IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Dissociative chemisorption of water on the Si(111) 7*7 surface studied at 150 K by X-ray photoelectron spectroscopy and energy loss spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 5855

(http://iopscience.iop.org/0953-8984/4/27/004)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.159
The article was downloaded on 12/05/2010 at 12:15

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 4 (1992) 5855–5862. Printed in the UK

Dissociative chemisorption of water on the Si(111) 7×7 surface studied at 150 K by x-ray photoelectron spectroscopy and energy loss spectroscopy

Dao-xuan Dai†, Fu-rong Zhu†, Yan-sheng Luo† and I Davoli‡

† Department of Physics, Fudan University, 200433 Shanghai, People's Republic of China

‡ Department of Mathematics and Physics, Camerino University, 62032 Camerino, Italy

Received 28 January 1992, in final form 8 April 1992

Abstract. The dissociative chemisorption of water vapour on the Si(111) 7×7 surface at 150 K and the effect of annealing have been studied using x-ray photoelectron spectroscopy and energy loss spectroscopy. From the data we may deduce that at 0.25 L the water molecule begins to adsorb on the adatom site and 'rest'-atom site of the unit cell and immediately dissociates to form a silicon hydroxyl Si–OH group (and probably an Si–H group), but no evidence for molecularly adsorbed water is observed. After subsequent annealing from 150 K up to 900 K, we observe decomposition of the Si–OH group, oxidation of the silicon surface and then re-establishment of the clean surface.

1. Introduction

Because of the development of semiconductor devices, fundamental research on semiconductor surfaces and interfaces has been one of the most active fields in the physics of semiconductors. The knowledge thus acquired has had considerable impact on the development of the technology of devices. Up to now the adsorption of water on the silicon surface has received much attention [1–19]. The key problem is whether molecularly adsorbed water exists. Fujiwara [5, 6], using UPS and AES, has reported that water molecules adsorbed onto Si(111) and Si(100) surfaces at room temperature, while Ibach *et al* [7], using HREELS at low temperatures, concluded that water dissociated after adsorption to form silicon hydride, Si–H, and hydroxyl, Si–OH, groups on Si(111) and Si(100) surfaces and also that no evidence for the molecular phase is found except for a physisorbed layer of ice. Kobayashi *et al* [9], using the same technique as Ibach *et al*, pointed out that partially dissociative adsorption is observed for water vapour on the Si(111) 7×7 surface and that molecularly adsorbed water does not exist at room temperature. The dissociative adsorption of water on the silicon surface has also been reported by Mayer [10] and Mayer and Urakking [11] and other workers [13, 15–17]. However, Scheafer *et al* [13], using HREELS and XPS at low temperatures, confirmed that molecular adsorption of water is found on the cleaved Si(111) 2×1 surface. As for the adsorption site we note that Avouris and Lyo [19] reported STM results at room temperature but did not provide the corresponding data at low temperatures.

In this paper we report data on water adsorbed on the Si(111) 7×7 surface at 150 K and the effect of subsequent annealing from 150 to 900 K using XPS and ELS.

0953-8984/92/275855+08$04.50 © 1992 IOP Publishing Ltd

The paper is organized in the following way. In the next section we describe the experimental equipment used and the procedures followed in preparing the surfaces. In section 3 we present the results of our work divided into two parts; in section 3.1 we give the low-temperature data and a preliminary discussion on the adsorption site while in section 3.2 we report the data for a brief exposure of water and successive annealing of the sample in a temperature range from 150 up to 900 K. In the last section a short summary is also attempted.

2. Experimental details

All the measurements were taken with an ESCALAB-5 electron spectrometer. This apparatus has been previously described elsewhere [20]. ELS data were obtained with an electron energy of 200 eV. We chose both XPS and ELS in this experiment because XPS can be used to identify the chemical environments of an element by comparison, whereas ELS not only is extremely sensitive to electronic structure at the surface but also can be used to detect the appearance of a chemical phase induced by new chemical bonding. The sample was an n-doped mirror-polished Si(111) wafer with a carrier concentration of about 10^{15} cm^{-3}. The Si(111) 7 × 7 clean surface was obtained starting from a polished surface which had been sputtered and then annealed up to 1100 K. We paid particular attention to ensuring a carbon- and oxygen-free surface. Water from a liquid-nitrogen-frozen deionized water ampoule was flowed over the sample. The Si(111) 7 × 7 surface was exposed to water for the time necessary to reach an exposure of 0.25–5 L (1 L = 1 × 10^{-6} Torr s) at 150 K. During the exposure, all the ionization gauges were switched off to prevent water molecule dissociation and to make sure that the surface was exposed to a 'molecular' water ambient.

