Enhanced electron field emission from oriented columnar AlN and mechanism

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(002) oriented AlN thin films with a columnar microstructure fabricated by vapor phase deposition with a sample bias exhibit excellent field emission properties. The field emission current density increases with smaller film thickness, and at a thickness of 400 nm, the current density reaches 9.9 $\mu A/cm^2$ and the turn-on field is close to 5 $V/\mu m$. Atomic force microscopy discloses nanoscale protrusions on the surface that greatly expand the emission area and efficiency. The Fowler-Nordheim plot reveals a linear dependence under low electric field (<17 $V/\mu m$), suggesting that the emission current originates from the quantum tunneling effect. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2216353]

Cold cathode field emission materials have stimulated extensive research interest due to their applications in optoelectronic devices and field emitters.[1,2] Among them, aluminum nitride (AlN), an important wide-band-gap semiconductor, is a promising field emitter because of its very small or even negative electron affinity, high mechanical stability, high thermal conductivity, and long-term stability in harsh environments.[3] A small or negative electron affinity means that electrons can be extracted from the surface easily when an electric field is applied, thereby giving rise to a large field emission current density. Some investigations have been conducted on the field emission properties of AlN. Kasu and co-workers studied the field emission current from heavily Si-doped AlN,[4,5] and Tondare *et al.* reported field emission from AlN nanotubes and nanoparticles.[6] The emission properties of AlN nanoneedles and nanorod arrays were also reported by Zhao *et al.* and Tang *et al.*, respectively.[7,8] However, these structures lack long-term emission stability and the difficulty to control the microstructure limit further applications.

Carbon nanotubes (CNTs) have been widely investigated and good field emission properties have been found.[1,9,10] Usually, nanotubes possess a high orientation and the field emission properties are enhanced gradually when carbon-based materials become more highly oriented, indicating that the excellent emission properties may be related to the preferential orientation. Hence, the orientation can be one of the key factors to obtain excellent field emission properties, and so it is possible that by controlling the microstructure and orientation, the field emission properties of other materials can be improved. In the work reported here, we study the effects of the microstructure and orientation on the field emission properties of AlN films fabricated by a simple vapor deposition method. Our results show that the thin film with the (002) preferential orientation exhibits excellent field emission properties that include a low turn-on field and high current density, whereas no obvious field emission current is observed from the amorphous AlN thin film.

Oriented AlN thin films with a columnar microstructure were fabricated using a solid $AlCl_3$ source by bias-assisted catalytic chemical vapor deposition (cat-CVD). During deposition, the temperature of the catalyst was very high (about 2000 °C), thereby providing enough energy for decomposition and reaction of the precursor gases, while the substrate was kept at a relatively low temperature of 190 °C. A negative dc bias voltage of 400 V was introduced to improve the orientation of AlN thin films.[11] The crystallinity of AlN thin films was examined using a MAC M21X/VAHF-type x-ray diffractometer (XRD) with a standard Cu $K\alpha$ radiation source. The thickness and cross-sectional microstructure of the thin films were evaluated by transmission electron microscopy (Philips CM200 FEG-TEM). The field emission properties of the samples were studied at room temperature in an ultrahigh vacuum chamber at a base pressure better than 2×10^{-8} Torr. The current density-field (J-E) characteristics were measured using a diode structure with a transparent indium tin oxide (ITO) plate as the anode. The sample surface and ITO anode were separated by 25 μm using a mica spacer and the emission area was about 0.3 cm^2.

Figure 1 shows the XRD spectra of AlN thin films with and without a sample bias during deposition. In the presence of the bias, the film possesses the (002) preferential orientation of the hexagonal phase (powder diffraction file: 25-1133). In contrast, the film deposited with the bias exhibits a very wide peak in the diffraction pattern, implying that the film is almost amorphous. It suggests that the negative bias can improve the crystallinity and leads to oriented growth. A typical cross-sectional TEM image of the oriented AlN sample is shown in Fig. 2(a). It can be seen that the oriented AlN thin film is mainly composed of columnar shape grains. The polycrystalline hexagonal phase of AlN (h-AlN) is revealed from the selected area diffraction pattern obtained by probing the columnar particles, and the results are consistent

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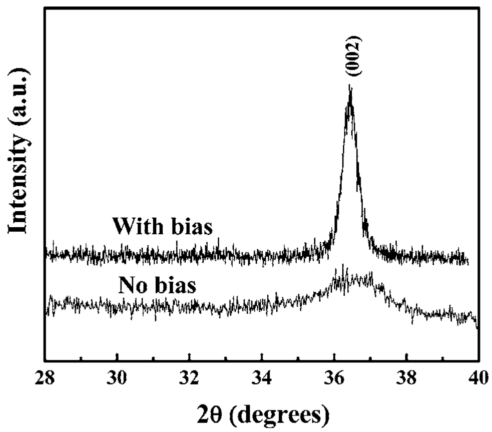

FIG. 1. XRD spectra acquired from AlN thin films prepared at different substrate biases.

