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Surface Vibrations of Silicon Detected by Low-Energy Electron Spectroscopy

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The energy loss of 5-eV electrons reflected from clean and from oxidized (111) silicon surfaces has been investigated. A surface phonon with $\hbar\omega \approx 55$ meV, $k \approx 0$ is found at the clean surface. After exposure to $\approx 10^{-5}$ Torr min oxygen, three energy losses at 48, 90, and 125 meV occur. Models for the electron-phonon interaction, the nature of the surface phonon, and the structure of the oxidized surface are proposed.

Recently the unexpected strong interaction of low-energy electrons with long-wavelength surface phonons of infrared-active materials has been demonstrated by the author.[1] The interaction with the electron is due to the electric field of the surface phonon in the vacuum above the crystal surface. A quantum-mechanical theory of surface-phonon excitation by low-energy electrons has been developed by Lucas and Šunjić.[2] The agreement with the experimental results is quantitative and complete.[3] The loss energy of the electron is characteristic for the bulk material and the appropriate boundary conditions. At the surface of a semi-infinite crystal, for example, the frequency of the surface phonon is determined by the condition $\mathrm{Re}\,\epsilon_n(\omega) = -1$, where $\epsilon_n(\omega)$ is the normal component of the bulk-dielectric tensor. Because of the strong interaction of the electron with the surface phonon it seems difficult to detect additional energy losses related to specific surface properties of infrared-active materials. Propst and Piper,[4] however, have shown that it is possible to detect localized modes of gases adsorbed on tungsten. Progress in the experimental technique as well as in the theoretical understanding of the electron-solid interaction enables us now to continue this early work. Details of the electron spectrometer are described elsewhere.[3]

Silicon (111) surfaces were prepared from 3000-Ω-cm p-type material by cleaving the crystals in ultrahigh vacuum of 2×10^{-10} Torr. A typical energy-loss spectrum after cleavage is shown in Fig. 1(a). Within the experimental accuracy the loss energy of 55 meV is independent of the impact energy between 3 and 20 eV. The relative intensity of the energy loss as compared with the elastically scattered intensity I_{el} decreases at higher impact energies. At 5 eV the relative intensity was $I_{55}/I_{\mathrm{el}} \approx 7\times10^{-3}$ for four different crystals. The inelastic intensity is strongly peaked in the forward direction. When the crystal was rotated, both the elastic and inelastic intensities diminished. For a two-dimensional periodic crystal surface the parallel component of the wave vector $k_{\parallel}$ is the appropriate quantum number for any type of vibration. From the angular resolution of the spectrometer of ±0.5° one may estimate that vibrations with $k < 1.5\times10^{-2}$ Å^{-1} give the maximum contribution to

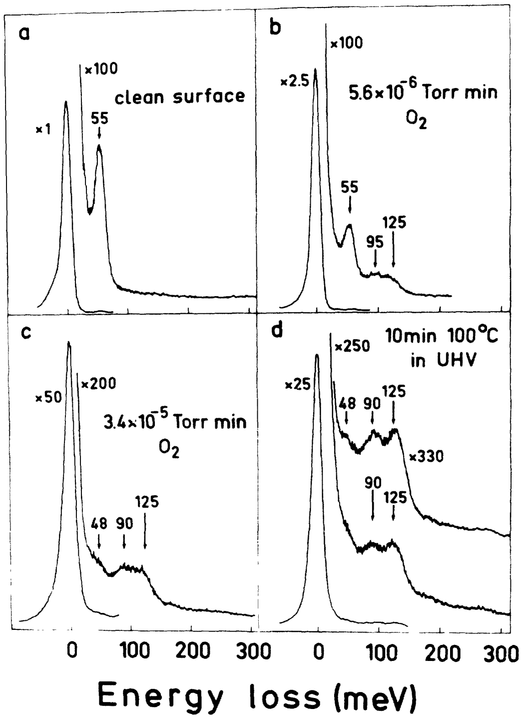


FIG. 1. Energy-loss spectrum of 5-eV electrons after specular reflection from a (111) silicon surface (recorder traces). The angle of incidence is 45°. The [112] direction is normal to the plane of incidence.

the observed energy loss. A slight increase in the observed relative intensity of the energy loss with the angle of rotation indicates some contribution of greater $k_{\parallel}$ vectors.