3. Results and discussion

3.1. *Water adsorption at 150 K*

3.1.1. ELS data. In figure 1, curve (a) shows ELS data at 150 K for the Si(111) 7 × 7 surface; curves (b)–(h) give ELS data at different water exposures. Curve (a) at 150 K is very similar to that at room temperature reported by Ibach and co-workers [7, 14]. In the set of curves obtained for successive water exposures, we note that at a low exposure of 0.25 L the labelled surface peaks S_1 and S_3 disappear, showing the beginning of water adsorption onto the silicon surface, whereas another surface peak S_2 remains virtually unchanged. In the meantime, the other $\hbar\omega_s$ peak of the surface plasmon decreases and broadens. When an exposure of 0.5 L is reached, S_2 shifts to a lower energy. We can also see that, when the exposure is higher than 2 L, all ELS data remain basically unchanged, indicating that the water adsorption has reached saturation and the sticking coefficient approaches zero. This means that a fast adsorption stage is followed by a very slow adsorption stage. Both AES and XPS measurements support the above statement. In the AES data we have observed that the intensity ratio of O KLL to Si LVV versus water exposure increases exponentially with increasing exposure until saturation adsorption takes place. The ratio of O 1s to Si 2p in the XPS data has a similar trend to the AES data. All this confirms that there

is a saturated adsorption state after 2 L. The thickness d ($\simeq 1.2$ Å) of saturated water adsorption on the Si surface can be estimated according to the relative intensity ratio $I_s^0/I_s \simeq 1.2$ (I_s^0 is the intensity of the bulk plasmon peak $\hbar\omega_p$ for a clean surface and I_s is the intensity of $\hbar\omega_p$ for a saturated surface at 2 L) and the effective escape depth of 6 Å for an electron energy of near 200 eV.

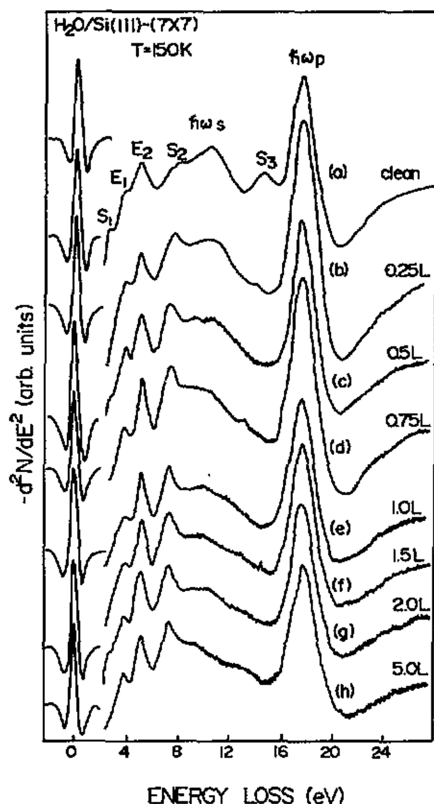


Figure 1. ELS spectra obtained at 150 K from an Si(111) 7 × 7 surface at different water exposures.

3.1.2. XPS data. Figure 2 and figure 3 show the XPS data of the O 1s peak. In figure 2 we report the O 1s peak as a function of water exposure at 150 K. In this figure the integrated areas are not normalized in intensity. We observe that, regardless of the water exposure, the binding energy (BE) E_b of the O 1s main peak remains at 531.7 eV. The constant BE from 0.23 to 5 L suggests that only a single adsorption state exists. Because our E_b is so low, we may deduce that it is related to the formation of the silicon hydroxyl (Si–OH) group. This statement is in reasonable agreement with the calculation by Katircloglu [17]. Also, the circumstantial evidence [13, 21, 22] supports our statement. Spitzer and Lüth [21] have measured the adsorption of water on oxygen pre-adsorbed on Cu (schematically H_2O/O/Cu(110)) in a temperature range from 90 to 300 K. They have found three different chemical species adsorbed on the Cu(110) surface depending on the temperature, i.e. the three E_b values of O 1s distinguish three different adsorption states. The peaks with high, medium and low E_b correspond to the molecular state, the OH group and the atomic adsorption state, respectively. Au *et al* [22] studied the H_2O/Cu(111) system by XPS, and similar results were obtained. Of course, we note that our single adsorption state is different

