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Total-current-spectroscopy studies of the electron states of the clean Si(100)2 × 1 and hydrogen-chemisorbed Si(100)1 × 1 surfaces

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Experimental data have been obtained on the clean Si(100)2 × 1 surface and hydrogen-chemisorbed Si(100)1 × 1 surface with use of total-current spectroscopy. Relative to the valence-band maximum, two empty surface states at 1.8 and 0.7 eV and four occupied surface states at −0.25, −0.45, −6.0, and −8.4 eV are observed on the clean Si(100)2 × 1 surface. Two hydrogen-induced surface states at −5.0 and −9.5 eV relative to the VBM on the hydrogen-saturated Si(100)1 × 1 surface have been observed. A preliminary interpretation of these data is also given.

I. INTRODUCTION

Total-current spectroscopy[1] (TCS) is a surface-spectroscopic technique particularly useful in materials characterization when band-structure effects play a decisive role. It can not only provide information on occupied states but also give information about unoccupied states, and so TCS has been used in studies of semiconductors, layered materials, and insulators. TCS has several additional advantages, such as low electron energies, low beam current, high surface sensitivity, and low cost. Two different approaches have been developed to date for explaining the mechanism of TCS. The approach proposed by Komolov and Chadderton[1] is based on an inelastic-scattering model (or interband-transition model), in which discrete interband transition and collective excitations occur directly when the appearance energy is equal to the excitation threshold. Møller and Mohamed[2] have implemented a computer code to extract the density of states (DOS) of valence and conduction bands from the experimental data derived from TCS. A second approach is based on an elastic-scattering model (or low-energy electron-diffraction model).[3,4] In this latter model, the TCS spectrum is interpreted as the energy dependence of the electron elastic reflectivity coefficient. The former approach has been used to interpret features in TCS spectra for semiconductors, such as Si, GaAs, InSb, and InAs, etc.[5,6] Recently, Dittmar-Wituski, Naparty, and Skonieczny[7] have shown a very high correlation between TCS and ELS (electron energy-loss spectroscopy) spectral features.

Although chemisorption of hydrogen on the Si(100) surface has been investigated extensively,[8-18] the central problem about whether the monohydride, the dihydride, and/or the trihydride phase is formed on the Si(100)1 × 1 surface is still open. Only a few investigations of the Si(111) surface have been done using TCS (Refs. 5 and 19) in order to explore the application of the TCS in surface studies and check the mechanism of TCS. In this paper, we have measured the total-current spectra of the clean Si(100)2 × 1 surface and hydrogen-saturated chemisorbed Si(100)1 × 1 surface: In this work, the approach proposed by Komolov and Chadderton[1] and by Møller and Mohamed[2] is adopted and the results obtained agree with existing data obtained by other methods.

II. EXPERIMENT

In a TCS measurement, the primary beam is incident perpendicularly on the solid surface and the total secondary emission is investigated by monitoring the current in the target circuit, with the primary current kept constant; then the derivative of the current collected by the sample is recorded. A schematic diagram of the total-current spectrometer is shown in Fig. 1. The DPR 304-type low-energy electron-diffraction (LEED) electron gun was from Riber Company, France. A constant accelerating voltage V_p of 150 eV was applied. The energy of this beam was decreased to $V_p + V_b = 10$ eV by the retarding voltage V_b. The energy E_0 of the primary electrons can be controlled by a sweeping voltage V_s. The beam orientation was perpendicular to the target. Differentiation of the target current with respect to the incident energy was obtained through a modulation voltage V_m with a frequency of 5 kHz. The size of the beam spots measured using a Faraday cup and a ZC 36-type picoammeter is less than 5 mm.

