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1. Introduction

Diamond-like carbon (DLC), an amorphous meta-stable carbon containing high sp³ bond, is one of the most attractive materials. Similar to genuine diamond films [1-9], DLC film also has a lot of advantages, including high thermal conductivity, low thermal expansion coefficient and so on [10-15]. Therefore, it is widely used in field emission display, gas sensors, microwave tubes and biomedical applications etc. DLC film is commonly prepared by microwave chemical vapor deposition method (MW-CVD) and hot-filament CVD technique (HF-CVD). It can even be deposited cheaply onto glass or plastic substrates at room temperature [13,16].

In electron field emission (FE) area, DLC and diamond films were extensively investigated as electron field emitters because of their unique properties, low or negative electron affinity. In principle, field emission from DLC, a semiconductor with a band gap varying from 1 eV to 4 eV according to its sp content, is easier than high quality diamond with a wide band gap of 5.5 eV. And several techniques also have been adopted to enhance the FE properties of DLC, such as using nitrogen to increase sp² banding of grain boundary [3,4], and using high aspect ratio tips to form DLC coated emitters [3,5,11,13,14,17]. Meanwhile, diamond nanotips [3,6], nanowires [4,7] and nanorods [8,9] were fabricated gradually, which could increase emission sites and reduce the turn-on field due to the typical FE structure with high aspect ratio. Yet to DLC films, few of works have been reports on crystal nanorods due to its chemical inertness [14,17]. Hence, DLC nanorods (DLCNRs), a nanostructure with high aspect ratio, would have great potential as a field emitter.

In previous works, we had fabricated highly ordered TiO₂/Ti nanotube arrays and investigated their FE properties [18]. The results were very interesting including moderate turn-on field, high FE current density, large field enhancement factors and good emission stability. We also planned to modify TiO₂ with carbon materials (carbon nanotube, DLC and diamond). It was a successful attempt in this modified process that DLC were synthesized on TiO₂/Ti nanotube arrays. Interestingly, the surface of DLC film, fabricated on TiO₂/Ti nanotube arrays deposited Ni nanoparticles, took on pagoda-shaped nanorods, a typical FE structure with high aspect ratio. Their tips seem to be pyramid and the edges and corners are aligned regularly on the body surface. What worth more to encourage is that DLCNRs/TiO₂/Ti has a low turn-on field, large field enhancement factors and good emission stability.

2. Experiment details

High purity titanium foils (99.9% purity, 0.5 mm thickness) were degreased in an ultrasonic bath with acetone for 5 min, rinsed in deionized water and dried in air at room temperature.
treated titanium sheet as an anodic and graphite as a cathode electrode, anodization was carried out for 3h in 0.5 wt% HF at 13V (direct current). The whole course of anodization was conducted at 0°C with magnetic agitation [19]. Finally, the anodized TiO2/Ti nanotube arrays were used as anode, put into 0.1M NiSO4·7H2O solution and were electrochemically deposited with Ni nanoparticles by applying DC voltage 1.2V for 70s.

A low-pressure CVD system was used to synthesize the DLCNRs films. The prepared TiO2/Ti nanotube arrays deposited Ni nanoparticles were placed in a quartz boat and were sent to a quartz tube furnace. Ni particles were reduced in a gas of H2 (6.0 sccm) at 650°C for 40min. Then, the furnace temperature increased to 750°C and the growth of DLCNRs was carried out at a mixture gas of CH4 (2.0 sccm) and N2 (18.0 sccm) for 1.2h. Finally, the reaction was terminated and the furnace was cooled to room temperature.

