.0\times 10^{-6}$ Pa.

results,[16,19] so more systematic investigations are required to understand the origin of this phenomenon.

The FE current-voltage characteristics were analyzed by using the simplified Fowler-Nordheim (FN) equation

$$I = (1.54 \times 10^{-10}\beta^2 V^2 A/d^2 \phi)\exp(-6.83 \times 10^3 \phi^{3/2} d/\beta V),$$

where I is the FE current, V is the applied voltage, ϕ is the work function of the emitting material, β is the field enhancement factor, and A and d are the area of emission and cathode-anode distance, respectively. The corresponding FN plots $[\ln(J/E^2)$ vs $1/E]$ of the AlN nanoplatelets at three sample-anode distances are shown in Fig. 3(b). The approximate linearity of the plots indicates that the recorded currents were indeed caused by FE. β can be calculated from the slope of the FN plot if the work function of the emitter is known. Using the reported work function of AlN (3.7 eV) (Ref. 6) and the slopes of FN plots in Fig. 3(b), the β's were calculated to be $\sim$1785, 1140, and 1015, respectively, at three sample-anode distances. Such high β values are consistent with the low E_{to} and E_{thr} values of AlN nanoplatelets.

The stability of the FE current is crucial for practical device applications. For a long-term FE current stability test, the applied field was set at 7.8 V/μm for an initial current density of 10.157 mA/cm^2, which is about ten times higher than the critical level of FED operation current density (1 mA/cm^2).[20] Figure 4 shows the result of FE current density versus time for a period over 5 h under a pressure of $\sim 7.0\times 10^{-6}$ Pa at a sample-anode distance of 50 μm. The AlN nanoplatelets show a rather high stability without detectable degradation of FE current during the test. The mean current density and the standard deviation are calculated to be 10.01 and 0.27 mA/cm^2, respectively, and their ratio is as small as 2.7%. To a certain emitter, the mechanical and thermal stabilities are two of the main factors influencing the emission current stability.[21] The FE device will exhibit poor stability if the emitter does not have good mechanical and thermal stabilities. In our case, the AlN nanoplatelets connect with each other to form a honeycomblike network and they are thicker at the bottom, which is helpful for enhancing the mechanical stability and preventing them from vibrating under the applied electric field. On the other hand, AlN has high excellent thermal conductivity ($\sim$320 W/m K) and our nanostructures have a large connection area with the Si substrate, so they can quickly transfer the heat caused by the high current density from the top edges to the substrate. Furthermore, like a ribbed radiator, the large side surface of the nanoplatelets can effectively disperse some of the heat, which protects them from being destroyed due to superheating.

In summary, 2D AlN nanoplatelets have been synthesized on a Si substrate using an etched Si wafer via a simple vapor phase method without catalyst. The nanoplatelets vertically grew on the Si substrate and connected with each other to form a honeycomblike network. The thickness of the single-crystalline nanoplatelets varies from 10 to 100 nm, and their height varies from several hundred nanometers to several microns. FE measurements showed that the synthesized honeycomblike network of AlN nanoplatelets has a low turn-on field of 3.2–5.0 V/μm for driving a current density of 10 μA/cm^2, and threshold field of 7.8–12.1 V/μm for driving a current density of 10 mA/cm^2 at sample-anode distances of 50–100 μm. Its fluctuation of FE current with density of 10 mA/cm^2 for 5 h is within 3%. The low turn-on and threshold fields and the small fluctuation of FE current demonstrate that this 2D AlN nanostructure is a good material for FE applications. In addition, this synthesis of etching Si wafer and vapor phase method may be widely used as a reference for fabricating 2D nanostructural materials on Si substrate.

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