ANOMALOUS IMPROVED ELECTRON FIELD EMISSION FROM HYBRIDISED GRAPHENE ON MO TIP ARRAYS

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ABSTRACT

A new, efficient electron field emitter geometry, based on monolayer graphene coated well aligned Mo tip arrays, is here reported. The rather anomalous, yet nonetheless beneficial contributions of this hybridized nanostructured film morphology is evaluated and discussed. Efficient and stable field emission with low turn on fields has been observed. Incorporation of graphene and Mo tip array results in noteworthy improvements in emission of these nanoscale heterostructure devices.

KEYWORDS

Graphene, molybdenum, tip array, field emission

INTRODUCTION

Background

Electron field emission (FE) is a quantum tunneling phenomenon whereby electrons are emitted from a solid surface under the action of a strong electric field [1]. Graphene and its derivatives have been found to be efficient field emitters due to their unique geometry and electrical properties [2]. Reports thus far indicate that the FE performance of nascent graphene is moderate [3] compared with other nano graphitic cathodes, such as carbon nanotubes [4]. Possibly associated with the deposition method, such as nominally planar chemical vapor deposition, such graphene flakes tend to lie parallel to or protrude at low angles from the substrate, thereby limiting their geometrical field enhancement. By comparison carbon nanotubes allow for simple, near ideal vertical alignment. Planar surfaces that have low enhancement factors, contingent on the emitters material properties, can require high turn on fields of up to 1000 V/μm [5]. Such high electric fields are undesirable as they can result in deleterious electrical discharge and vacuum breakdown [6]. Practically, as a result, field emitters are engineered to have needlelike shapes with sharp tips in order to dramatically reduce the turn-on electric fields by several orders of magnitude due to the local field enhancement at these tips [7].

In this paper, we outline our work on an optimized means of transferring graphene onto Mo tip arrays in order to produce a new nanostructured electron source. Compared with the field emission characteristics of bare Mo tips, and graphene on flat bulk Mo, though rather anomalously, for the graphene coated Mo tip arrays improved emission was evident with a reduced turn-on field observed.

Field emission theory

Fowler–Nordheim (F–N) theory [8, 9] is one of the most-commonly used models for explicating electron emission from electron dense surfaces under intense electric fields and has been widely used to investigate the electron-emission behavior of various materials [10]. Though its validity at the nanoscale remains under some debate, it does nonetheless coarsely approximate the field emission current (I) as a function of the applied electric field (E) from

$$I = \frac{(aA\beta^2 E^2)}{\varphi} \exp(-b\varphi^{3/2} / \beta E)$$

Where $a = 1.54 \times 10^{-6}$, $b = 6.83 \times 10^{7}$, A is the emission area, β is the field enhancement factor and E ($=V/d$) is the applied electric field. d is the cathode to anode distance.

The emission current is highly dependent on both the geometry of the cathode and the material properties. Based on this, at specific fields, lower work function materials with high aspect ratio emitters are capable of producing higher emission currents [11, 12].

Among the most promising method to increase the FE performance is the hierarchical development of the cathode through the use of nanoscale surface engineering. Here the emitting surface, comprising primarily of microstructures, is complemented with 1D or 2D nanostructured adlayers [13], which augment the emission properties. Molybdenum, along with other refractory metals, is one of the most common FE materials used to date, while graphene and its derivatives are expected to come to the fore due to their unique geometry and electrical properties [14]. The high aspect ratio of monolayer graphene could potentially give dramatic field enhancement, if suitably aligned, when combined with its novel transport properties. In the present study, we transfer graphene to Mo tip array in an optimized way.

FABRICATION

A schematic description of the fabrication process is illustrated in Fig. 1. The Mo tip array fabrication process is reported in detailed elsewhere [15]. For brevity, and as shown in Fig. 1(a), a double-side-polished, 400 mm thick, 4-inch high purity (99.95%) Mo wafer was first coated with an evaporated 500 nm thick Al film to form etch

mask. The tip array was subsequently patterned by photolithography (Fig. 1b and c), with the Al patterned by dry etching in CH_3F plasma (Fig. 1d). The Mo tip array was etched using an anisotropic SF_6 dry etch in a commercial ICP etcher (Sentech PTSA 500) (Fig. 1e). Residual Al was removed by ultrasonication (15 W) for 60 s (Fig. 1f). PMMA/graphene films were transferred onto the Mo tips (Fig. 1g) by standard PMMA transfer [16], outlined later, with the PMMA subsequently removed by heating to obtain the sample with graphene uniformly covering the Mo tips (Fig. 1h).

