Electron emission of carbon nitride films and mechanism for the nitrogen-lowered threshold in cold cathode

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Carbon nitride films have been deposited by rf reactive magnetron sputtered graphite carbon in an N₂ discharge. The process parameters, viz., nitrogen partial pressure (P_N₂), substrate temperature (T_s), and substrate bias (V_b) were varied in order to investigate their influence on the field emission properties. The effective work function for carbon nitride films determined using the Fowler–Nordheim equation is in the range of 0.01–0.1 eV. Insight is presented into the nitrogen-lowered threshold of cold cathode electron emission of carbon from the perspective of nitride tetrahedron bond formation. The involvement of nonbonding (lone pair) and lone-pair-induced antibonding (dipole) states is suggested to be responsible for lowering the work function and hence the electron emission threshold. It is found that the substrate temperature of 200 °C, floating potential at the substrate, and nitrogen partial pressure of 0.3 Pa are favorable to promote the reaction that lowers the work function. © 2003 American Institute of Physics. [DOI: 10.1063/1.1594822]

I. INTRODUCTION

Electron field emission of carbon-based materials has attracted tremendous interest in recent years due to its high potential for display applications.1 Electron emission was observed to occur under moderately low electric field from diamond.2–4 nitrogenated diamond,5,6 diamond-like carbon,7,8 carbon nanotubes,9–11 and nitrogenated amorphous carbon (amorphous carbon nitride).12–16 Field emission from polycrystalline diamond grown using chemical vapor deposition is slightly easier17,18 than from high quality diamond due to its much lower resistivity.19 Both boron and phosphorous doped diamonds have relatively high threshold field of emission, while nitrogen doped diamonds lower the fields significantly.6,19 The band gap of diamond-like carbon (DLC or α-C) varies from 1 to 4 eV depending on the fraction of sp³ bonding.19 Field emission from α-C is generally much easier than from diamond. Incorporating nitrogen into an α-C matrix could ease the electron field emission further.13 Since the α-C and the nitrogenated α-C (α-C:N) films are deposited at low temperatures, they are of particular interest for the applications of field emission displays.20

Numerous mechanisms5,19,21,22 have been proposed for the low-threshold emission of carbon such as negative electron affinity,23 defects bands in diamond,18 space charge induced band bending,3 surface states,17 and surface dipole.19 However, the mechanism for electron field emission from nitrogenated carbon is poorly known, thus further study is necessary. In this work, we present the intrinsic property of the field emission from α-C:N films caused by the chemical bonding states.

II. EXPERIMENT

Carbon nitride films were deposited on Si(001) substrates using rf magnetron sputtering high purity (99.99%) pyrolytic graphite (100 mm in diameter) in a pure N₂ discharge. Prior to deposition, the chamber was pumped down to the base pressure of 5 × 10⁻⁷ Pa. For different depositions, the process parameters, viz., nitrogen partial pressure, substrate temperature, and substrate bias were varied, respectively, whereas the sputtering power was kept constant at 150 W. The deposition conditions are as follows: (1) nitrogen pressure varied from 0.3 to 1.0 Pa, while substrate was held at ambient temperature and voltage was kept at floating; (2) substrate temperature was changed from ambient temperature to 500 °C with the voltage kept at floating at fixed nitrogen partial pressure of 0.3 Pa; (3) substrate bias was varied from 0 to ~150 V at ambient temperature and nitrogen partial pressure of 0.3 Pa. The deposition time was 30 min, and the thickness of the film was determined in the range of 100–500 nm. The experimental details have been described elsewhere.24

The field emission from as-deposited films was measured in an ultrahigh vacuum of 10⁻¹⁰ Pa. During testing, the carbon nitride films coated on Si(001) substrate and an indium tin oxide (ITO) coated glass plate were considered as the cathode and the anode, respectively. The spacing distance between the anode and the cathode was kept at 100 μm. Current density (J) flowing to the ITO electrode as a function of the applied electric field (E) was recorded.