from those on the cleaved Si(111) 2 × 1 surface measured by Schaefer *et al* [13] from 0.1 to 5 L. This difference may be induced by using different reconstructing surfaces and different methods of sample preparation. Finally, in figure 2, we also observe a very substantial shoulder near 530 eV at 0.25 L which is much weaker at 2 L. At present, however, no conclusion as to its origin can be made. Because of the decrease in its intensity with increasing exposure, it may perhaps correspond to a certain pre-adsorbed state.

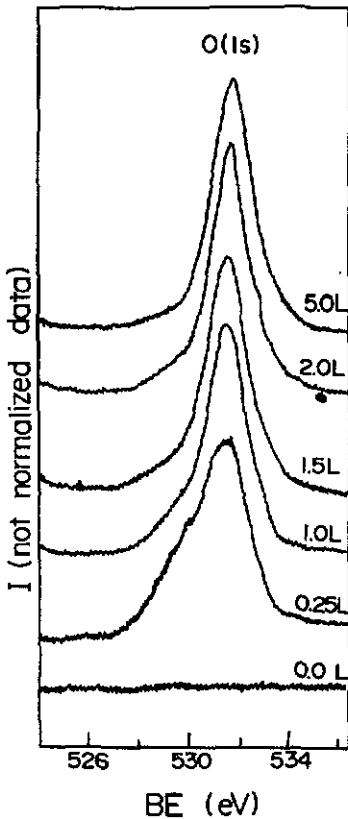


Figure 2. O 1s core-level spectra obtained at 150 K from an Si(111) 7 × 7 surface at different water exposures. The intensity data are not normalized.

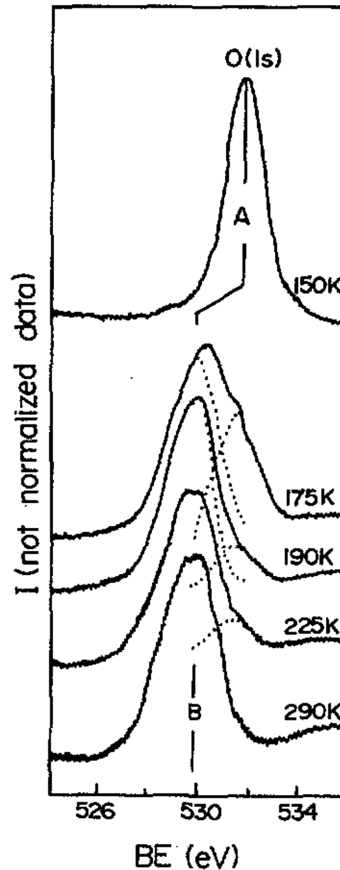


Figure 3. O 1s core-level spectra obtained from an Si(111) 7 × 7 surface exposed to 5 L of water for different temperatures ranging from 150 to 290 K.

3.1.3. LEED data. The Si(111) 7 × 7 LEED pattern was found to be stable with respect to water exposure. No increase in the background intensity of the LEED pattern has been observed as a result of water exposure. The result is in agreement with that of Ibach *et al* [7], but Scheafer *et al* [13] observed that the system is disordered at an exposure of 1 L.

3.1.4. Discussion on the adsorption site. Here we may deduce some information about the adsorption site from the ELS data in figure 1. Ibach *et al* pointed out that S_1 can be associated with the initial states due to dangling bonds at an energy near the valence band maximum (VBM). Recently two occupied surface states S′ and S″ near

