

Surface electronic density of states of tetrahedral amorphous carbon investigated by scanning tunneling spectroscopy and *ab initio* calculations

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The surface electronic density of states of tetrahedral amorphous carbon has been measured by scanning tunneling microscopy and calculated by density functional theory. An analysis of these results and their comparison is presented here for a series of structures with different microscopic mass densities. The experimental structures were obtained by pulsed laser deposition with varying conditions resulting in diamond-like carbon thin films. The calculated carbon structures were generated by simulating a melting-cooling cycle with molecular dynamics using the density functional energetics within the local density approximation. The experimental and calculated densities of states show good agreement. Graphitic-like surface reconstruction is both observed at the sp^3 -rich tetrahedral amorphous carbon (ta-C) sample and found in the calculated ta-C slab structure. © 2000 American Institute of Physics. [S0003-6951(00)01719-8]

Proposed extraordinary electronic properties¹ of tetrahedral amorphous carbon (ta-C) are currently of much interest due to potential applications in field emission devices. Especially, the ta-C surfaces have been studied intensively, since the field emission efficiency is defined by surface properties, and the ta-C film acts as an electron emitter. Depending upon the way ta-C is formed, it can be electrically conducting, or semiconducting. Other properties of ta-C include heat and radiation resistance, optical transparency over a wide spectral range, chemical inertness, and low or negative electron affinity.

In a recent work by Dong and Drabold,² the calculated structural and electronic properties of ta-C surfaces were reported. The fraction of sp^3 atoms at the surface was shown to be near 50% and the major feature of the ta-C surfaces was chain or ring formation of the threefold-coordinated atoms.² Therefore, ta-C surfaces were found to be smooth and highly graphite like, that is consistent with experimental findings. Electronic states were found to evolve from bulk-like extended states inside the bands to localized surface-like states in the band tail or band gap. Surface sp^2 graphitization was found to delocalize surface states.

Arena *et al.*³ have studied electronic properties of the ta-C surfaces by means of scanning tunnelling spectroscopy (STS). The surface density of states (DOS) of a sp^3 -rich sample was shown to have narrower band gap than bulk DOS due to sp^2 -rich bonding on the surface. The band gap was found to be around 2 eV. In addition, the valence band intercept was shown to lie closer to the Fermi level at 0 eV than the conduction band intercept. This indicates that un-

doped ta-C films are intrinsically *p*-type semiconductors.³

Amorphous diamond-like carbon (DLC) thin films studied in this work were produced by pulsed laser deposition (PLD) on *n*-type silicon substrates.⁴ An XeCl excimer laser (wavelength 308 nm, pulse length 20 ns) was used for deposition and the laser intensities are in the range 10^8 – 5×10^9 W cm⁻². The incident laser radiation is focused onto the pyrolytic graphite target at an angle of 45°. During the deposition, the target is rotated around its axis in order to avoid the drilling effect. The deposition is performed at room temperature with a vacuum chamber base pressure around 10^{-3} Pa.

The STS characterization of DLC thin films is made by means of scanning tunneling microscope (STM) in air. A commercial STM/atomic force microscope (AFM) (Digital Instruments NanoScope® II) system is used to investigate surface DOS. In the STS, tunneling tip is brought close to sample surface to establish tunneling current within sample and tip. To obtain current-voltage (*I*–*V*) characteristics, tunneling conditions for STM imaging is first achieved. At this state, a Pt–Ir tip is frozen still by keeping the tip-sample distance and position constant, and the tunneling current is measured at different sample bias voltages. A typical sample bias (V_b) and tunneling current (I_t) for STS from DLC are –3 V and 1–10 nA, respectively. It was found, that higher values of the V_b and I_t produced more stable spectroscopic behavior, although, good STM imaging conditions are obtained with smaller values.

I–*V* curves were measured by interrupting the feedback and measuring the tunneling current as a function of sample voltage. Making *I*(*V*) spectroscopic measurements involves setting the V_b and running the feedback to establish I_t . The V_b is then ramped between $\pm$ scan range/2 and modulated by

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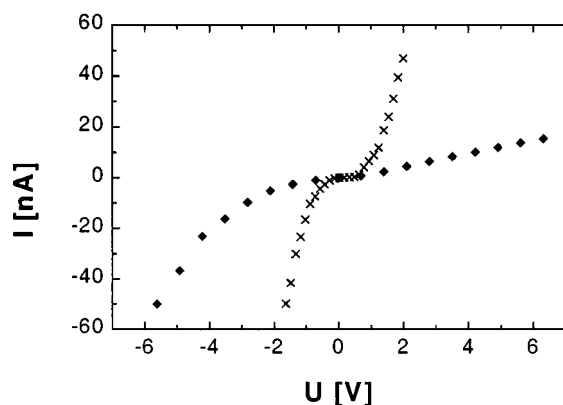


