# Surface structure of C(100)-(2×1)-H studied by a quantitative LEED analysis

Y. M. Wang
*Department of Physics and Material Science, City University of Hong Kong, Hong Kong, China*

K. W. Wong
*Department of Chemistry, Chinese University of Hong Kong, Hong Kong, China*

S. T. Lee
*Department of Physics and Material Science, City University of Hong Kong, Hong Kong, China*

M. Nishitani-Gamo, I. Sakaguchi, and K. P. Loh
*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

T. Ando
*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
*and National Institute for Research in Inorganic Materials (NIRIM), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
(Received 31 August 1998)

The structure of the hydrogen terminated, $(2\times1)$ reconstructed diamond (100) surface has been investigated by low-energy electron-diffraction (LEED) intensity versus energy $[I(E)]$ measurements in combination with tensor LEED calculations. It has been found that the surface corresponds to the formation of symmetric dimers on the top C layer, with a dimer length of 1.60 Å. The top layer shows slight inward relaxation; the interlayer spacing between the first and second C layers reduces to 0.81 Å, which corresponds to an ~7% contraction compared to the bulk value. The structural details of the first four carbon layers have been determined and are compared to those given by theoretical calculations. [S0163-1829(99)00715-8]

## INTRODUCTION

The surfaces of diamond have received considerable attention in the past decade due to the advances in diamond film growth by chemical vapor deposition (CVD) methods. Since the growth of atomically smooth C(100) surfaces became possible by homoepitaxial CVD,[1] a large amount of research has been devoted to understanding the atomic structure of this surface, with the ultimate goal of providing guidance for atomically controlled diamond CVD.

The (100) surface of diamond has two dangling bonds per C atom for the ideal surface geometry. This leads to very rich surface chemistry. In particular, the adsorbed hydrogen plays a critical role in determining the structures of the surface. For example, a fully hydrogen-passivated C(100) surface would contain two hydrogen atoms per carbon atom and thus stabilize the simple truncated-bulk surface structure of $(1\times1)$ symmetry. On the other hand, loss of hydrogen leads to a reconstruction of the surface, achieving a $(2\times1)$ symmetry.

The surface structure of the hydrogen-terminated C(100) surface has been the subject of many investigations using a variety of experimental and theoretical methods.[2–17] Earlier experimental studies[2–6] indicated that the as-polished or acid cleaned C(100) surface exhibits $(1\times1)$ LEED pattern and that annealing the surface to a temperature $\geqslant$1273 K produces the two-domain $(2\times1)$ LEED pattern. The change was attributed to desorption of hydrogen from the original surface. Meanwhile, a number of studies[6,7] have pointed out that exposure of the $(2\times1)$ surface to hydrogen could restore the $(1\times1)$ LEED pattern. Although debate still remains, in both theoretical and experimental aspects, regarding the stable configuration of the hydrogenated C(100) surface (monohydride or dihydride structure), it is generally agreed that the hydrogen-terminated, $(2\times1)$ surface involves monohydrides.[8,9] Furthermore, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) observations[1,10,11] have revealed rows on the hydrogenated, $(2\times1)$ reconstructed C(100) surface, which were interpreted as evidence of dimer formation. To date there are numerous theoretical studies on the search for a stable configuration for the hydrogenated C(100) surface. The level of sophistication ranges from slab-MINDO (modified intermediate neglect of differential overlap) and empirical tight-binding methods to non-self-consistent local-density-functional (LDF) calculations. Among them, several calculations[12–15] have given results which support the dimer formation model for the H-terminated, C(100)-$(2\times1)$ surface. Additionally, these studies provided structural details for the surface, which can be compared with experimental results.

Overall, it appears that the majority of the experimental and theoretical studies carried out so far agree on the dimer formation model for the hydrogenated C(100) $(2\times1)$ surface. However, there is still no sufficient experimental evidence to definitely discriminate several qualitatively different models, which can equally produce the $(2\times1)$ reconstruction pattern. To address this problem, we have un-

 

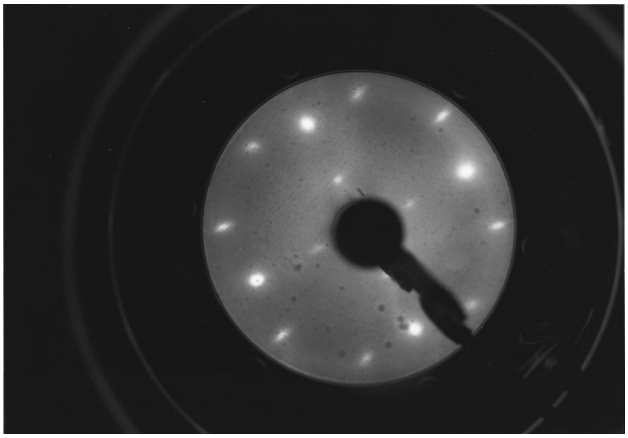

FIG. 1. Low-energy electron-diffraction pattern acquired at 90 eV from hydrogen terminated C(100) surface.

