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Surface-state densities on clean semiconductor surfaces measured by ellipsometry

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Ellipsometric measurements of chemical adsorption reactions on clean semiconductor surfaces yield information on the change in surface-state densities due to the adsorbed layer. The results can be compared directly with those obtained by photoemission experiments.

I. INTRODUCTION

Recently, surface-state distributions have been measured directly by photoemission experiments. Eastman and Grobman[1] studied the photoelectron emission of clean and oxygen-covered surfaces of Si(111), Ge(111), and GaAs(110). Wagner and Spicer[2] also examined the Si(111) surface. A peak which was present in the energy-distribution curves (EDC) of the electrons emitted from the clean surface disappeared gradually upon oxygen adsorption. For Si(111) an exposure of 10^{-3} Torr sec (about one monolayer) was used. The difference in the EDC of the clean and the covered surface was attributed to surface states associated with the "dangling" bonds of the surface atoms at the clean surface, which are compensated by the oxygen adsorption. On the assumption that the transition probability for emission of electrons from surface states is constant throughout the band, Gaussian-shaped bands of surface states are derived with a width at half-maximum of ~1 eV. The maxima of these surface states bands for the different crystal surfaces lie at 0.4 – 0.8 eV below the valence band edge. On the further assumption that the transition probability for emission of an electron from a surface state is the same as that for an electron from a bulk state, the total number of filled surface states was calculated to be $\sim 10^{15}$ cm^{-2}, which corresponds to the number of dangling bonds (one per surface atom). The photoemission data, therefore, appear to give information on the number and energy distribution of the filled surface states.

Rowe and Ibach[3] reported electron-energy-loss spectra with an incident electron beam of 100 eV. Small peaks in the loss spectra of silicon were observed, which disappeared upon oxygen adsorption. These loss peaks were interpreted as due to surface-state transitions. In this type of experiment the imaginary part of the inverse of the dielectric constant ($\text{Im}\epsilon^{-1}$) is measured and both the initial and final states are involved. Loss peaks were observed at 2.0 ± 0.4 and 1.7 ± 0.4 eV for Si(111) and Si(100), respectively.

We have reported[4] ellipsometric measurements of physical and chemical adsorption reactions on clean semiconductor surfaces. Ellipsometry is an optical method and the ellipsometric effects contain not only information on the thickness and index of refraction of the adsorbed layers but also on optical changes in the surface region of the substrate caused by the adsorption reactions. In the present paper it will be shown that these optical changes can be related to the changes in surface-state distributions upon chemical adsorption as derived from photoemission and electron-energy-loss measurements.

II. EXPERIMENTAL

The ellipsometric apparatus has been described previously.[4] The accuracy of the ellipsometric readings is 0.01°, whereas the reproducibility of the ellipsometric effects due to an adsorbed layer is typically 10%.

The measurements on Si, Ge, and GaAs have been performed at a few chosen wavelengths by using interference filters. The results for GaP have been obtained by Morgan[5] using a monochromator. In the latter case the data points were taken at intervals of 10 nm.

The silicon crystals have been cleaned by heating to 1200 °C for several minutes in an ultra-high-vacuum (UHV) chamber (< 10^{-9} Torr), or have been cleaved [the Si (111) plane only] in UHV. The germanium crystals have been cleaned by heating to 800 °C for several hours and the GaAs(110) surface has been obtained by cleaving in UHV. Auger-electron spectroscopy showed that the surface impurity concentration in the case of heat-cleaned Si surfaces was below the detection limit of the method (< 0.02 monolayer in the case of C and O), whereas some residual carbon (~5% of a monolayer) was observed on the Ge surfaces. No Auger measurements have been carried out for the cleaved Si and GaAs surfaces.

