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Full Length Article

Nickel-induced transformation of diamond into graphite and carbon nanotubes and the electron field emission properties of resulting composite films

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ABSTRACT

The metal-induced transformation of diamond into graphite and carbon nanotubes (CNTs) was achieved by catalytic deposition with nickel as the catalyst. The quality of catalytic products was assessed by scanning electron microscopy, Raman spectroscopy and transmission electron microscopy. Results showed that the catalytic process could be controlled by adjusting the carbonaceous concentration in the deposition atmosphere, and new information concerning the diamond/Ni/graphite multi-phase mixed interface between diamond and carbon nanotube has been analyzed. A model was put forward to elucidate the mechanism of catalytic etching and growth on the diamond surface. In addition, the resulting diamond/CNTs composite film (10% CH_4) was found to exhibit the lowest turn-on field of 6.9 V/μm as well as good current emission stability compared to the other composite films.

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1. Introduction

Carbon-based materials with various structure and unique properties have been examined extensively in a wide range of fields for decades. Diamond films exhibit excellent physical properties, such as high electron mobility, high thermal conductivity (20–22 $W\,cm^{-1}K^{-1}$), and good chemical and thermal stability [1]. Graphite materials, such as microcrystalline graphite and carbon nanotubes (CNTs) have good electrical properties. Especially, the latter one exhibits superior structure advantages over other allotropes on emitting electrons, since its unique sharp emitting nanotips can make it easy to increase local field strength [2]. Recently, carbon composite nanostructure has attracted increasing attention because it can integrate advantages of various carbon film materials, thus obtaining desired properties and broadening its application field. Currently, lots of sp^2-bonded materials, like microcrystalline graphite, single-walled nanotubes and multi-walled nanotubes have been grown directly on diamond films, and the consequent enhanced composite performance showed large potentials in some application areas, such as electron field emission (EFE) materials [3], electrochemical detection [4], micro electro mechanical system (MEMS) [5,6]. Thus, the need for endeavor to investigate the internal transformation mechanism of different carbon allotropes is highlighted in view of the superiority of composite.

Until now, the transformation mode of carbon allotropes mainly focused on the catalytic growth of CNTs, which remains to be an open topic. Bokx et al. [7–9] proposed that it was the concentration gradient of carbon atoms in the catalytic intermediate carbides that drive the carbon transport to form filamentous carbon. Puretzky et al. [10] reported that no nanotube growth was observed at a slow heating rate, and proposed that the carbon diffusion rate was one of the key factors to the growth of nanotube. Zhong et al.

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[11] emphasized that the determining step of growing rate was the gaseous diffusion of hydrocarbon. And Bokhonov et al. [12,13] investigated the interaction of nickel with diamond, and suggested that the graphitic products should be taken into consideration in the growth of carbon nanotubes. No matter how different these theories were, it should be noted that the carbon diffusion is the key point in the whole catalyst growth process. And in spite of so many research findings, roles of carbon concentration and phase (solid state or gaseous state) which have an important effect on the carbon diffusion in the structural transformation of carbon allotropes have not been fully unveiled. Thus, the need for endeavor to investigate the transformation mechanism of different carbon allotropes with different gaseous carbon source concentration is highlighted in view of this issue.

In this paper, we aimed at thoroughly investigating the catalyst mechanism of diamond surface by regulating the carbon concentration in catalytic deposition atmosphere. By controlling the substrate, temperature and catalyst, we attempted to reveal the internal relations between the catalysates and the carbon source concentration (methane). Meanwhile, we firstly reported the discovery of a three-phase-mixed layer and hereby optimized the relevant growth mechanism. Additionally, effects of superficial morphologies on the performance of electron field emission were also investigated.

2. Experimental

⟨100⟩ silicon substrates (10 mm × 10 mm × 0.6 mm) were firstly ultrasonically cleaned in acetone for 20 min, ethanol and deionized water for 10 min successively. The cleaned Si substrates were then ultrasonically seeded in a suspension of diamond nanopowders for 30 min to enhance diamond nucleation. A diamond layer was subsequently obtained by hot-filament chemical vapor deposition (HFCVD) using a mixture of methane (CH_4, 3 sccm) and hydrogen (H_2, 97 sccm), and diborane (B_2H_6, 0.2 sccm). Doping the diamond with only a small amount of boron helps to enhance the electrical conductivity of diamond and thus to improve the EFE properties of films [14]. The substrate temperature maintained at around 750 °C and the chamber pressure kept at 3×10^3 Pa for 240 min. Next, a nickel coating of 30 nm thickness was sputtered on the diamond surface by DC magnetron sputtering, which was carried out under an argon atmosphere held at 0.4 Pa for 60 s. The as-sputtered nickel/diamond film was further catalytically treated in the same CVD reactor at 10 kPa at 800 °C for 40 min. A gas mixture consisting of 0%, 0.5%, 5% and 10% methane in hydrogen, and a total gas flow rate of 50 sccm was introduced, respectively. Thus, diamond-based composite films were finally obtained and denoted as 0% CH_4, 0.5% CH_4, 5% CH_4 and 10% CH_4, respectively.

