No-catalyst growth of vertically-aligned AlN nanocone field electron emitter arrays with high emission performance at low temperature*

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The AlN nanostructures with a wide band-gap of 6.28 eV are considered as ideal cold cathode materials because of their low electron-affinity. Many methods have been devoted to fabricating AlN nanostructures, but high growth temperature over 800 °C and the use of the catalysts in most methods limit their practical application and result in their poor field-emission behaviours in uniformity. This paper reports that without any catalysts, a simple chemical vapour deposition method is used to synthesize aligned AlN nanocone arrays at 550 °C on silicon substrate or indium tin oxide glass. Field emission measurements show that these nanocones prepared at low temperature have an average turn-on field of 6 V/μm and a threshold field of 11.7 V/μm as well as stable emission behaviours at high field, which suggests that they have promising applications in field emission area.

Keywords: AlN nanocone, low-temperature growth, no-catalyst, field-emission

PACC: 7280E, 6150C, 8116, 7970

1. Introduction

Since Geis[1] first demonstrated that diamond film have excellent field emission (FE) properties, wide band-gap semiconductors have attracted great interest in research. Compared with bulk materials, the wide band-gap nanostructures should deserve being paid more attention because of their larger aspect ratio and more unique properties as well as a negative or a little positive electron affinity,[2−6] which can do favours for emission operation in FE applications. Among them, AlN nanostructures are very particular due to the high melting-point (> 2300 °C), high thermal conductivity ($K \sim 320$ W/m·K), large exciton binding energy and strong endurance to harsh environments.[7−10] Recent researches on AlN nanostructures have stimulated the proceeding of their controlled growth techniques, and as a result different morphologies of AlN nanostructures are synthesized in aligned arrays, such as nanotips,[11−13] nanorods,[14,15] nanowires,[16−18] and nanobelts.[19] But it is noted that these known preparing methods are usually found to have some troubles in fabrication of nanometer scale devices, which have restricted their applications in FE area, for example high growth temperature (> 800 °C) and the use of catalysts. On the one hand, high-temperature growth way increases the production costs and keeps them from synthesizing on the substrate with low melting point. As known to us, indium tin oxide (ITO) glass is a widely-used substrate in flat panel display, whose melting point is lower than 600 °C. The known methods cannot meet the requirement of the mass production in flat panel display industry because high growth temperature will destroy the ITO glass. On the other hand, the use of catalysts will do harmful for nanotechnology because the catalysts will introduce some impurities and take effects on their field emission

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properties by affecting the contact resistance between the nanostructure and the substrate. Lastly, the AlN nanostructures in previous reports do not exhibit excellent field emission properties as expected, in which they have a high turn-on field and threshold field and exhibit poor emission uniformity. The existence of the above-mentioned factors holds back the rapid development of their application in FE area. Therefore, developing a catalyst-free and low-temperature way to fabricate highly-oriented AlN arrays with excellent field emission behaviours becomes a challenging and important subject from the point of practical applications.

Chemical vapor deposition (CVD) is a more simplified and low-cost method to obtain high-yield and high-quality nanostructures in comparison with anodic aluminum oxide (AAO) template method, sol–gel method or laser ablation method, so our strategy is adopting this way to realize the controllable growth of AlN nanostructures. In this paper, at low temperature of about 550 °C and without using any catalysts, vertically-aligned AlN nanocone arrays have been successfully synthesized on the Si or ITO substrate by CVD way. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), and Raman spectroscopy are used to characterize their morphology and crystalline structures. Their growth mechanism and FE properties are also investigated here.

2. Experimental

Large area AlN nanocone arrays have been synthesized by using $AlCl_3$ powders (purity: 99.99 %) as source materials in a two-temperate zone tube furnace, which has been described in our previous paper.[20,21] No catalysts were used in the whole experimental process, and Si(100) wafer or ITO glass was used as substrate. Moreover, the growth temperature has increased to be lower than 550 °C, which can be suitable for the use of commonly-used ITO glass. A ceramic boat loaded with $AlCl_3$ was put into low-temperature region A of the furnace when the substrate was placed into high-temperature region B. The temperature of region A was set to exactly reach 150 °C as soon as that of region B arrived at 550 °C. Then the mixed gas consisted of N_2 and NH_3 was introduced into the chamber, whose flow rate ratio is ranging from 300:10 to 300:20 standard cubic centimeters per minute (sccm). The whole reaction lasted 1–2 hours and the growth pressure was kept at 2–5×10^3 Pa. After the furnace is cooled to room temperature, a white film was deposited on the surface of the substrate.