III. RESULTS AND DISCUSSION

A. Ellipsometric results

In ellipsometry two parameters are measured corresponding to the relative phase change (Δ) and the relative amplitude ratio change (Ψ) of the two components of the polarized light wave, parallel with and perpendicular to the plane of incidence, upon reflection from a surface. The changes in these parameters ($\delta\Delta$ and $\delta\Psi$) upon gas adsorption on the surface were recorded as a function of the wavelength of the light λ at which the ellipsometric measurements were performed. For optically nonabsorbing adsorbed layers (simple inorganic and organic molecules in the near ir visible and near uv spectral regions), it is expected from theoretical considerations[4] that the $\delta\Delta$ varies roughly proportionally to $1/\lambda$ and that the $\delta\Psi$ values are very small. This behavior was observed for physically adsorbed layers, such as Kr on Si(111) at liquid-nitrogen temperature. The $\delta\Delta$- and $\delta\psi$-vs-λ curves for chemically adsorbed layers, however, showed a large amount of structure, which appeared to be independent of the type of adsorbate. This effect has been interpreted as due to a substrate change upon chemical adsorption, i.e., the compensation of the dangling bonds of the surface atoms. It was shown that the substrate effect increased linearly with the number of adsorbed molecules[4] up to the saturation coverage where all dangling bonds had been compensated. The substrate effect was described phenomenologically as the effective disappearance of a transition layer present at the clean surface. This transition layer with an arbitrarily chosen thickness of 5 Å (this value has no influence on the model[6]) has optical constants different from the bulk, due to the difference in electronic structure between the surface layer (dangling bonds) and the bulk (sp^3-type bonds). Chemical adsorption to saturation coverage largely restores the normal tetravalent bond configuration of the surface atoms.

The ellipsometric effects $\delta\Delta_t$ and $\delta\psi_t$ due to the substrate change alone have been obtained from the relations

$$\delta\Delta_{\text{meas}} = \delta\Delta_{\text{ads}} + \delta\Delta_t \quad , \tag{1}$$

$$\delta\psi_{\text{meas}} = \delta\psi_{\text{ads}} + \delta\psi_t \quad , \tag{2}$$

where the subscript t refers to the transition layer. The $\delta\Delta_{\text{ads}}$ and $\delta\psi_{\text{ads}}$, i.e., the ellipsometric effects of the adsorbate itself, have been calculated using the results of calibration experiments (gas-volumetric-adsorption measurements on powder surfaces,[4] later supported[7] by simultaneous measurements with ellipsometry and Auger-electron spectroscopy on single-crystal surfaces). Typical results are given in Fig. 1.

The validity of the assumptions used in the calculation of the effects of the adsorbed layer ($\delta\Delta_{\text{ads}}$ and $\delta\psi_{\text{ads}}$) and the separation into an adsorbate and a substrate effect has been discussed in Ref. 4. Without going into detail the following points can be made in favor of the above treatment.