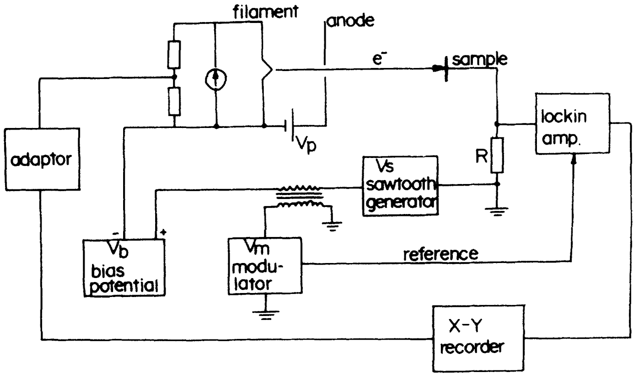

FIG. 1. Experimental apparatus of TCS.

All experiments were carried out in an ion-pump UHV system equipped with LEED and quadrupole mass spectrometer. The base pressure was less than 1×10^{-9} Torr. The sample used in this experiment was a lightly p-type mirror-polished single-crystal Si(100) wafer with a resistivity of 10 Ω cm. To obtain Ohmic contact between the sample and the holder, a p^{+}-type doped layer was formed on the back of the sample. The experimental procedure for surface cleaning and hydrogen adsorption was done in accordance with Refs. 10 and 15. After insertion into the UHV system, the sample was heated to 850 °C for 10 min and then annealed at 700 °C for 5 min. This procedure can give a clean surface showing the well-known sharp 2×1 LEED pattern.

III. RESULTS AND DISCUSSIONS

The TCS spectra of clean Si(100)2×1 and hydrogen-saturated chemisorbed Si(100)1×1 surfaces are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2, the electron energy E_0 is measured with respect to the vacuum level E_{vac}.

A. Clean surface

In this paper, a TCS spectrum of the clean Si(100)2×1 surface is given and an attempt has been made to understand the mechanism of the electronic transitions and the origin of the TCS peaks. It has been demonstrated theoretically[1] and experimentally[2] that at very low incident energy (less than 20 eV) the fine structure in the TCS spectra is dominated by inelastic electron-electron scattering processes, resulting in interband transitions that can be analyzed through a convolution over the DOS under the approximations of a constant-transition-matrix element, energy conservation, and momentum nonconservation in the scattering process. According to the interband-transition model, the probabilities are high for primary electrons to be scattered to empty states of high density and for electron excitation to take place between DOS maxima. Since energy must be conserved during the whole process, the transition energy ΔE can be written as

$$\Delta E=\varepsilon_i-\varepsilon_f=E_f-E_i\ , \tag{1}$$

where ε_1 and ε_f are the electron energies of the initial and final states for primary incident electrons, respectively. E_f and E_i are the energies of the final and initial states for excited electrons, respectively. According to formula (1), each measured TCS peak does not correspond to a unique transition due to the nonconservation of the momentum in the scattering process.

No good theoretical results of the electronic structure for the Si(100)2×1 surface are available; therefore, in order to relate TCS bulk peaks to corresponding interband transitions for our present purpose, the result proposed by Chelikowsky and Cohen[20] is used (see Fig. 3). In Fig. 3, the energy origin is taken to be at the valence-band maximum (VBM). There are two possible final states, D_1 and D_2, in Fig. 3. D_1 is a maximum of the calculated DOS at 5.3 eV above the VBM and D_2, the other maximum near the vacuum level, 4.3 eV above VBM. The data on Γ_{15} at 3.1 eV and secondary conduction-band maximum L_1 at 2.05 eV of Lassailly *et al.*[21] are also reproduced in Fig. 3. As shown in Fig. 2(a), seven peaks, S_1, E_1, E_2, S_2, $\hbar\omega_s$, S_3, and $\hbar\omega_p$ at 2.2, 3.7, 7.7, 9.0, 11.7,