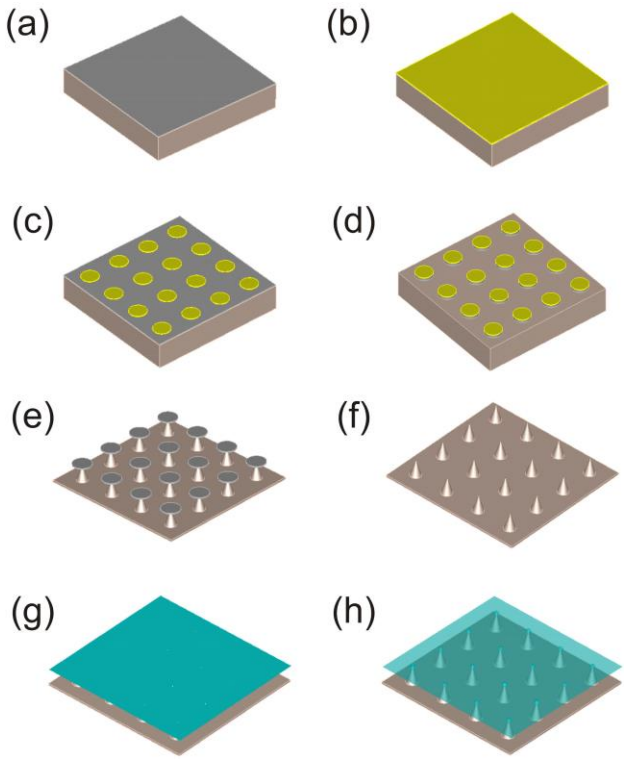

Figure 1: Schematic of the processes of transferring the CVD graphene onto the Mo tip array: (a) deposition of 300nm Al, (b-c) photoresist patterning by optical lithography, (d) ICP etching of Al, (e) Mo tip forming ICP etch, (f) removal of Al mask, (g) PMMA/graphene film transfer, and (7) PMMA removal by heating.

This optimized transfer of graphene is described in Figure 2. PMMA was spin coated onto the Cu-foil-supported CVD-graphene at 4,700 rpm for 60 s (Figure 2b), and then cured at 180°C for 1 min. Since graphene grows on both sides of the Cu foil only one side of the Cu/graphene was coated with PMMA, the opposite side was exposed to O_2 RIE plasma treatment to remove the underside graphene. The 1 cm × 1 cm × 25 µm thick Cu substrates were then etched in aqueous ammonium persulphate (0.1M concentration) over 12 h (Figure 2c). The PMMA mechanically supports the graphene until the metal etching is complete. The PMMA/graphene stack was then rinsed in deionized water (Figure 2d) and placed on the target substrate using a silicon wafer fragment for support. Transferred samples were then dried at room temperature for 12 hours. Samples were subsequently baked on a hot plate at 350°C in air to remove the PMMA support (Figure 2e). When treated for <3 h, we found there was poor adhesion between the graphene and the transfer substrate, whilst when heated for >12h at 350°C (Figure 2f), the PMMA/graphene film adhered well and the PMMA block could be peeled off effectively.

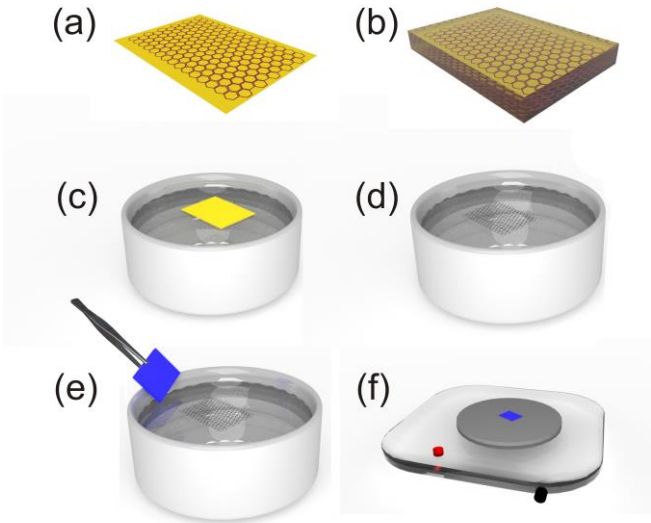

Figure 2: Schematic depiction of the graphene transfer processes. (a) Copper-supported graphene (b) Spin-coated PMMA on graphene/copper foils at 4700 rpm for 60s. (c) The PMMA/graphene film floated on the surface of ammonium persulfate (0.1M) which etches the Cu catalyst. (d) The PMMA/graphene film is then rinsed in deionized water several times to ensure full removal of residual etchant(e) Mechanical transfer of the PMMA/graphene film onto the destination sample (f) After drying for several hours, the sample was heated at 120°C for 15 mins and then heated at 350°C for 12.