The FE type SEM (XL-SFEG SEM, FEI Corp.) was used to examine the morphology of the AlN nanocone arrays across the entire wafer, while their crystalline structures and growth direction were characterized by TEM (Tecnai-20 TEM, PHILIPS), selected area electron diffraction (SAED), Raman spectroscopy (Reinshaw, inVia) and XRD (Rigaku RINT 2400). And FE measurements on the AlN nanocone arrays were carried out in our self-built FE analysis system.

3. Results and discussion

The XRD measurement was performed on the as-prepared product and the corresponding XRD pattern is shown in Fig. 1. It is indicated in Fig. 1 that these collected products on Si substrate are well crystallized, which is close to the XRD pattern of the products on ITO substrate. All these three diffraction peaks are indexed as the AlN phase with a wurtzite structure according to the data of the Joint Committee for Powder Diffraction Standards (JCPDS) card No. 25-1133. Moreover, only a very sharp and strong (002) peak can be found in this pattern except two very weak peaks, which proves that the AlN nanocones are well-aligned single crystals and grow preferentially along *c*-axis orientation. No peak belonging to Si substrate is observed in this XRD pattern. We have compared several AlN nanocone films in different growth densities on Si(001) substrate. It is found that the Si peak can be indexed only for the AlN film with lower

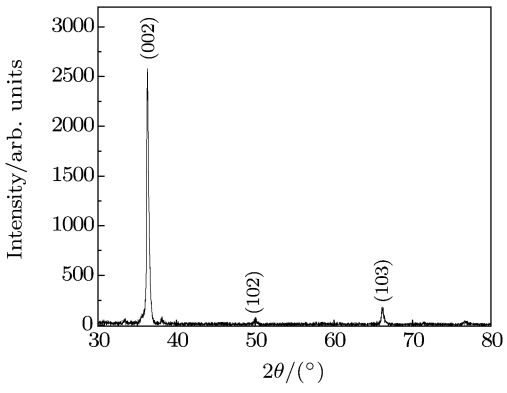


Fig. 1. XRD pattern of AlN nanocone film collected on Si(100) substrate.

growth density. In this situation, part of the Si substrate is exposed to the illumination of x-ray in the measurements, so the signal of Si is observed in the XRD pattern. If the AlN film is in higher growth density, no Si peaks can be found in the XRD pattern. At the same time, we change the substrate from Si(001) to Si(100) and the similar experimental result is observed, which suggests that the densely-packed AlN film can prevent the collection of Si substrate signals from the detection of x-ray irradiation.

Figure 2 shows the SEM image of the AlN nanocones on Si substrate, in which their morphological characters can be observed. From Fig. 2(a), the AlN nanocones are seen to cover the whole silicon substrate with a very high density. The as-synthesized AlN nanocones stand vertically to the substrate and parallel to each other. One can see that they have similar morphology and sharp tip, as provided in the top-view image (Fig. 2(b)). The high-resolution SEM image of the nanocone arrays is given in Fig. 2(c). It is seen that these nanocones exhibit a mean diameter of 20 nm at the apex, 70 nm at the base and a length of about 1 μm. Also, the AlN nanocone arrays can be synthesized on ITO substrate in the same reaction conditions with those grown on Si substrate, whose images are provided in Figs. 2(d)–2(f).

