Modulating the work function of carbon by N or O addition and nanotip fabrication

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Abstract

A model is presented for the lowering of the work function for high-efficiency electron emission. It is suggested that: (i) an oxide or nitride tetrahedron formation creates nonbonding lone pairs that induce the anti-bonding dipoles associated with density of states added above the Fermi level and; (ii) that nanofabrication could densitify the charges in the confined region due to the coordination number (CN)-imperfection-induced bond contraction. However, over dosing N or O may cause hydrogen-like bond formation with a 'dipole/+' valence state which could explain the reduced work function. Closely packed nanotips also reproduce the work function of a flat surface. It is anticipated that the work function of a surface can be lowered by proper co-doping O or N with metals of low-work function to the miniaturized tips. Predictions agree with various experimental observations. © 2003 Elsevier Ltd. All rights reserved.

The work function (Φ) or the threshold (V_T) in cold-cathode field emission of materials such as diamond, diamond like carbon (a-C) or carbon nanotubes (CNTs), can be modulated by doping proper amount of properly selected elements besides the geometric enhancement of the emitters. An addition of N to the CVD polycrystalline diamond thin films significantly reduces the V_T of the diamond. The V_T of the N-doped diamond is even lower than the V_T of the diamond doped with boron and phosphorous [1–5]. The work function of carbon nitride films could be reduced to ~0.1 eV deposited at 200 °C substrate temperature under 0.3 Pa nitrogen sputtering pressure [6].

The N-lowered V_T has been attributed to a certain yet unknown sub-band formed above E_F due to N addition. However, such a band is lacking with P or B doping because boron is a shallow substitutional acceptor in diamond with a

level at 0.38 eV above the valence band edge E_V, and phosphorus can act as a shallow donor with a level 0.46 eV below the conduction band edge E_C [7]. Boron nitride coated graphite nanofibers also emit electrons at much reduced V_T (from 1.5 to 0.8 V/μm) with high (10^2 level) current intensity compared with the uncoated carbon fibers [8]. It is explained that introducing BN nanofilm to the surface leads to a significant reduction in the effective potential barrier height, or the Φ. A tendency of N-buckling outward the BN nanotubes has been derived theoretically, which was explained as arising from the different hybridizations of B and N in the curved hexagonal layer and the N-bucking is expected to form a surface dipole [9]. It was expected that Cs- and Li-doping should add their higher energy states directly to the conduction band of diamond to reduce the Φ of the diamond. Unfortunately, this measure was proven less effective [10]. Similarly, adding proper amount of oxygen to the surface also lowers the Φ and hence improves the efficiency of the emission. It has been found that O_2 and O_3 adsorption could increase the emission current of the CNT array by ~800% along with a decrease

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of the V_T from 0.8 to 0.6 V/μm [11]. First-principles calculations by Park et al. [12] suggest that the calculated emission currents of CNTs are significantly enhanced because oxidation could change the electronic structure, which increases the local field at the adsorption site. However, higher oxygen exposures (>65 Langmuir) cause detrimental effect on the field emission of the CNT array [13]. Surprisingly, adding both Cs and oxygen atoms to the surface [14] could reduce the Φ of diamond to ~ 1.25 eV. Lin [15] further proved experimentally that lowering the Φ of a cathode by adsorbing both oxygen and electropositive metallic elements on its surface is more effective than by adsorbing simply the metallic element or oxygen. Lin noted that an appropriate quantity of oxygen adsorbed on the cathode surface would be essential to result in a better dispenser cathode and also higher quantum yield of negative electron-affinity photo cathodes, while fluorine would play an important part in the electron emission stability.

However, understanding the mechanism for the chemically modulated work function of carbon is a great challenge though numerous models have been proposed, including the negative affinity [16–18], antenna effect of conducting channels [19], impurity gap states [5,20], band bending at depletion layers [21] and surface dipole formation [22]. According to the impurity gap state argument, N locates at a distorted substitutional site in the host matrix with one long but weak C–N bond, which forms a deep singly occupied donor level, ~ 1.7 eV below the E_C. On the other hand, two neighboring nitrogen atoms relax away from each other due to the weak lone pair interaction, which form doubly filled states located ~ 1.5 eV above the E_v. These two mid-gap impurity levels are suggested to play dominant roles in lowering the V_T. Furthermore, N may create a depletion layer that causes band bending at the back contact. At sufficiently high donor concentrations, this band bending narrows the tunneling distance there, and allows emission into the diamond conduction band.

Questions may arise as following: How could the electronegative additives turn the electron affinity of a diamond to be negative? Why does the addition of the low-Φ metal effect-less? Where have the conduction electrons of the low-Φ metals gone upon being added to the carbon surface? Why is co-doping with the low-Φ metal and oxygen highly effective? Why the overdosed oxygen causes detrimental effect on the e-emission? We need to answer these questions satisfactorily. For example, the electron affinity of a specimen is defined [23] as the separation between vacuum level, E_0, and the bottom edge of the conduction band, E_C. Negative affinity means that the conduction band is raised to a position that is above the E_0. Electrons in such a conduction band should fly away from the surface without needing any excitation. Chemical reaction can change the work function but never the electron affinity [23]. If the N-induced mid-gap impurity levels (1.7 eV $< E_C$ and 1.5 eV $> E_V$) are dominant, the carbon

co-doped with P and B should perform better than the carbon doped with N, as the P- and B-derived states (0.46 eV $< E_C$ and 0.38 eV $> E_V$) appear to be more beneficial. Therefore, an atomic scale understanding of the electronic process of threshold reduction due to nitrogenation and oxidation is highly desirable.