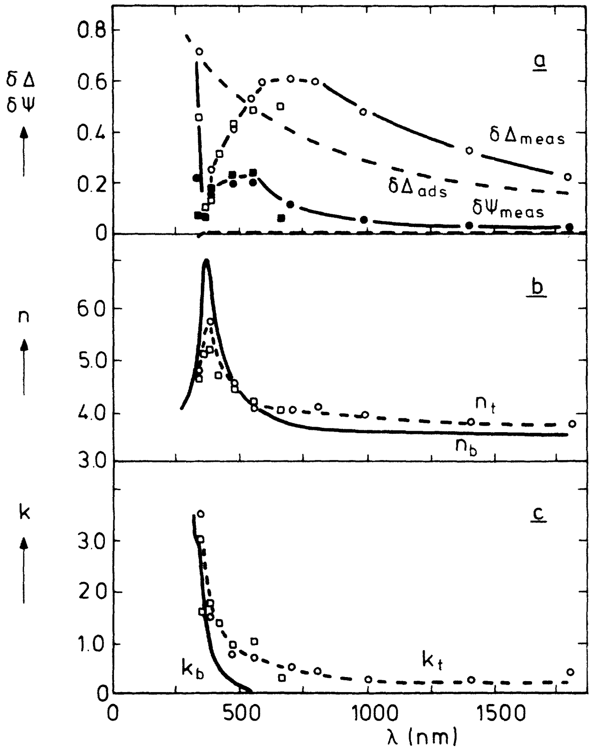

FIG. 1. Ellipsometric results for oxygen adsorption on a clean Si(111) surface. Circles refer to $\delta\Delta_{\text{meas}}$ and $\delta\Psi_{\text{meas}}$ for Si(111) cleaned by flashing to 1200 °C, squares refer to the same data for a Si(111) surface cleaved in uhv. The measurements have been performed at an angle of incidence of 62.4°. The dashed lines in (a) represent the calculated values of $\delta\Delta_{\text{ads}}$ and $\delta\Psi_{\text{ads}}$. The optical constants of the transition layer n_t and k_t as given in (b) and (c), respectively, have been calculated using $d_t = 5$ Å. The bulk values n_b and k_b are taken from Ref. 8.

(i) The $\delta\Delta_t$ and $\delta\psi_t$ at saturation coverage seemed to be independent of the type of chemically adsorbed layer, allowing for errors up to 15%.

(ii) No extra structure in the $\delta\Delta_t$- and $\delta\psi_t$-vs-λ curves is introduced by subtracting the calculated adsorbate effects from the measured ellipsometric effects. This implies that conclusions based on this structure (positions of maxima and minima) are not influenced by the details of the calculation.

(iii) The n_t and k_t values cannot be independent from each other, but must be related through Kramers-Kronig relations. The absorption coefficient [Fig. 1(c)] integrated over the total wavelength region determines the value of the index of refraction at the long-wavelength limit n_∞. The "extra" absorption in the wavelength region 500–1500 nm implies, therefore, also a higher value of n_∞ for the transition layer. The difference between the index of refraction of transition layer and bulk $(n_t - n_b)_{\lambda=\infty}$, is given by

$$\delta n_\infty = (n_t - n_b)_{\lambda=\infty} = \frac{2}{\pi}\int_{\lambda=500}^{\lambda=1500} \frac{k_t - k_b}{\lambda}\, d\lambda \quad , \qquad (3)$$

where the subscript b refers to bulk properties. The calculated value of δn_∞ appears to be 0.25 which proves to be consistent with the difference between n_t and n_b at the longest wavelength measured[6] as shown in Fig. 1(b).

B. Surface states

The transition layer model can be interpreted in terms of transitions between bands of filled and empty surface states. The relevant parameter for the transition probability between the bands is the imaginary part of the dielectric constant of the transition layer $\mathrm{Im}\epsilon_t (= 2n_t k_t)$. The $\mathrm{Im}\epsilon_t$ and $\mathrm{Im}\epsilon_b$ curves for silicon as a function of photon energy $h\nu$ are given in Fig. 2. The surface-states transitions appear at the low-energy side of the $\mathrm{Im}\epsilon$-vs-$h\nu$ curves. At photon energies between 2 and 3 eV the $\mathrm{Im}\epsilon_t$ becomes approximately equal to $\mathrm{Im}\epsilon_b$. In order to estimate the number of surface states the assumption has been made that the $\mathrm{Im}\epsilon_t$ and $\mathrm{Im}\epsilon_b$ curves coincide for photon energies higher than 3.0 eV. The total integrated area under the $\mathrm{Im}\epsilon$-vs-$h\nu$ curve then corresponds to the total number of valence electron states (bulk and surface) in a 5-Å-thick layer, i.e., 10^{16} states/cm^2. The integrated area under the surface states peak $\mathrm{Im}\epsilon_t$-ϵ_b $\mathrm{Im}(\epsilon_t - \epsilon_b)$ is about $\frac{1}{10}$ of the total peak area.[6] This corresponds to ~ 10^{15} surface states/cm^2, in agreement with photoemission results, if a similar assumption is made regarding equal transition probabilities for transitions of electrons from surface and bulk states.

