Research Article

The Field Emission Properties of Graphene Aggregates Films Deposited on Fe-Cr-Ni alloy Substrates

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The graphene aggregates films were fabricated directly on Fe-Cr-Ni alloy substrates by microwave plasma chemical vapor deposition system (MPCVD). The source gas was a mixture of H₂ and CH₄ with flow rates of 100 sccm and 12 sccm, respectively. The micro- and nanostructures of the samples were characterized by Raman scattering spectroscopy, field emission scanning electron microscopy (SEM), and transparent electron microscopy (TEM). The field emission properties of the films were measured using a diode structure in a vacuum chamber. The turn-on field was about 1.0 V/μm. The current density of 2.1 mA/cm² at electric field of 2.4 V/μm was obtained.

1. Introduction

Graphene has grabbed appreciable attention due to its exceptional electronic and optoelectronic properties [1]. One of the potential applications of graphene is in field emission (FE) displays. Malesev et al. synthesized vertically aligned few-layer graphenes (FLGSs) using plasma-enhanced chemical vapor deposition (PECVD) on titanium substrate, and turn-on field of the field emission from the graphene layer was as low as 1 V/μm [2]. Qi et al. prepared FLGSs by radio-frequency PECVD on Si(100) substrates without any catalyst, and turn-on field of its emission was 3.91 V/μm [3]. We previously reported that nanocrystalline graphitic films on ceramic substrates by MPCVD using Fe-Ni-Cr layer as catalyst were deposited, the turn-on field of 1.26 V/μm was obtained [4].

In this paper, we present the field emission characteristics of the graphene aggregates films, which were synthesized by MPCVD directly on stainless steel substrate without any catalyst. The structure of the films was also studied.

2. Experiment

The Fe-Cr-Ni alloy substrates were polished with abrasive paper of W7 (particle size was about 15 μm) and then

ultrasonically cleaned with deionized water and acetone. The graphene films were deposited directly on the substrates without any catalyst by MPCVD. The source gas was a mixture of H₂ and CH₄ with flow rates of 100 sccm and 12 sccm, respectively. During the deposition, the total pressure of 6.0 KPa, substrate temperature of 700°C, and microwave power of 1600 W were kept for 10 mins.

The structure of deposited films were analyzed by Raman scattering, SEM, and TEM. The field emission properties were measured using a diode structure, which was placed in a vacuum chamber. The deposited film with area of 0.2 cm² was used as a cathode. The anode of an indium tin oxide (ITO-) coated glass was separated from the cathode by a mica spacer with thickness of 600 μm. The base pressure in the vacuum chamber was maintained below 1 × 10⁻⁴ Pa during the measurements. The voltage was stepped up from 0 to 2500 V.

3. Results and Discussion

The Raman spectrum of the sample was shown in Figure 1. The G- band appearing at 1583 cm⁻¹ originates from in-plane vibration of sp² carbon atoms and is a doubly degenerate (TO and LO) phonon mode (E_{2g} symmetry) at

FIGURE 1: Raman shift of the as-grown sample.

FIGURE 2: SEM and TEM images of the sample; (a) top-view SEM image of as-grown sample, (b) SEM of an enlarged image, (c) TEM image of agglomerated graphene sheets, and (d) HRTEM image of graphene sheet.

the Brillouin zone center. The band located at 1353 cm^{-1} corresponds to the D band of graphitic carbon species, which is a disorder-activated Raman mode and is associated with the TO branch near the K-point. The 2D band at 2700 cm^{-1} originates from a two-phonon double resonance Raman

process, and it is closely related to the band structure of graphene layers and is to be used to confirm the presence of graphene [5, 6]. The band at 1620 cm^{-1} , termed as D', which arises from phonon scattering at the crystal-lattice defects. The band at 2950 cm^{-1} originates from D+G mode

FIGURE 3: I-V curve and its F-N plot of the sample.

[7]. The Raman spectrum of the sample indicated that the deposited film was graphene film.

The morphology of the graphene film was shown in Figure 2. Figures 2(a) and 2(b) showed the top-view SEM images of as-grown sample, and it seemed to be consisted of petal-like clusters of graphene sheets. Such kind of film was named graphene aggregates film. The sizes of the clusters were about 100–300 nanometers. In order to further examine and confirm the nanostructure of the sample, TEM measurements were performed. To prepare TEM samples, the sample was ultrasonically treated in alcohol directly, then dropped onto holey grids. Figure 2(c) revealed the TEM image of agglomerated graphene sheets around an amorphous carbon particle, which may hint that the growth of the graphene sheets probably originated from amorphous carbon structure. In the experimental condition, the detailed growth mechanism of the agglomerated graphene needs further study. The layered structure shown in HRTEM image (Figure 2(d)) confirmed the structure of graphene. It also revealed the defects such as wrinkles and edge loops in graphene sheet.

The field emission characteristics of the graphene aggregates film were tested. The turn-on field of about 1.0 V/μm and the current density of 2.1 mA/cm² at electric field of 2.4 V/μm were obtained. Figure 3 showed the current versus voltage (*I*-*V*) curve of the field emission, and the corresponding Fowler-Nordheim (F-N) plot was inserted in Figure 3, which characterized the tunnel effect of the field emission from the graphene aggregates film. The F-N plot exhibited two different slopes at low-field region and high-field region. The current saturation of the emission and the slope deviation of the F-N plot at high-field region were observed in Figure 3. The same phenomena were observed for carbon nanotubes emitter, reported by Choi et al. [8]. In the present case, we suggested that the current saturation and F-N plot deviation were attributed to the same reason, which was adsorbate desorption effect, especially hydrogen-adsorbate desorption during the emission measurement. We had also reported the hydrogen desorption effect during

the emission measurement for amorphous carbon emitter [9]. During the graphene film deposition by CVD method, hydrogen atoms were adsorbed on the surface and edges of graphene aggregates to form the localized states near the Fermi level, which were responsible for the emission. During the emission measurement, the hydrogen adsorbates gradually desorbed, and the localized states disappeared, which probably led to the current saturation and F-N plot deviation phenomena.

The above measured results indicate that the graphene aggregates film was a good material for field electron emitter. The good field emission properties would be attributed to two possible mechanisms. (1) The graphene sheets were extending to a height of several hundreds of nanometers vertically aligned to their surfaces along the applied electric field, and the field sites of which would cause a large-field enhancement factor [10]. (2) the defects of the graphene sheet lowered electron affinity that provided a low-energy barrier and enhanced electron emission. Filletter et al. reported that energy barrier of single-layer graphene grown epitaxially on 6H-SiC (0001) had been determined to be 135 ± 9 meV by means of the Kelvin probe force microscopy [11], which was much lower than that of 4.5 eV for graphite.

4. Conclusion

In summary, we have demonstrated that the graphene film can be directly grown on stainless steel surface employing methane as the source gas in about a 10-min growth time. The growth temperature was about 700°C. The graphene aggregates emitter has a very low turn-on field of only about 1 V/μm and an emission current density of 2.1 mA/cm² at an applied field of 2.4 V/μm. This promising field emission performance can be attributed to the electric field enhancement, and the defects induced low-work function of the graphene aggregates film.

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