

Effect of surface treatments on the electronic properties of ultra-nanocrystalline diamond films

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Abstract

We present the soft x-ray spectroscopic study of the ultra-nanocrystalline diamond (UNCD) films with different surface treatments. The samples were prepared by means of microwave plasma enhanced chemical vapor deposition (MPECVD) and the different surface treatments are applied to alter their field emission properties. The electronic properties were subsequently examined by the soft x-ray absorption and x-ray emission spectroscopy at carbon $1s$ threshold. From the experimental results, there is no significant variation in electronic structure of oxygen- and hydrogen-plasma treated UNCD films. On the other hand, the biased treated UNCD film shows more remarkable change on the sp^2 and sp^3 states. The formation of sp^2 bonding and the reduction of sp^3 bonding are the consequence of the improved electron field emission properties.

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1. Introduction

Diamond is a very attractive material with extensive theoretical and experimental studies owing to its unique physical and chemical properties, such as extreme hardness, high surface stability, high thermal conductivity, large energy gap, and so forth [1]. Therefore, diamond is an excellent candidate for the industrial applications. The properties of nanomaterials may differ from those of the bulk either in geometric structure or electronic band structure owing to the symmetry breaking or to the quantum size effects. In the last few decades, there are substantial studies on the properties and applications of microcrystalline diamond (MCD) [2], especially for the electron field emission properties [3]. Diamond is the most promising electron emitting materials due to its low and negative electron affinity [4]. The improvement of this material becomes significant.

Thus, very recently large focus has been directed towards the intriguing properties and applications of nanocrystalline (NCD) and ultra-nanocrystalline diamond (UNCD) films [2]. It has been found that either by suitable doping or reducing the grain size can improve the electron field emission property. The n-type conductivity of UNCD can be induced by nitrogen doping [5]. Moreover, the high field emission of UNCD film is the result of the presence of electron conducting channels in the grain boundary [6]. It is believed that the sp^2 and sp^3 hybrid is one of the most important facts to characterize the field emission property. X-ray absorption (XAS) and x-ray emission (XES) spectroscopy are ideal techniques for studying the bonding structure of diamond and directly measure, respectively, the density of unoccupied and occupied electronic states [7]. In particular the sp^2 versus sp^3 bonding ratio can be straightforwardly probed. The main effort of this study is to investigate how the electronic structure influences the field emission properties of the UNCD films. The effects of different surface treatments on the nitrogen incorporated UNCD films have been studied.

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2. Experiment

The C *1s* x-ray absorption and x-ray emission measurements were carried out at the Lawrence Berkeley National Laboratory (LBNL), Advanced Light Source (ALS) at beamline 7.0.1. The beamline is equipped with a 99-pole, 5-cm period undulator and spherical grating monochromator. The XAS spectra were obtained in the total electron yield mode by measuring the photocurrent directly from the sample. The XES spectra were recorded by using the high resolution grazing incidence grating spectrometer with a two dimensional detector [8]. The resolutions were set to 0.1 eV at 290 eV (in the vicinity of the C *1s* edge) for both XAS and XES. The highly oriented pyrolytic graphite (HOPG) was used as the standard samples to calibrate the monochromator. The energy scale in the XES spectra was calibrated by using the elastic peaks.

These nitrogen incorporate UNCD films were prepared by means of microwave plasma enhanced chemical vapor deposition (MPECVD) and the different surface treatments were applied to these films, H-terminated surface by hydrogen plasma treatment, O-terminated surface by air plasma treatment, and the film with negative bias applied. All the UNCD films in the present study show the similar grain size ~10 nm, based on the scanning electron microscope (SEM) image, the detail of the preparation is given elsewhere [9].

3. Results and discussion

In Fig. 1 the XAS spectra are presented, from top to the bottom, in the order of as-grown, air plasma treatment, hydrogen

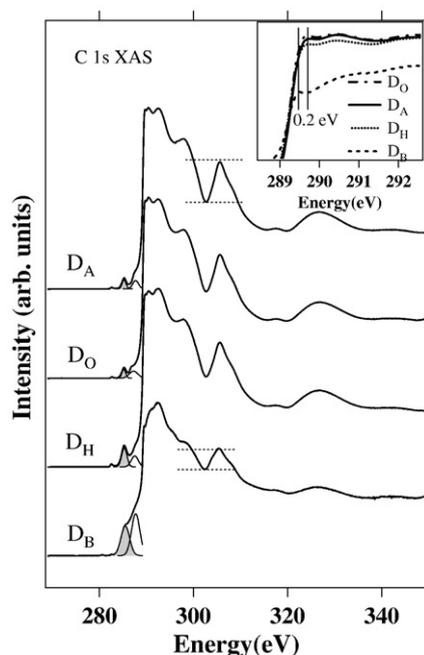


Fig. 1. The C *1s* absorption spectra of different surface treatment UNCD films. The as-grown, air plasma, hydrogen plasma and bias treatment UNCD films are denoted as D_A , D_O , D_H and D_B , respectively. The shadow represents the sp^2 contribution. The dotted line indicates the depth of the second band gap. The exciton region is expanded in the inset.