Field emission scanning electron microscopy (FE-SEM, S4800-6 and JSM-6701F) was used to characterize the morphology of TiO2/Ti nanotube arrays and DLCNRs. The evidence of DLCNRs formation and its purity was analyzed by characterizing the samples with Raman spectrometer (LabRAM HR8000uv, 512 nm). FE current was measured in a vacuum chamber at the pressure 4.0×10−3Pa by a diode structure. A copper rod electrode served as an anode and the sample of TiO2/Ti nanotube arrays or DLCNRs/TiO2/Ti directly acted as a cathode. A mica sheet with 100μm thickness was used as a spacer. The area of the hole in the spacer is about 1mm². The diameter of the hole in the spacer was about 1 mm². Interestingly, DLC films with large grains, but not nanorod, can be gained on bare TiO2/Ti nanotube arrays, as shown in Fig. 2(b). It is clearly that Ni plays a crucial role in the formation of DLCNRs. The high-resolution images of DLCNRs are shown in Fig. 2(c) and (d). Compared with other similar works [7–9], some new features about the nanorods were observed. The nanorods have a pagoda shape. The tips of most nanorods seem a sharp pyramid (inset of Fig. 2(c)), while some are rectangular parallelepiped (inset of Fig. 2(d)). The edges and corners are aligned on the body surfaces of nanorods regularly, which indicate that the clear crystal faces distribute on the body surface. Meantime, the crystalline nanorods are exposed completely without evident graphite sheath. Moreover, TiO2/Ti nanotube arrays deposited Ni were first used as the substrate to grow DLCNRs, this was a successful attempt. And an ordinary CVD reactor set up by ourselves was used for growth of DLCNRs at a low temperature 750°C, which is a simple and low cost method.

Raman spectra were measured to evaluate the crystalline quality of DLCNRs and DLC films, as shown in Fig. 3. Two peaks about 1332 and 1598 cm−1 are observed both in DLCNRs and DLC films. However, Raman peaks of DLCNRs are stronger and sharper than that of DLC films. The peak about 1332 cm−1 is well-defined diamond peak. The peak about 1598 cm−1 is assigned to G band, and it is related to sp2-bonded carbon residing at grain boundaries. It is worthy that the presence of N can increase sp2 banding at the grain boundaries and a low temperature can lead to high density of defects incorporated in the films [3,4,16,22,23], thus, the Raman peaks of such samples are broadened as a band.

Based on the above results, the formation mechanism of pagoda-shaped DLCNRs was suggested. Nanocrystalline diamond was firstly nucleated both on the TiO2/Ti surface and in the nanotube. With the prolonging of time, the ball-shaped diamond nucleuses grew up gradually. Unfortunately, without catalyst Ni nanoparticles, grains could not grow into rod but polycrystalline shape like nanocrystalline diamond, as shown in Fig. 2(b). Only those grains under catalyst Ni nanoparticles quickly grew into faceted nanocrystal grains. The crystal faces, such as (110) and (100), distribute on the surface of the nanocrystal grains. It is well known that the growth rate of diamond is fairly larger along the (110) direction than along the (100) direction [8,9]. The faceted nanocrystal grains grew into the DLCNRs. At the same time, the further growth of nanorods took place both on the tips and body surfaces. In addition, the ends and corners were formed on the body surface due to the different growth rates along the different crystal directions. Consequently, the pagoda-shaped DLCNRs were grown. It was worthy that Ni was one of the key factors for fabricating DLCNRs. It was favorable for enhancement of diamond nucleation and sharply enhanced preferred orientation in the growth of DLCNRs at a low temperature.

Fig. 2(a) is the low-resolution FE-SEM images of the DLCNRs fabricated on aligned TiO2/Ti nanotube arrays, with Ni nanoparticles on its surface shown in the inset of Fig. 2(a). It is obvious that the DLCNRs distribute randomly on the surface of TiO2 substrate and their length is the range of 3–10μm. Interestingly, DLC films with large grains, but not nanorod, can be gained on bare TiO2/Ti nanotube arrays, as shown in Fig. 2(b). It is clearly that Ni plays a crucial role in the formation of DLCNRs. The high-resolution images of DLCNRs are shown in Fig. 2(c) and (d). Compared with other similar works [7–9], some new features about the nanorods were observed. The nanorods have a pagoda shape. The tips of most nanorods seem a sharp pyramid (inset of Fig. 2(c)), while some are rectangular parallelepiped (inset of Fig. 2(d)). The edges and corners are aligned on the body surfaces of nanorods regularly, which indicate that the clear crystal faces distribute on the body surface. Meantime, the crystalline nanorods are exposed completely without evident graphite sheath. Moreover, TiO2/Ti nanotube arrays deposited Ni were first used as the substrate to grow DLCNRs, this was a successful attempt. And an ordinary CVD reactor set up by ourselves was used for growth of DLCNRs at a low temperature 750°C, which is a simple and low cost method.

