

PHOTOEMISSION STUDY OF DIAMOND (100) SURFACE*

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ABSTRACT

The electronic structure of the diamond C(100)-(2×1)/(2×2) has been investigated by means of angle-resolved photoelectron spectroscopy for the first time. A surface-related shift has been observed in the C 1s core level spectrum. The surface-state band dispersion was measured along the symmetry axis Γ -J' in the surface Brillouin zone. For $k_{\parallel} = 0$, there is a very pronounced surface state 1.5 eV below Fermi level E_F , and it disperses downwards with increasing k_{\parallel} . Near the boundary of the surface Brillouin zone J', we find two states with binding energies of 1.9 and 2.4 eV with respect to E_F .

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I. INTRODUCTION

The numerous unique properties possessed by diamond has raised growing interest in this material and the potential of its application in the semiconductor industry. Investigation of the diamond is also inspired by recent breakthroughs in depositing polycrystalline diamond films under metastable conditions by chemical vapor deposition (CVD) technique on various substrates. However, the understanding of the diamond growth process is still very poor, which roots, to large extent, from lack of understanding of the diamond, particularly its surface electronic structures. Few studies, both theoretically and experimentally, have ever been conducted for diamond and its thin films before. In comparison, for other members in the same column of the periodic chart such as Si and Ge, extensive theoretical and experimental studies have been carried out, [1] resulting in tremendous progress in terms of our understanding about these materials and astonishing improvement of the device processing. We believe that there is an urgent and unmet need to study the nature diamond and its surfaces and gain some basic understanding of them. In past year, work on diamond surfaces has mainly been focused on the C(111) surface which is relatively easy to prepare, [2-7] few studies of the C(100) surface, which may be more important in terms of device applications, have been reported. [7-10]

In this work, we have studied the surface structure of natural diamond C(100) surface using angle-resolved core level and valence band photoemission spectroscopy (ARPES). To best of our knowledge, our work is the first study of this kind on the C(100) surface. One chemically shifted component in the C1s core level has been resolved, that is attributed to the surface dimer of the C(100) surface. We have observed two surface related states in the valence band spectra and determined their dispersion along Γ -J' direction in the surface Brillouin zone. These results will be

compared with the Si(100) surface, a much better understood surface that has the similar structure as diamond.

II. EXPERIMENTAL

The photoemission study of C(100) surface was conducted at Stanford Synchrotron Radiation Laboratory on a multi-undulator beam line V-2 with photon energy ranging from 20 to 1000 eV. A VG ADES-400 angle resolved ultra high vacuum system that consists of a main chamber housing a low energy electron diffraction (LEED) optics, a hemispherical energy analyzer, and a sample load lock system was used. The sample manipulator was equipped with an azimuthal rotation mechanism and an e-beam heater for high temperature annealing. The base pressure of the chamber during the experiment was $<2 \times 10^{-10}$ torr. The angular resolution of the ADES 400 analyzer is $\sim 2^\circ$ and the overall energy resolution is about 250 meV.

The natural type IIB C(100) surface studied here was mechanically polished on a rotating wheel of cast iron periodically replenished with a mixture of diamond grit and olive oil. During the polishing the grit itself is eroded, and its size at the end of polishing process is believed to be well below $1 \mu\text{m}$. [4, 11] The olive oil acts as a hydrogen source to terminate the diamond surface, which behaves like a passivation layer for the surface. The sample was then cleaned for UHV system and transferred into the experimental chamber through the load lock system and outgassed at 500°C until the chamber pressure recovered close to the base pressure. We found that the hydrogen terminated diamond surface is very stable even at a temperature of $\sim 800^\circ\text{C}$. The clean C(100) surface was finally created by annealing the sample at $\sim 1100^\circ\text{C}$ for 10 minutes with a $(2 \times 1)/(2 \times 2)$ LEED pattern. Another experimental concern is the possible charge accumulation on the sample during the photoemission process since diamond is a wide band gap semiconductor with a band gap of 5.5 eV. But a previous study [4] has indicated that

sample charging would not become a serious problem during the photoemission study as long as the edge of the sample surface held a good electrical contact to ground.

