Long-Range Quasielastic Scattering of Low-Energy Electrons by Conduction-Band Surface Plasmons on Si(111)7×7

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Conduction-band surface-plasmon excitations are seen to contribute to the quasielastic scattering of low-energy electrons from clean Si(111)7×7 surfaces. We have analyzed these observations by means of a multiple-scattering theory and show that these excitations are localized below the surface space-charge layer. A comparison of the deduced surface-charge-density profile is in good agreement with the Fermi-level pinning at this surface.

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Considerable interest exists in the transport properties and the nature of the space-charge region at a semiconductor surface. Distinct energy-loss features due to conduction-band surface plasmons have recently been observed on compound semiconductors by electron energy-loss spectroscopy (EELS).[1-3] In contrast, the conduction-band surface-plasmon losses in silicon with similar carrier densities are expected to be observed as a broadening in the energy distribution of the elastically scattered electrons.[4] This difference results from the lower plasmon energies and the overdamped response due to the lower mobility in comparison to compound semiconductors (e.g., GaAs). Consequently the scattering probability peaks at zero energy loss for carrier densities $\sim 10^{16}$ cm^{-3} and gives rise to the observed Gaussian line shape in the scattered electron distribution. Recent EELS studies have demonstrated that an analysis of the quasielastic line shape is a viable method for obtaining valuable information about the electronic properties of semiconductor surfaces.[5,6]

In this paper we present the first experimental observation of this quasielastic scattering by *conduction-band* surface plasmons on the Si(111)7×7 surface.[7] We show that this quasielastic scattering is influenced by the conduction-band density through impurity doping and thermal activation of free carriers across the silicon band gap. We have quantitatively analyzed these observations using a multiple-scattering theory and show that the observed surface-plasmon excitations are localized below the depletion layer at the semiconductor surface as a result of the strong band bending. These results demonstrate, for the first time, that the quasielastic scattering of low-energy electrons observed from semiconductor surfaces can be used to quantitatively study the surface space-charge layer. This long-range probing depth follows directly from the very small momentum transfer involved in the low energy of these excitations, typically a few millielectronvolts. The deduced surface-charge density profiles obtained from these measurements are in good agreement with calculations based on the Fermi-level pinning at this surface.

The experiments were performed in an ion, turbomolecular, and titanium sublimation pumped ultrahigh vacuum system with a base pressure of 4×10^{-11} Torr. The samples consisted of single-crystal *n*-type As-doped silicon with impurity concentrations ranging from 6.6×10^{12} to 5.6×10^{16} cm^{-3}. The bulk carrier concentrations n were determined by conventional resistivity measurements. The samples were cleaned by Ne-ion bombardment (500 eV) and repeated cycles of oxidation and annealing to 1125 K. Clean surfaces produced well-ordered, low-background 7×7 LEED patterns. The EEL spectrometer consists of a double-pass 127° cylindrical deflection monochromator and analyzer. The impact energy referenced to the vacuum level was 6.8 eV. The incident angle was 60° with respect to the crystal normal, and the angular acceptance of the analyzer is 1.8° full width at half maximum (FWHM). All measurements were made in the specular direction with an (8 ± 1)-meV-FWHM overall spectrometer resolution.

The quasielastic scattering, measured by the FWHM of the elastic peak, as a function of temperature is shown in Fig. 1. For the nearly intrinsic sample (lowest curve) the temperature dependence is characteristic of the metallic nature of the 7×7 surface.[7] However, as the impurity concentration is increased above $\sim 10^{15}$ cm^{-3} an additional broadening is observed as evidenced by the increased slopes of the two upper curves in Fig. 1. This increased broadening is due to the increased conduction-band electron density due to ionization of the additional impurities. This effect is more dramatically observed in Fig. 2 where the conduction-band density is increased by thermal activation. Here a significant increase in the width of the quasielastic peak is observed for temperatures above 500 K.

A general characteristic of a number of semiconductors is the presence of a large density of surface states which fall in the band gap and pin the Fermi level at the surface.[8] For the Si(111) surface the depth of the surface depletion layer, d, can be estimated from the

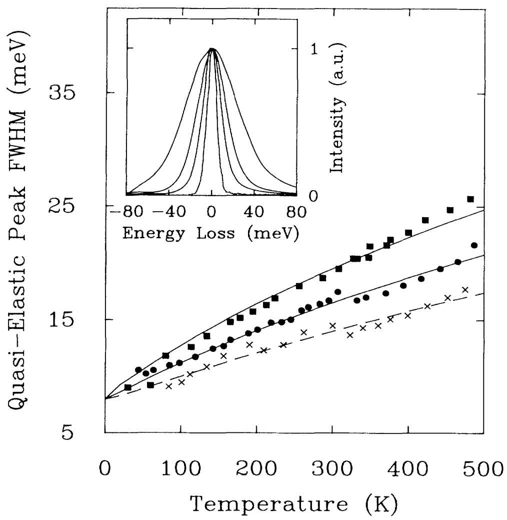

FIG. 1. Temperature dependence of the quasielastic-peak linewidth (FWHM) for different bulk impurity densities. The lower dashed line is given by the expression for the broadening due to excitation in a two-dimensional surface-state band (Ref. 11). The upper two solid lines are obtained with an additional contribution from the conduction-band free carriers, using Eq. (2), with depletion depths of 1050 and 1900 Å. The bulk carrier densities are (crosses) 6.6×10^{12}, (circles) 8.9×10^{15}, and (squares) 5.6×10^{16} cm^{-3}. The inset shows the measured quasielastic peak at 80, 514, 701, and 881 K for the case of circles.