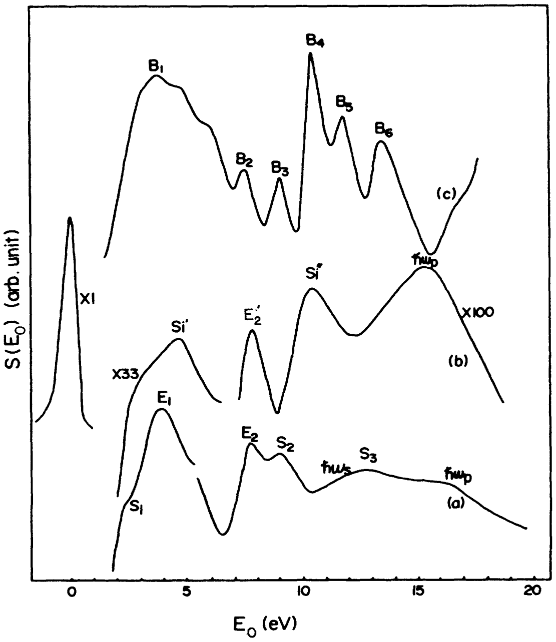

FIG. 2. TCS spectra. (a) Clean Si(100)2×1 surface. (b) H-saturated Si(100)1×1 surface. (c) Results calculated by us.

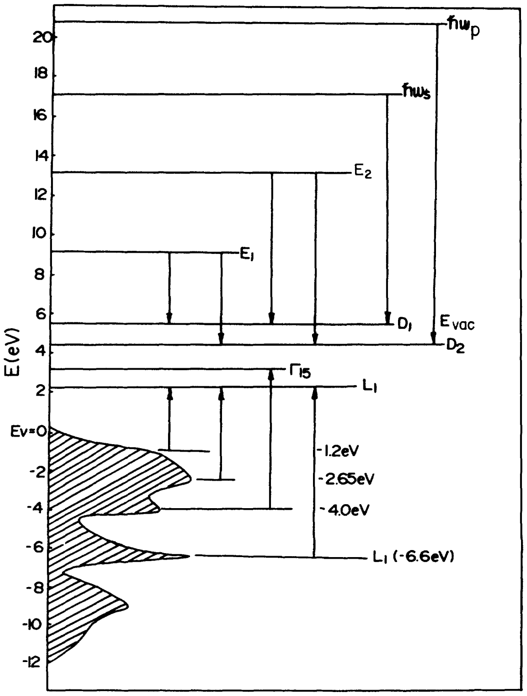

FIG. 3. Theoretical bulk density of state of silicon.

13.0, and 15.7 eV, respectively, can be observed. First, we attempt to distinguish surface peaks from bulk peaks, depending on whether the peak quenches upon hydrogen adsorption. Since S_1, S_2, S_3, and $\hbar\omega_s$ peaks are quenched after saturated hydrogen adsorption, as shown in Fig. 2(b), they can be associated with surface states. E_1, E_2, and $\hbar\omega_p$ are the bulk peaks. The possible transitions associated with E_1 and E_2 are shown in Fig. 3. Second, we will relate the TCS surface peaks S_1, S_2, and S_3 to their corresponding interband transitions, for which the results of surface DOS calculated by Ciraci *et al.*[11] (shown in Fig. 4) are used. According to the relation $\varepsilon_i = E_0 + \xi$ and Eq. (1), the value of E_i will be determined as follows. By using an ionization energy ξ of 5.28 eV as given by Ranke and Xing[22] and the relation $\varepsilon_i = E_0 + \xi$, ε_i can be obtained from the measured TCS peaks. ε_f and E_f can be obtained from theoretical calculations or experimental measurements. Then Eq. (1) can be used to assign E_i to various levels. Thus, the surface peaks S_1, S_2, and S_3 can be considered as corresponding to interband transitions from surface states in Fig. 4. The energy difference as indicated by the arrows corresponds to the energy loss.