The graphene functionalized Mo tips, and the planar bulk Mo chips functionalized with graphene were characterized by scanning electron microscopy, as shown in Figure 3(a-f). A Mo tip array, of 10 µm pitch, were realized with good uniformity and an aspect ratio ≈ 1.8 with a tip radius of 91 nm.

In the case of the pristine Mo tips, four dominant factors influence the level of field emission, the emitter tip radius r, emitter height h, inter-emitter pitch D, and the electric field E. Controlling the tip areal density was also an important factor in determining the field emission performance, as electron screening from neighboring tips must be minimized. Our simulations suggest that the emission current density reaches a maximum when the distance D is approximately three times the height h (to be reported elsewhere). For the Mo tip array, D/h≈ 1.6, suggesting that the cones are likely overly closely packed for optimal emission. Upon coating of the Mo tip with the CVD graphene we note the occurrence of new conical surface features, where the dimensions of these new cones are comparable to those of the original Mo tips, though the height of the new cones are somewhat shorter, with D remaining broadly the same, thus enlarge the D/h_{new} and ths adjustingthe emission current density.

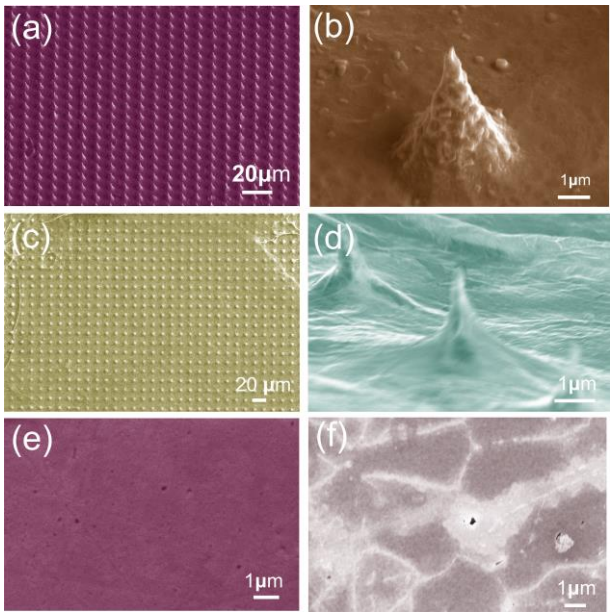

Figure 3: SEM of (a) Mo tip arrays (b) Perspective view of single Mo tip (c) Mo tip arrays with graphene (d)Perspective view (e) Bulk Mo (f) Bulk Mo with graphene.

Raman shifts of the graphene coated Mo tips and graphene coated flat Mo are shown in Figure 4(a). The increase in the I_D/I_G ratio of the Mo tips/graphene and SEM micrographs indicates an increase in defect density in the Mo tips/graphene, likely induced by the transfer process and high basal plane stresses induced at the Mo tip apexes. Such defects likely provide additional new emission sites as the variation in field is much larger at defects, edges, and ripples at the atomic scale, which leads to larger local electric fields. The surface roughness of the graphene sheets on the Mo tips is shown in Figure 4(b).

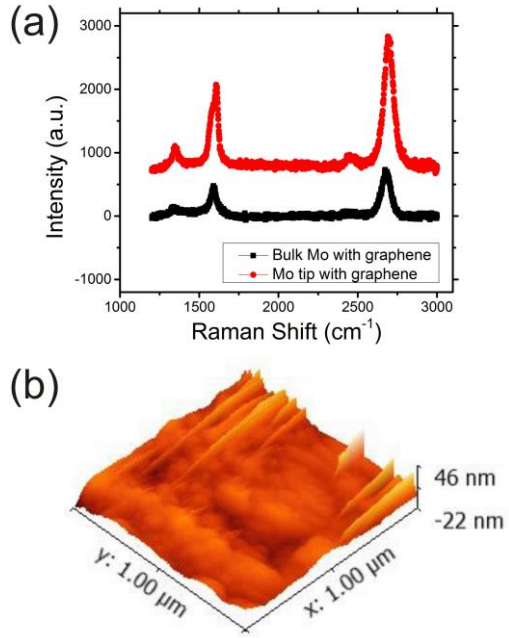

Figure 4: (a) Raman shift of bulk Mo/graphene and Mo tips/graphene (b) Surface roughness of the graphene on the Mo tips.