The surface character of the 55-meV loss is proved by the oxygen-adsorption experiments. Oxygen was admitted by a heated silver tube. After exposure to 5.6×10^{-6} Torr min O_2, two, weak extra energy losses were observed in addition to the 55-meV loss [Fig. 1(b)]. The 55-meV loss completely disappears after exposure to some 10^{-5} Torr min O_2 [Fig. 1(c)], and a new energy loss at approximately 48 meV occurs. Again the 90- and 125-meV losses are poorly separated. After oxygen adsorption a considerable angular divergence of the elastic and inelastic peaks was observed, and probably for this reason the elastic intensity scattered into the angular aperture of the analyzer was decreased by a factor of ≈50 [see Figs. 1(a) and 1(c)]. Heating the oxidized crystal to 100°C for 10 min in ultrahigh vacuum enhances the elastic intensity, and the 90- and 125-meV losses are resolved better [Fig. 1(d)]. However, the half-widths of the loss peaks still seem to be greater than the half-width of the elastic peak. The upper spectrum in Fig. 1(d) was obtained from another crystal after the same treatment. Further exposure to oxygen and heating to higher temperatures (300°C) produced no significant changes in the energy-loss spectrum. The relative intensities indicated in the different figures and the intensities for the different crystals are normalized to the current measured at the crystal and therefore contain uncertainties due to a possible change in the total reflection coefficient. The relative intensities between the 48-, 90-, and 125-meV losses seem to be constant for different crystals even with considerable contamination of the crystal surfaces indicated by strong extra resonances in the region expected for OH, SiH or CO, and CH bands. Phonon scattering of low-energy electrons most commonly has been attributed to single or multiple scattering from localized atomic potentials at positions correlated in space and time.[5] However, no strong selection rules for small-phonon wave vectors are derived from either the kinematical or dynamical scattering theory. Furthermore, according to these theories the inelastic intensity scattered into the angular aperture of the spectrometer at 5-eV impact energy should be 2 orders of magnitude lower than has been found in the reported experiments. On the other hand, strong inelastic phonon scattering in the forward direction is known from infrared active materials, where the electrons are scattered by the electric fields of long-wavelength surface phonons. For symmetry reasons no polarization and hence no electric field is associated with long-wavelength phonons in silicon. However, this statement only holds for the bulk material and not for the surface atoms. The two atoms in the unit cell of silicon are in different positions with respect to the surface. This will give rise to an effective ionic charge; and, just as in a ZnS lattice, a vibration of the two different atoms against each other will set up a dipole moment. For the following discussion we therefore consider the silicon surface to consist of a thin infrared-active layer on the bulk material. It is interesting to note that Bootsma and Meyer[6] in ellipsometric measurements have found optical constants at clean silicon surfaces different from the bulk.

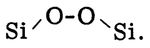
Inelastic scattering of low-energy electrons from thin dielectric films in specular reflection has been calculated by Lucas and Šunjić. From Fig. 1 of Ref. 2 relative intensities for the scattering from the ω_+ normal and the ω_- tangential modes are estimated for 5-eV electron:

$$I_{\omega_+}/I_{\rm el} \approx 0.3 \text{ and } I_{\omega_-}/I_{\rm el} \approx 2.4.$$

These values refer to an oscillator strength like that in ZnO. The actually measured intensity ratio at the clean silicon surface is 7×10^{-3}. An effective ionic charge of $\approx 10^{-1} e_0$ may therefore be derived for the silicon surface layer. For small oscillator strength the frequencies of surface and bulk modes in a thin layer are close to each other. At the present stage it can therefore not be decided whether the 55-meV loss corresponds to either a tangential or a normal vibration. The strong forward scattering, however, indicates that dipole scattering rather than scattering from localized atomic potentials is the relevant scattering mechanism at silicon surfaces at least for low electron energies. Furthermore it should be noted that the frequency of the surface phonon ($\hbar\omega = 55$ meV) is considerably lower than the frequency of the correspondent bulk mode ($\hbar\omega = 65$ meV).

Oxygen adsorption on silicon (111) surfaces has been studied by several authors. It is known from low-energy electron-diffraction experiments[7] that adsorbed oxygen does not produce a periodic structure. This explains the observed angular divergence of the elastic and inelastic intensities.

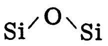
Bootsma and Meyer[6] reported finding a coverage of one oxygen atom per silicon surface atom at exposures of some 10^{-1} Torr min and proposed a formation of peroxide groups[8]:



$$\mathrm{Si}\diagup^{\mathrm{O\text{-}O}}\diagdown\mathrm{Si}.$$

Such a structure has five nondegenerate normal modes with a dipole moment,[9] which have not been found in the experiments reported here.

Corosella and Comas[10] have measured the oxygen coverage versus exposure at annealed surfaces using proton-activation analysis. They found a rapid decrease of the sticking coefficient at 10^{-6} Torr min exposure and a total number of $(3-4)\times 10^{14}$ oxygen atoms per square centimeter for exposures between 10^{-6} and 5×10^{-4} Torr min, which corresponds to one oxygen atom per two silicon surface atoms. Then a configuration like



$$\mathrm{Si}\diagup^{\mathrm{O}}\diagdown\mathrm{Si} \qquad (1)$$

seems more likely. For a (111) surface there are three different sites with the same configuration. A random distribution over these sites would give the required nonperiodic structure. Oxygen in a configuration like (1) introduces three nondegenerate normal modes. This agrees with the spectra in Fig. 1. A formation of peroxide bridges cannot be strictly ruled out. However, by assuming a structure as given by (1) at least for sufficiently low exposures the experimental results are explained without additional assumptions.