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The FE characteristics were analyzed by the Fowler–Nordheim theory [24–26], using the following equation,

\[
J = \frac{E^2 \beta^2}{\Phi} \exp \left( -\frac{B \Phi^{1/2}}{E \beta} \right).
\]

where \(E, \beta\) is the applied field and the FE enhancement factor, respectively; \(\Phi\) is the local work function of diamond and TiO2. Here, they are assumed to be 4.7 eV and 4.4 eV respectively [27–30]; \(B\) is a constant of \(-6.83 \times 10^9\ \text{eV}^{-3/2} \ \text{V m}^{-1}\). The turn-on electric field of DLCNRs/TiO2/Ti, as shown in the Fig. 4(a), is 3.0 V/μm and the FE current density reaches rapidly about 4.4 mA/cm² at 8.6 V/μm, compared with the FE of bare TiO2/Ti nanotube.
arrays (the turn-on field is 11.4 V/mm) [18]. The Fowler–Nordheim (FN) plot shown in the inset of the Fig. 4(a) clarifies that the current is indeed caused by electron FE only due to their strong line relationship. It can also be used to calculate FE enhancement factor $\beta$ of emitter by the slope $(B\Phi^{3/2}/\beta)$. Here, the $\beta$ of DLCNRs/TiO$_2$/Ti and TiO$_2$/Ti nanotube arrays can be calculated about 2455 and 660, respectively. It is clearly that the FE of samples is improved after deposition of DLCNRs. In prior works [18], we discussed that the moderate FE of TiO$_2$/Ti nanotube arrays were mainly attributed to the unique structure including small radius of curvature of tube end, moderate tube density and tight adherent. After deposition of DLCNRs, the FE of samples is mostly caused by DLCNRs, which have predominant structure. DLCNRs possess elegant pagoda shape with sharp pyramid tips. The edges and corners are aligned regularly on the nanorods body surface, which increase emission sites greatly. Meantime, nitrogen incorporated into nanorods increases sp$^2$ bonding at the grain boundaries, which is favorable to enhancement of FE by promoting the ability to move electrons through the graphitic carbon. The enhanced emission from a-C:H:N had been gained by Gehan and Amaratunga [31] etc.in 1996. In their views, as the N content increases, a higher field across the films at a given applied voltage between the n$^{++}$-Si and the metal anode can be obtained for an increase in the concentration of ionized donor centers. In addition, the FE stability has also been studied, as shown in Fig. 4(b). The emission current density of DLCNRs/TiO$_2$/Ti is about 3.4 mA/cm$^2$ at 8.3 V/µm, and has no obvious decay in 480 min, compared with the emission current density of TiO$_2$/Ti is about 2.3 mA/cm$^2$ at 18.8 V/µm.

Fig. 2. (a) FE-SEM images of the DLCNRs films with pagoda shape. Inset: the substrate of aligned TiO$_2$ nanotube arrays with Ni nanoparticles. (b) FE-SEM images of the DLC films with smooth surface. Inset: the substrate of aligned TiO$_2$ nanotube arrays without Ni nanoparticles. (c) And (d) high-resolution FE-SEM images of the DLCNRs films. Inset: top end shapes of the nanorods: (c) pyramid and (d) rectangular parallelepiped, respectively.

Fig. 3. Raman spectra of the DLCNRs and DLC films.

![Raman spectra of the DLCNRs and DLC films.](image)
4. Conclusion

Using TiO2/Ti nanotube arrays deposited Ni as the substrate, the novel pagoda-shaped DLCNRs have been successfully synthesized by a low cost CVD at low temperature 750°C in nitrogen atmosphere. In formation of DLCNRs, the catalyst of Ni plays an important role. DLCNRs possess pagoda-shape including the sharp pyramid on the tips, the edges and corners aligned regularly on the body surface. The field emission characteristics of DLCNRs/TiO2/Ti have also been studied. They possess a low turn-on electric field 3.0 V/μm, a high field emission current density 4.4 mA/cm² at 8.6 V/μm and good emission stability. Consequently, the DLCNRs/TiO2/Ti with a pagoda-shape has a bright developing prospects as a field emitter.

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