III. RESULTS

Figures 1–3 show J–E profiles and Fowler–Nordheim (FN) plots of the electron field emission from carbon nitride
films prepared under various conditions. Generally, the field emission from the as-grown carbon nitride films was observed to be stable with low threshold electric field. It is found that the nitrogen partial pressure of 0.3 Pa, substrate temperature of 200 °C, and floating potential at the substrate are favorable to lower the work function. The effective work function determined using FN plots for all the carbon nitride films is lower than 0.1 eV, which changes little with nitrogen partial pressure, substrate temperature, and substrate bias. The very low threshold of electron field emission observed here is beyond the explanation of existing models. However, we found that the model of bonding and band-forming for oxides and nitrides could provide a more feasible mechanism for lowering the threshold of carbon nitride emitters in cold cathode emission.

IV. MODEL

According to the model of bonding and band-forming for oxides and nitrides, it is essential for a nitrogen atom, N, to hybridize its sp orbital upon interacting with carbon, C, to form a quasi-tetrahedron, NC₄, with the involvement of bonding (sharing electron pair), nonbonding (lone electron pair), and antibonding (lone-pair induced dipole) states. Energy states near the edge of valence band, Eᵥ, or below Fermi-level (Eᵥ) are emptied by transporting electrons to the bonding orbital of N and the antibonding orbital of C. The antibonding states are located well above Eᵥ of the C due to the polarization. The nonbonding and bonding bands are slightly higher and lower, respectively, than the 2p level of an isolated N atom. The presence of bonding, nonbonding lone-pair, and the lone-pair-induced antibonding states is of key importance to a nitride. Being well acclaimed by existing evidence, this model has provided consistent insight into the physical properties of some nitrides and oxides, such as the origins of the N-enhanced magnetization of rare earth and ferromagnetic metals, the blueshift in light emitting of group-III nitride, and wear and corrosion resistance as well as the ultrahardness and super elasticity. We believe that
this model should enable us to have deeper insight into the enhanced emission properties of the $\alpha$-C:N compounds in which the localized nonbonding and atomic-bonding could somewhat lower the threshold of field emission.

Figure 4 shows the schematic of the nitride quasi-tetrahedron (NC$_4$) model. The N atom hybridizes and interacts with carbon atom in solid phase during the film deposition, through four directional orbitals. The smaller spheres are C and the larger one is the lone-pair induced C dipoles with an expansion in size and elevation of energy states. When a reaction takes place, all atoms change their sizes and valence states. The N–C bonds are mainly polar-covalent due to its slight difference in electronegativity ($\sim 3$ and 2.5 for N and C, respectively) between the constituents.

The cluster bonding results in a change of density of states (DOS) of a semiconductor, as illustrated in Fig. 5.

1. The $sp^3$-hybrid bonding states of N are slightly lower in energy than the $2p$ level of an isolated N.

2. The N $sp^3$-nonbonding (lone pair) states are slightly higher than the $sp^3$-bonding states. The nonbonding should not change the system energy in principle.

3. The antibonding (dipole) states being well above the $E_F$ reduce the work function.

4. Holes are produced under $E_F$ by the process of bond and antibond formation. During the reaction, the electron in the outmost shell of C (in the conductance or valence band) transits either to N $sp^3$-bonding states or to the outer empty shell of C, antibonding (dipole) states. This process of electron–hole production alters a metal to a semiconductor such as Al$_3$N, or widens the band gap of a semiconductor such as SiN.

(2) With this model, we have improved our understanding of the mass transport, phase formation, atomic dislocation, electron localization, and energy state variation occurring in a
wide range of oxide and nitride surfaces.25–27 For example, relative to SiC, two additional DOS features have been observed in nanometric SiN.28 The one DOS feature is at ~3.3 eV below \( E_F \) and the other is 1.0–3.8 eV above \( E_F \). The former was ascribed as the N-2p lone-pair \( \pi \) orbital at the top of the valence band while the latter is yet to be known. The latter may be identified as the antibonding subband (Fig. 5) based on the current modeling scheme. In calculating carbon nitride, Hughbanks and Tian29 found that the N-N lone-pair repulsion causes a ~2.31 eV antibonding-energy. Matar30 also noted an antibond feature at ~3 eV above the \( E_F \) of Fe,N compound in his calculation. Therefore the presence of nonbonding lone pairs and antibonding states is unambiguously intrinsic for nitride compounds.

