Band-gap dependence of field emission from one-dimensional nanostructures grown on *n*-type and *p*-type silicon substrates

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Field emission of electrons from narrow-band-gap and wide-band-gap one-dimensional nanostructures were studied. *N*-type silicon substrates enhanced the emission from the low-band-gap silicon nanowires and carbon nanotubes, whereas *p*-type substrates were a better choice for field emission from wide-band-gap silicon carbon nitride nanocrystalline thin films and nanorods. The role of the substrate-nanostructure interface was modeled based on different junction mechanisms to explain, qualitatively, the fundamentally different emission behavior of these nanostructures when *n*- and *p*-type silicon substrates were used. The results could be explained on the basis of simple carrier transport across the silicon-silicon nanowire interface and subsequent tunneling of electrons for the silicon nanowires. Schottky barrier theory can explain the better field emission of electrons from the *n*-type silicon supported carbon nanotubes. The decreased barrier height at the interface of the silicon-silicon carbon nitride heterojunction, when *p*-type silicon substrate was used, could explain the superior field emission in comparison to when *n*-type silicon substrates were used.

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The development of vacuum microelectronics was intimately linked with the realization of reliable high intensity electron sources. The thermionic emission from conventional cathode materials was challenged by the field emission from gated molybdenum and silicon microtip¹ cold cathode emitters, for low power applications, that could be scaled down to micrometer sizes to utilize the high electric field to extract electrons. The advent of nanotechnology then provided efficient electron emitters through a wide gamut of nanostructures, nanorods, nanotubes, and nanowires, of different elements and even compounds. The microgeometry of these nanostructures demonstrated how some of the parameters of the Fowler-Nordheim equation,² especially the field enhancement factor, used to describe field emission in metals, could be tailored to achieve lower threshold voltages for electron emission. The material,³ its microstructure,⁴ the microgeometry (that is, whether the emitter is a tip, tube or rod),^{5,6} any adsorbed species and surface modifications,^{7,8} and electrical and other physical properties of the emitting material were thoroughly studied to give us an insight into this phenomenon of field emission. However, these nanostructures are often supported on attractive substrates such as silicon, for future integration to the device technology, whose role in determining the emission efficiency has been unclear. The substrate-nanostructure interface is of paramount importance since the availability of electrons undergoing tunneling from

one-dimensional nanostructured emitters depends on the efficiency of the electron injection mechanism from the substrate across this interface. This paper, instead of scanning the much visited nanostructure-vacuum interface, proceeds to examine the substrate-nanostructure interface that had a remarkable effect on the field emission patterns of low band gap nanostructures namely, silicon nanowires (SiNWs) and carbon nanotube (CNTs), and wide-band-gap nanostructures, namely, silicon carbon nitride (SiCN) nanocrystallites, and nanorods, supported on *n*- and *p*-type crystalline silicon substrates.

SiNW, multiwall CNTs (MWCNT), and SiCN nanocrystalline thin films and nanorods were deposited on doped Si substrates namely, *n*⁺ (resistivity~2–5 mΩ cm), *n* (resistivity~1–10 Ω cm), and *p* type (resistivity~1–10 Ω cm). The field emission properties were measured on a parallel-plate diode type device structure,⁸ where the nanostructures grown on silicon served as the cathode and an indium tin oxide coated glass plate served as the anode. The distance between these two electrodes could be controlled, and was kept at ~50 μm. This distance was used to calculate the apparent field at the tip. A vacuum level of 10⁻⁸ Torr was maintained during the measurements.