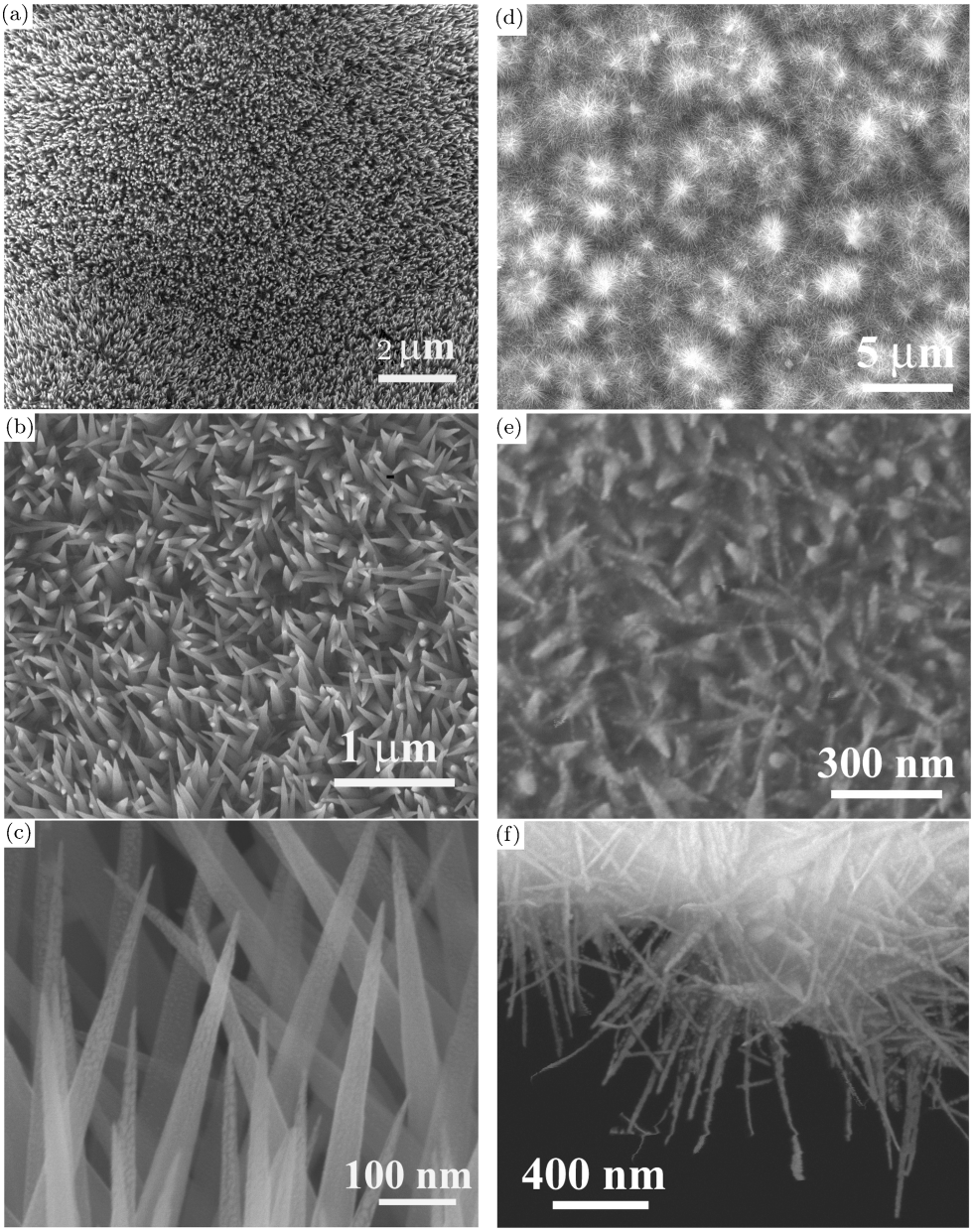


Fig. 2. The SEM images of AlN nanocone arrays: (a) low magnification image of large area AlN nanocone arrays on Si substrate; (b) and (c) top and side view of AlN nanocones on Si substrate; (d) low-resolution SEM image AlN nanocone arrays on ITO substrate; (e) and (f) their corresponding top and side view images.

From Fig. 2(d), the alignment of the AlN nanocone array is relatively worse and their growth density is lower than the AlN nanocones synthesized on Si substrate, which possibly comes from the different lattice mismatches between the substrate and the AlN film. They are observed to have a mean length of about 1 μm and a mean top diameter of about 20 nm in Figs. 2(e) and 2(f), which is similar with those of the AlN nanocones on Si substrate. Both of the AlN nanocone arrays are observed to have uniform conelike shapes and smooth surface as well as a high aspect ratio of 50, which is beneficial for FE.