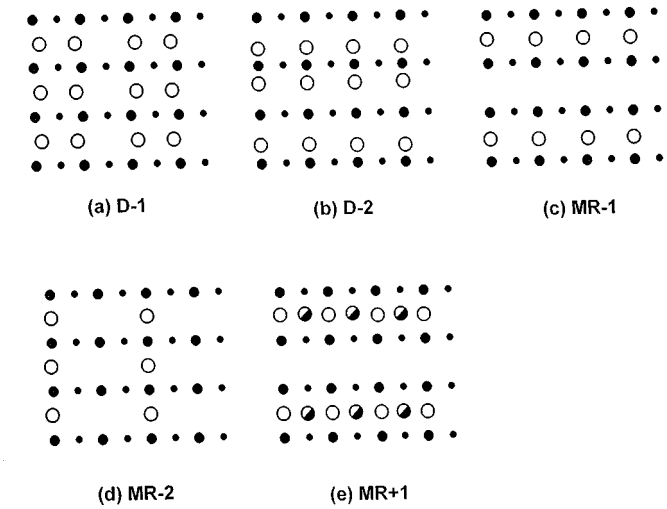


FIG. 2. A schematic top view of model types included in the TLEED analysis for the hydrogen terminated, $(2\times1)$ reconstructed C(100) surface. Note that hydrogen atoms are neglected in the analysis. Open circles represent the first-layer atoms. The gray circles indicate atoms in the second layer and small solid circles are the third-layer atoms. In model MR+1, those atoms which were removed to generate the MR−1 model are introduced back to the system and placed on the bridge sites of the first-layer atoms; they are shown by half-shaded circles.

dertaken a LEED crystallographic analysis for the C(100)-$(2\times1)$-H surface. The purpose of this paper is to present a structural model of the surface which passes the LEED tests. Additionally, detailed structural features determined for the surface are compared to the values given by theoretical calculations.

## METHODS

The experiments were carried out in an ultrahigh-vacuum (UHV) facility with a base pressure of around $1\times10^{-10}$ Torr, as described elsewhere.[18] For LEED $I(E)$ spectra measurements, a CCD camera connected to a personal computer via a frame grabber board was used. All LEED data were taken with the electron beam at normal incidence.

The sample used was a 1-$\mu$m-thick, *p*-type homoepitaxial diamond (100) thin film. The film was deposited on the high-pressure and high-temperature synthetic diamond substrate by microwave plasma assisted chemical vapor deposition using $CH_4$-$B_2H_6$-$H_2$ mixture. The $CH_4$ concentration was 1.0% and $B_2H_6$ concentration was 2 ppm. The substrate temperature was measured by an optical emission pyrometer and kept at 800 °C. Incident microwave power was 750 W and the reaction pressure was kept at 40 Torr. The growth layer was a *p*-type semiconductor with 1 $\mu$m thickness. Following growth of the homoepitaxial film, the sample was exposed to the microwave generated hydrogen plasma at 800 °C. It was found that the plasma treatment produced large, atomically flat (100) terraces and left the surface hydrogen terminated.[19] The plasma treated surface is stable in air and the Auger electron spectrum showed that the sample was free of contaminants and graphitic carbon. On this hydrogen plasma treated C(100) surface, a sharp, two-domain $(2\times1)$ LEED pattern was observed. Figure 1 shows the pattern acquired at an incident electron energy of 90 eV. Half-order spots were visible at incident energies as low as 40 eV. The LEED patterns were recorded, at room temperature, in the energy range 50–252 eV in steps of 2 eV. Intensity versus energy $[I(E)]$ curves for diffraction spots that are symmetrically equivalent were compared to verify normal incidence and were averaged to improve the quality of the data and enhance the signal-to-noise ratio. Three integer and three fractional order symmetrically independent beams, designated as (10), (11), (20), (1/20), (11/2), and (03/2), were used in the analysis.