Randomly oriented Si nanowires [inset, Fig. 1(a)] grown by catalyst-assisted chemical vapor deposition on *n*-type silicon substrates showed superior field emission properties than

FIG. 1. Emitted current density as a function of applied field for (a) silicon nanowires grown on ($\square$) *n*-type Si and ($\blacktriangle$) *p*-type Si substrates (the inset shows scanning electron micrograph of randomly oriented silicon nanowires grown on silicon substrates); (b) well aligned multiwall carbon nanotubes grown on (∇) *n*-type Si and ($\blacktriangledown$) *p*-type Si substrates at a deposition temperature of 1000 °C and on ($\square$) *n*-type Si and ($\blacksquare$) *p*-type Si substrates, for CNTs deposited at 800 °C, (inset shows scanning electron micrograph of well aligned multi wall carbon nanotubes grown on silicon substrates).

those grown on *p*-type silicon substrates [Fig. 1(a)]. The SiNWs grown on *n*-type substrates showed a two-order higher emission current density than those grown on *p*-type substrates at an applied electric field of 17.5 V/μm. Assuming a slightly higher band gap for SiNWs (1.4 eV) than Si (1.1 eV) (neglecting any significant quantum confinement effects), and a small band bending at the interface, the predominant term for the field emission of electrons is the carrier transport across the substrate-SiNW interface followed by tunneling from the SiNW to vacuum. In contrast to the energy barrier faced by electrons in the acceptor level of *p*-type Si substrates to inject into the SiNWs, the electrons from the donor level of the *n*-type Si substrate can be easily injected into the conduction band of the SiNW against a much smaller energy barrier and then tunnel into vacuum. The smaller barrier at the substrate-nanostructure interface explains the higher field emission for the *n*-type substrates.

Well aligned MWCNTs [inset, Fig. 1(b)] were grown by the microwave plasma enhanced chemical vapor deposition route, on *n*- and *p*-type silicon substrates, using iron as a catalyst and hydrocarbon feedstock gases.^{6,9} Here, the *I*-*V* characteristics [Fig. 1(b)] shows that, for the CNTs grown on the *n*-type substrates, the field emission is superior to that of the CNTs grown on *p*-type substrates. MWCNTs grown at higher substrate temperatures (1000 °C) were found to be less defective than the ones grown at lower substrate temperatures (800 °C). Raman spectroscopy showed a higher intensity ratio of the 1580-cm⁻¹ mode (*G* band) to the 1345-cm⁻¹ mode (*D* band) for the CNT grown at 1000 °C. Nevertheless, both sets of MWCNT samples showed better field emission when *n*-type substrates were used. If a turn-on field (V_{on}) for field emission is defined as the field required for 10 μA/cm² of emitted current then the V_{on} for the *n*- and *p*-type substrates were 2.8 and 3.8 V/μm, respectively, for the MWCNT grown at 1000 °C. For the MWCNT grown at 800 °C, the V_{on} for the *n*- and *p*-type substrates were 7.0 and 9.4 V/μm, respectively.

To explain this result, we utilized the theory of Schottky barriers. Fullerene tubules have been shown to have a carrier density similar to that of metals and a zero band gap at room temperature.¹⁰ CNTs were shown to have a band gap of a few hundred meV at room temperature.¹¹ We can then treat the CNT-Si interface as a metal-semiconductor interface and apply the theory for Schottky barriers on this system. Since field emission is measured by applying a negative bias to the substrate, the situation of a Si (*n*-type)-MWCNT combination is somewhat similar to a forward biased Schottky junction, whereas a Si(*p*-type)-MWCNT combination is similar to that of a reverse-biased Schottky junction. The built in potential (V_{bi}) in each of these cases can be written as

$$V_{bin} = (\phi_{Bn} - V_n) - V_F \quad (1)$$

and

$$V_{bip} = (\phi_{Bp} - V_p) + V_R \quad (2)$$

for the Si(*n*-type)-MWCNT and Si(*p*-type)-MWCNT cases, respectively. Here qV_n and qV_p stand for the energy difference between the Fermi level and the conduction or valence band for *n*- and *p*-type Si; V_F and V_R stand for the forward and reverse bias voltages; and $q\phi_{Bn}$ and $q\phi_{Bp}$ denote the barrier heights for the *n*- and *p*-type substrates, respectively. Here, the difference between qV_n (~0.22 eV) and qV_p (~0.16 eV) is negligible. In other words, the effective built-in potential is reduced in case of the *n*-type substrates and increased for the *p*-type substrates under the nature of biasing used in the field emission measurement. This difference in the built-in field, that opposes the transfer of electrons from the substrate to the MWCNT, determines the difference in the observed field emission current levels. It should be mentioned that the barrier heights $q\phi_{Bn}$ and $q\phi_{Bp}$ increase as the work function of the CNTs increases. It can be shown that in thermal equilibrium, the built-in potential on *n*-type Si is always less than that of *p*-type Si for a CNT work function smaller than 4.57 eV. The presence of V_F and

