Investigation of field emission properties of carbon nanotube arrays defined using nanoimprint lithography

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We have previously shown that ordered arrays of individual multiwalled carbon nanotubes (MWCNTs) emitters could be achieved by combining lithography for growth catalyst definition and plasma enhanced chemical vapor deposition (PECVD) for MWCNT growth.1 In Ref. 1, electron beam lithography (EBL) was used to create patterns on the substrate followed by deposition of a conductive diffusion layer and the catalyst resulting, after growth, in localized spaced CNTs. The spacing between CNT emitters is necessary to avoid screening effects during field emission measurements.2 However, the EBL method previously used to create arrays of individual spaced MWCNTs is not suitable for mass production of emitters or microcathodes on a wafer/large scale due to the high cost of a high throughput EBL instrument. The need for low-cost high throughput self-assembly nanotechnology has resulted in the development of the nanoimprint lithography (NIL) technique.3,4 NIL can be used to produce any mark/space ratio (e.g., 1/100) in the pattern, in contrast to other lithographies (e.g., interferometry and nanosphere lithography) whose mark/space ratios are, to a certain extent, fixed. The resolution of NIL is not limited by effects of wave diffraction, scattering, and interference unlike photon or particle based lithographies. Additionally, NIL can pattern sub-10 nm features and has been used to produce patterns over 15 cm/6 in. in diameter uniformly. In this letter, we demonstrate NIL as a route for producing large arrays of individual localized MWCNTs simultaneously for use in the production of self-assembly of CNT-based field emitters.

The NIL method is based on a hard master with predefined patterns pressed into a substrate with a soft layer of polymer resist such as polymethyl methacrylate (PMMA) at temperatures above the polymer glass transition (Tg). The master is then released after a few minutes, resulting in pattern transfer followed by reactive ion etching (RIE) to remove the remaining residue in the patterned areas. Here, for the substrate preparation, a Si(100) wafer was first immersed in hydrofluoric acid for approximately 1 min. The acid removed the superficial layer of SiO2 as its presence causes electrical discharges during field emission—this is highly undesirable for field emission source devices. The wafer was then cleaned ultrasonically using acetone and isopropanol. Finally, the resist PMMA [950 K diluted in 4 vol % anisole (A4)] was spun at 2300 rpm and hard baked to remove any solvent still present (140 °C for 1 min). The thickness of PMMA was measured to be 250–280 nm using a Dektak profilometer. The Si wafer employed for the master fabrication was cleaned in a similar way as the substrate. The resist (PMMA A4) was spun on the wafer, followed by e-beam exposure (50 kV, 50 pA), Mo sputtering, and then lift-off to yield a hard mask pattern of Mo round dots. Reactive ion etching using CF4 was then used to transfer the Mo pattern into the silicon as pillars, followed by removal of the Mo using wet acid etch. Note that EBL is only needed once in the overall process, that is, in the fabrication of the master. The master can then be used multiple times with cleaning to fabricate multiple wafers of emitters. Figure 1(a) shows a scanning electron microscopy (SEM) image (FEI Philips XL30, operating at 5 kV) of the master used for process optimization; the words NANO IMPRINT can be seen in reverse (mirror image). Figure 1(b) shows the master with Si pillars used for the CNT array fabrication with 10 μm pitch, 270–280 nm diameter, and 230–250 nm height. The height of the Si pillars was less than the thickness of the resist polymer film, so that direct contact between master and substrate is avoided. During nanoimprint, the PMMA can adhere to the master, making its subsequent removal difficult. To ensure effective release of the master, its surface was perfluorinated/made nonwetting by exposing the master to 1H,1H-2H,2H perfluorodecyltrichlorosilane (FDTS) in a dessicator for 2 days.

The actual nanoimprint experiments were performed with an Obducat™ nanoimprint tool. The pressure and temperature during imprint were varied from 40 up to 60 bars
and from 160 up to 190 °C, respectively. The release temperature was optimized at 70 °C after 5 min in vacuum. The imprint was performed under vacuum to avoid the formation of air bubbles in the resist. The imprint temperature was increased approximately 80 °C above the glass transition temperature \( T_g \) of PMMA to reduce the resist viscosity. PMMA residue still present after imprint was removed by RIE (~0.2 mbar), in 25:25 SCCM (standard cubic centimeter per minute) \( \text{O}_2: \text{Ar} \) with an etch rate of typically 3.5–4.0 nm s\(^{-1}\).

