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Synthesis and field emission properties of graphene-Ni hybrid composites

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ABSTRACT

Nickel decorated vertically aligned graphene sheets (VGSN1) and vertically aligned graphene sheets-graphene shell/nickel core (VGSN2) hybrids have been synthesized by radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD). The surface morphology, microstructure and growth mechanisms of VGSN1 and VGSN2 hybrids were investigated. The field emission (FE) studies indicated that the graphene-Ni hybrids delivered better FE performance than pristine graphene (VGS/Si) due to the insert of Ni particles. The influences of the morphologies and structures on FE performance have been revealed. Our approach provides a novel way to fabricate highly efficient graphene-based field emitters for the development of practical electron sources.

1. Introduction

Electrons can be emitted from the surface of metal or semiconductor into vacuum via thermionic emission, photoemission or field emission. The field emission (FE) is a quantum mechanical tunneling phenomenon in which electrons are emitted by the application of an external electric field [1–9]. Therefore, the cold cathode field emitter attracts more attention due to its fast turn-on process, low working temperatures, ultrahigh energy efficiency and miniaturized device size, and provides a high emission current density at low electric fields [10–13]. Since the first demonstration of electron FE from carbon nanotubes [14], carbon-based cold cathodes including nanotubes, graphene and related composites have garnered growing interest as potential emitters in field emission displays [15–25]. In particular, graphene, a two-dimensional honeycomb lattice material bonded with a single layer of sp^2-hybridized carbon atoms, exhibits extremely high electronic mobility, excellent thermodynamic stability and great elasticity for future electronic structures [26–29]. It's well known that the electron emission from graphene is strong directional dependence with extremely low out-of-plane conductivity, and the electron emission is mostly from the edges of graphene. Therefore, vertically aligned graphene nanosheets (VGS) are considered to be good candidates for field emitters free from Joule heating, owing to the exposed sharp edges, non-stacking morphology, high aspect ratio and the unique physical properties of graphene [30–32].

Recently, combining graphene with low-dimensional nanomaterials as the hybrid nanostructure is an innovative avenue to obtain improved FE properties and nano-electron emission devices [33–36]. Vankar et al. [37] have demonstrated that graphene films grafted with metal nanoparticles by thermal evaporation showed enhanced electron field emission and reduced turn on and threshold fields. Zhang et al. [33] have reported an improved FE property from the graphene–Au nanoparticles nanocomposite and the decoration of Au nanoparticles on graphene was deployed by thermal evaporation. Yan et al. [34] have fabricated a graphene/patterned ZnO nanorod array composite by covering the patterned ZnO nanorod arrays with graphene thin layer, and this composite exhibited better field emission than graphene/compact ZnO nanorod arrays. However, the weak adhesion between graphene and low-dimensional nanomaterials in graphene-based composites obtained by above methods will limit the electronic transmission speed during FE process. Promising FE properties of VGS and related materials have been reported [30,37–39]. And we have reported FE studies on VGS-graphite shell/Cu core hybrids in our previous work [31]. The study revealed that the hybrids synthesized by RF-PECVD exhibit superior FE properties in comparison with pure VGS due to the existence of Cu and the tightly surrounded of graphene on Cu surface. This structure could decrease the contact resistance between graphene and Cu, and then improved the FE properties. It is worth noting that Ni is a better catalyst than Cu when it is used to grow the graphene films, because Ni provides faster growth rate than Cu and helps in the growth process by providing the nanoclusters of a polycrystalline film containing very small particles [37,40,41]. These studies have inspired us

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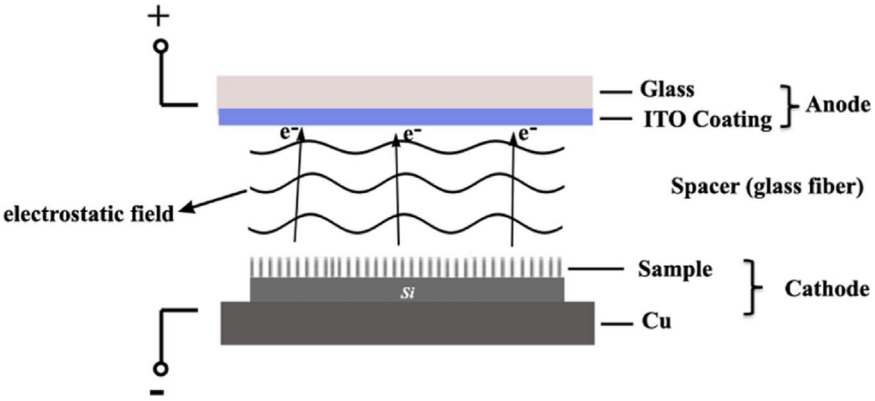

Fig. 1. A schematic of the setup for field emission measurement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