V. DISCUSSION

As a consequence of nitrogen inclusion discussed in this work, the local work function changes with altering the surface atomic valences. The dipole towards the open end of a surface will easily emit electrons under an external electrical stimulus. This may provide a more feasible yet simple mechanism for lowering the threshold voltage of emitters in cold-cathode field emission.

It is known that the emitting-current density \( (J) \) follows the Fowler–Nordheim (FN) relation:

\[
J = \frac{A E^2}{\phi} \exp \left( -\frac{B \phi^{3/2}}{\beta E} \right),
\]

where \( A \) and \( B \) are constant, \( \beta \) is the dimensionless field enhancement factor, and \( E \) and \( \phi \) are the external electric field and the work function, respectively. Obviously, reducing the work function is the most effective means to enhance the capability of a cold cathode. The possible mechanisms of reducing the work function may include the charge tunneling, surface roughening, or nanostructuring that enlarge the local curvature of the emitters, as well as chemical adsorption. However, it should be noted that only the field emission governed by the chemical adsorption on the surface of the emitters is intrinsic.

The low-threshold effect of the cold-cathode field emission due to nitrogen addition could be clear evidence for the bonding and band-forming modeling predictions. The presence of the antibonding states above \( E_F \) lowers the work function that eases the cathode field emission. Actually, the phosphorous-3p electrons are more mobile than the N 2p and O 2p electrons, but P doping offers little reduction of the threshold with respect to the O and N doping. The \( sp \) hybridization of P appears to be harder than N and hence P doping could not produce the nonbonding and antibonding features. Hence the interpretation of the mechanism using the impurity energy level can only be applied to P doping but not N addition. The work function of Cs and Li (~3.5 eV) is much lower than that of other metals (~5.0 eV). However, adding the Cs and Li to the diamond surface does not enhance much emission. Therefore lowering the threshold of field emission is the unique ability of electronegative N additives that adds indeed a subband above the \( E_F \). There has been sufficient evidence for the lone pair interaction in nitride.25–27 Based on the existing mechanisms of electron field emission, the work functions of \( a-C \) and \( a-C:H \) are estimated in the order of 3.5–4.0 eV,18 while that of the diamond with graphitic patches is 3–4.2 eV,32 depending on whether the surface is hydrogenated. However, in the case of nitrogenated diamond, \( a-C:H:N \), and \( a-C:N \), extremely low work functions (0.01–1.0 eV) have been reported,11,12,18,19,22,23 including the results of this work. The low work function of nitrogenated diamond can be explained by the fact that the film has a rough outer surface and heterogeneous bonding, which may lead to large field enhancement factors in the system.18 But, \( a-C:H:N \) and \( a-C:N \) surfaces are smooth and as such the geometric field enhancement is unlikely.18 The huge difference in the work functions for \( a-C:H:N \) and \( a-C:N \) is therefore beyond the explanation based on the mechanisms proposed previously. It is worth emphasizing that this difference can be narrowed by using the bonding and band-forming model which indicates that N interacts with carbon atoms and forms the antibonding states. The antibonding (dipole) states being well above the \( E_F \) reduce the work function by 2.2–3.0 eV,29,30 Therefore the work functions of 0.01–1.0 eV are possible according to the bonding and band-forming model.

VI. SUMMARY

According to the model of bonding and band-forming, a nitrogen atom hybridizes its \( sp \) orbital upon interacting with C to form a NC(4) quasi-tetrahedron. This leads to the formation of nonbonding (lone pair), antibonding (dipole), and electron–hole states. The presence of antibonding states above \( E_F \) lowers the work function and hence the electron emission threshold for the C:N compound, which may provide a more feasible mechanism for lowering the threshold electric field of emitters in cold cathode emission.

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