The results from photo emission and ellipsometry, therefore, refer to roughly the same surface state densities. The width at half-height of our $\mathrm{Im}(\epsilon_t - \epsilon_b)$ curves of 1.5 eV, as shown in Fig. 3, also agrees with the width of ~ 1.0 eV measured in photoemission, since in the present experiments both the initial and the final states are involved.

The photoemission data suggest that the maximum density in the filled surface-states band lies 0.4–0.8 eV below the valence band edge. Combining this result with the ellipsometric data where transitions between these filled states and a band of empty surface states are measured, makes it possible to measure the energy position of the maximum density of the latter band. These maxima lie 0–0.8 eV above the conduction band edge for the crystal surfaces measured in this study.

The relevant data for silicon, germanium, GaAs, and GaP are given in Table I. (The data on GaP have been taken from a recent paper by Morgan.[5]) It appears that the ellipsometric results can be described phenomenologically by transitions between a band of filled surface states and a band of unfilled surface states positioned roughly symmetrical with respect to the band gap.

The surface states distribution on Si(111) and Si(110) appears to be similar, whereas the data on Si(100) show a second peak[9] in the $\mathrm{Im}\epsilon_t$-vs-$h\nu$ curve at 1.3 eV. Comparison with the data of Rowe and Ibach[3] shows reasonable agreement with the presently observed peak at 2.6 eV. About 0.3 eV should be added to the electron energy-loss values to compare them with the present data, since $\mathrm{Im}\epsilon^{-1}$ is measured instead of $\mathrm{Im}\epsilon$ as obtained from optical data.

Chiarotti *et al*[10] have measured optical absorp-

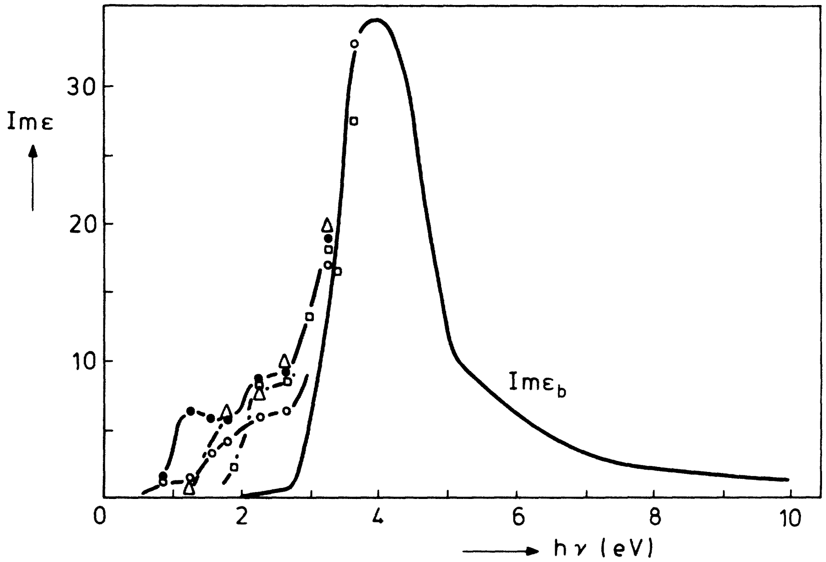

FIG. 2. $\mathrm{Im}\epsilon_t$ and $\mathrm{Im}\epsilon_b$ of silicon as a function of photon energy. Open circles, Si(111), flashed; squares, Si(111), cleaved; triangles, Si(110), flashed; and closed circles, Si(100), flashed. The $\mathrm{Im}\epsilon_b$ values (solid line) are taken from Ref. 8.