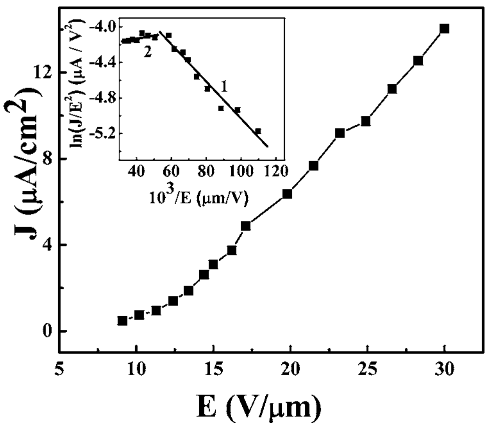

FIG. 3. *J-E* curve of field emission derived from the (002) oriented AlN thin film and the corresponding FN curve is shown in the insert plot.

with the XRD results. Furthermore, an amorphous layer at the interface of AlN/Si is clearly observed which is confirmed by the selected area diffraction pattern shown in Fig. 2(a). The formation of the amorphous AlN thin layer adjacent to the substrate during the initial growth can be attributed to the existence of an amorphous SiO_2 thin layer and such a phenomenon has been observed.[12] In fact, the initial amorphous AlN phase is a thermodynamically metastable one. The polycrystalline layer on the amorphous AlN matrix is considered to arise from recrystallization due to energetic ion bombardment under the substrate bias. In general, the bias activates the plasma and enhances the ion energy. The activated adsorbed species can thus have sufficient energy to overcome the nucleation energy barrier and crystallization is promoted. Ion bombardment may also provide energetic adatoms that promote their surface migration. Furthermore, the (0001) plane of the AlN crystal is the densest plane. The nuclei growth along the (0001) plane is much faster than that on the other planes. If the orientation of the original nuclei is assumed to be random, those nuclei on the (0001) plane will grow perpendicularly to the surface, leading to nucleation with a *c*-axis orientation.[11] As time elapses, the polycrystalline AlN crystallites with the (002) preferential orientation grow upward, resulting in a columnar shape structure as observed in Fig. 2(a). Figure 2(b) shows the atomic force microscopy (AFM) micrograph disclosing small protrusions on the nanoscale on the surface. These protrusions greatly expand the emission area and efficiency.

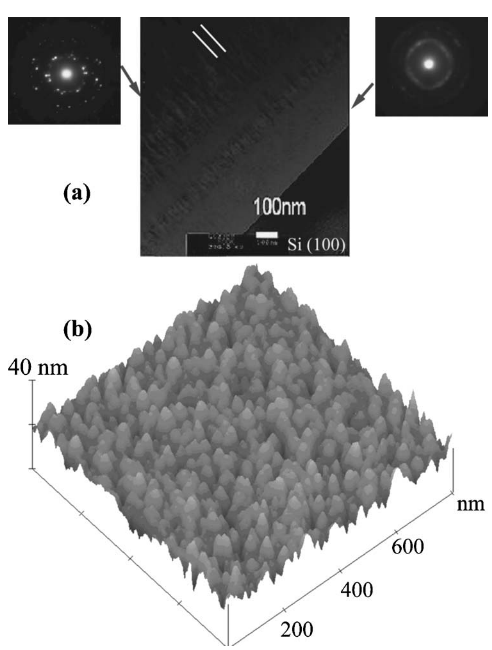

FIG. 2. (a) Cross-sectional TEM images of oriented AlN thin films and selected area diffraction patterns. (b) Corresponding AFM image indicating the surface morphology.

The field emission characteristics of the AlN thin films are evaluated based on the current density versus electric field (*J-E*) curves. Figure 3 shows the *J-E* curve of the sample described in Fig. 2. Because it is difficult to calculate the real emitting area exactly, the emission properties of the materials are usually roughly characterized by the current density J which is based on the measured current/planar sample area.[7,8] A remarkably stable and low turn-on field of about 9 $V/\mu m$ is observed from the oriented AlN thin film. The field emission current density reaches 4.9 $\mu A/cm^2$ at an applied field of 17 $V/\mu m$, and it is very similar to that of a Si-doped AlN sample reported by Taniyasu *et al.*[5] The field emission current-voltage characteristics can be analyzed by the Fowler-Nordheim (FN) equation:

$$J = A\left(\frac{\beta^2 E^2}{\phi}\right)\exp\left(\frac{-B\phi^{3/2}}{\beta E}\right),$$

where J is current density, E is the applied field, ϕ is the work function of the emitting material, β is the field enhancement factor, and A and B are constants with values of 1.54×10^{-10} A V^{-2} eV and 6.83×10^{3} V $eV^{-3/2}$ μm^{-1}, respectively. The corresponding FN plot shown in the inset of Fig. 3 indicates a linear dependence in region 1 under low electric field (<17 $V/\mu m$), suggesting that the emission current originates from the quantum tunneling effect. The field enhancement factor β can be calculated from the slope of the linearly fitted FN curve if the work function of the emitter is known. Based on the reported value of the AlN work function of 3.7 eV, the β value is about 216 which is sufficient for various applications in field emission, although it is lower than that of CNTs.[8] Under a high electric field (>17 $V/\mu m$), the *J-E* curve shows a linear relationship ($\bar{j} = \sigma \bar{E}$), meaning that the material has been broken down. The FN plot in region 2 further confirms this property $[\ln(J/E^2) = \ln \sigma - \ln E]$.