The surface structure analysis was done within the tensor LEED approach using the TLEED programs provided by Van Hove.[20,21] Layer stacking was performed with the renormalized forward scattering method, and the search algorithm worked with the reliability factor, $R_P$, introduced by Pendry.[22] The atomic phase shifts for carbon were included to $l=7$. The effect of atomic vibrations was taken into account using a Debye temperature of 1860 K, and inelastic damping was included by an imaginary potential of −8 eV. The real part of the inner potential was continuously refined during each set of TLEED calculations. The hydrogen atoms were neglected due to their weak scattering power.

Five different models were analyzed using TLEED and they are shown schematically in Fig. 2. Note that only those models which can ''create'' the $(2\times1)$ LEED pattern were considered here. These models can be divided into two groups.

(i) Dimer models. For these models, carbon atoms in the first layer form symmetrical dimers. In model D-1 [see Fig. 2(a)], the dimers are formed between the atoms within the same row. Model D-2 [Fig. 2(b)] is similar to D-1, except that in this case, the dimers are formed by pairing the column atoms.

(ii) Missing row models. The missing row structures were obtained by removing alternating row atoms (as in model MR−1) or column atoms (as in model MR−2) in the first layer from the ideal unreconstructed (100) surface. In the third missing row model (referred to as MR+1), those atoms removed to generate the MR−1 structure were placed on the bridge sites along the rows formed by the remaining atoms.

TABLE I. Optimized $R_P$ values of various models tested.

| Model | $R_P$ |
|---|---|
| Dimer models | |
| D-1 | 0.19 |
| D-2 | 0.41 |
| Missing row models | |
| MR−1 | 0.35 |
| MR−2 | 0.30 |
| MR+1 | 0.37 |

## RESULTS AND DISCUSSION

The final $R_p$ value after the TLEED optimization for each model type is reported in Table I. The minimum $R_p$ value (0.19) was achieved for model D-1. Using Pendry's statistical estimate,[22] we obtained $\Delta R_p = 0.06$ as the uncertainty in $R_p$. According to this criterion, the model type D-1 is clearly favored over the other models tested. Figure 3 compares experimental $I(E)$ curves with those calculated for the model D-1, which is favored by TLEED analysis. For model D-1, the surface dimers were originally kept symmetrical and unbuckled during TLEED optimization. When displacements which lower the symmetry were included, the $R_p$ value was reduced by a further 0.03. However, considering the uncertainty in $R_p$, (0.06) such a reduction may not be significant. Furthermore, visual inspection of $I(E)$ curves indicated that the resulting changes are small, although in this case more parameters were made available in the fitting process. Therefore the symmetrical dimer model seems to have contained all the significant features of the surface structure.

A pictorial representation of aspects of the optimized D-1 model is shown in Fig. 4 and some corresponding geometrical parameters are listed in Table II. The uncertainties in the geometrical parameters were estimated using the scheme proposed by Anderson *et al.*[23] In the optimum geometry, symmetrical dimers are formed on the top layer (designated as first layer) by pairing atoms within the same row. The

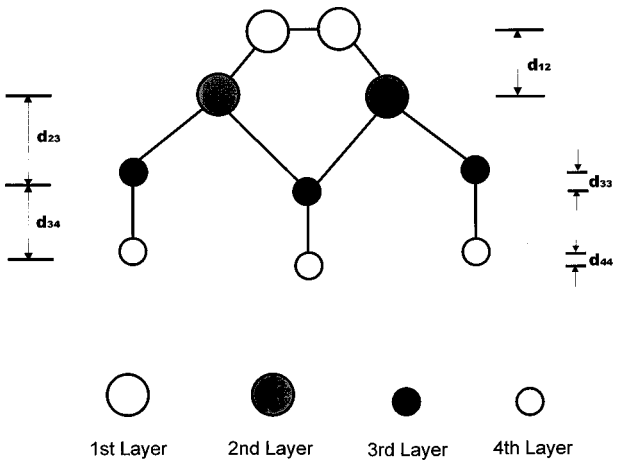


FIG. 4. Side view of the best-fit geometry for the model D-1.

dimer length is determined to be 1.60 Å, slightly longer than the single C-C bond length in hydrocarbon (1.55 Å). The first interlayer spacing ($d_{12}$) is 0.81 Å, which corresponds to a 7% contraction compared to the bulk value (0.87 Å). The corresponding C-C bond length formed between the carbon atoms in the first and second layers is 1.57 Å, close to the value in the ideal (1×1) bulk geometry (1.53 Å). The reconstruction in the top layer induced bucklings in the third and fourth layers (by 0.08 and 0.06 Å, respectively) since there are now two types of C atoms in the layers (one just below the surface dimers and the other below the intervals of the dimers). However, the magnitudes of lateral displacements of C atoms in the third and fourth layers, indicated by TLEED calculations, are within the range of the uncertainties. The fifth layer does not show significant relaxations and essentially maintains the bulk geometry. The average bond lengths between the second and third as well as third and fourth layers are 1.54 and 1.52 Å respectively; both values are close to that in the bulk geometry.