III. RESULTS AND DISCUSSION

In Fig. 1 we have shown the C 1s core level spectra for the hydrogen terminated and reconstructed clean diamond (100) surfaces. For the hydrogen terminated diamond surface that has been annealed at 800°C, the computer least-square fitting indicates that the spectrum only consists of a single component. The (1 × 1) LEED pattern depicts that this surface has the same type of geometrical structure as the unreconstructed truncated diamond. When this surface is annealed at 1100°C, rather drastic changes take place. The (1 × 1) LEED pattern has been replaced by a (2 × 1)/(2 × 2) pattern and the core level spectrum now contains two components. We have determined that the lower binding energy component originates from the diamond surface by varying the probing depth, which can be achieved by either changing the incident photon energy or the emission angle of the photoelectrons. The separation between the surface and bulk component is about 0.93 eV.

As the other group-IV semiconductors, an ideal truncation of the bulk diamond would result in a (100) surface with two dangling bonds on each surface carbon atom. This situation is not energetically favorable. A rearrangement of the surface atoms to lower the surface energy then takes place, resulting in a surface unit cell which is larger than that for the ideal surface and with fewer dangling bonds. That is exactly what has been observed here for the diamond with a (2 × 1) reconstruction. In this case, the surface carbon atoms are in a different electronic environment compared with the bulk carbon atoms. This is reflected by the chemically shifted component in the C 1s core level spectrum for the reconstructed diamond (100) surface. The surface core level components have also been observed for other group IV semiconductors. For the hydrogen terminated diamond surface, all the dangling bonds are believed to be saturated

by hydrogen atoms. As a result, the top layer carbon atoms see a rather similar environment as their bulk partners, which is reflected by a single component in the photoemission core level spectrum. We also notice that the line width of the C 1s core level from H:C surface is about a few tens eV wider than that from the clean C(100) surface. This may be because for the hydrogen terminated C(100), the top surface carbon still show little amount of shift that can not be resolved with our energy resolution. The broadening could also come from inhomogeneity of this surface. Finally we have observed a peak shift of the bulk component for the hydrogen terminated diamond with respect to that of the clean diamond surface. This essentially represents the change of the surface band bending of these two surfaces, where the H-C(100) shows 0.55 eV more in band bending.

Semiconductor surface atom arrangement has been always an interesting topic and there have been extensive studies in this regard. [1,12] It is generally agreed that the surface Si and Ge atoms tend to form dimers on the clean (100) surfaces. Whether these dimers are symmetric or asymmetric remains to be answered. For the C(100) our results are consistent with a recent theoretical study attributes that it is most likely that the carbon atoms on the C(100) surface will form symmetric dimers. But we must point out that higher resolution must be employed to determine the accuracy of the geometric model.

The clean C(100) surface shows a (2×1) LEED pattern actually corresponding to a two-domain (2×1) reconstruction with the two domains at 90° to each other. The surface Brillouin zones of this surface is illustrated in Fig. 2, showing superimposed surface Brillouin zones of the two different domains. The ARPES valence band spectra ($h\nu=40\text{eV}$) of the reconstructed C(100) surface as a function of the photoelectron emission angle taken along $[011]/[0\bar{1}\bar{1}]$ directions are presented in Fig. 3. We have observed several features highlighted by the tic-marks. The energies of these features are referred to the Fermi level (E_F) which was determined from a platinum metal sample.

The most pronounced feature, S_1 , observed in this set of spectra is the peak located around 1.5 eV below the E_F close to Γ point of the Brillouin zone. We did vary the incident photon energy and saw no dispersion of this state as a function of the photon energy. This indicates that this feature has surface state character. Furthermore, in Fig. 4 the normal emission valence band spectra for the clean and hydrogen terminated C(100) surface are shown. The spectrum for the hydrogen terminated diamond surface has been shifted by -0.55 eV to correct for the band bending of this surface. Clearly, for the hydrogen covered C(100) surface there is no emission observed from the area near the Fermi level. This further confirms that the feature near the Fermi level from the reconstructed C(100) surface originates from the surface state emission. Also, with the help of the valence band spectra taken on hydrogen terminated C(100) surface, we have determined that all the features with binding energy of 4 eV or higher originate from bulk contribution.

