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Fabrication of patterned reduced graphene oxide nanosheet field-emission cathodic film at room-temperature

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ABSTRACT

Well defined patterns of SU-8 photoresist were fabricated using typical photolithographic process on high conductive silicon substrate. Electrophoretic deposition of reduced graphene oxide nanosheets (RGOS) on patterned SU-8 photoresist was conducted at room-temperature. The thin SU-8 photoresist could prevent the transverse deposition of RGOS over the photoresist areas to some extent. A little amount of RGOS at SU-8 photoresist areas were removed by rinsing treatment due to the hydrophobic nature of SU-8 and result in the formation of patterned RGOS films. The field-emission properties of patterned RGOS films show low turn-on electrical field and high current density. The low-cost and scale-up fabrication method can be easily utilized for assembly and integration of RGOS into patterned RGOS film for the field emission display applications at room-temperature.

1. Introduction

Carbon based cold cathodes have been studied intensively over the past decades as potential candidates for field emission displays (FEDs). Graphene, a rising star in material science, has atomic thickness, high aspect ratio (the ratio of lateral size to thickness), excellent electrical conductivity, and good mechanical properties, which qualify it as an attractive candidate for the use of field emission source [1,2]. Furthermore, the presence of rich edges renders graphene for the tunneling of electrons. For graphene to become a viable engineering material for FED application, an efficient deposition process at room-temperature is attractive compared to the high-temperature CVD process [3]. Several room temperature deposition processes have been developed to assemble graphene into functional structure by a variety of chemical or physical approaches such as inkjet printing, Langmuir–Blodgett method, electrophoretic deposition (EPD) [4–6].

The EPD is the charged colloidal particles dispersed in a liquid-phase suspension moving toward and depositing on the oppositely charged electrode by applying voltage. The EPD has high deposition rates and throughput, good uniformity, large-area deposition, and controllable thickness for fabrication of film. The EPD has been used to produce highly packed microstructural carbon nanotube (CNT) films exhibiting excellent electron-field-emission characteristics from colloidal CNT suspensions [7]. Hasan et al. [8] have fabricated large-area graphene oxide films on stainless steel using EPD. Cheng and coworkers [9] fabricated graphene nanosheets (GNS) film with good field emission properties using EPD process after the addition of a charger to render them positively charged then a bias voltage of 100–60 V was applied to the solution.

Much attention has been paid to the fabrication of patterned graphene films. Therefore, well-aligned graphene field emission arrays were fabricated using as-grown graphene on copper foils via simple photolithography techniques and oxygen plasma etching. Field emission measurement of the patterned graphene film revealed a turn-on field of 7.2 V/μm at 100 nA/cm^2 [10]. The integration of micro-fabrication and electrophoretic deposition offers the ability to fabricate ordered two-dimensional patterned graphene film [11–14]. SU-8 is one kind of the insulating photoresist. SU-8 layer on the conductive silicon substrate could prevent the electrophoretic deposition of graphene. SU-8 pattern would restrain the transverse deposition of RGOS over the insulating SU-8 areas as EPD carried out [15].

In this paper, the reduced graphene oxide nanosheets (RGOS) were prepared by a chemically reduced method. Well defined patterns of SU-8 photoresist on high conductive silicon had been fabricated using typical photolithography. The EPD and SU-8 photoresist patterns were combined with for fabrication of the large-area patterned RGOS film. The charged RGOS are coherently deposited onto an electrically conductive silicon substrate and

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seldom on unconductive SU-8 area. Further, a small quantity of RGOS deposited on SU-8 area could be rinsed away due to hydrophobic properties of crosslinked SU-8. The patterned RGOS film including strip and lattice with linewidth and size of 20 μm, 40 μm were obtained. The field-emission properties of cathodic patterned RGOS films have been measured using two-electrodes facility in vacuum. The turn-on field for 10 $\mu A/cm^2$ of current density was found to be 3.34 V/μm and the maximum current density of field emission can reach the 33 mA/cm^2 at the electrical field of 9 V/μm. The patterned RGOS films display better field-emission properties with low turn-on electric field and high current density than the patterned graphene reported [10].

2. Experimental

2.1. Preparation of RGOS

Graphite powders purchased from Baotou Graphite Co. (China) with platelet sizes ranging from 10 to 50 μm were used for the preparation of graphite oxide. Graphite oxide was synthesized by a well-known modified Hummer's method [16]. Firstly, 0.3 g of graphite powders was added into 10 ml of H_2SO_4 (98 wt%) under stirring in a flask that had been cooled to 0 °C using an ice bath. Next, 0.75 g of $KMnO_4$ was added slowly to the flask keeping the temperature below 10 °C. Subsequently, the ice bath was removed and the flask was heated to 35 °C. The temperature was maintained for 30 min, followed by the slow addition of 100 ml of de-ionized (DI) water. The temperature of the reaction mixture increased to 90 °C upon the addition of water and the reaction vessel was maintained at this temperature for 15 min. The suspension was further treated with 30% H_2O_2 until the cessation of gas evolution. Finally, the suspension was vacuum filtered and left to dry under a vacuum after washing with copious amounts of DI water.

