

22nd International Conference on

THE PHYSICS OF SEMICONDUCTORS

Volume 1

Vancouver, Canada
August 15 – 19, 1994

Editor

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National Research Council of Canada
Institute for Microstructural Sciences
Ottawa, Canada

 **World Scientific**
Singapore • New Jersey • London • Hong Kong

MICROSCOPIC THEORY OF THE OPTICAL PROPERTIES OF Si(111) - 7×7

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We studied the origin of electronic transitions at Si(111)- 7×7 . Within a tight-binding approach, we have calculated the surface electronic structure, optical and Electron-Energy-Loss (EEL) spectra. In all cases, good agreement between our calculations and the experimental data was obtained.

1. Introduction

For more than three decades much attention has been paid to the study of the Si(111)- 7×7 reconstructed surface. In spite of all these efforts, the large size and complexity of its unit cell have hampered establishing a conclusive theory, and some questions, especially concerning its spectroscopy, are still open. Several structural models have been proposed¹, but only one reproduces almost all the important features of this surface; the Dimer- Adatom- Stacking fault (DAS) model of Takayanagi *et al.*², shown in Fig. 1. The DAS model has 12 adatoms (ADs), 6 restatoms (RAs), 1 corner hole (which altogether yield 19 dangling bonds (DBs) per unit cell), 9 dimers and a stacking fault in one half of its cell.

Although optical techniques are a powerful tool to characterize surfaces, only a few experimental results have been reported for Si(111)- 7×7 ³⁻⁵. On the other hand, theoretical results about its optical properties have only been obtained in terms of the Si(111)- 2×2 , and Si(111)- 3×3 models⁶. Calculations that take into account the full unit cell with all its atoms and building elements are still lacking. In this paper, we present microscopic calculations of the electronic and, for the first time, of the optical properties of the Si(111)- 7×7 surface based on the DAS model described before.

2. Electronic Structure

The electronic structure and the optical properties of the Si(111)- 7×7 have been calculated using a sp^3s^* semi-empirical tight-binding approach⁷; the formalism used here has been extensively described in Ref. 8. The system consists of a slab of 7 Si layers, including ADs, and a hydrogen layer at the bottom surface to saturate the Si DBs, with a total of 347 atoms. The Si(111)- 7×7 atomic geometry was taken from an *ab-initio* molecular dynamics simulation⁹. The main surface axes are shown in Fig. 1, while the Z -axis is normal to the surface. In order to reproduce the known experimental electronic structure¹⁰⁻¹², we moved the RAs outward in the Z direction by 0.5 \AA with respect to the positions reported in Ref. 9.

In our calculations, a weak dispersion (less than 0.1 eV) of the surface states at different points in the irreducible part of the Surface Brillouin Zone (SBZ) has been found. Hence, we show in Fig. 2 the calculated surface band structure of Si(111)- 7×7 , at only one special point (SP), whose position in the SBZ is shown in the same figure. The Fermi energy E_F was found at 0.43 eV above the top of the valence band, while the measured experimental value is 0.6 eV¹³. Around E_F there are filled and empty DB- like surface states mainly localized on ADs. Given the small gap between these states, we expect a metallic behavior of the

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surface. (In the rest of the paper energies will be referred to E_F). There are two groups of occupied surface states at -0.65 eV and between -0.75 eV and -1.25 eV. Those at -0.65 eV are DBs located at restatoms (RAs), while the other ones are mainly AD backbonds. The surface states observed around -1.7 eV also show an AD backbond character, with a small contribution from dimers. Above E_F there are two overlapping groups of empty states. The states at lower energy (0.5 eV) are mainly DBs located at ADs, while the states at higher energy (0.7 eV) are mainly AD back-antibonds. AD back-antibonding states also are found between 1.3 and 1.5 eV (not shown in Fig. 2). These findings are in good agreement with experimental results¹⁰⁻¹³, and with previous theoretical calculations for 3×3^6 and 7×7^9 models.