Our conclusion that the C(100)-(2×1)-H surface reconstructs via the formation of C-C dimers is consistent with the results of theoretical studies,[12–14] which indicated that the dimer formation is an energetically favorable process. That

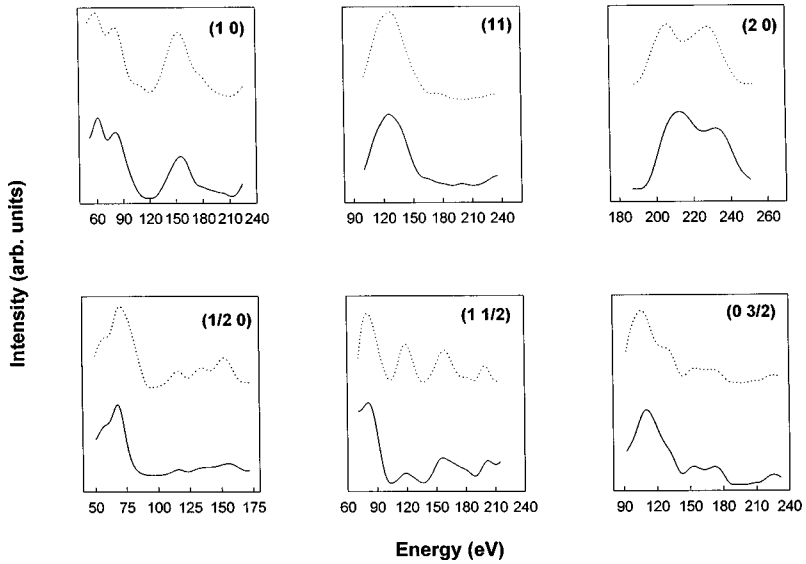


FIG. 3. $I(E)$ curves for six diffracted beams at normal incidence for C(100)-(2×1)-H surface. The dotted lines represent experimental curves while the solid lines represent curves calculated for model D-1 with optimum geometry given by TLEED optimization.

TABLE II. Some TLEED optimized parameters for model D-1.

| Parameters (Å) | C(100)-(2×1)-H |
|---|---|
| dimer length | 1.60±0.05 |
| $d_{12}$ | 0.81±0.03 |
| $d_{23}$ | 0.90±0.06 |
| $d_{33}$ | 0.08±0.05 |
| $d_{44}$ | 0.06±0.05 |
| $d_{\text{bulk}}$ | 0.87 |

the dimer formation model is favored over the missing row models agrees with the energy calculations by Halicioglu,[16] in which the Brenner potential function was used. However, we note also that the same type of calculation by Halicioglu, when a different potential function (i.e., Tersoff function) was used, gave the model MR+1 as the most stable configuration for the surface structure. While the question still remains regarding which potential represents more closely the properties of carbon phase on the surface, it would be useful that further independent energy calculations be carried out to clarify this uncertainty. Nevertheless, the result of the present LEED analysis does add some support to the calculation results using the Brenner function.

Another attribute of the favored model is the formation of symmetrical dimers rather than the asymmetrical ones. This is again in agreement with several theoretical calculation results.[12–14] In particular, the SLAB-MINDO calculation by Zheng *et al.*[17] indicated that the asymmetrical dimer structure was higher in energy by 1.11 eV per surface atom, when compared to the symmetrical dimer configuration. The symmetrical dimer formation on H-terminated C(100) surface is in contrast to the formation of asymmetrical dimers on the corresponding Ge(100) (Refs. 24 and 25) and Si (100) surfaces.[26] The difference was attributed to different character in the electronic surface states. Indeed, despite many similarities, carbon does behave somewhat differently from Si and Ge in terms of structure. For instance, higher-order reconstruction like those found on the Si (100) and Ge (100) surfaces has not yet been observed on C(100) surface.