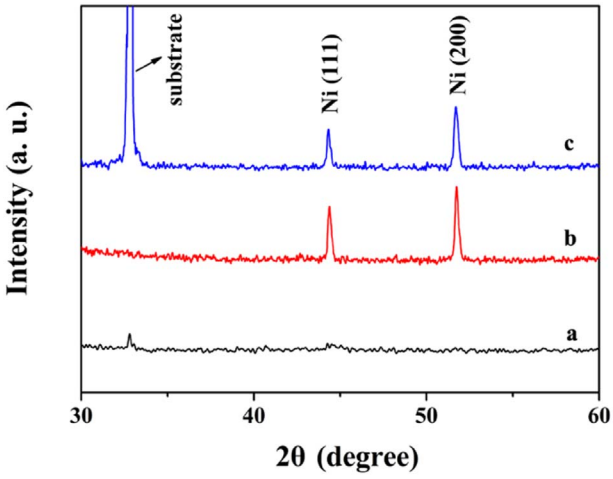

Fig. 2. XRD patterns for N2 film (a) before and (b) after annealing, (c) XRD pattern for VGSN2 sample grown for 35 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to further investigate field emission performance in graphene-Ni composites.

Herein, we try to obtain two kinds of vertically aligned graphene sheets-Ni hybrids by using RF-PECVD. Meanwhile, we reveal the growth mechanism and investigate how the variations in morphologies and structures of hybrid composites influence their FE properties.

2. Experimental

2.1. Synthesis of hybrid composites

Using direct-current magnetron sputtering, we firstly deposited Ni films with a thickness of about 1 nm (N1) and 20 nm (N2), respectively, on Si (100) wafers. VGS were synthesized on Ni catalyst films by RF-PECVD at the substrate temperature of 800 °C in mixture of CH_4/Ar gases with the gas flow rate ratio CH_4/Ar = 20 sccm/50 sccm (sccm denotes standard cubic centimeter per minute at STP). The discharge power, total gas pressure and growth time were kept at 200 W, 800 Pa and 2–35 min, respectively. The fabrication of VGS has been reported previously [31]. The resulting samples were named VGS/Si, VGSN1 and VGSN2 corresponding to the Ni films with a thickness of 0, 1 and 20 nm, respectively.

2.2. Characterization of prepared samples

The obtained samples were characterized by X-ray diffraction (XRD) using a Bragg-Brentano diffractometer (D8_tools) in θ-2θ configuration with a Cu Kα line at 0.15418 nm as a source, scanning electron microscopy (SEM) (JEOL JSM-6700F), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F operated at 200 kV) and Raman spectra measurement (T64000 (Horiba) with a 514.5 nm Ar^+ laser excitation). The electron field emission measurements of the samples were carried out at a pressure of 2×10^{-4} Pa using a diode configuration at room temperature. An indium tin oxide (ITO) plate and sample mounted on Cu plate were used as the anode and cathode, respectively. A schematic setup of electron field emission from samples is presented in Fig. 1.

3. Results and discussion

3.1. The microstructure and morphology of samples

The XRD patterns of N2 film before and after annealing are shown in Fig. 2a and b, respectively. Fig. 2c is the XRD pattern for VGSN2 sample grown for 35 min. Two diffraction peaks at 44.4° and 51.7° in curves b–c correspond to the (111) and (200) planes of cubic Ni (JCPDS-ICDD Card No. 04-0850). However, no reflections from either nickel oxide or carbide were observed in Fig. 2(b–c), which confirms that the VGS have protect the nickel particles from oxidation and the nickel is chemically stable during graphene deposition. In addition, diffraction signals from Ni peaks for VGSN1 sample, N1 film and N2 film are too weak to be detected.

Fig. 3(a–b) exhibit the SEM images for N2 film before and after annealing. Fig. 3c is the SEM image for N1 film after annealing. It can be found that Ni particles sparsely dispersed on the substrate surface caused by surface energy minimization through the liquid-like flow after annealing [42]. The size distributions of Ni particles for N2 and N1 film after annealing are shown in Fig. 3(d–e), respectively. As the thickness of Ni catalyst film was 1 nm, up to 92% of Ni particles have diameters of 14.5–29.5 nm (Fig. 3e). However, Ni particles evolved from Ni film with a thickness of 20 nm have a wide distribution of particle size (50–300 nm) (Fig. 3d), attributing to the attachment of species in the quasi-liquid phase of Ni film on the bare surface of Si substrate as well as the previously existing Ni particles.

Fig. 4(a–c) compares the surface morphologies of VGSN2 samples after growing for 6, 15, and 35 min. It is well known that the Ni catalyst will provide an efficient way to improve the nucleation of VGS, and contributes to the VGS growth [43]. As the deposition time is 2 min (Fig. 4e), only a few small sizes of sharp protrusions appear on the surfaces of Ni particles. As the deposition time is increased from 6 to 35 min, more and more graphene sheets vertically align on the surface of Ni particles and apparently enlarge. Finally, hedgehog-like particles with the VGS extend from the surface of Ni were formed. In

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