FIG. 2. Emitted current density as a function of applied field for (a) silicon carbon nitride nanocrystals grown on (■) p -type Si and (○) n -type Si and (△) n^+ -type Si substrates, (inset shows scanning electron micrograph of silicon carbon nitride nanocrystals grown on silicon substrates); (b) silicon carbon nitride nanorods grown on (■) p -type Si and (□) n -type Si substrates [the inset shows the scanning electron micrograph (SEM) of silicon carbon nitride nanorods grown on silicon substrates with silicon carbon nitride nanocrystalline buffer layers].

V_R will shift this limiting work function to higher values encompassing the commonly observed MWCNT work functions in the range of 4.6–4.8 eV.¹² As a consequence, n -type substrates will always show better field emission properties by virtue of a lower built-in potential.

Nanocrystalline SiCN films were deposited via electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD).¹³ Controlling the ECR-PECVD conditions both high and low density of SiCN crystallites [inset, Fig. 2(a)] were prepared on n^+ -, n -, and p -type Si substrates. It must be noted that the density of these nanostructures, as exemplified in the case of CNTs, has a profound effect on the field emission behavior.¹⁴ The I - V emission characteristics [Fig. 2(a)] clearly reveals that the SiCN nanocrystallite samples produced on p -type silicon substrates emit a higher current density as compared to those grown on n -type or n^+ -type silicon; this is true for any given field and irrespec-

FIG. 3. Band-edge photoemission spectrum from a nanocrystalline SiCN film. Minimum work function is 4.5 eV above the Fermi level of the back contact.

tive of the crystallite density. In this case, V_{on} for the nanocrystallites grown on p -, n -type, and n^+ -type silicon substrates are 14.5, 16.9, and >20 $\text{V}/\mu\text{m}$, respectively.

SiCN nanocrystalline films were used as buffer layers for the growth of SiCN nanorods via microwave chemical vapor deposition [inset, Fig. 2(b)].¹³ High density SiCN nanocrystalline films produced high density SiCN nanorods. Interestingly, the SiCN nanorods grown on these nanocrystalline SiCN buffer layers also show a higher field emission when grown on p -type Si substrates than those grown on n -type silicon [Fig. 2(b)], irrespective of the nanorod density. The emission pattern is reproducible over several observations and independent of morphological differences such as density and length of the nanorods. V_{on} for the SiCN nanorods grown on p - and n -type silicon substrates is 9.7 and 11.0 $\text{V}/\mu\text{m}$, respectively.

The simple transport as that occurring in case of SiNW or the Schottky barrier effect as in a CNT, is inadequate to explain the observed results. To explain the results we revert to semiconductor heterojunctions. The analogy of the present system, SiCN on Si, with that of a semiconductor heterojunction is valid owing to the large difference in their band gaps and resistivities. The SiCN material has a high electrical resistivity and a wide band gap (4.2 eV)¹⁵ in comparison to the low electrical resistivity and low band gap (1.1 eV) of the doped silicon substrates. From an independent ab-initio calculation, the work function for SiCN was found to be 5.5 eV,¹⁶ whereas that for n -type Si is ~ 4.15 eV.¹⁷ Our x-ray photoemission spectroscopy measurements on SiCN determined a minimum work function of 4.5 eV above the Fermi level of the back contact, as seen in Fig. 3. It is evident that the electron affinity (χ) of wide-band-gap SiCN is less than that of the low band gap silicon ($\chi = 4.01$ eV).¹⁷

The model being introduced is still valid for a range of χ for SiCN, unless it is too small to make SiCN strongly p type. Assuming an electron affinity $\chi \sim 2.5$ eV for SiCN (Fig. 4), we obtain a “straddled” heterojunction wherein the band gap of the SiCN completely overlaps the band gap of silicon.