plasma treatment, and bias treatment UNCD films, and they are denoted as D_A , D_O , D_H , and D_B , respectively. All spectra exhibit a sharp feature at ~289.7 eV and a dip at ~302.7 eV. The former is the excitonic transition which is the result of the bound electron-hole pair, while the latter is the second absolute band gap. Both are characteristics of the diamond structure spectrum. The exciton peak and the dip are often used to evaluate the quality of diamond [10].

The spectra can be basically divided into two regions, at ~285.3 eV and relatively broad band between ~290 and 303 eV, which are assigned to the unoccupied π^* and σ^* bonds, respectively. The π^* feature is the characteristic of the sp^2 C=C bond, while the σ^* feature is the characteristic of the sp^3 tetrahedral C–C bond. In addition a very weak peak at about 287.5 eV, observed between the π^* and σ^* bonds is attributed to C–H bond. In perfect diamond with 100% of sp^3 hybridized carbon, the unoccupied states exhibit pure σ^* character. On the other hand, in impure diamond or nanodiamond, a π^* feature located at 285.5 eV is expected to be appeared [11] due to structural differences between surface and bulk, the tetrahedral network of bonds is discontinued at the surface or interface [12]. The increment of the π^* peak is also consistent with other study with nitrogen added [13]. As nitrogen is incorporated at the grain boundaries, new electronic states associated with carbon and nitrogen are introduced into the band gap of diamond, leading to semi-metallic property [14]. It has been not just observed experimentally [15] but also predicted theoretically [14] the semi-metallic property is ascribed to the presence of π -bonding.

Compared with the pure diamond that all the spectra are similar, indicating that these UNCD films are diamond in nature with a small fraction of sp^2 carbon. The origin of the peak appeared below the π^* peak at about 282.5 eV is still not well understood yet. It has been ascribed to the C *1s* surface exciton [16,17], while other reports speculated that it originates from the disordered, most likely amorphous carbon [18,19]. As bias applied to the UNCD film, the sp^2 (sp^3) bonding increases (decreases) drastically, indicated by the decreasing diamond exciton peak and the increase of the π^* bonding state. This may be due to a larger amount of grain boundaries [18]. Although all the films show similar grain size ~10 nm [9], the bias treated UNCD film shows extreme rough granular surface and others present smooth and similar surface morphology. The rough surface may bring about larger total volume of grain boundaries. For a quantitative study, we have integrated the intensity of the π^* feature of the sp^2 state, using Gaussian function after background subtraction, as shown in the bottom of each spectrum. The enhancement of the sp^2 features and reduction of sp^3 features, indicate that the film is becoming more graphitic in nature when applying the bias to the film. It is likely that at D_B , electrons find the conduction path and therefore a relatively lower onset electric field. This may be due to the grain boundaries at the rough surface contain more graphitic carbon.

The peak at ~287.5 eV is ascribed to C–H bonding in diamond, and is commonly observed in H-terminated diamond surface [20]. It is originated from the absorption of hydrocarbon to the dangling bonds at surface. It has highest intensity in the

H-treatment film. However, others still show this feature, so this C–H bond would be due to the more or less surface contamination. The water vapor is inevitable within the chamber during the bake out process and would be the main source of the surface contamination. The diamond exciton, located at 289.5 eV, reduces in the spectrum of D_B , along with the reduction in depth of the diamond second band gap, indicates that as bias is applied, the degree of short-range order is reduced. This is consistent with the observation from HRSEM [9]. Close inspection reveals that the D_B exhibits a slightly broader and weaker exciton transition with a 0.2 eV shift to lower energy in comparison to other UNCD films. This might be due to increase in the lifetime of the core-hole excitation. Besides, this shift implies the increased exciton radius or the shrinking of the band gap [11].

The dip at ~ 303 eV is originated from the second absolute band gap of diamond. The depth of the gap depends on the crystalline size or the size distribution [21]. Besides, this gap is also a fingerprint of semiconducting-like or insulating-like materials. It has been shown that the dip is absent in amorphous diamond which has semi-metallic character due to the presence of sp^2 state. Here we observe the dip is shallow in D_B along with the increased sp^2 state. This may correlated to the field emission property.