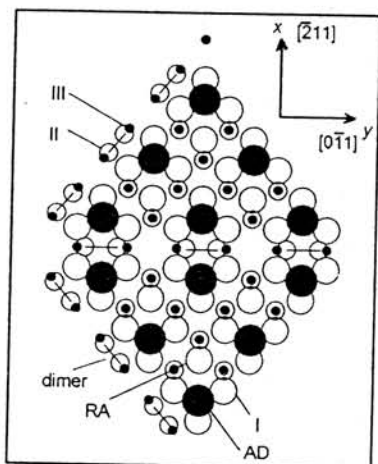


Fig. 1. Unit cell of the Si(111)-7x7 surface, top view. The atomic positions of the four top layers are indicated, as well as the surface axes.

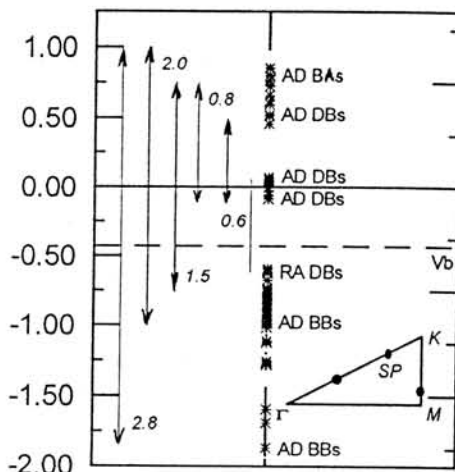


Fig. 2. Surface band structure at SP. Dots (stars) denote bulk (surface) states. The 3 special points in the irreducible SBZ are indicated. The main transitions between empty and filled states are also indicated (eV).

3. Optical Properties

In order to calculate the correction to Fresnel formula of reflectivity due to the presence of a surface, we used the expressions for s- and p- polarized light derived in Ref. 14. The imaginary part of the dielectric constant was calculated at three special points¹⁵ in the irreducible SBZ (see Fig. 2). Transitions up to 13 eV were taken into account. Therefore, the calculated real part of the polarizability, obtained by using the Kramers-Kronig transform, is accurate up to about 6 eV⁸. The optical response is isotropic for light polarized in the surface plane.

To interpret the electronic transitions observed experimentally³⁻⁵, we have calculated the difference of the reflectance between the clean surface and the H-covered one, that is the differential reflectance (DR). In the case of the H-covered surface, we have taken a slab of Si atoms at their bulk ideal positions, terminated at the top and bottom surface by a monolayer of H atoms. In Fig. 3 we show the DR for s (full line), and p (dashed line) polarizations, at an angle of incidence of $\theta = 60^\circ$. The optical spectra, for s-, and p-polarized light, have very similar lineshapes, the main difference being their intensity: the response to p- polarized light is sensibly larger than the response to s- polarized one.

Analyzing the spectra, we find that up to 2.0 eV the response is dominated by surface

to surface (s - s) transitions, and from 2.0 eV to 3.0 eV by surface to bulk (s - b) transitions. The bulk to surface (b - s) transitions are weak compared with the other contributions. The main s - s and s - b transitions are indicated by arrows in Fig. 2. They occur at 0.1 eV, 0.6 eV, 0.8 eV, and 1.45 eV, where the first one at 0.1 eV involves the filled and empty AD-DB states near E_F . The second peak at 0.6 eV can be attributed to transitions among (i) AD-DB below E_F and AD-DB at 0.5 eV, and/or (ii) between RA-DB and AD-DB near E_F . The structure at 0.8 eV is attributed to transitions from AD-DB states to AD-BB states. The peak at 1.45 eV is due to transitions from AD-BB states to (i) AD-DB states at 0.5 eV, and (ii) AD-BB states; and/or from AD-DB to AD-BB at 1.4 eV (not shown in Fig. 2). The s - b component shows a broad structure from 2.0 eV to 3.5 eV mainly due to transitions between AD-BB and bulk states in the conduction band, where the bottom of the conduction band (C_b) is found at 1.4 eV respect to the top of the valence band (V_b). For energies above 3.0 eV, the spectrum is mainly dominated by s - b and bulk to bulk (b - b) transitions, and shows a minimum at 3.2 eV and a structure with three maxima at 3.5 eV, 3.8 eV, and 4.2 eV. We found similar transitions at the same energy positions as in a previously calculated spectrum for the 3×3 model⁶.