to the VBM have been measured using current imaging tunnelling spectroscopy by Hamers *et al* [23]. S′ at 0.25 eV above the VBM is localized on 12 adatoms of the unit cell according to dimer–adatom–stacking fault model of Takayanagi *et al* [24], while S″ at −0.15 eV below the VBM is localized at three spots in each half of the unit cell, i.e. dangling bonds on the 'rest' atoms in the first full atomic layer. The peak S_1 of 2.0 eV measured by us may be assigned to one of the following two transitions according to the energy conservation of interband transitions. One transition is from the S′ level to the secondary conduction band minimum L_1 at 2.05 eV above the VBM [25] corresponding to an excitation energy of 1.8 eV, and the other is from S″ to L_1 with an excitation energy of 2.2 eV. Both of these two excitation energies are in reasonable agreement with the measured loss energy of 2.0 eV for S_1 within the experimental error range. The fact that the peak S_1 quenches at 0.25 L in figure 1 shows that, in order to saturate the dangling bonds, a water molecule is adsorbed on both adatom and 'rest'-atom sites of the unit cell and then decomposed immediately (or simultaneously) to form an Si–OH group (and a probable Si–H group) according to the constant E_b of O 1s in figure 2. Fortunately, similar results have been given at room temperature using STM by Avouris and Lyo [19]. Our discussion is simply a crude description of the adsorption site; however, it should be a heuristic starting point for further observations at low temperatures by STM.

3.2. *Water exposure and successive annealing of the sample*

XPS and ELS measurements versus different annealing temperatures of the sample were done in order to clarify the adsorption mechanism.

3.2.1. XPS data. In figure 3 the photoemission data on O 1s are presented. The curve at 150 K has an FWHM of 1.9 eV and is located at 531.7 eV while the curves for higher annealing temperatures have broader peaks and their maxima shift to lower BEs. The FWHM of the curve at 175 K increases to 3.5 eV and the peak position shifts to 530.6 eV. A further increase in annealing temperature to 190 K further narrows the O 1s peak; its FWHM decreases to 2.2 eV and the peak position decreases slightly to 530.2 eV. For higher temperatures, E_b and FWHM remain the same up to 700 K. These results, including the O 1s peak position shift to a lower energy and the fact that its FWHM first increases and then decreases with increasing annealing temperature, are similar to those reported by Spitzer and Lüth [21]. We note that the displacement of 1.5 eV between the medium and lower E_b is nearly equal to the value of 1.3–1.5 eV measured by others [19, 20]. Within the detectable limit of XPS the presence of only two adsorption states rather than three states leads to the conclusion that no water molecule adsorption exists for which there would be a third state with E_b higher than 531.7 eV. The modification of the emission lines with increasing temperature can be understood by fitting the curve at 175 K to two Lorentzian curves, positioned at 530.2 eV and 531.7 eV, respectively. In the fitting procedure the extreme O 1s spectra at 150 K and at 290 K are used as the reference. The calculated Lorentzian curves are shown as dotted curves in the figure. The peaks measured in the intermediate temperature range are considered to be due to mixing of adsorption states A and B in the figures. Because the area of the curves in figure 3 remains unchanged during annealing, we believe that no oxygen atoms desorb from the surface. The increase in temperature induces the breaking of OH bonds. The transition from state A to state B starts at 175 K when the temperature is high enough to break the OH group and to establish an Si–O bond (530.2 eV). We cannot say

anything about what happens to the H atoms, although other reports [7, 19] have claimed the possibility of formation of an Si–H group.

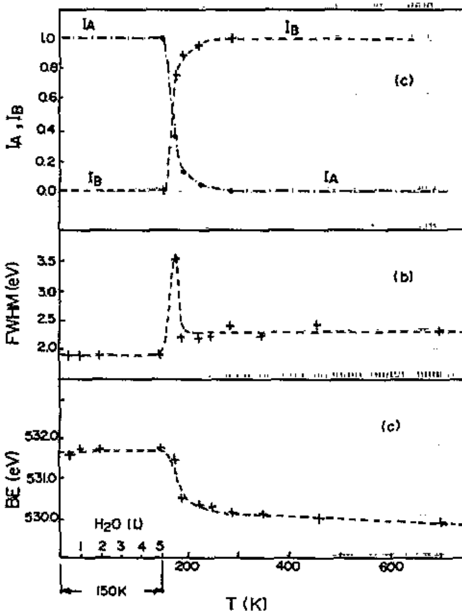


Figure 4. The changes in the O 1s core level obtained on an Si(111) 7 × 7 surface exposed to 5 L of water at 150 K followed by annealing at different temperatures: (*a*) BE, (*b*) FWHM and (*c*) normalized intensities of adsorption states A and B.