FIG. 4. Representative band diagrams for (a) Si (*n*-type)-SiCN and (b) Si (*p*-type)-SiCN heterostructures, in thermal equilibrium. E_C , E_V , and E_F represent the conduction band, valence band, and Fermi level of SiCN material, respectively; E_{CN} , E_{VN} , and E_{FN} represent the conduction band, valence band, and Fermi level of *n*-type Si; and E_{CP} , E_{VP} , and E_{FP} represent the conduction band, valence band, and Fermi level of *p*-type Si.

After constructing the band diagram based on the available data on silicon and SiCN, it was found that SiCN is slightly *p* type. Indeed, amorphous SiCN was found to be slightly *p* type.¹⁸ When Si and SiCN come into intimate contact and a thermal equilibrium is established (Fig. 4), band bending occurs at the interface.¹⁷ We expect a difference in the barrier heights for electrons and holes in such an abrupt heterojunction between Si and SiCN. For a Si (*n*-type)-SiCN junction, the large difference in the Fermi levels of *n*-type Si (E_{FN}) and SiCN (E_F) before equilibration, would necessitate a larger flow of electrons to SiCN to obtain Fermi level alignment in equilibrium. This will in turn give rise to a severe band bending and a higher barrier for further electron movement from silicon to SiCN. In the case of a Si (*p*-type)-SiCN heterojunction, however, the Fermi level in silicon (E_{FP}) is lower than the Fermi level of SiCN (E_F) before equilibration, and will necessitate some flow of electrons from SiCN during the Fermi level alignment. This will result in band bending at the Si-SiCN interface, but this time, instead of a barrier, a well is formed. The flow of electrons across this junction and subsequent tunneling during field emission would be efficient for the *p*-type silicon substrate due to the absence of the energy barrier. If there is any voltage drop within the thickness of the material the work function may be more than 4.5 eV. Even if we assume a higher work function (up to 5.5 eV) for SiCN as found from theoretical estimates, a barrier at the Si (*p*-type)-SiCN interface will exist but will be smaller than that existing in the Si(*n*-type)-SiCN interface, because $E_{FP} - E_F$ will be always less than E_{FN}

$-E_F$.^{17,19} For *p*⁺ Si substrates E_{FP} and E_F will be even closer and a lower barrier height will be seen by the electrons tunneling into SiCN. Hence, larger field emission currents were observed for the Si (*p*-type)-SiCN case as compared to the Si (*n*-type)-SiCN case. This model is oversimplified since we have neglected the effects of interface states, diffusion effects, and possibly some contribution from the external biasing used during the measurements, however, it gives a plausible qualitative explanation of experimentally observed effects.

In general, the different nanostructures studied here have different morphologies, electrical conductivities, and surface states that may influence the order of emission current densities in different cases. The change in the emission pattern from these nanostructures when the substrates are changed from *n*-type silicon to *p*-type silicon, however, is related to the substrate-nanostructure interface, and has been explained by different junction mechanisms determined by their band gaps. The change in emission pattern effected by a change of substrate conduction may be enhanced by proper doping of these nanostructures, especially in the case of SiCN where it can even be reversed depending on the Fermi level positioning in the band diagram (Fig. 4).

In short, the field emission from silicon nanowires, well aligned carbon nanotubes, silicon carbon nitride nanocrystalline thin films, and nanorods were studied. The effect of the *p*- and *n*-type silicon substrates in limiting or enhancing the field emission currents from the nanostructures has been demonstrated. The *n*-type silicon substrates proved to be bet-

ter for field emission from low-band-gap silicon nanowire and carbon nanotubes systems. The energetically higher Fermi level in *n*-type silicon was conducive for electron transport across the Si-SiNW interface assisting in field emission. Field emission from carbon nanotubes was explained with the help of the Schottky barrier theory, where an *n*-type silicon substrate offered a lower built-in potential to carrier transport. The results of improved field emission in the case of wide-band-gap nanocrystalline SiCN thin films and SiCN nanorods on *p*-type silicon substrates were explained based on band diagram considerations in semicon-

ductor heterojunctions. *P*-type silicon substrates offered a significantly lower injection barrier height, which resulted in larger field emission currents.

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