The optimum geometrical parameters given by TLEED analysis are in general agreement with the *ab initio* calculation by Furthmüler *et al.*[15] The latter calculation gave a structural model involving a dimer length of 1.61 Å and a contraction of 8% for the first interlayer spacing. However, the magnitudes of bucklings in the third and fourth layers indicated by this study were about 50% smaller compared to the results by Furthmüller *et al.*[15]

In summary, the present LEED crystallographic analysis for the C(100)-(2×1)-H surface favors the symmetrical dimer formation model rather than the missing-row reconstruction. The optimum geometry given by TLEED analysis involves a dimer length of 1.60 Å, a 7% contraction in the first interlayer spacing, and bucklings in the third and fourth C layers. The model is in accordance with previous experimental observations[1,8,10,11] and the structural details agree closely with those given by *ab initio* calculations.[15] The LEED investigations confirm that the dimer reconstruction occurs on the C(100) monohydride surface.

## ACKNOWLEDGMENT

We thank Dr. M. A. Van Hove (Lawrence Berkeley Laboratory) for supplying the TLEED computation codes.

[1] L. F. Sutch, M. S. Thompson, C. J. Chu, R. H. Hauge, J. L. Margrave and M. P. d'Evelyn, Appl. Phys. Lett. **70**, 1685 (1991); C. J. Chu, M. P. d'Evelyn, R. H. Hauge, and J. L. Margrave, J. Appl. Phys. **70**, 1695 (1991).
[2] B. B. Pate, Surf. Sci. **165**, 1356 (1990).
[3] J. B. Marsh and H. E. Farnsworth, Surf. Sci. **1**, 3 (1964).
[4] P. G. Lurie and J. W. Wilson, Surf. Sci. **65**, 453 (1977).
[5] R. E. Thomas, R. A. Rudder, and R. J. Markunas, J. Vac. Sci. Technol. A **10**, 2451 (1992).
[6] S. T. Lee and G. Apai, Phys. Rev. B **48**, 2684 (1993).
[7] A. V. Hamza, G. D. Kubiak, and R. H. Stulen, Surf. Sci. **237**, 35 (1990).
[8] B. D. Thoms and J. E. Butler, Surf. Sci. **328**, 29 (1995).
[9] T. Aizawa, T. Ando, M. Damo, and Y. Sato, Phys. Rev. B **48**, 18 348 (1993).
[10] Th. Frauenheim, U. Stephan, P. Blaudeck, D. Porezag, H. G. Busmann, W. Zimmermann-Edling, and S. Lauer, Phys. Rev. B **48**, 18 189 (1993).
[11] H. Sasakż, M. Aokż, and H. Kawarada, Diamond Relat. Mater. **2**, 1271 (1993).
[12] Y. L. Yang and M. P. d'Evelyn, J. Am. Chem. Soc. **114**, 2796 (1992); Y. L. Yang and M. P. d'Evelyn, J. Vac. Sci. Technol. A **10**, 978 (1992).
[13] S. P. Mehandra and A. B. Anderson, Surf. Sci. **248**, 369 (1991).
[14] B. N. Davidson and W. E. Pickett, Phys. Rev. B **49**, 11 253 (1994).
[15] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **53**, 7334 (1996).
[16] T. Halicioglu, Diamond Relat. Mater. **1**, 963 (1992).
[17] X. M. Zheng and P. V. Smith, Surf. Sci. **256**, 1 (1991).
[18] K. W. Wong, S. T. Lee, R. W. M. Kwok, Y. W. Lam, and H. Kawarada, Jpn. J. Appl. Phys., Part 1 **35**, 5444 (1996).
[19] B. D. Thoms, M. S. Owens, J. E. Butler, and C. Spiro, Appl. Phys. Lett. **65**, 2957 (1994).
[20] P. J. Rous, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **226**, 15 (1990); A. Wander, M. A. Van Hove, and G. A. Somorjai, Phys. Rev. Lett. **67**, 626 (1991).
[21] M. A. Van Hove, W. Moritz, H. Over, P. J. Rous, A. Wander, A. Barbieri, N. Materer, U. Starke, and G. A. Somorjai, Surf. Sci. Rep. **19**, 191 (1993).
[22] J. B. Pendry, J. Phys. C **13**, 937 (1980).
[23] J. N. Anderson, H. B. Nielsen, L. Petersen, and D. L. Adams, J. Phys. C **17**, 173 (1984).
[24] M. Needles, M. C. Payne, and J. D. Joannoupoulos, Phys. Rev. Lett. **58**, 1765 (1987).
[25] L. Spiess, A. J. Freeman, and P. Soukiassain, Phys. Rev. B **50**, 224 (1994).
[26] W. S. Yang and F. Jona, Phys. Rev. B **28**, 2049 (1983).