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Field emission characteristic study on bristling few-layer graphite/diamond composite film

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ABSTRACT

The purpose of this study is to fabricate a composite film of bristling few-layer graphite on an octagonal shaped diamond-tip array and to measure the field emission characteristics. The composite film of bristling few-layer graphite on an octagonal shaped diamond-tip array is firstly proposed to improve the field emission effect and lifetime because of the high pitch height ratio of bristling few-layer graphite and the high stability of diamond. The microcrystalline and ultra-nano-crystalline diamond-tip arrays with the shape of an octagonal cone are formed by microwave plasma-enhanced chemical vapor deposition on a silicon substrate. Changing the flow rates of gasses when the bristling few-layer graphite are deposited on the diamond film leads to different results and find out the ideal fabrication parameters for improving field emission. The diamond-tip arrays and bristling few-layer graphite morphology are then examined by Raman spectroscopy and scanning electron microscopy. The field emission effect with different few-layer graphite/diamond composite arrays is also examined.
In this study, the composite film of bristling few-layer graphite structures on diamond-tip arrays grown by $N_2/H_2/CH_4 = 40/80/20$ showed excellent field emission stability and high field emission characteristics with low turn-on field of 2.60 V/μm and the field enhancement factor of 1921.

1. Introduction

The field emission theory was proposed by Fowler and Nordheim [1]. It states that when the material is applied an electric field, the barrier at the surface of an electron conductor becomes rounded triangular, and individual electrons can escape from the material in various circumstances.

In recent years, a lot of field emission studies used carbon nanotubes (CNTs), graphene, diamond and other carbon materials as cathodes [2,3]. Although CNTs have good field emission effect, the lifespan of the CNTs and the screening effect limits its applications. Studies on the screening effect, a phenomenon in which the current density decreases when the distance of each emitter is too close to each other and interferes with the electric field of emitters, of CNTs have been proposed [4–6].

Diamond possesses excellent physical and chemical properties, including high hardness, high corrosion resistance, high thermal conductivity, high stability, high electron mobility, and negative electron affinity [7,8]. These outstanding characteristics make diamond widely utilized in industrial grinding, cutting tools and electronic related components in recent years. Diamond related materials that could be deposited on silicon substrates, including microcrystalline diamond (MCD), nano-crystalline diamond (NCD) and ultra-nano-crystalline diamond (UNCD), are suitable candidates for being stable and reliable field emission emitters [9–12]. Many researchers used micro/nano-crystalline diamonds to improve stability and lifetime of CNTs. Varshney et al. grew CNTs on free standing diamond films and hierarchical flower-like carbon nanotube clusters on UNCD films, which both have excellent field emission lifetime and stability [9,10]. Yang et al. fabricated vertically aligned CNTs/diamond double-layered structure to improve field electron emission stability [11]. Tsai et al. fabricated MCD/CNT double-layered pyramid arrays to improve field electron lifetime of CNT [12].

Graphene has become a popular material recently, because of its excellent field emission properties, including high electric mobility, low resistivity, and low energy barrier [13,14]. Graphene is also used in the fabrication of super-hydrophobic and the super-hydrophilic devices [15]. In general, graphene can be fabricated by three methods: mechanical exfoliation, reduced from graphene oxide and chemical vapor deposition. In the method of chemical vapor deposition, the nickel and the copper are often used as the substrate to grow the graphene [16,17].

Furthermore, the number of layers of graphene less than 10 is called few-layer graphene while graphene with 10 to 100 layers are called few-layer graphite. The synthesis of few-layer graphene by microwave plasma-enhanced chemical vapor deposition has been proposed in recent studies [18]. Zhu et al. proposed that the hydrogen is the main

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factor about growing carbon nanosheet [19]. The carbon atoms will grow a graphite and amorphous carbon layer on the substrate at nucleation sites in the beginning. When the carbon atoms are deposited on the nucleation points, hydrogen will etch more amorphous carbon. Then crystalline graphitic structures and the carbon nanosheet will grow at the same time subsequently. Another type of graphene called the vertical graphene was first discovered in the process of fabricating carbon nanotube [20,21]. Vertical graphene is used as an electrode of the super capacitor, which is expected to replace the conventional capacitor device, because of its high surface area [22]. Few-layer graphite grown in this study is similar to the vertical graphene in terms of structure, but with the exception of having a diamond core within its layers of graphite.

This study proposes the fabrication of the bristling few-layer graphite/diamond composite film, which shows excellent field emission properties, longer lifespan, and less screening effect. In this composite film the bristling few-layer graphite (BFG) acts as the field emission emitters and the MCD or UNCD deposited conducts away heat to improve field emission properties. In order to decrease screening effect, the nitrogen flow rates are adjusted during growing BFG to alter the morphology of BFG in the hope of finding the most optimal field effect results and the octagonal silicon tip arrays are used as the substrate. In this study, the morphology and structure of bristling few-layer graphite/diamond composite film were observed by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The characteristics of bristling few-layer graphite are examined by Raman spectroscopy (514 nm), and the field emission proprieties of the composite film with tip arrays are also studied. In addition, the relationship between the BFG morphology and fabrication parameters are also discussed.

2. Experiment

In this experiment, octagonal shaped tips have first been created with lithography techniques. After that the diamond layer was grown with chemical vapor deposition methods. Finally, the bristling few-layer graphite was grown on the resulting substrate surface.