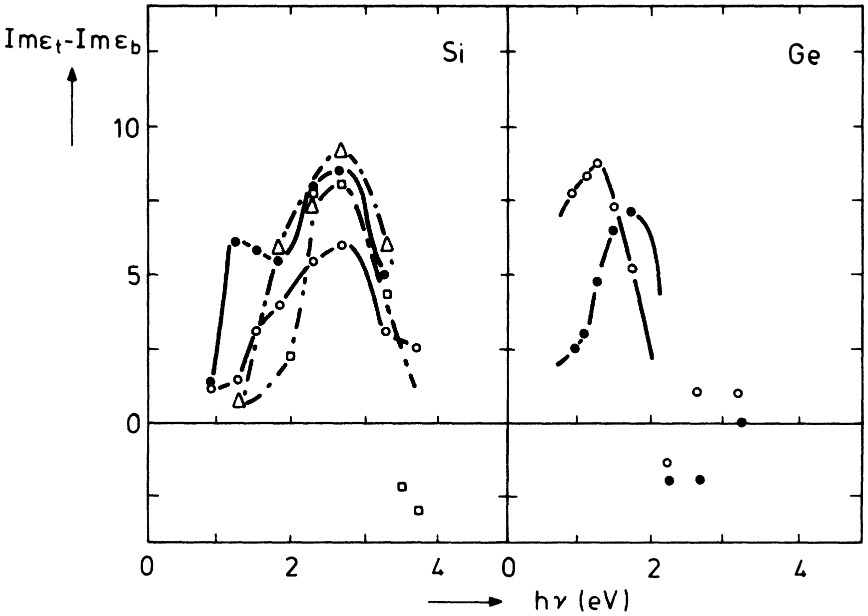

FIG. 3. Difference between $\mathrm{Im}\epsilon_t$ and $\mathrm{Im}\epsilon_b$ for several crystal planes of Si and Ge as a function of photon energy. The maxima correspond to the E_{max} in Table I. On the left-hand side, open circles, Si(111), flashed; squares, Si(111), cleaved; triangles, Si(110) flashed; and closed circles, Si(100) flashed. On the right-hand side, open circles, Ge(111), ion-bomb. and annealed and closed circles, Ge(100), ion-bomb. and annealed.

tion in clean Si(111) and Ge(111) surfaces at 0.5 eV, using the method of total internal reflection. The data were interpreted as transitions between two extremely sharp bands of surface states both lying in the band gap. Our optical measurements could not be extended below 0.7 eV and we cannot compare, therefore, their results with ours. In photoemission measurements,[1,2] however, this sharp surface states band has not been observed.

Recent calculations[11–13] of surface-states distributions on the Si(111) surface place the maximum surface state density very close to the top of the valence band. Bortolani *et al.*[12] carried out their calculations for a crystallographically ideal surface, whereas Appelbaum and Hamann[13] took surface relaxation into account. The latter authors show the direct relation between dangling bonds and surface states. Ellipsometry cannot solve the discrepancy between the calculated maximum density at the valence band edge and the maximum density 0.6 eV below the valence band edge as observed in photoemission, since the ellipsometric data give only information on the energy gap between filled and unfilled states and not on their absolute energy position.

IV. CONCLUSION

There appears to be a strong correlation between results obtained by ellipsometry and by photoemission pertaining to the surface-states distribution on semiconductor surfaces. Both methods give approximately the same total number of surface states ($\sim 10^{15}/\mathrm{cm}^2$) if the same assumptions are applied in the interpretation. Photo-

TABLE I. Surface-state information from ellipsometry and photoemission. E_{max} refers to the energy where the total transition probability between filled and unfilled surface states is at maximum. $(E_{\mathrm{max}} - E_{\mathrm{gap}})/2$ gives the maximum surface state densities below the valence band edge, derived from ellipsometry, assuming a symmetrical distribution around the middle of the gap. E_{max} (filled states) refers to the maximum density of filled surface states below the valence band edge, as derived from photoemission data (Refs. 1 and 2).