Now we discuss the corresponding interband transitions for the three surface peaks S_1, S_2, and S_3. The first surface peak S_1 at 2.2 eV may correspond to two possible transitions when primary electrons are scattered to D_1: One transition is from the first occupied level O_1 to the empty states D_i^*. Here, the occupied level O_1 at -0.45 eV is from the dangling-bond band S_u,[11] and the empty state D_i^* at 1.8 eV stems from an antibonding dimer bond previously measured by us[23] using inverse photoelectron spectroscopy (IPES). The excitation energy $E_f - E_i$ of 2.25 eV calculated from the above data is in good agreement with the corresponding loss energy of 2.2 eV. Another transition occurs from the second occupied level O_2 to L_1. This occupied level, O_2, is an occupied dangling-bond state and its energy position of -0.15 eV obtained by us in in reasonable agreement with -0.35 eV of ultraviolet photoelectron spectroscopy (UPS) measured by Himpsel and Eastman[24] within our experimental error. The second surface peak S_2 of 9.0 eV can be assigned to two transitions. One is from the other occupied level S_{DB} calculated by Ciraci *et al.*[11] to another empty surface state, D_{down} (Ref. 25) while the other one is from the occupied level S_{PB} to Γ_{15}. The S_{DB} level at -8.4 eV originates from an *s*-type dimer bond and the S_{PB} level at about -6.0 eV is resonance-state localized at backbonds.[11] D_{down}, at about 0.7 eV, originates from dangling bonds at the down atoms of the asymmetric surface dimer. The energy position of D_{down} deduced by us not only is consistent with the values of 0.5–0.7 eV obtained by Himpsel and Fauster,[26] by Batra, Nicholls, and Reihl,[27] and by us,[23] but also is in good agreement with the value of 0.68 eV calculated by Chadi.[28] Similarly, the third surface peak S_3 at 13.0 eV may correspond to the following two transitions from the occupied band S_b: One is from the occupied state near -10.0 eV to Γ_{15} and the other is from the occupied state near -11.8 eV to L_1. Since the S_b band is mainly produced by the second-layer silicon *s* orbit,[11] the corresponding local DOS structure does not appear in Fig. 4; therefore, this interpretation of the S_3 peak is somewhat unexpected. We would like to point out that all the S_1, S_2, and S_3 peaks measured by TCS are also in reasonable agreement with those measured by Rowe and Ibach[29] using electron-energy-loss spectroscopy (ELS), within experimental errors. In fact, Ciraci has interpreted their theoretical results using ELS, although ELS has a large experimental error (± 0.4 to ± 0.8 eV). Our TCS results further support Ciraci's calculation with a smaller experimental error of ± 0.1 eV using these results on Γ_{15} and L_1.[21] In Table I a summary of the TCS peak positions, electron energies of the initial and final states, the corresponding transition energies, and the ELS data are given.

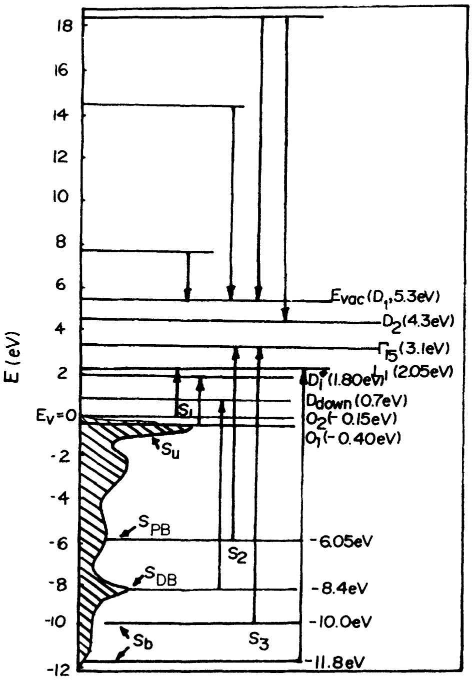

FIG. 4. The theoretical surface density of state of the clean Si(100)2×1 surface and interband transitions from surface states.