Localized modes of bulk interstitial oxygen in a similar configuration have been fairly successfully treated by regarding the configuration (1) as a free hypothetical molecule.[11,12] In a valence force-constant model the angle of bond and the distance between the Si and O atoms may be estimated from the experimentally measured frequencies.[13] One obtains $2\alpha \approx 130°$ and $d_{\text{Si-O}} = 1.56$ Å which in spite of the over-simplified model is in surprisingly good agreement with the distances known from the different quartz modifications (1.54–1.59 Å).

It has been shown that low-energy electron spectroscopy is a very sensitive tool for studies of surface vibrations. Further information about the structure of adsorbed species may be gained from the experiments when the relative intensity is measured versus angle of incidence. One expects a different angular dependence for the different normal modes, and it should be possible to work out selection rules within the framework of the dipole scattering theory.

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Convective and Absolute Instabilities in Semiconductors Exhibiting Negative Differential Mobility

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It is shown that, in a semiconductor exhibiting negative differential mobility, the coupling between diffusion effects and the tendency for space-charge accumulation can lead to temporal growth rather than spatial amplification if the dielectric relaxation frequency exceeds a certain threshold value. This conclusion results from an analysis of the dispersion relation for longitudinal waves in the semiconductor. The criterion for temporal growth is a condition for *absolute* instability, as opposed to *convective* instability, which would indicate rather spatial amplification.

The formation of a growing accumulation layer in GaAs biased in the region of negative differential mobility (NDM) is known to be associated with a *convectively* unstable space-charge wave which grows as it travels along at the carrier velocity.[1,2] In the limit of small diffusion and low frequencies, this wave is essentially unaffected by diffusion effects, at least in the small-signal approximation. However, a study of the dispersion relation for longitudinal waves also yields a second solution whose existence is mainly a result of diffusion.[3] This other solution represents a backward wave which, in the limit of small diffusion, is heavily damped and for this reason has mainly been neglected.

It is the purpose of this Letter to clarify the meaning of this backward wave and to stress its importance in NDM materials, where it can lead to an *absolute* instability, i.e., temporal growth rather than spatial amplification. The analysis which follows assumes a uniform, infinite semiconductor in which the carriers are drifting at a constant velocity v_0 under the influence of an applied field E_0. For a small wavelike perturbation of the form $\exp[i(\omega t-\beta z)]$, the dispersion relation $F(\omega,\beta)=0$ is obtained by solving the linearized set of equations

$$j_1=\omega_c\epsilon E_1+v_0\rho_1-D\partial\rho_1/\partial z, \tag{1}$$

$$\epsilon\partial E_1/\partial z=\rho_1, \tag{2}$$

$$\partial j_1/\partial z+\partial\rho_1/\partial t=0, \tag{3}$$

where D is the diffusion coefficient (assumed constant) and $\omega_c=\mu\rho_0/\epsilon$ is the dielectric relaxation frequency, μ being the differential mobility $\partial v_0/\partial E_0$ and $\rho_0=n_0e$ the background charge density. Here the subscript 1 indicates that the corresponding quantities are small perturbations superimposed on the zero-order solution (subscript 0). For the assumed $\exp[i(\omega t-\beta z)]$ dependence, the derivation of the dispersion relation from (1)-(3) is straightforward. We obtain

$$F(\omega,\beta)\equiv D\beta^2-iv_0\beta+\omega_c+i\omega=0. \tag{4}$$

This quadratic equation for β has two solutions expressed as

$$\beta=i\frac{v_0}{2D}\pm i\frac{v_0}{2D}\left(1+4\frac{\omega_cD}{{v_0}^2}+4i\frac{\omega D}{{v_0}^2}\right)^{1/2}. \tag{5}$$

In the limit of small diffusion and low frequencies ($\omega_cD/{v_0}^2$ and $\omega D/{v_0}^2\ll1$), the square root can be expanded to yield the two simple solutions,[3]

$$\beta_{\mathrm{I}}\simeq\beta_e-i\beta_c, \tag{6}$$

$$\beta_{\mathrm{II}}\simeq-\beta_e+i\beta_d, \tag{7}$$

where $\beta_e=\omega/v_0$, $\beta_c=\omega_c/v_0$, and $\beta_d=v_0/D$. The first one represents a traveling space-charge wave which is damped or amplified, depending whether ω_c is positive or negative. Within the limits of the approximation used, it is not affected by diffusion. The second wave, on the other hand, is a heavily damped backward wave in which diffusion effects play a dominant role. In order to understand better the meaning of these