Figure 4 summarizes the changes in E_b, the FWHM of the O 1s emission lines and the normalized intensities I_A and I_B for state A and state B, respectively, (taking $I_A + I_B = 1$) versus the annealing temperature. It is very interesting that 175 K is the critical temperature where all our data have a discontinuity. In figure 5 the area ratio of the O 1s peak normalized to the Si 2p peak versus the annealing temperature is shown. The data are obtained from successive annealings, starting from 190 K and proceeding up to 830 K. The sample surface was exposed to 5 L of water at 150 K. The area ratio remains nearly unchanged between 150 and 300 K, indicating that when Si–OH groups decompose, all oxygen atoms remain on the surface and readily form the surface silicon oxide SiO_x ($x < 2$). This measurement also supports the viewpoint that the molecular adsorption of water is not present. If molecular water were adsorbed on the surface at low temperatures, it would be desorbed from the adsorbed surface when the annealing temperature reaches 300 K and would induce a decrease in the O 1s-to-Si 2p area ratio. The area ratio begins to drop slightly near 400 K, which corresponds to the start of oxygen loss. Above 830 K the area ratio approaches zero, indicating that the surface recovers and becomes clean.

3.2.2. ELS data. Figure 6 shows ELS data of water (5 L) adsorbed on an Si(111) 7 × 7 surface as a function of annealing temperature. At 180 K we observe a new loss peak S'_3 (13.6 eV), which is very near the peak at 13.1 eV observed at room temperature by Ibach and Rowe [14] and is attributed to a transition from occupied to unoccupied electron states in the oxygen-covered silicon surface layer. This is further evidence that state A in figure 3 is related to atomic oxygen adsorption below 290 K, above which it disappears. When the peak S'_3 disappears at about 400 K, the silicon oxide

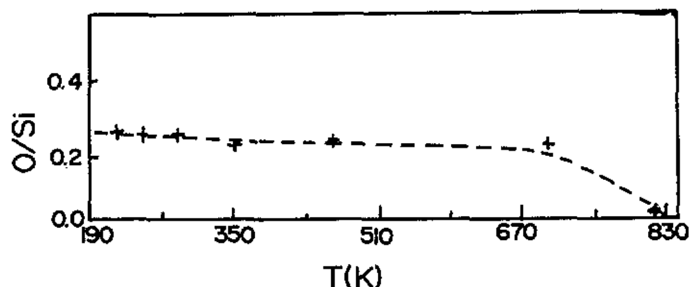


Figure 5. Area ratio of O 1s normalized to the Si 2p core level obtained on an Si(111) 7 × 7 surface.

decomposition and oxygen desorption process take place (this is in agreement with the result in figure 5). It persists up to 800 K when the surface peak S_3 again appears, showing the re-establishment of a clean surface and complete desorption of all adsorbed groups.

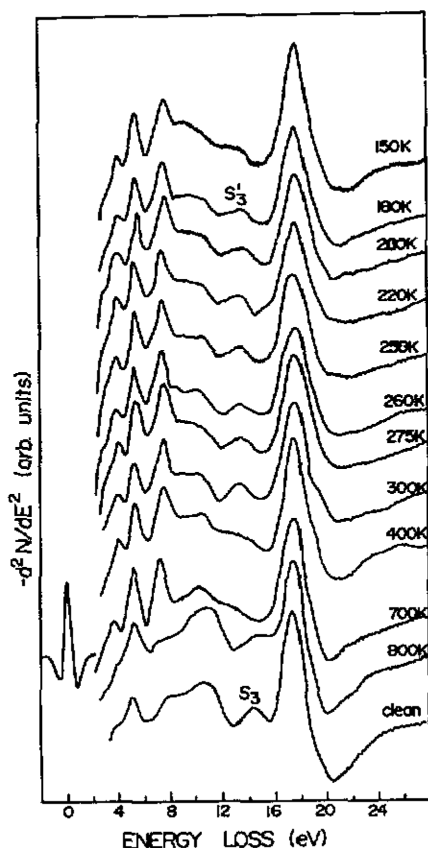


Figure 6. ELS spectra obtained on an Si(111) 7 × 7 surface exposed to 5 L of water at 150 K followed by an anneal at different temperatures.

3.2.3. LEED data. During the annealing procedure at a temperature lower than 300 K, an increase in the background intensity and consequent fading of the spots in the LEED pattern have been observed; this may be due to a slight disorder array in SiO_x. Above 300 K the background intensity begins to decrease again and the LEED spots to become increasingly brighter. At temperatures above 800 K we can see a well

defined Si(111) 7 × 7 pattern. This is further evidence that the adsorbed surface returns to being totally clean at the corresponding temperature.