For CNT growth, we used an ITO diffusion barrier (15 nm) and a Ni (7 nm) catalyst prepared by sputtering, which were then lifted off to form catalyst dot islands resembling the pattern on the master. The growth of aligned MWCNTs was performed by PECVD (Ref. 1) using acetylene and ammonia (\( \text{C}_2\text{H}_2:54 \text{SCCM}, \text{NH}_3:200 \text{SCCM} \)) at 725 °C. The bias for these set of experiments was increased slightly from the usual 600 to 630 V to produce CNTs with a smaller tip apex—this is due to the Ni catalyst being etched away by higher energy ions in the plasma as the CNT grows upwards.

For these needlelike structures, the field enhancement \( (\beta) \) is related to the aspect ratio height/radius, in the form \( \beta = h/r \). Figure 2(a) shows SEM images of CNTs grown using the master shown in Fig. 1(a); NANO IMPRINT letters formed by CNTs can be observed, where each letter consist of multiple aligned CNTs, made from a master bearing the pattern in mirror image. Figure 2(b) shows the SEM image of a 500×500 \( \mu \text{m}^2 \) array of CNTs using the master shown in Fig. 1(b). Figure 2(c) shows an enlarged area of the array with CNTs spaced 10 \( \mu \text{m} \) apart. The CNTs were 3–4 \( \mu \text{m} \) in height and 20–40 nm in tip radius. The inset in Fig. 2(c) shows an individual CNT with a Ni catalyst present. The measured tip radius was 30.5 nm, and the tube was 3.53 \( \mu \text{m} \) in height. Therefore, for this particular CNT the field enhancement factor \( (\beta_{\text{SEM}} = h/r) \) should be \( \beta \approx 3530/30.5 = 115.7 \).

Scanning anode field emission microscopy (SAFEM) was performed to obtain information on the current-voltage \( (I-V) \) characteristics, the field enhancement \( (\beta) \), and the maximum emission current of single CNT emitters. In addition, statistical information on the distribution of field emission properties in the CNT field emitter array was measured using this technique, as described in Ref. 6. The sample was introduced in the SAFEM without prior treatment. Bias-distance curves were recorded at a constant emission current of 11 nA, with the tip centered above an emitter. The measured \( V-d \) characteristic indicated a linear increase in voltage with increasing tip-sample distance with a corresponding slope of 27.5 V \( \mu \text{m}^{-1} \), which is the applied electric field \( (E_a) \). Furthermore, if we now fix \( d \), and since \( E_a = V/d \), for a fixed field of 27.5 V \( \mu \text{m}^{-1} \) at 11 nA obtained using 193 V, one can determine the distance \( d \) to be 7 \( \mu \text{m} \).

The field at the tip of this emitter is related to the applied electric field by the relation \( E_{\text{local}} = E_a \beta \). Assuming a work function of \( \Phi = 4.9 \text{ eV} \) previously determined for MWCNTs (Ref. 9) it can be predicted theoretically that an emission current of 11 nA requires a local electric field of 3850 V \( \mu \text{m}^{-1} \). Thus, \( \beta = 3850/27.5 = 140 \). This corresponds to a particular emitter with a 3.5 \( \mu \text{m} \) height and a radius of curvature at the CNT apex of 25 nm. From SEM measurements the average tube heights were \( \sim 3.5 \mu \text{m} \) and the aver-
emitter arranged on a 10 μm pitch array, but, with different values of the field enhancement resulting in the intensity differences in the map. As can be seen from the map there are a number of holes where emitters are supposed to be active. The emitters on these sites could have been previously destroyed during prior measurements which determined the maximum current carrying capability of the emitters. In this map 225 emitters have been found. As we had fabricated emitters with a pitch of 10 μm, and the map size was 250×240 μm², we expect approximately 600 emitters (i.e., 1×10⁷ cm⁻²). Therefore, 37.5% of the nominal number of emitters could be imaged/were active corresponding to an emission site density (ESD) of 3.75×10³ cm⁻² for an applied electric field of 27.5 V μm⁻¹. From the ESD the field enhancement values for all the 225 emitters have been determined, and Fig. 3(d) shows the statistical distribution (histogram). The bulk of the emitters shows a Gaussian distribution centered at β₀=97 with a full width at half maximum (FWHM) of 37. Here the β₀ value obtained is consistent with the βSEM values for the CNTs derived from the aspect ratio measured in the SEM. The Gaussian distribution, indicated by the solid line in Fig. 3(d), strongly suggests the presence of regular emitter arrays with a certain deviation in emitter height and radius of curvatures. However, there are some emitters falling outside the Gaussian distribution. This asymmetry to higher field enhancement values is due to inhomogeneities related to the radius of curvature of the CNT emitter. Here, the maximum radius is given by the diameter of the CNT which varies in a rather narrow range. However, small protrusions on the spherical apex of the CNT can reduce the effective radius of the emitter significantly. As the field enhancement factor depends on the inverse of the radius, one can therefore observe factors considerably larger than what would be expected from the average radius of curvature of the emitter apex.

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