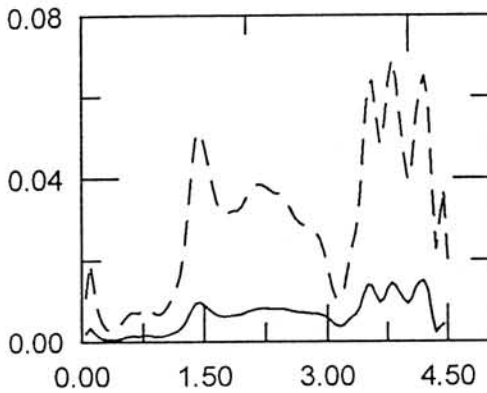


Fig. 3. Differential reflectance for s - (full line) and p - (dashed line) polarizations vs. energy (eV).

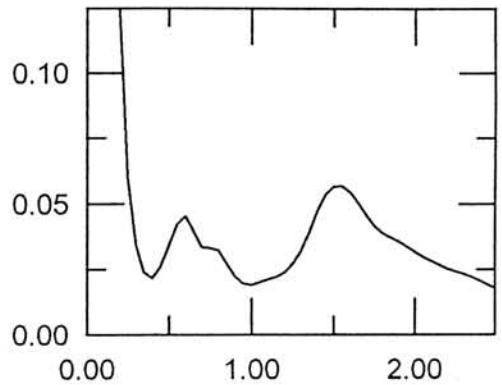


Fig. 4. Electron scattering probability (arb.u.) as a function of the energy loss (eV).

Chiarotti *et al.*⁴ have measured the surface absorption constant for the Si(111)- 7×7 surface, using unpolarized, normally incident light in the near infrared. The weak structure observed from 0.3 eV to 0.8 eV with an intensity of $\sim 0.8\%$, agrees with our theoretical results. Wierenga *et al.*³ measured the differential reflectance in the energy range from 1.0 to 3.0 eV, using also unpolarized, normally incident light. They found two peaks at 1.76 eV and 2.9 eV. Similar transitions, with an additional peak at 4.2 eV, were observed later by Alameh and Borensztein⁵. In this last work, both s - and p -polarized light were used in a wider energy range, from 1.2 to 5.0 eV, at an angle of incidence of 60 degrees. Both experiments^{3,5} measured the difference of reflectance between the clean Si(111)- 7×7 surface and the oxidized one; similar results have been obtained¹⁶ using a hydrogenated surface instead of the oxidized one. The first experimental peak at 1.76 eV can be associated with the present calculated s - s transition at 1.45 eV in Fig. 3, while the second experimental peak at 2.9 eV might correspond to the calculated s - b structure between 1.8 and 3.0 eV, where the intensities of both calculated spectra fit very well with the experimental ones⁵.

However, the intensity of the calculated peaks at 1.45 eV, 3.5 eV, 3.8 eV, and 4.2 eV is larger than those observed in Ref. 5.

Using our theoretical results of the surface dielectric constant, we calculated the EEL spectrum in the low energy regime according to the formalism of Ref. 17. We show in Fig. 4 the electron scattering probability as a function of the loss energy, calculated at an angle of incidence $\varphi_i = 45^\circ$, and a primary beam energy of $E_0 = 15$ eV. At 0.1 eV there is a peak with an intensity 8 times larger than the structure shown in the figure. Further transitions are observed at 0.6 eV, 0.8 eV, and 1.5 eV. The first peak at 0.1 eV is in agreement with the experimental peak observed at 95 meV by Demuth et al.¹³. The following two calculated transitions together could correspond to the measured one at 0.9 eV, while the structure at 1.5 eV can be related with the experimental transition at 1.7 eV. There is a remarkable agreement of the relative intensity as well as the shape between the present results and the experimental ones. The origin of the electron transitions between surface and bulk states shown in Fig. 4 are the same as those discussed before in the DR case.

4. Conclusions

We have calculated the electronic structure and optical properties of the Si(111)-7 \times 7 surface. The surface band structure calculated here shows a very good agreement with the experimental results. The optical and EEL spectra are interpreted in terms of electron transitions between surface and/or bulk states. We have found a good agreement with the available experimental data, especially for the EEL spectra.

This work has been supported in part by the European Community programme ESPRIT Basic Research, within the Action no. 6878, EASI. One of the authors (C.N.) also acknowledges the partial support of the *Dirección General de Asuntos del Personal Académico* of the *Universidad Nacional Autónoma de México*, (México) under project IN-102493.

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