For the surface state, as we vary the photoelectron emission angle along the $[011]/[01\bar{1}]$ directions dispersion does occur. The dispersion of surface state is presented in Fig. 5, where their initial energies as a function of the wave vector $E(\mathbf{k}_{\parallel})$ are plotted. The main surface state feature, which is a pronounced peak at normal emission, disperses downwards from -1.5 at the zone center to -2.4 eV at the zone boundary at J' (see Fig. 3). Additionally, a second peak S_2 at -1.9 eV is seen near the zone boundary at J' , which might be degenerated in energy with the main peak seen at Γ . It should be pointed out that since the surface has mixture of (2×1) and (1×2) domains, the dispersion shown in fig. 5 should also be considered as the combination of the surface state dispersion along both $[011]$ and $[01\bar{1}]$ directions.

Overall, the surface related features S_1 and S_2 of the C(100) valence band spectra and their dispersion appear to be very similar to those observed on the Si(100) surfaces, [1] although the magnitude of dispersion may differ to certain extent. This apparently roots from the similar structures of the two semiconductors. It should be mentioned that

certain surface related features observed for the Si(100) surface, such as S₃-S₅, have not been detected for the diamond surface. Main reason is that those feature are usually observable along the [010] direction, while in our case we only investigated the dispersion along the [011] / [01 $\bar{1}$] directions. Future careful and systematic studies of this surface may reveal more features.

IV. CONCLUSIONS

We have studied the reconstruction diamond (100) surface electronic structure using both core level and angle resolved valence band photoemission spectroscopy for the first time. One surface component of the C 1s core level spectrum is observed and it is in agreement with the theoretical calculation that this surface is most likely to consist of only symmetrical dimers. In the valence band spectra we have identified the emission from the surface states and mapped out the dispersion along [011] / [01 $\bar{1}$] directions. The results from this study have been compared with those from reconstructed Si(100) and Ge(100) surface, and we have found that they share large similarity in the surface electronic structures.

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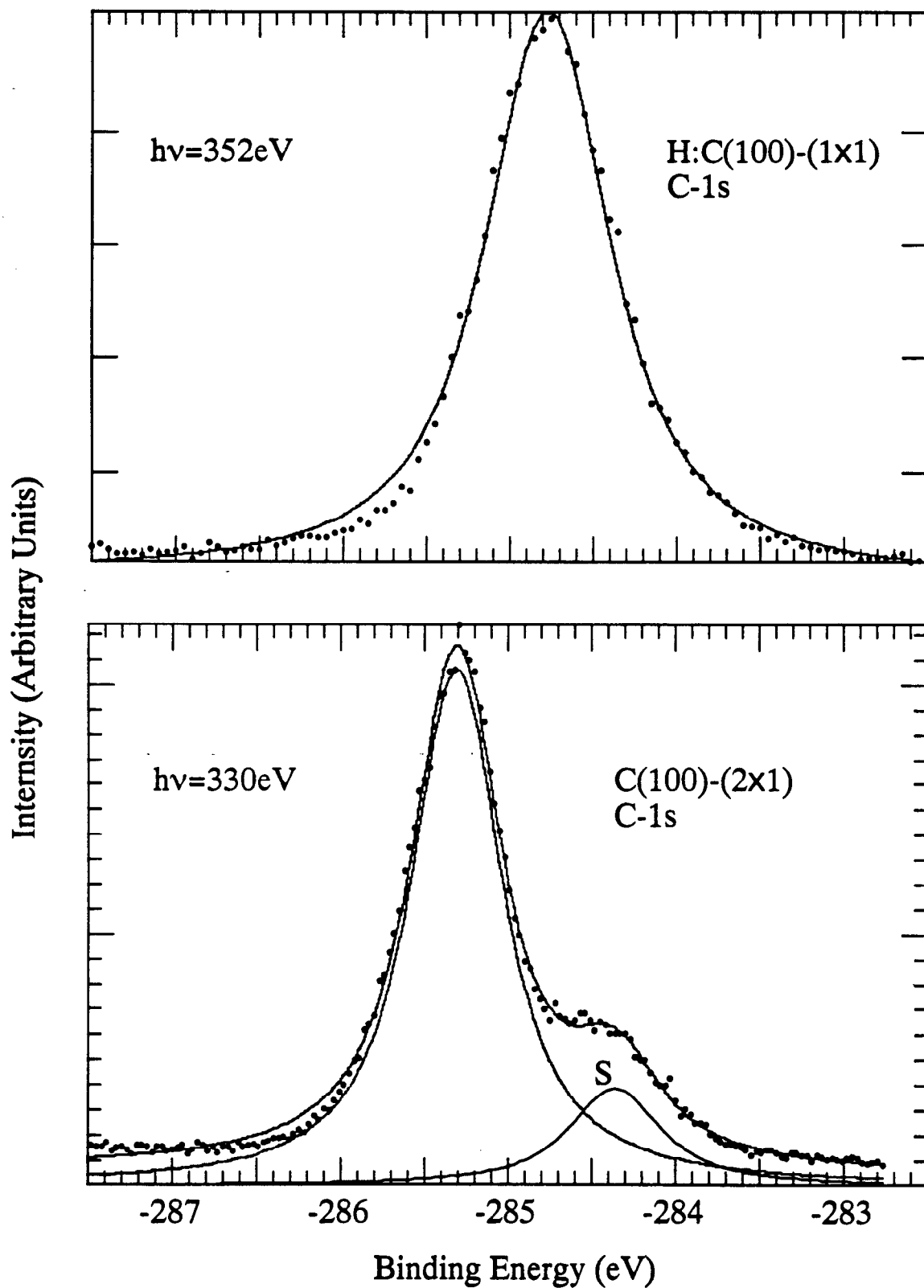