Because the growth process is catalyst-free, the possible growth mechanism of the AlN nanocones cannot be interpreted by the VLS mechanism. We think that the VS mechanism should be suitable for illustrating their growth process. A simple growth model is depicted as follows. Firstly, $AlCl_3$ powder was vapourized at low temperature (< 150 °C) and reacted with NH_3 to form continuous AlN thin film on Si(100) or ITO glass substrate. The chemical reaction equation can be expressed as:

$$AlCl_3\,(g) + NH_3\,(g) \rightarrow AlN\,(s) + HCl(g). \qquad (1)$$

In some researches,[22] it is believed that the function of the catalysts is crucial because only AlN particles can be obtained when no catalyst is used in the experiment. But not any catalyst is used in this process, which implies that the incorporation of the catalyst is not essential for the dissociation of $AlCl_3$ vapour and NH_3 vapour, which is different from the illustrations in Ref. [22]. Here we prefer that the saturated vapour pressure of the reaction gas in the vacuum chamber is the key factor in determining the formation of AlN film. We designed a series of experiments to test this conclusion. When kept other reaction conditions unchanged and no catalysts were used, the AlN nanocones can be synthesized even at 550 °C, which is different from the observation of previous paper. But it is found that the AlN film cannot be synthesized if the growth pressure is adjusted to be lower than 500 Pa, which further proves that our current propositions should be more suitable for the formation of AlN nanocones in experiments. Secondly, because the strong strain coming from the lattice mismatch between the substrate and AlN film turned larger and larger with the increase of the temperature, continuous AlN thin film was destroyed and divided into many nanoparticles. When we used ITO glass or ceramic plate as the substrate in place of silicon wafer, the growth density of AlN nanocones differs with the change of the substrate at the same growth conditions due to different strain existed between the substrate and AlN film. Moreover, the growth temperature is adjusted to lower than 400 °C, only AlN nanoparticles can be found on the substrate, which is due to the decrease of the strain force and the saturation vapour at low temperature. Combined with previous research results, it comes to a conclusion that the growth density of the AlN nanocones is strongly dependent on the strong strain. Thirdly, these nanoparticles served as the nucleus of the following AlN clusters and started to grow along the energy favourable orientation [001] with the progress of the reaction. Finally, one-dimensional AlN nanocones were obtained on the surface of the substrate. Of course, the flow rate ratio of N_2 to NH_3 can affect the growth of the AlN nanocones. The main function of N_2 is to transport the evaporated Al atoms to the substrate region, controll the content of the reaction gas and adjust the reaction pressure for the formation of AlN nanocones. Through a series of experiments, it is found that only the AlN nanoparticle film can be found on the substrate if the flow rate of N_2 to NH_3 is lower than 300:5 sccm. At this situation, the low supplement of NH_3 usually forms a thin continuous AlN film, and there is a relatively smaller strain force between the substrate and the AlN film, which cannot produce the nanoparticles for the nucleus of the AlN nanocones. Moreover, it is also found that if pure NH_3 gas is introduced into the chamber, the content of the HCl gas formed in the reaction process is often very high and corrupts the substrate to a great extent, in which case lots of AlN nanocones are peeled off. The addition of the N_2 gas can effectively decrease the HCl concentration in the chamber and provide a more suitable pressure for the formation of the AlN nanocones. Until now, the most suitable ratio of N_2 to NH_3 is found to be ranging from 300:10 to 300:20. And the alignment of the nanocone arrays possibly results from the steric overcrowding.[20,23,24]

To confirm the crystalline structure of the AlN nanocones synthesized at 550 °C, the TEM technique was applied to characterize the product. Figure 3(a) gives a typical TEM image of an AlN nanocone. We find that the AlN nanocone has a smooth shape and its diameter decreases from 60 nm to 20 nm, which is resemble to our observed results in Fig. 2(c). The ripple-like contrast in TEM image should originate along from the existence of strains *c*-axis. From the

high-resolution TEM (HRTEM) image (Fig. 3(b)), the AlN nanocone is found to have a mean lattice spacing of 0.298 nm between two adjacent crystalline planes. This growth plane can be confirmed to be (002) plane based on the JCPDS card No. 25-1133, which proves that their growth direction is [001] orientation. The inset is the corresponding SAED pattern, where one can see that the diffraction spots are clear and sharp. Combined with these measurement results, it is revealed that the AlN nanocones are perfect single crystals with a wurtzite structure. Moreover, according to our result of analysis, there are not any crystalline defects existed in the nanocones prepared at low temperature. So it can be a conclusion that the crystallinity of AlN nanocones prepared at low temperature does not turn worse in comparison with those prepared at high temperature, which ensures that the low-temperature growth technique of AlN nanocones can meet the requirements of FE applications.