FIG. 1. Typical I - V curves for as-deposited diamond-like carbon samples with different bulk sp^3 fractions measured using a small sample bias voltage ($V_b = -100$ mV) and tunneling current, ($I_t = 1$ nA). Therefore, the tip is located close to the sample surface and these I - V curves represent the bulk properties. (×) Low sp^3 fraction, and (♦) and high sp^3 fraction.

modulation voltage V_{mod} ($V_{\text{mod}} \ll V_b$) and tunneling currents are measured at $V_b \pm V_{\text{mod}}/2$. Using these values, normalized differential conductivity, which is proportional to surface electronic DOS, can be calculated. Normalized differential conductivity is defined as $(dI/dV)/(I/V)$, where dI is the average of the currents measured at $V_b \pm V_{\text{mod}}/2$, dV is modulation voltage, I is tunneling current I_t , and V is sample bias voltage.

Figure 1 shows typical I - V curves for as-deposited DLC samples with different bulk sp^3 fractions, measured using small V_b , therefore, allowing the tip to locate close to the sample surface. This, according to Arena *et al.*,³ means that these I - V curves represent the bulk properties. At the low sp^3 fraction limit the I - V curve is symmetric around 0 eV indicating that the Fermi level is located in the middle of the band gap. At the high sp^3 fraction limit, the I - V curve is clearly asymmetric and rectifying characteristics are observed. A similar effect has been observed earlier from amorphous diamond (a-D)⁵ and it indicates that undoped a-D thin films with the sp^3 fraction are intrinsically p -type semiconductor materials. Therefore, the DLC on the n -Si forms an ideal p - n heterojunction, with negative bias applied on the n -Si operating as a forward-biased cathode emitter.⁵

In our previous work,⁶ a series of bulk ta-C structures with different microscopic mass densities were generated by running molecular dynamics for a melting-cooling cycle and using the density functional theory (DFT) with a local density approximation (LDA).^{7,8} The Harris functional formalism was used to evaluate the energetics for molecular dynamics. It offers a fast algorithm for evaluation of forces from DFT.⁹ The initial configuration of atoms was a simple periodic cubic lattice with diamond structure, which contained 64 atoms. The sample densities varied from 2.0 g/cm³, which is close to the graphite density, to the diamond density, 3.54 g/cm³. The structural and electronic properties of the simulated models were calculated and it was shown that with increasing mass density, the average bond length, bond angle, sp^1 , sp^2 , and sp^3 fractions, and electronic properties all came closer to those of diamond-like amorphous carbon.

In this work, bulk models with a cubic unit cell of 64 atoms generated in Ref. 6 are taken as a starting point. To

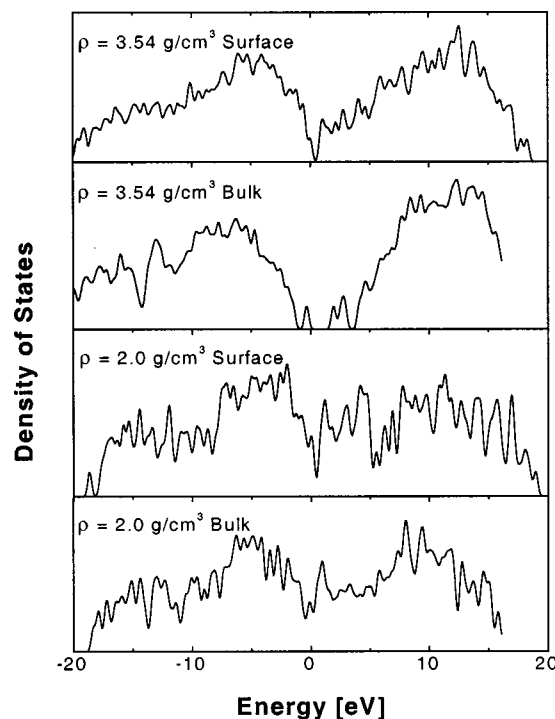


FIG. 2. The calculated electronic density of states for slab and bulk structures with mass densities of 2.0 and 3.54 g/cm³. The Gaussian broadening with a line width of 0.5 eV is used for smoothing and the Fermi level is set to 0 eV.

model the surface the unit cell dimension in z direction is doubled leaving the other half empty. Thus, periodic slab models ($x, y, 2z$) with two surfaces are generated. The dimensions $x=y=z$ were 8.5 Å and 7.112 Å at the highest and lowest density, respectively. These structures are relaxed at 300 K using the same DFT-LDA method described above. It is found that relaxation time of 100 fs is long enough to allow the singly bonded surface atoms to relocate and form chain or ring structures on the surface, but short enough to prevent bulk atom relaxation. With a longer relaxation time, the slab density (occupied volume) is modified due to the total energy minimization. As a result of 100 fs relaxation, about half of the atoms are relocated.