Figure 1 C-1s core level spectra from hydrogen terminated and reconstructed surfaces.

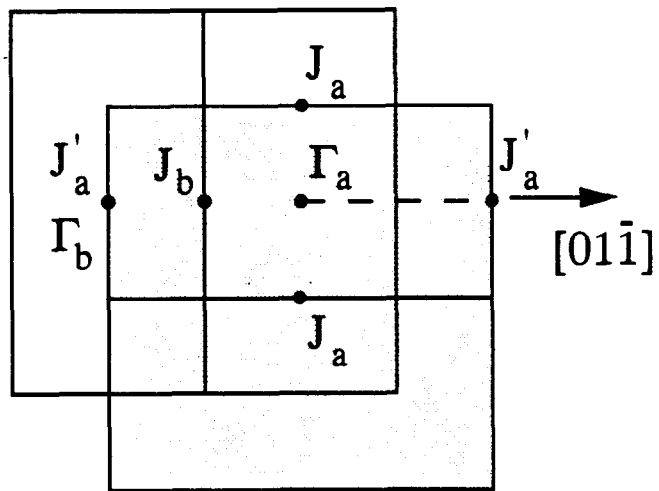


Figure 2 Surface Brillouin zones for a two-domain 2x1 reconstruction on C(100)

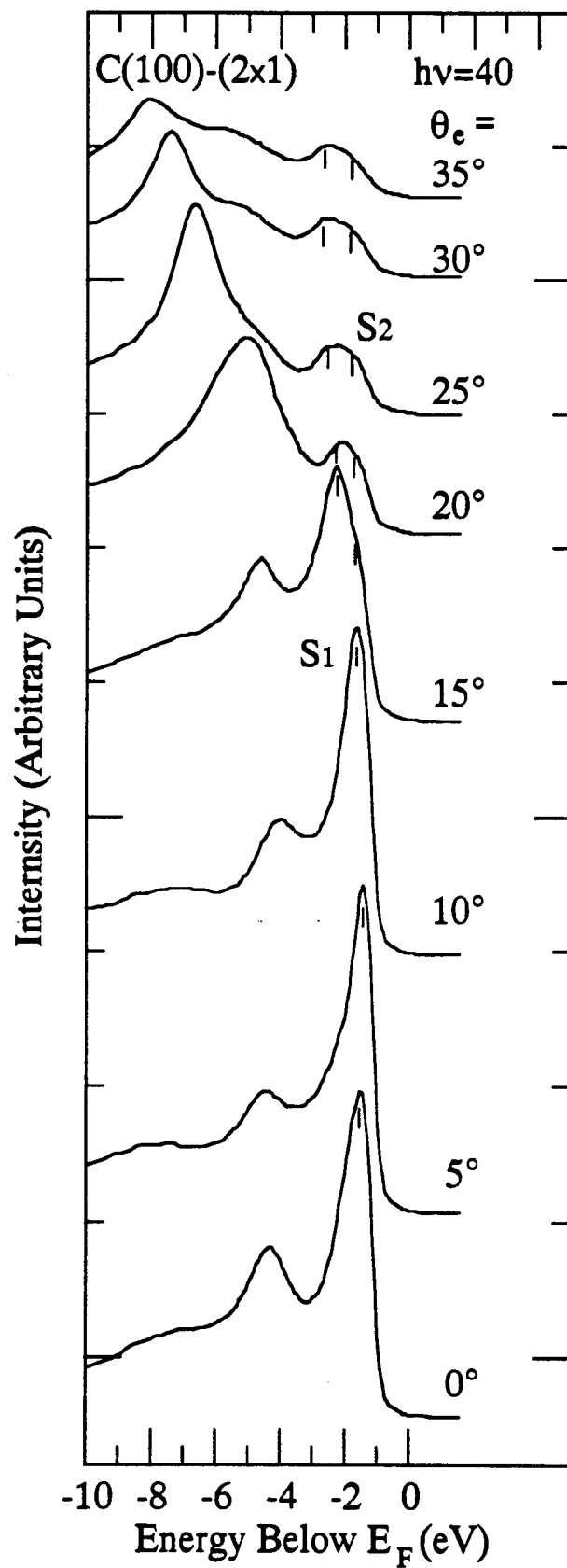


Figure 3 An angular series of spectra from C(100)-(2x1) surface, recorded with 40 eV photon energy and incident angle 45° .