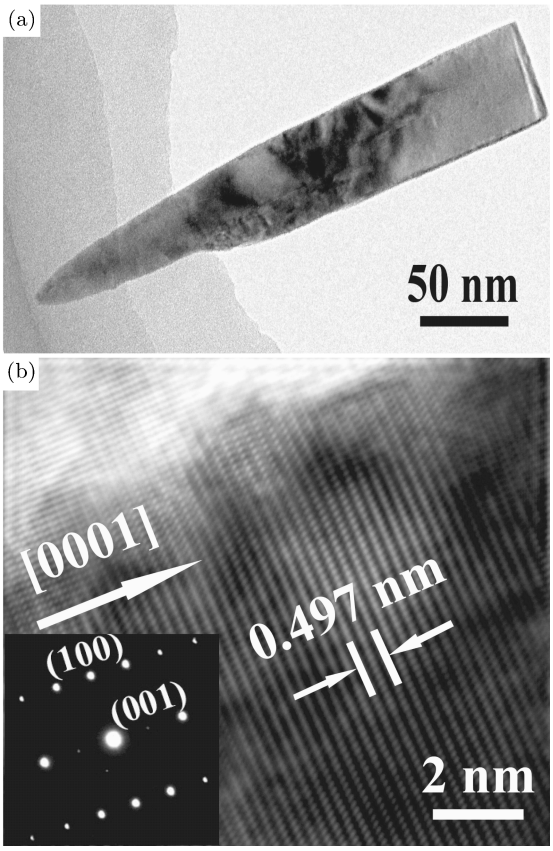


Fig. 3. The TEM and HRTEM images taken from an AlN nanocone: (a) typical TEM image of an AlN nanocone, (b) the corresponding HRTEM image of the AlN nanocone. The inset is the SAED pattern of the AlN nanocone.

Raman scattering is an effective tool to evaluate the crystallinity and the presence of lattice strain for nanostructures, so it is used to explore the AlN nanocone arrays. Room-temperature Raman spectra of the as-fabricated AlN nanocone arrays are indicated in Fig. 4. In our Raman spectrum, only two distinct peaks (612.5 cm^{-1} and 656 cm^{-1}) can be found, which is respectively assigned to the A_1 (transverse optical) and E_2 (high) phonon mode. But there are usually six characteristic peaks existing in the Raman spectrum of the space group of bulk AlN materials with a wurtzite structure, corresponding to E_2 (low), E_2 (high), A_1 (transverse optical), A_1 (longitudinal optical), E_1 (transverse optical), and E_1 (longitudinal optical).[25] The absence of some phonon modes should be attributed to the special angle between the wave vector of the phonons and the c axis of one-dimensional AlN nanocones in the near backscattering geometry.[22,26] Compared with the Raman spectrum of the AlN nanocones prepared at 700 °C,[22] it is found that the peaks at 522 cm^{-1} and 902 cm^{-1} are not seen in this spectrum. The absence of the peak at 522 cm^{-1} can interpret the existence of thick AlN nanocone film, which prevents the detector from collecting the signal of the silicon wafer. Whereas for the loss of the peak at 902 cm^{-1}, it can be attributed to the fact that larger lattice strain may exist between the substrate and the AlN nanocone film with the absence of the Ni layer. In addition, it is also found that the Raman spectrum of our sample exhibits asymmetry and the characteristic peaks move to low wavenumber followed by the broadening of their widths, which possibly results from the size effects or the existence of the internal strain.[27–30] From the Raman spectrum, we further prove that the crystallinity of AlN nanocone does not change distinctly with the decrease of the growth temperature.