EMISSION PROPERTIES

The field emission performance of the samples was measured at a base pressure of $<10^{-7}$ mbar in a custom-built, automated field emission system. An ITO/glass anode was positioned adjacent to the emitting surface and the emission area of all the three samples was 12.5 mm^2. All measurements were performed at a cathode-to-anode distance of 1 mm.

Typical I-V characteristics are shown in Figure 5(a), with the corresponding F-N plots shown Figure 5(b). The emission characteristics were measured from 0–5 kV, at 50 V increments, with spectra consisting of both up and down sweeps. The emission current was averaged (n=3) at each bias.

Three different FE cathodes were tested and compared: pristine Mo tip arrays, graphene functionalised Mo tip arrays, and graphene coated flat bulk Mo. The maximum emission current of graphene/Mo tips was 1.27×10^{-04} A, around an order of magnitude greater than the maximum emission current of the unfunctionalized Mo tips (5.70×10^{-06} A). There was little measurable emission current above the SMU noise floor from the graphene sheets on flat bulk Mo, even under the maximum applied electric field of 5×10^{6} V/m, as shown in Figure 5a. We observe that the maximum emission current characteristics of the fabricated devices markedly enhance when the Mo tips/graphene field emitters are used as the cathodes. The observed enhancement of the FE performance may be attributed to the gradual formation of the increased electric field at the wrinkled graphene protrusions [17], though further studies of this rather anomalous effect are underway.

After coating the Mo tip array with graphene, field emission occurred at considerably lower turn on fields. We attribute this to the possible formation of a triple junction between Mo, graphene and vacuum [18] coupled to the increased areal density of atomically sharp, though admittedly small, yet sharp protrusions. In a triple junction, the surface potential undergoes a step change at the junction between the graphene and Mo due to the difference in work function. This surface potential irregularity may modify the local potential in the vicinity of the junction. In this regard, it is possible to explain the electron emission for the graphene functionalized Mo tips as follows: emission from the Mo tips/graphene/vacuum triple junction occurs due to an enhancement of the applied field brought about by an augmented aspect ratio, which is possibly further amplified by triple junction affects. The planar Mo/graspect was especially low, and though triple junction effects may indeed enhance the observed emission, it appears that aspect ratio affects dominate the emission improvements noted. .

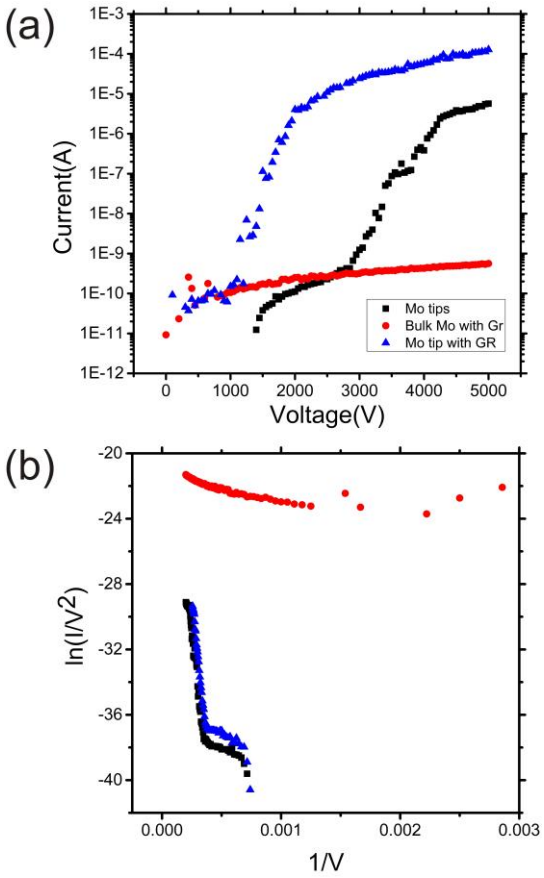

Figure 5: I-V curves of Mo tips, Bulk Mo/graphene and Mo tips/graphene cathodes. (b) Corresponding FN plots.

CONCLUSIONS

In this paper, a simple and general methodology for the fabrication of hybrid graphene/Mo tip array has been demonstrated. The present methodology results in an anomalous lowering of the turn on field and improved maximum emission currents. The ability to deposit wrinkled graphene sheets in large scale will allow fundamental studies as well as exploiting the unique 2D structure for applications and will pave the way for future electron emission 2D heterostructure nano devices.

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