The obtained graphite oxide was exfoliated in DI water under ultrasonication for 2 h to form stable graphene oxide suspension. Sodium hydroxide was added to the exfoliated graphite oxide dispersion described above until the pH reach 11. The solution was then stirred for 2 h and a homogeneous light yellow-brown solution was obtained. Then 5 ml hydrazine hydrate was added into the solution. The reaction mixture was then stirred for 4 h at 90 °C under the protection of nitrogen. The resulting suspension was filtered and dried in vacuum. A stable RGOS dispersed in dimethylformamide (DMF) solution was obtained by sonicating 3 h in 100 W supersonic wave, which produced completely dispersed RGOS suspension.

2.2. Fabrication of patterned RGOS film

Patterned substrate with different surface properties is the prerequisitive to fabricate patterned RGOS film. Oxygen plasma is commonly used for surface activation purpose because it contains high energy species including electrons, ions, and radicals which strongly oxidize the organic species on the surface. The oxygen plasma treated surfaces were characterized using contact angle measurements with DI water as probe liquid to assess the wettability. Silicon substrate exhibited a low water contact angle and was stable at 1–5° for at least 1 month at room temperature after oxygen plasma treatment. A freshly prepared SU-8 surface is not hydrophilic, with a static water contact angle of 73 ± 5°. Contact angle measurements revealed oxygen plasma treatment of the SU-8 surface revender an effective hydrophilization ($\theta < 5°$). However the hydrophilic surface of the oxidized SU-8 surface recover its hydrophobicity with contact angle about 45° in several day exposure to air.

All work to produce SU-8 pattern was done in a clean room. Substrates to be deposited RGOS were first patterned with alternating SU-8 and silicon regions that are 20–100 μm in linewidth and 20 μm, 40 μm in size. The schematic diagram of fabrication of SU-8 pattern on silicon substrate was illustrated in Fig. 1(a). Single crystal highly N-doped silicon N(1 0 0) (resistivity of 0.001–0.005 Ω cm) was used as the substrate. The silicon substrate was cleaned with piranha solution (mixture of 3:1, v/v of H_2SO_4 and H_2O_2) at 80 °C, blown dry in nitrogen. The substrate was baked in an oven at 180 °C for 30 min to dehydrate the surface. Appropriate amount of SU-8 2010 (MicroChem Corp., MA, USA) resist was applied at the center of the wafer. The wafer was spun at 500 rpm for 15 s to spread the resist. To get the desired thickness of 10 μm, the wafer was further spun at 3000 rpm for 30 s. The resist was prebaked at 60 °C for 5 min and 95 °C for 7 min on a hot plate. The SU-8 photoresist was exposed through the patterns that designed previously in the forms of strip or lattice with different dimension. The exposure system is Intelligent Micro Patterning's SF-100 Xtreme Maskless Photolithography System without precious mask. The substrate was subsequently rinsed and dried with nitrogen after the development for 5 min in SU-8 developer. Then the resist was postbaked at 60 °C for 10 min

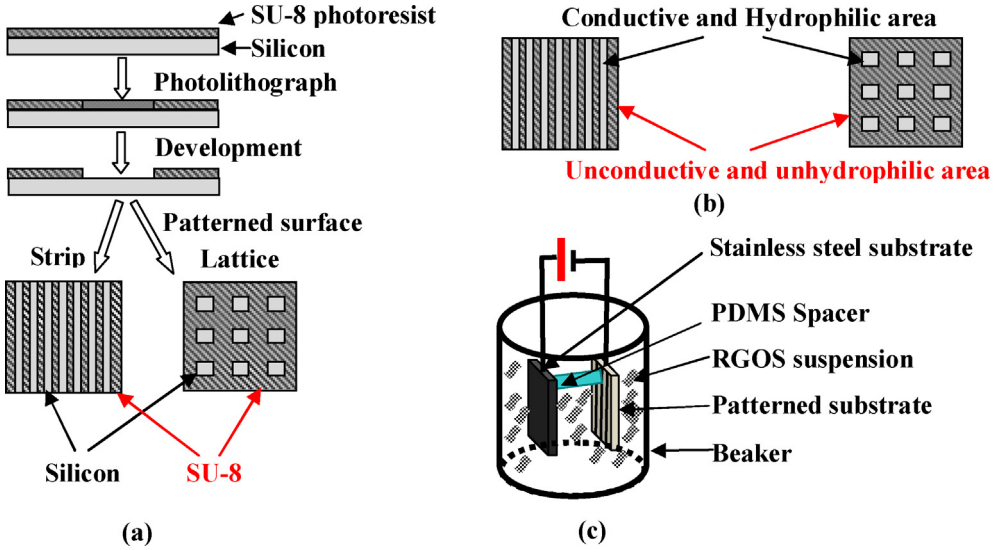

Fig. 1. Schematic diagram of the fabrication processes of patterned RGOS film. (a) Preparation of patterned substrate. (b) Conductive and surface properties of patterned substrate. (c) Electrophoretic deposition of RGOS on patterned substrate.