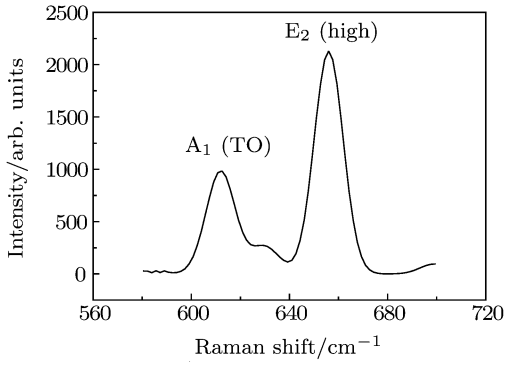


Fig. 4. Raman spectrum of the as-prepared AlN nanocone arrays.

The surface electron affinity is one of the determinant parameters strongly affecting FE property of cathode materials. And AlN nanostructures may have

a little positive or negative affinity on (001) crystalline plane, which makes most researchers consider them as one of the promising cathode materials in future. So we applied ultraviolet photoemission spectroscopy (UPS) technique to investigate the electron affinity of the AlN nanocones before the beginning of FE measurements. Figure 5 shows the UPS spectrum of the sample. To confirm that the detector can collect all emission electrons from the valence band, a voltage of -5 V was applied to the sample. The spectral width ($W_{\rm spectra}$) of the sample can be calculated by linearly extrapolating the emission onset edges to zero intensity at both the low kinetic energy cutoff and the high kinetic end, which are equal to the energy difference between the deepest level in the valence band and the edge of the valence band for semiconductor. Based on this method, the width is determined to be about 14.3 eV. The surface electron affinity χ of a sample may be obtained by using the following equation:[31]

$$\chi = h\gamma - E_{\rm g} - W_{\rm spectra}, \tag{2}$$

where $E_{\rm g}$ is the energy band gap, and $h\gamma = 21.2$ eV, which is the radiation energy of He I line. The energy band gap of AlN nanocones can be assumed to be the same as that of bulk AlN, i.e., 6.28 eV.[32] Then the χ values are deduced to be 0.62 eV, which suggests the electron affinity of the as-prepared AlN nanocones is low enough for electron emission at low field operation in FE area.

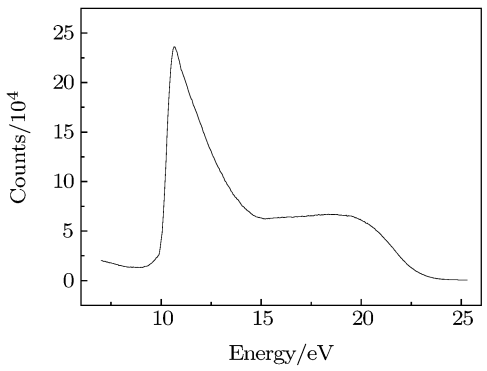


Fig. 5. UPS spectrum of aligned AlN nanocone arrays on silicon substrate.

The AlN nanostructures usually exhibit good FE properties, and whether the synthesized AlN nanocones should have the same or better FE performance is still needed to be testified, which is very essential for their applications. The FE measurements were carried out in our self-built FE analysis system with a basic pressure lower than 2×10^{-7} Pa. Transparent anode method is an effective way to measure the FE properties of cathode film, which can provide the experimental data more accurately and obtain the emission images of cathode film simultaneously in comparison with other ways. So we applied this way to measure the FE properties of the as-synthesized AlN nanowire arrays. The AlN nanocones prepared on Si substrate at 550 °C were used as the cathode and the area of the sample is about 2×1 cm^2. A clean ITO glass was used as the anode and the distance between the anode and the cathode is about 400 μm in the experiment. Moreover, in order to avoid the occurrence of the emission uniformity coming from the unequal distance between the anode and the cathode, the AlN nanowire film is fixed to parallel to the ITO glass by placing two pieces of designed ceramic plates with an equal thickness. The digital camera is placed to face the observation window of the measurement to obtain the emission images of the sample *in situ*. Typical current density versus electric field (J–E) curve is shown in Fig. 6(a). It is seen that the turn-on field (defined as the electric field for $J = 10$ μA/cm^2) and the threshold field (defined as the electric field for $J = 1$ mA/cm^2) of AlN nanocone arrays is about 6 V/μm and 11.7 V/μm, respectively. Moreover, the maximum current density of the sample reaches 2.16 mA/cm^2 when the electric field increases to 15.85 V/μm. Their corresponding Fowler–Nordheim (FN) plots are indicated in the inset. One can observe that their FN plots are close to straight line, which suggests that the emission is a field-tunnel process and can be illustrated by the classical FN equation.[33] So according to the FN equation, the dependence of FE current density of AlN nanocone arrays on the electric field can be written as