Recent progress [24–26] has revealed that it is essential for oxygen or nitrogen atom to hybridize its sp-orbital upon interacting with a solid surface, which has led to a bond-band-barrier (BBB) correlation mechanism for the behavior of atoms and valence electrons in the process of reaction. N or O forms a quasi-tetrahedron with four surrounding atoms with bonding share electron pairs and nonbonding lone electron pairs [24]. Due to the different valence values, N possesses one and O has two lone pairs. This difference determines the group symmetry of an oxide from that of a nitride quasi-tetrahedron, and some properties such as the chemical stability. The lone pair induces an anti-bonding dipole with expansion of size and elevation of electronic energy. For clusters with more additive O or N atoms, some dipoles become $+$/dipole and hence hydrogen-like bonds are formed. These bond, nonbond, anti-bond will add corresponding density-of-states (DOS) to the valence band and above of the host. Bond forming alters the sizes and valences of the involved atoms and causes a collective displacement of these atoms, which corrugate the morphology or the potential barrier of the surface. These events are essential yet often overlooked in practice. Fig. 1 illustrates the proposed NC$_4$ quasi-tetrahedron and the corresponding DOS of the bonding, nonbonding, holes and the lone-pair-induced anti-bonding (dipole). The anti-bonding states are well above the Fermi level, which lowers the Φ and hence the threshold of field emission. Hole production due to bonding and dipole formation widens the band gap of the host solid. Lone pair states stay within the band gap and the bonding states are lower than the 2p level of an isolated N or O atom. H-like bond formation transfers electrons from the anti-bonding states to the bonding state, and hence, narrows the anti-bonding sub-band and restores the Φ-reduction, which explains why over dosing oxygen to CNT could cause adverse effect on the field emission [13].

On the other hand, according to the recent bond-order-length-strength (BOLS) correlation mechanism [27], the coordination number (CN) imperfection causes the remaining bonds of the lower coordinated atoms to contract spontaneously associated with magnitude increase of bond energy in the relaxed surface region. The confined electrons are denser and more localized in the surface region. For a nanosolid of size D, the work function satisfies [25]:

$$\phi_L = E_0 - E_F; \text{ and } E_F \propto n^{2/3} = \left(\frac{N_e}{V}\right)^{2/3} \propto \bar{d}^{-2} \qquad (1)$$

E_0 is the vacuum level. N_e being the total number of electrons of a nanosolid is conserved. The mean lattice
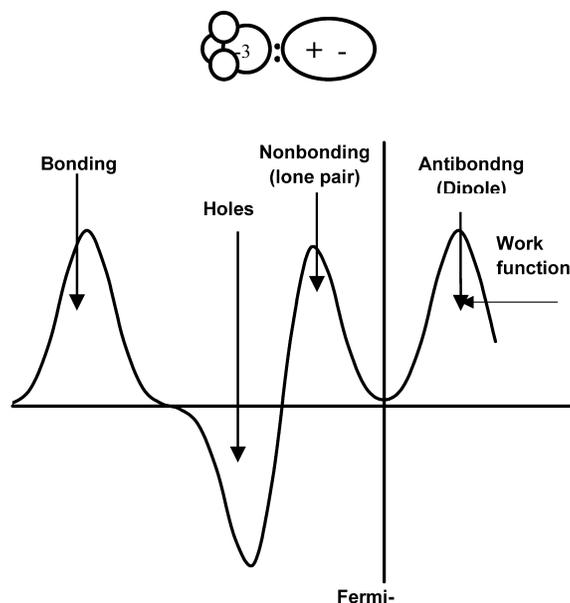
Fig. 1. The primary NC_4 nitride quasi-tetrahedron model. Smaller ions donate electrons to the central N of which the sp-orbital hybridizes with production of a nonbonding lone pair. The larger sphere is the lone-pair-induced C dipole, and the N-induced DOS difference $[n(NC_4) - n(C)]$ of a semiconductor. The lone-pair polarized anti-bonding state lowers the work function and hence the threshold of field emission. The processes of bonding and anti-bonding generate electron holes close to E_F.