B. Saturated chemisorbed surface

LEED pattern changes to (1×1) from (2×1) when hydrogen atoms are saturation adsorbed on the clean Si(100) surface; two features which appear in the TCS spectrum are clearly seen in Fig. 2(b). First, all surface peaks S_1, S_2, S_3, and $\hbar\omega_s$ are quenched, as the dangling bond and backbonding bond have been saturated by hydrogen atoms. Second, two additional hydrogen-induced peaks S' and S'' at 4.6 and 10.3 eV, respectively, have been observed. This result is different from that obtained by Maruno *et al.*[10] In addition, the E_1 peak becomes stronger and broader.

Various models have been proposed to explain the

TABLE I. The peak position of TCS, and electron energy of initial and final states due to interband transitions. The energy origin coincides with VBM.

Surface peaks	E_0	Primary initial energy (eV) ε_i	Electron final energy (eV) ε_f	Excited initial energy (ev) E_i		Electron final energy (eV) E_f	ELS (Ref. 29) (eV)
				ours	others		
S_1	2.2	7.5	5.3	0.40	−0.45 (Ref. 11)	1.8 (Refs. 11 and 23)	1.7±0.4
			4.3 (Ref. 20)	−0.15	−0.35 (Ref. 24)	2.05 (Ref. 21)	
S_2	9.0	14.3	5.3	−5.9	−6.05 (Ref. 11)	3.10 (Ref. 21)	8.4±0.8
				−8.3	−8.4 (Ref. 11)	0.7 (Ref. 27)	
S_3	13.0	18.3	4.3 (Ref. 20)	−11.95	−11.8 (Ref. 11)	2.05 (Ref. 21)	14.7±0.8
			5.3	−9.9	−10.0 (Ref. 11)	3.10 (Ref. 21)	

hydrogen-saturated Si(100)1×1 phase. Sakurai and Hagstrum[8] considered the H-saturated (1×1) phase at room temperature as a uniform dihydride phase (two H per Si atom) with each surface Si atom relaxing to the bulklike arrangement. This model has been supported by Ciraci *et al.*[11] and by Oura *et al.*[16] and is widely accepted.[30–31] Because no detailed structural model of the (1×1) surface is available, here we would like to use this model and a DOS calculation of the (1×1) surface to interpret our TCS data. The DOS of the (1×1) surface calculated by Ciraci *et al.*,[11] which is shown in Fig. 5, reveals two distinct maxima. Two additional hydrogen-induced surface peaks S' and S'' obtained by our TCS may correspond to the transitions from the first maximum near −5 eV and the second maximum at −9.5 eV to L_1, respectively.

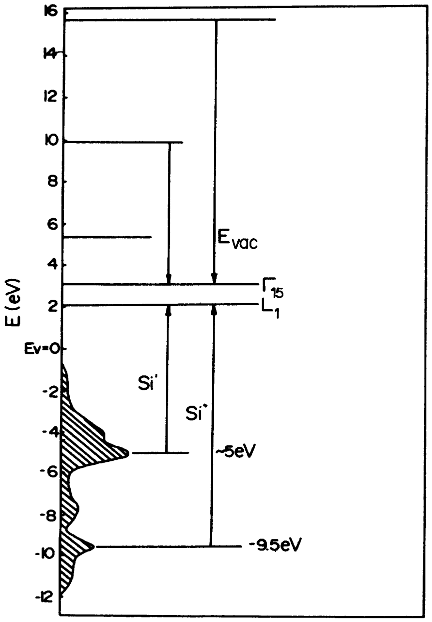

FIG. 5. The theoretical surface density of state of the H-saturated Si(100)2×1 surface and interband transitions from H-induced surface states.