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

where $A = 1.57\times10^{-10}$ (A·V^{-2}·eV), $B = 6.83\times10^{9}$ (V·m^{-1}·eV$^{-3/2}$), and ϕ is the work function of AlN nanocone, which adopts the work function (3.7 eV) of bulk AlN materials. Then the average field enhancement factor β is calculated to be about 1600. In some reports,[21] the AlN nanocones at high temperature have a turn-on field of 12 V/μm and a threshold field of 32 V/μm, which is too high to be applied in FE field. But using this improved no-catalyst growth method, we have successfully enhanced the FE behaviours of AlN nanocones to a large extent. The reasons for the improvement of the emission ability are summarized as follows. One is that the substrate used in this experiment is the silicon substrate differ-

ent from the initial experiment, which has been removed from the surface oxide layer. At this situation, the contact resistance between the substrate and the AlN nanocones has been decreased to a low extent in comparison with the silicon substrate with oxide layer in our initial report because higher effective voltage is applied between the cathode and the anode. If we do not remove the surface silicon oxide layer before the beginning of the fabrication of the sample, the AlN nanocones usually perform poor emission behaviours in FE measurements as previous report. So it is concluded that contact resistance is the crucial factors determining their FE performances. Secondly, the aspect ratio (50) of the as-prepared AlN nanocones is higher than that (20) of the AlN nanocones by using catalysts. As known to us all, higher aspect ratio will result in higher field enhancement factor. So the AlN nanocones prepared without catalysts should have much higher electric enlargement ability than the AlN nanocones by using catalysts at the same applied voltage, which leads to their better FE performance. Using catalyst, when we tried to fabricate the AlN nanocones with the aspect ratio of 20 on Si substrate without the surface oxide layer, we find that the emission ability does not exhibit an obvious change (turn-on field of 7 V/μm and a threshold field of 12 V/μm). So we can draw a conclusion that this factor is an influence factor for their FE properties, which is not the key factor. In addition, the as-prepared AlN nanocone arrays without using catalysts have relatively lower turn-on field and higher enhancement factor than many nanomaterials commonly used as cathodes, such as ZnO, GaN and WO_3, this fact proposes that they can be applied for various FE areas.

The AlN nanocones usually exhibit poor emission uniformity in most researches because different contact modes between the substrate and the nanowire often result in their different work performance because of the existence of the catalyst. Although the as-prepared AlN nanocone arrays at low temperature have the same contact mode because no catalyst is used, they should perform better emission properties based on the above-mentioned theory. A typical emission image of the AlN nanocones is demonstrated in Fig. 6(b). And the inset gives the profile of the sample. From Fig. 6(b), it is observed that over 90% emission sites uniformly distribute on the sample and almost all the emission sites have the similar luminance, which shows that the AlN nanocones prepared without catalyst have excellent emission homogeneity.