In Fig. 2, the calculated DOS for surface slab and bulk structures with mass densities of 2.0 and 3.54 g/cm³ are shown. The Gaussian broadening with a line width of 0.5 eV is used for smoothing and the Fermi level is set to 0 eV. Details of the results from bulk calculations have been discussed earlier in Ref. 6. In the calculated DOS for the slab structures, the number of π^* states decreases as the density increases, and therefore, the electronic properties of the slab structures come closer to those of diamond which has no π states. At mass density of 2.0 g/cm³, both slab and bulk DOS have a pronounced π^* state at 1 eV. Although there are states at the region 2–4 eV above the Fermi level in the slab DOS, which arise from amorphous structure, both DOS show the graphitic, sp^2 bonded, nature of the sample. There are more states above the Fermi level in the surface DOS than in the bulk DOS at a mass density of 3.54 g/cm³. These states arise from the surface sp^2 bonds of the slab structure. This indicates that the slab surface structure is more graphite like than the bulk structure.

Let us now investigate the case of the high-density limit

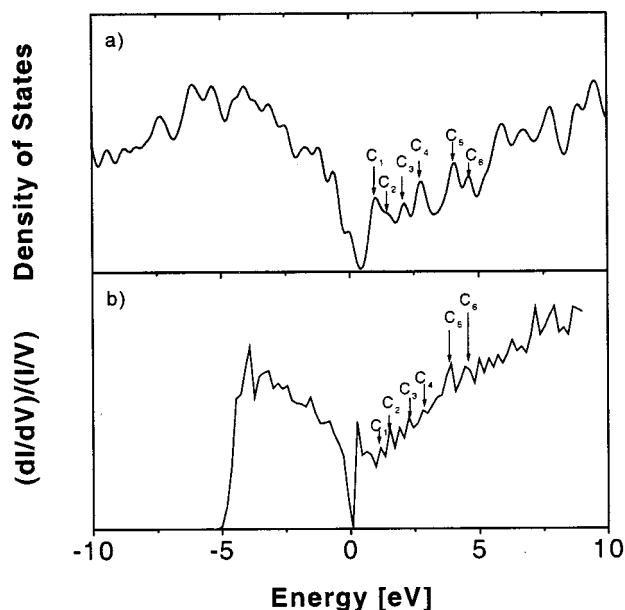


FIG. 3. (a) Calculated DOS of the slab ta-C structure with mass density of 3.54 g/cm³. (b) Normalized conductivity of the pulsed laser deposited DLC sample with a high sp^3 fraction measured by means of STM.

spectra in detail. In Fig. 3 normalized conductivity of the pulsed laser deposited DLC samples with high sp^3 fraction together with calculated DOS of the slab structures at the high-density limit are shown. The sp^3 fraction of the DLC sample has been measured by x-ray near edge absorption spectroscopy (XANES) and reported in Ref. 4. The experimental STS spectrum of high-density limit DLC sample reassembles well with the calculated surface DOS of a ta-C slab structure. In the recent work by Arena *et al.*,³ states due to localized π bonding in surface DOS measured by STS were reported. These states were at 1.7, 2.8, and 3.6 eV. In the case of graphite, peaks fairly close to these, 1.7, 2.5, and 3.5 eV, have been assigned as π^* band, an extrinsic surface state and a bulk state, respectively.¹⁰ In the present work, DOS features at 1.0 (C₁), 1.5 (C₂), 2.15 (C₃), 2.7 (C₄), 4.0 (C₅), and 4.6 eV (C₆) are observed in the calculated surface electronic DOS of ta-C structures with high the sp^3 fraction. Peaks C₂, C₄, and C₅ visible in STS spectra from a sp^3 -rich DLC sample, show the graphitization of the surface layer of the calculated ta-C structures and sp^3 -rich DLC films. Exact peak positions for the different spectra are given

TABLE I. C_n peak positions in Figs. 3(a) and 3(b).

	DLC, 75 sp^3 fraction (eV)	Ta-C, high sp^3 fraction (eV)
C ₁	1.2	1.0
C ₂	1.6	1.5
C ₃	2.35	2.15
C ₄	2.85	2.7
C ₅	3.9	4.0
C ₆	4.5	4.6

in Table I. In our earlier work,⁶ we assigned the C₁ state to be the π^* state that reassembled well with the C 1s $\rightarrow \pi^*$ transition in the experimental XANES.⁴ Therefore, we suggest that the presence of a well-defined C₁ state on spectra reported here is also a clear indication of the graphitic reconstruction of the surface.

In conclusion, calculated surface electronic DOS and experimental surface DOS measured by STS are in good agreement. Features are found in the DOS of sp^3 -rich DLC samples and calculated DOS of ta-C structures that indicate graphitic surface reconstruction. In addition, ta-C structures and sp^3 -rich DLC films are shown to be intrinsically p -type semiconductors.

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