The XES spectra with excitation energy 320 eV are presented on the left side of Fig. 2. The feature at about 270–272 eV is related to states with $2s$ character while the more intense fluorescent features close to the highest occupied orbitals arise from states with $2p$ character. The XES spectra map the energy of the highest occupied states. Spectral features of D_A , D_H , and D_O are essentially similar, consisting of a broad main peak around 279 eV and a high energy shoulder peak near 282 eV. These features therefore suggest that chemical bonding and local structures are very similar. The main peak and the high energy shoulder peak are probably due to the σ and π orbitals,

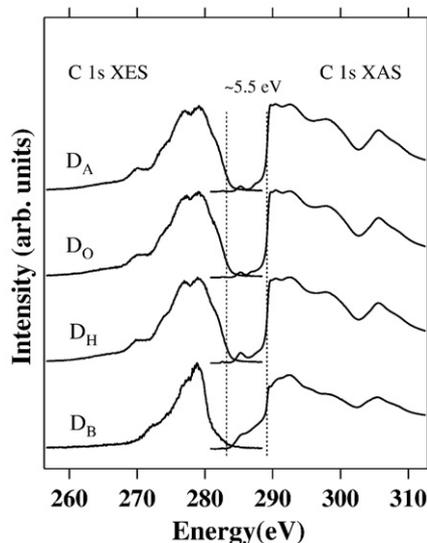


Fig. 2. The C 1s XES spectra (left) and XAS spectra (right) for different surface treatment UNCD films.

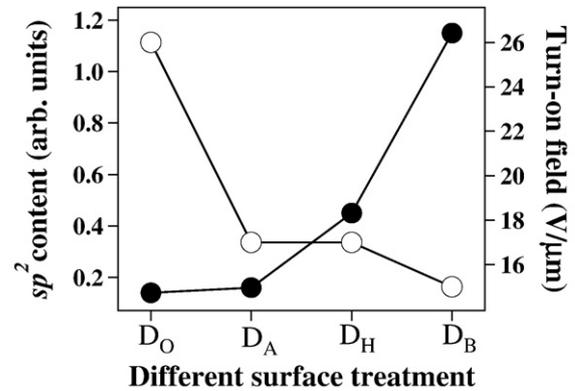


Fig. 3. The sp^2 carbon concentration (closed symbols) versus the turn-on electric field (open symbols).

respectively [22]. This is consistent with the bulk diamond [23]. However, the D_B show the different spectral shape particularly the intensity distributions and it resembles the spectrum of diamond clusters [24]. In the spectrum of D_B , the valence band becomes narrower and the $2s$ state is shifted toward the valence band maximum and close to states with mainly p character. Thus the stronger sp hybridization is expected. The HOMO-LUMO gaps were then estimated by comparing the XAS together with XES. Considering the valence band maximum (VBM) of diamond at 283.8 eV [25] and the conduction band minimum (CBM) estimated by a standard method [26]. The Lorentzian and arctangent functions were used to describe the exciton state and the conduction band edge, respectively [27]. The CBM is estimated to be about 289.9 eV and then the energy gap is yielded to be about 6.0 eV, as shown by dotted lines in Fig. 2. This value is slightly larger than the well-known energy gap of 5.5 eV for bulk diamond. It has been found that the conduction band edge is shifted to higher energy with reduce the grain size of UNCD films due to the quantum confinement effect [27]. According to the SEM image all these UNCD films show similar grain size of about 10 nm. Consequently, the enlargement of the energy gap compared with bulk diamond may be indicative of the quantum confinement effect.

Electron field emission property measured from J–E curves and Fowler–Nordheim (F–N) plots yielded the emission current density (J_e) and turn-on-field (E_0). E_0 is plotted as open circles in Fig. 3. Meanwhile, the XAS spectra were decomposed into the primary components, most notably the π^* state at 285.5 eV in order to determine sp^2 contribution. As shown in Fig. 3 (closed circles), the number of sp^2 increases from 0.14 in D_O , 0.16 in D_A , 0.45 in D_H , and finally to 1.15 in D_B . The increase of the sp^2 feature is the signature of the formation of graphite like structure. Considering that the grain boundaries generally consist of sp^2 carbon and the boundary volume increases with the decrease of grain size or the rough surface, it is reasonable that the sp^2 carbon concentration increases with increasing the rough surface for bias treated UNCD film. These numbers are found to be in line with the field emission properties. The enhancement of the sp^2 features and reduction of sp^3 features suggest the graphitization of films enhances the electron emission behavior.

4. Conclusions

In conclusion, the electronic properties were examined by the soft x-ray absorption and x-ray emission spectroscopy at carbon $1s$ threshold. From our experimental results, we found that surface treatments of air and hydrogen had nearly no effect on both the valence and conduction band structures, as the C $1s$ emission and absorption showed no differences. For bias treated UNCD film, the feature ~ 285.3 eV is enhanced, suggesting that bias treatment induced some of the sp^2 states from the surface. The enhancement of sp^2 bonding induced the electron conducting path are the consequence of the improved electron field emission properties.

Acknowledgments

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