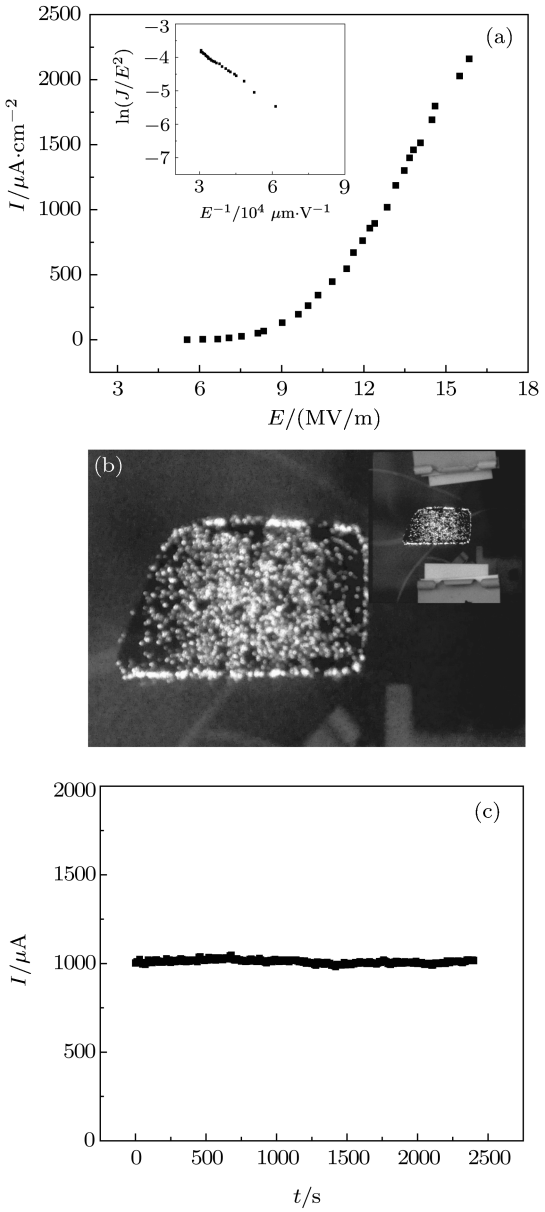


Fig. 6. (a) The J–E curves of aligned AlN nanocone arrays. The inset is their corresponding FN plots. (b) The spatial distribution of the emission sites on the sample. The inset gives the figuration of the sample. (c) The emission stability curve of the AlN nanocones at electric field of 11.7 V/μm.

Clearly, the AlN nanocones prepared without catalyst have more uniform emission than those prepared by using catalysts in other reports. We also attribute these phenomena to the change of the contact resistance and the detailed analysis is depicted as the following. When the catalysts are used in the experiment, the contact resistance usually changed with the binding force between the AlN nanocones and the substrate. It is known that the growth mechanism is various for the existence of different contact forces.[34]

If the binding force is strong at the growth stage, the AlN nanocones often adopt the bottom-growth model, i.e., the catalysts exist at the bottom of the nanocones and contact with the substrate. But if a weak binding force exists between the substrate and the AlN nanocones (top-growth model), the catalyst will occur at the top of the nanocones, i.e., the nanocone will straightly contact with the substrate. It is obvious that the contact resistance is different in these two situations. Then, using the catalyst at the growth stage, we have no way to ensure that all the nanocones have the same contact model with the substrate, this fact must lead to their different contact resistances in the experiment and result in different effective voltages falling between the anode and the nanocones. Without using the catalysts, the contact resistance between the AlN nanocones and the substrate is usually similar. So the AlN nanocones prepared without catalysts should have more excellent emission uniformity than the AlN nanocones using catalysts based on our analysis, which is in good agreement with our observed results.

Finally, field emission stability measurements are performed on aligned AlN nanocone arrays, which is significant for their actual applications. Figure 6(c) displays the representative FE stability curve of the sample. The whole measurement lasted 4 h, and the initial emission current was 1 mA when the applied field was fixed at 11.7 V/μm. It is seen that the current fluctuation is lower than 3% throughout the measurement, this fact suggests that AlN nanocone arrays synthesized at low temperature can meet the stability requirements of FE application at high current density.

4. Summary

In conclusion, we have synthesized vertically-aligned AlN nanocone arrays without using any catalyst and at a low temperature of 550 °C by simply nitriding $AlCl_3$ powders. The as-synthesized AlN nanocones have a mean length of 1 μm and a sharp tip of about 20 nm. And they are identified as perfect single crystals with a wurtzite structure and have a growth direction of [001]. The FE measurements show that aligned AlN nanocone arrays prepared at low temperature still have excellent FE performances comparable to most of the excellent cathode materials, this fact suggests that they should have potential applications in FE areas. Moreover, this no-catalyst and low-temperature growth technique can produce AlN nanocones with better FE performance than the AlN nanocones synthesized by using catalysts at high temperatures, this fact may provide a new way for fabricating AlN nano-electronic and nano-optical devices on ITO substrate with low melting-point in future.

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