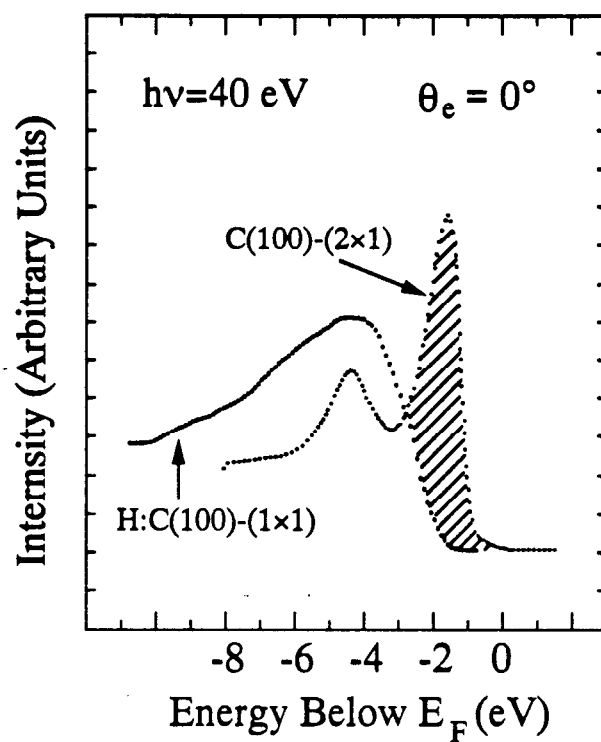


Figure 4 ARPES spectra of clean and H-terminated C(100)-(2x1) surface. The shadowed area corresponds to surface state emission.

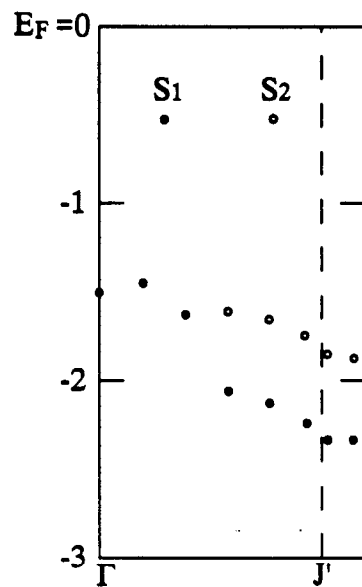


Figure 5 Experimental surface state dispersion for C(100)-(2x1) in the $[01\bar{1}]$ direction