contraction of a nanosolid follows the relation [28]:

$$\begin{cases} \dfrac{\overline{d(D)}}{d_0} = \displaystyle\sum_{i \leq 3} \gamma_i c_i \\ \gamma_i = N_i/N = V_i/V \\ c_i = 2/\{1 + \exp[(12 - z_i)/8z_i]\} \end{cases} \quad (2)$$

where d_0 is the lattice constant of the bulk; c_i being the bond contraction coefficient depends on the effective CN (z_i) of the specific atom and γ_i the number (N) or volume (V) portion of the ith atomic layer over the entire solid of any shape. At the lower end of size limit ($D < 3$ nm), the average bond length is around 10% shorter than the bulk value and hence the work function will reduce to $0.9^{-2} \sim 80\%$, according to Eq. (1). Using He–II ultraviolet beam source of 21.2 eV, Abbot et al. [29] measured the work function of diamond {111} surface about 4.8 eV at grain size of 108 μm. They found that the work function decreases with particle size to a minimum of 3.2 eV at an average grain size of about 4 μm. The work function recovers to a maximum of 5.1 eV at diamond particle size of 0.32 μm. Kappes and Schuhmacher [30] measured the work function of Na particles around 0.4–2.0 nm to vary inversely with size D from 2.25 eV to the bulk value of 2.75 eV as the particle size increases. It appears that the measured size-dependent work-function change for

diamond and Na nanosolids is in conflicting with the BOLS prediction. However, one needs to note that if the particles are closely packed, the system is identical to a smooth surface. At a certain range of particle sizes, the work function is indeed lower than the values at the both ends of size limit. Recently, it has been confirmed [31] that hydrogen-rich or oxygen-containing CVD precursors promote electron field emission for discrete diamond particles and noncontinuous diamond films. This holds not for high quality and continuous diamond films as well as nanocrystalline diamond or glassy carbon coatings containing conductive graphitic carbon. Agreement between observations in Refs. [29,31] indicates the significance of separation between the nanoparticles.

The lone pair and the lone-pair induced dipole at nitride and oxide surface has been evidenced by many theoretical and experimental observations. For instance, two additional DOS features have been measured from nanometric SiN compared to the DOS of nanosolid SiC [32]. The one at ~ 3.3 eV below E_F corresponds to the N-2p lone-pair at the top of the valence band and the other, 1.0–3.8 eV above E_F to the anti-bonding sub-band in the current DOS configuration (Fig. 1). For carbide, neither lone pair nor anti-bonding dipole could form upon reaction. However, a ~ 2.31 eV anti-bond-energy feature has been obtained in calculating carbon nitride [33]. It is unambiguous that N or O adds indeed an anti-bond sub-band above E_F due to the dipole formation, disregarding the host element [24,25]. The preferential oxidation of the densely packed diamond {111} plane evidences the geometrical selectivity of the oxide tetrahedron and the existence of the loosely bounded dipoles (0.05 eV binding energy) that are readily eroded away of the surface [34].

The BBB correlation mechanism could be able to answer the aforementioned questions regarding chemical effect on the work function. The 3sp orbitals of a P atom are hard to be hybridized compared to the 2sp orbitals of O and N because the 3sp electrons are more mobile than are the 2sp electrons of N and O. The de-localized 3sp electrons determines that the P acts as a n-type donor that adds simply a DOS feature to a position 0.46 eV below the E_C of a diamond [7]. That P-doping gives little reduction of the work function compared to O or N doping [5] means that the impurity gap levels narrow the band gap but contribute insignificantly to the work function reduction. Unlike P and B, O and N could expand the band gap of a semiconductor instead, through compound formation [23]. Therefore, N and O act not simply as impurity donors or acceptors of which no charge transport is involved. The work function of Cs and Li (~ 3.5 eV) is much lower than that of other metals (~ 5.0 eV). However, adding Cs and Li to the diamond surface is effect-less in improving the emission properties. In fact, one is unable to prevent carbide formation in the mixture of metal and carbon. In the process of carbide formation, the conducting electrons of the metal will 'flow' into the empty p-orbital of carbon, which lowers the

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occupied DOS of the doping metals. However, doping with both low-Φ metal, such as Li or Cs, and electronegative additive, such as N or O could form metal dipoles at the surface, which reduces the work function of the low-Φ metals even further (~ 1.25 eV < 3.5 eV). Therefore, co-doping low-Φ metals with O or N could be promising practice [14,15] in lowering the work function of carbon. However, it is anticipated that the production of the H-like bond at the surface due to O or N over-dosing may have detrimental effect on the work function reduction, such as the case of CNTs with over-doped oxygen [13]. Appropriate doping would be necessary [15] to avoid H-like bond formation that raises the work function.

With the BBB correlation as origin, the impurity gap levels (lone pair) [5,20] and the surface dipole formation [22] models would be correct and complete. The lone pair impurities contribute indirectly to the work function reduction as they induce the anti-bonding dipoles. Other effects such as conducting channels [19], band bending at depletion layers [21] may play some supplementary roles in lowering the V_T, as these effects exist depending less on the presence of oxygen or nitrogen. On the other hand, nanofabrication of the emitters also lowers the work function by at most 20%, due to the CN-imperfection localized surface charges. However, densely packed nano-tips will annihilate the size effect. Joining the effects of size reduction in BOLS correlation and dipole formation in BBB correlation, the work function will be substantially lowered for enhancing the efficiency of filed emission. New understanding may help designing and controlling work function for electron source applications.

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