C. Interband transition model

Our TCS data on both the clean Si(100)2×1 surface and the H-saturated Si(100)1×1 surface have been interpreted by use of the interband-transition model proposed by Komolov and Chadderton. In order to examine further this model, two different approaches were made in analyzing the TCS spectrum of the clean surface. One approach is to calculate the energy positions of the TCS spectrum using an elastic-scattering model; unfortunately, the discrepancy between experiment and theory is so large that this model has to be abandoned. Another approach is to calculate the TCS spectrum using the interband transition model.

We take the structure of the TCS to be the sum of the structures due to elastically and inelastically scattered electrons. According to the Komolov-Chadderton model and calculations,[1,2] the intensity of elastically scattered electrons is modulated by the onset of inelastic-scattering channels. Thus, the connection between the TCS spectrum and the band structure is effected by noting the dependence of inelastic mean free path L_2 on the DOS of the valence and conduction bands (N_c and N_v). Under the approximations of the constant-transition-matrix element, conservation of energy, and nonconservation of the momentum in the scattering process, it is possible to obtain a direct relation between L_2 and the DOS as follows:

$$\begin{aligned}\frac{1}{L_2}&=\frac{W(E)}{V}\\&=\frac{W_0}{V}\int_{\Delta}^{E}N_c(E-\varepsilon)\\&\quad\times\left[\int_{-\varepsilon}^{-\Delta}N_v(E_0)N_c(E_0+\varepsilon)dE_0\right]d\varepsilon\ .\end{aligned} \tag{2}$$

where, $W(E)$ is the inelastic-scattering probability, W_0 is a constant, V is the velocity of electron in the solid, E is the energy of the scattered electron measured from the bottom of the conduction band, E_0 is the energy of the initial state in the valence band, ε is the energy loss in the scattering such as interband transition, and Δ is the width of the energy gap.

In this theoretical calculation we should consider the contributions of both the bulk band and the surface DOS, thus making the problem too complex. So, for simplicity, we shall only consider the contribution of bulk-band DOS and make the assumption of a single final state that has been used to explain the transition of the ELS data by Rowe and Ibach[29] and the TCS spectrum by Dittmar-Wituski, Naparty, and Skonieczny.[7] Taking $\xi=5.33$ eV and an electron affinity $\chi=4.21$ eV as given by Ranke and Xing,[22] we obtain the results shown in Fig. 2(c). These results show not only that the bulk peaks B_1 and B_2 calculated from Fig. 2(c) are in agreement with the bulk peaks E_1 and E_2 measured from Fig. 2(a), respectively, but also that both shapes are similar. Although peaks B_5 and B_6 seem to coincide with the peaks $\hbar\omega_s$ and S_3, respectively, it is, perhaps, unjustified to think that B_5 and B_6 make certain contributions to the TCS spectrum, since they still have not been quenched completely after hydrogen absorption [see Fig. 2(b)]. Besides, we expect not to see the surface peak S_1 in Fig. 2(c). The reason why some bulk peaks like B_3 and B_4 are also missing in Fig. 2(a) may be the neglect of the contribution of the surface DOS and/or the approximation of constant-transition-matrix elements. Briefly, our simple calculation shows that the interband-transition model is applicable to this experiment on silicon.

IV. CONCLUSION

In this paper, we have studied the electronic states on the clean Si(100)2×1 surface and the hydrogen-saturated Si(100)1×1 surface observed with use of TCS. Two empty states (D_i^* and D_{down}) and four occupied states (O_1, O_2, S_{pb}, and S_{db}) on the clean surface have been identified, since they are quenched upon hydrogen saturation adsorption. The assignment of D_i^*, D_{down}, O_1, and O_2 is supported by previous studies using IPES and UPS. Two additional hydrogen-induced surface peaks, S' and S'', on the hydrogen-saturated surface have been observed, in agreement with the calculation of Ciraci *et al.* All experimental data on the clean and hydrogen-saturated surfaces as well as a simple calculation on the clean surface, show that the interband-transition model is effective in developing an understanding of the electronic states obtained on both the clean and the hydrogen-saturated silicon surfaces with use of the TCS technique.

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