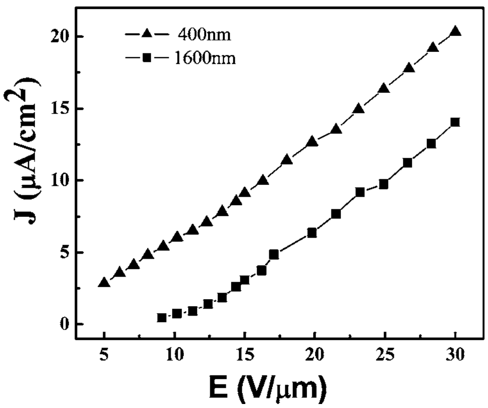

FIG. 4. *J-E* curves of field emission obtained from the (002) oriented AlN thin films with thicknesses of 400 and 1600 nm.

Since no obvious emission current can be observed from the amorphous AlN thin film, the excellent emission properties can be inferred to result from the preferential orientation. The origin of the electron emission from the oriented film can be understood from the change of the energy band structure and the area of electron emission accumulation. In general, the different orientation can result in the change of the band gap. For instance, CNTs can be transformed from insulating to conducting depending on the orientations.[13] Similarly, in AlN, the preferential orientation can induce the energy band gap shift and accelerate electron emission at a high electric field. The single preferential orientation of the AlN thin film may be beneficial to electron accumulation and subsequently field emission. This phenomenon has, in fact, been reported for closed-dome CNTs by Rinzler *et al.*[10] Hence, by adjusting the preferential orientation, it is possible to improve the emission properties of AlN thin films and this method can conceivably be applied to other field emission materials.

The effects of the film thickness on the field emission characteristics of the oriented AlN thin films are studied and the results are shown in Fig. 4. As the thickness is reduced, the field emission current density is enhanced and the turn-on field diminishes. When the thickness of the (002) oriented AlN thin film is 400 nm, the current density reaches 9.9 $\mu A/cm^2$ and the turn-on field is close to 5 V/μm. The thickness of the oriented film can thus influence the emission properties which appear to be mainly attributed to the difference of the surface roughness. As the film becomes thinner, the surface roughness increases. The root-mean-square roughness (R_m) values determined by AFM are 1.708 nm for the 400 nm thick film and 0.995 nm for the thicker sample that is 1600 nm thick. The surface morphology affects the local field enhancement and the emission current density has been observed to increase with surface roughness.[14] Consequently, enhanced field emission properties can be obtained from thin oriented AlN films.

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[1]W. A. De Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[2]K. Okano, S. Koizumi, S. R. P. Silva, and G. A. J. Amaratunga, Nature (London) **381**, 140 (1996).
[3]S. P. Grabowski, M. Schneider, H. Nienhaus, W. Monch, R. Dimitrov, O. Ambaher, and M. Stutzmann, Appl. Phys. Lett. **78**, 2503 (2001).
[4]M. Kasu and N. Kobayashi, J. Cryst. Growth **221**, 739 (2000).
[5]Y. Taniyasu, M. Kasu, and T. Makimoto, Appl. Phys. Lett. **84**, 2115 (2004).
[6]V. N. Tondare, C. Balasubramanian, S. V. Shende, D. S. Joag, V. P. Godbole, S. V. Bhoraskar, and M. Bhadbhade, Appl. Phys. Lett. **80**, 4813 (2002).
[7]Q. Zhao, J. Xu, X. Y. Xu, Z. Wang, and D. P. Yu, Appl. Phys. Lett. **85**, 5331 (2004).
[8]Y. B. Tang, H. T. Cong, Z. G. Zhao, and H. M. Cheng, Appl. Phys. Lett. **86**, 153104 (2005).
[9]G. Pirio, P. Legagneux, D. Pribat, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, and W. I. Milne, Nanotechnology **13**, 1 (2002).
[10]A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colber, and R. E. Smalley, Science **269**, 1550 (1995).
[11]A. P. Huang, G. J. Wang, S. L. Xu, M. K. Zhu, G. H. Li, B. Wang, and H. Yan, Mater. Sci. Eng., B **107**, 161 (2004).
[12]J. H. Choi, J. Y. Lee, and J. H. Kim, Thin Solid Films **384**, 166 (2001).
[13]S. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. J. Dai, Science **283**, 512 (1999).
[14]W. M. Tsang, S. P. Wong, and J. K. N. Lindner, Appl. Phys. Lett. **84**, 3193 (2004).