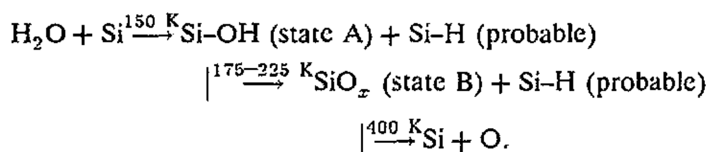
4. Summary

(i) The water is first adsorbed on the adatom and 'rest'-atom sites and immediately dissociates to form an Si–OH group (and a probable Si–H group).

(ii) The Si–OH group, after an anneal above 175 K, dissociates to form silicon oxide SiO_x ($0 < x < 2$) and a probable hydride Si–H. Only two adsorption states A and B are observed. No evidence of molecular adsorption is found.

(iii) The SiO_x is desorbed completely above 800 K; the adsorbed surface returns to an Si(111) 7 × 7 clean reconstructing surface again.

(iv) The mechanism of water adsorption and desorption on the Si(111) 7 × 7 surface may be represented as follows:



$$H_2O + Si \xrightarrow{150\ K} \text{Si–OH (state A)} + \text{Si–H (probable)}$$
$$\quad | \xrightarrow{175-225\ K} SiO_x \text{ (state B)} + \text{Si–H (probable)}$$
$$\qquad | \xrightarrow{400\ K} Si + O.$$

Acknowledgments

The authors would like to thank Professor Xide Xie for her kind guidance and Professor Youhua Qian for reading our manuscript. The work was supported by the National Natural Science Foundation in China.

References

[1] Russo N, Toscano M, Barone V and Lelj F 1987 *Surf. Sci.* **180** 599
[2] Ibach H and Rowe J E 1974 *Phys. Rev.* B **9** 1951
[3] Ciraci S, Erkoc S and Ellialioglu S 1983 *Solid State Commun.* **45** 35
[4] Cao P L 1986 *Chinese J. Semicond.* **7** 617
[5] Fujiwara K 1981 *Surf. Sci.* **108** 124
[6] Fujiwara K 1981 *J. Chem. Phys.* **75** 5172
[7] Ibach H, Wagner H and Bruchmann D 1982 *Solid State Commun.* **42** 457
[8] Schmeisser D 1984 *Surf. Sci.* **137** 197
[9] Kobayashi H, Kubota T, Oachi M and Nishijima M 1983 *Phys. Lett.* **95A** 345
[10] Mayer F 1971 *Surf. Sci.* **27** 107
[11] Mayer F and Urakking J J 1973 *Surf. Sci.* **38** 2515
[12] Rowe J E and Ibach H 1973 *Phys. Rev. Lett.* **31** 102
[13] Schaefer J A, Anderson J and Lapeyre G J 1985 *J. Vac. Sci. Technol.* A **3** 1443
[14] Ibach H and Rowe J E 1974 *Phys. Rev.* B **10** 710
[15] Schmeisser D, Himpsel F J and Hollinger G 1983 *Phys. Rev.* B **27** 7813
[16] Koehler B G, Mak C H and George S M 1989 *Surf. Sci.* **221** 565
[17] Katircioglu S 1987 *Surf. Sci.* **187** 569
[18] Podólsky B S, Ukraintsev V A and Chernov A A 1991 *Surf. Sci.* **251–2** 1033
[19] Avouris Ph and Lyo In-Whan 1991 *Surf. Sci.* **242** 1
[20] Dai Daoxuan and Zhu Furong 1991 *Phys. Rev.* B **43** 4803
[21] Spitzer A and Lüth H 1985 *Surf. Sci.* **160** 353
[22] Au Chak-tong, Berza J and Roberts M W 1979 *Chem. Phys. Lett.* **66** 340
[23] Hamers R J, Tromp R M and Demuth J E 1987 *Surf. Sci.* **181** 346
[24] Takayanagi K, Tonishiro Y, Takahashi M and Takahashi S 1985 *J. Vac. Sci. Technol.* A **3** 1502
[25] Lassailly Y, Chiaradia P, Hermann C and Lampel G 1990 *Phys. Rev.* B **41** 1266