Sample	Cleaning	$E_{\mathrm{max}} \pm 0.2$ eV	E_{gap} (eV)	$\frac{1}{2}(E_{\mathrm{max}} - E_{\mathrm{gap}})$	E_{max} (filled states)
Si(111)	Cleavage in UHV	2.6	1.1	0.75	0.45 or 0.60
Si(111)	Flashed to 1200 °C	2.6	1.1	0.75	···
Si(110)	Flashed to 1200 °C	2.6	1.1	0.75	···
Si(100)	Flashed to 1200 °C	2.6 and 1.3	1.1	0.75	···
Ge(111)	Cleavage in UHV	···	0.7	···	0.75
Ge(111)	Ion-bomb. + anneal at 800 °C	1.3	0.7	0.30	···
Ge(100)	Ion-bomb. + anneal at 800 °C	1.7	0.7	0.50	···
GaP(110)	Ion-bomb. + anneal at 500 °C	3.4	2.4	0.50	···
GaAs(110)	Cleavage in UHV	3.0	1.4	0.80	0.50

emission establishes the absolute energy position of the filled surface states band, whereas ellipsometry gives information on the relative positions of filled and unfilled surface states bands. Combination of the results, therefore, gives the position of the unfilled surface-states band.

The ellipsometric results can be compared directly to those obtained by electron energy-loss measurements. The methods yield Imϵ and Imϵ^{-1} due to surface states transitions, respectively. Ellipsometry will provide in general a higher-(optical-) energy resolution.

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[1] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

[2] L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).

[3] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 31, 102 (1973).

[4] F. Meyer, E. E. de Kluizenaar, and G. A. Bootsma, Surf. Sci. 27, 88 (1971).

[5] A. E. Morgan, Surf. Sci. 43 (1974).

[6] The transition layer is described by three parameters, its optical constants n_t and k_t, and its thickness d_t, whereas there are only two measured parameters, $\delta\Delta_t$ and $\delta\Psi_t$. Although there is no unique solution for all three parameters, unique values can be calculated in good approximation for $d_t(n_t-n_b)$, $d_t(k_t-k_b)$, and $d_t\,\mathrm{Im}(\epsilon_t-\epsilon_b)$. Insertion of a chosen value of d_t and literature values of n_b and k_b yields a set of transition layer values, dependent on d_t. The ratio $(n_t-n_b)/(k_t-k_b)$, however, is not dependent on d_t and the conclusion drawn from relation (iii) is valid irrespective of the choice of d_t. The number of surface states per cm^2 N is given by the ratio of the integrated peak areas of the $\mathrm{Im}(\epsilon_t-\epsilon_b)$- and Im ϵ_b-vs-E curves multiplied by the total number of valence electron states in the transition layer d_tD, where D is the density of states (2.10^{23}) per cm^3:

$$N=d_tD\int \mathrm{Im}(\epsilon_t-\epsilon_b)\,dE\Big/\int \mathrm{Im}\,\epsilon_b dE.$$

N is independent of the choice of d_t since $d_t\,\mathrm{Im}(\epsilon_t-\epsilon_b)$ is a parameter uniquely derived from the ellipsometric data.

[7] F. Meyer and J. J. Vrakking, Surf. Sci. 33, 271 (1972).

[8] H. R. Phillip and E. A. Taft, Phys. Rev. 120, 37 (1960).

[9] T. E. Fischer (private communication) suggested that the "extra" peak at 1.3 eV for the Si(100) surface might arise from the break-down of normal momentum conservation in the surface layer. This peak would then arise from bulk states, instead of surface states.

[10] G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[11] F. Flores and J. Rubio, J. Phys. C 6, L258 (1973).

[12] V. Bortolani, C. Calandra, and M. J. Kelly, J. Phys. C 6, L349 (1973).

[13] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973).