The surface topography of the composite films was observed by field emission scanning electron microscopy (FEI, Nova NanoSEM 230). The crystalline quality and bonding state of the films were characterized by Raman spectroscopy (HORIBA, LabRAM HR800; λ = 488 nm). Focused ion beam (FIB, Helios Nanolab 600i, FEI Electron Optics B.V, USA) was utilized to prepare the cross-sectional sample, and transmission electron microscopy (TEM, TECNAI G2, FEI Electron Optics B.V, USA) was used to characterize the microstructure.

The field emission characteristic of the samples was tested in a custom built setup, where a parallel-plate diode structure was used. The effective area of metal anode and the anode-cathode space were fixed as 19.63 mm^2 and 200 μm, respectively. I–V characteristic was obtained using Keithley 6485 Piacoammeter at ambient temperature in high vacuum and the result was analyzed using the classical Fowler-Nordheim (F-N) theory.

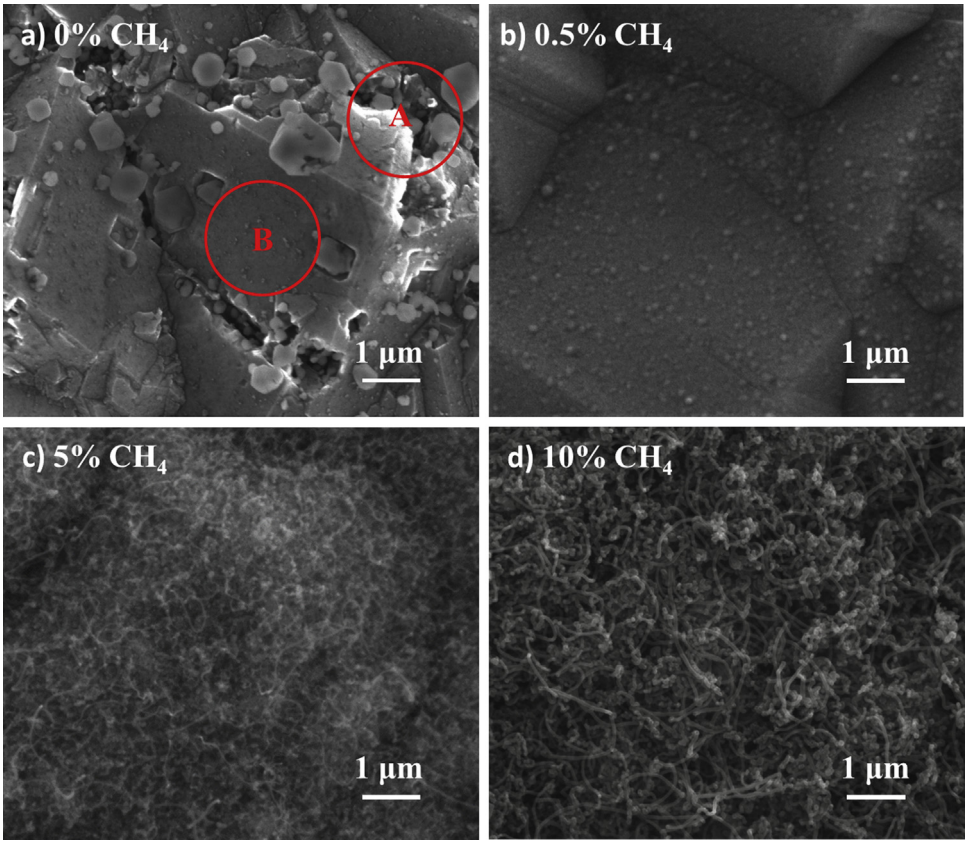

Fig. 1. SEM images of films obtained at different methane concentration of 0%, 0.5%, 5% and 10%.

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