2.1. The silicon tip with the lithography

The substrate with octagonal tips was made by photolithography and anisotropic etching processes. For the photolithography process, the pattern of the mask is a square array, in which the spacing of each square is 10 μm and the size of the square is 40 × 40 μm^2. Firstly, a square shaped titanium barrier layer of thickness 2000 Å was deposited on the silicon substrate, then a 3 μm thickness photoresist (AZ-P4620) was coated on the titanium. The photoresist was exposed to a pattern of ultraviolet light and a square shaped array of photoresist was developed. Finally, the square-shaped array of the titanium was fabricated by wet etching (NH_4OH:H_2O_2:D.I. water = 1:1:2). After that, the substrate was soaked into the solution of acetone, isopropanol and deionized water to remove the residual photoresist. The resulting substrate surface is as shown in Fig. 1.

The silicon substrate with the square pattern was then anisotropically etched by 5 M KOH and 1 M IPA at 60 °C for 50 min to fabricate the octagonal tip array. When the top of octagonal tips first appeared, the titanium layer was drifted away from octagonal tips due to the surface area of contact becoming nearly negligible (only the tip is in contact with the titanium layer at this point).

2.2. Diamond films and bristling few-layer graphite

The microwave plasma-enhanced chemical vapor deposition was used to grow the diamond films and the BFG in this study. Before the diamond film was grown, diamond nucleation sites were ultrasonically seeded on the substrate in a solution with diamond powders (diameter of 4–12 nm), titanium powders, and methanol for 45 min. The residual powders on the substrate were removed by the methanol and acetone, subsequently. Afterwards, the chamber was then evacuated to 3 × 10^{-2} Torr by a mechanical pump, and an MCD or UNCD film was deposited. MCD films were deposited with the microwave power of 1200 W at 80 Torr with flow rates of gasses of 1 sccm methane, 50 sccm argon and 49 sccm hydrogen for 60 min; UNCD films were deposited at the power of 1200 W and 130 Torr with flow rates of gasses of 4 sccm methane and 196 sccm argon for 60 min. After the growing of micro/nano-crystalline diamonds, the power was increased to 1500 W and different flow rates of gasses, shown in Table 1, were tested out. Fig. 2 shows the flow chart of the overall fabrication process.

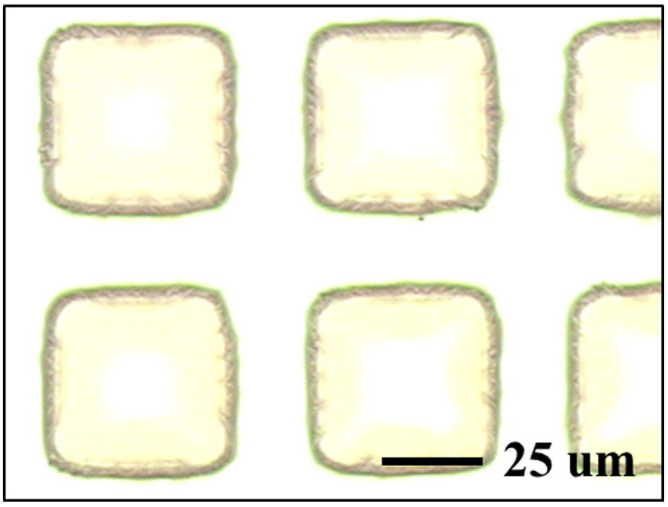

Fig. 1. The square-array pattern of the titanium barrier layer.

3. Results and discussion

3.1. The octagonal silicon tip

A novel process of creating octagonal shaped diamond tip arrays are proposed in this study. As shown in Fig. 3, the square-array pattern was anisotropically etched by 5 M KOH and 1 M IPA solution at 60 °C for different periods. Fig. 3(a) and (d) shows the sample of a 40-minute etched surface, which looks like an octagonal platform array. Fig. 3(b) and (e) shows the sample of a 50-minute etched surface, which shows an ideal octagonal tip array. Fig. 3(c) and (f) shows the over-etched result of a 60-minute etched surface. It is manifested that the optimal etching time of fabricating the octagonal silicon tip array is 50 min and is used in this study.

According to the literature [23], the lattice of the octagonal silicon tip surface is [211]. The morphology of the octagonal tip results from

Table 1
All label and parameters of samples.

Parameters	Pressure (Torr)	Power (w)	CH_4 (sccm)	H_2 (sccm)	N_2 (sccm)	Growth time (min)
BFG/MCD(UNCD)-N_2^1	80	1500	20	80	10	30
BFG/MCD(UNCD)-N_2^2	80	1500	20	80	20	30
BFG/MCD(UNCD)-N_2^3	80	1500	20	80	30	30
BFG/MCD(UNCD)-N_2^4	80	1500	20	80	40	30
BFG/MCD(UNCD)-N_2^5	80	1500	20	80	50	30
BFG/MCD(UNCD)-N_2^6	80	1500	20	80	60	30
BFG/MCD(UNCD)-N_2^7	80	1500	20	80	70	30
BFG/MCD-H_2^7	80	1500	20	70	40	30
BFG/MCD-H_2^6	80	1500	20	60	40	30
BFG/MCD-H_2^5	80	1500	20	50	40	30

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