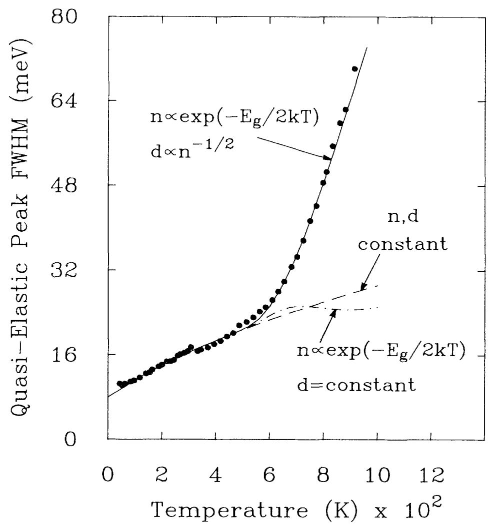

FIG. 2. Temperature dependence of the experimental width (FWHM) of the quasielastic peak showing the dramatic increase at high temperatures (circles). The lines are the calculated quasielastic broadening with (i) $n=8.9\times10^{15}$ cm^{-3}, $d=1900$ Å (dashed line), (ii) $n\propto\exp(-E_g/2kT)$, $d=1900$ Å (dot-dashed line), (iii) $n\propto\exp(-E_g/2kT)$, $d\propto n^{-1/2}$ (solid line).

measured Fermi-level position by use of a simple Schottky model. With the Fermi level at 0.53 eV below the conduction-band minimum,[9] $d\sim10^3$ Å for carrier densities $\sim10^{16}$ cm^{-3}. Thus to probe plasmons below the depletion layer a long-range interaction is required. In the conventional description[4] the surface plasmon is accompanied by a long-range electric field which decays exponentially from the surface into the vacuum and into the crystal with a decay length equal to the inverse of the momentum transfer parallel to the surface, $q_\parallel^{-1}$. According to the dipole scattering theory the momentum transfer $q_\parallel\sim(\hbar\omega/2E)k$, where k and E are the incident electron wave vector and energy, respectively. Thus for energies of a few millielectronvolts the momentum transfer is very small and results in a large effective probing depth $\sim10^4$ Å. It is this large probing depth at small loss energies which makes EELS effective in probing the surface space-charge layer.

An analysis of the quasielastic scattering requires a multiple-excitation theory because of the large scattering probability at the small loss energies involved. With allowance for multiple-scattering events at finite temperature the probability for scattering an incident electron is given by[10,11]

$$P(\mathbf{q}_\parallel,\omega)=\int_{-\infty}^{\infty}(dt/2\pi)e^{-i\omega t}\exp\{\int_0^\infty d\omega'\int d^2q'_\parallel\, f(\mathbf{q}_\parallel-\mathbf{q}'_\parallel)P_s(\mathbf{q}'_\parallel,\omega')\times[(n_{\omega'}+1)(e^{i\omega' t}-1)+n_{\omega'}(e^{-i\omega' t}-1)]\},\quad(1)$$

where $n_\omega=[\exp(\hbar\omega/k_BT)-1]^{-1}$ is the Bose-Einstein factor, P_s is the standard dipole single-loss probability,[4] and f is a function describing the spatial resolution of the spectrometer. The analysis is simplified by calculating the quasielastic linewidth instead of the full line shape. With use of Eq. (1) the linewidth of the quasielastic peak is given by[11]

$$\langle(\Delta\omega)^2\rangle=\int_0^\infty d\omega\,\omega^2(2n_\omega+1)\int d^2q_\parallel\, f(\mathbf{q}_\parallel)P_s(\mathbf{q}_\parallel,\omega).\quad(2)$$

The single-loss probability P_s is proportional to the loss function, $\mathrm{Im}g(q_\parallel,\omega)$, which describes the energy absorption in the medium. For the Si(111) surface there are two contributions to the quasielastic linewidth, excitations within the metallic surface-state band and the additional broadening due to conduction-band free-carrier excitations. The loss function can then be separated into two terms given by

$$\mathrm{Im}g = (\mathrm{Im}g)_{\text{surface state}} + (\mathrm{Im}g)_{\text{conduction band}}. \tag{3}$$

This separation is in agreement with experimental data in which the surface-state and conduction-band linewidths were measured separately on low-impurity clean samples and high-impurity adsorbate-covered samples, respectively. The resulting combined broadening measured on clean impurity-doped samples is found to be in agreement with Eq. (3). The temperature-dependent linewidth given by the first term in Eq. (3) has been described previously[11] and is shown by the lower dashed curve in Fig. 1.

Focusing on the conduction-band term, the loss function is given by $\mathrm{Im}g(q_{\parallel},\omega) = \mathrm{Im}\{-1/[1+\epsilon(q_{\parallel},\omega)]\}$, where $\epsilon(q_{\parallel},\omega)$ is the dielectric function of the medium. We use a three-layer model composed of vacuum, depletion layer, and substrate to simulate the semiconductor surface. The depletion layer is composed of a semi-infinite slab of thickness d and dielectric function ϵ_s on top of a substrate with a dielectric function ϵ_b. The effective dielectric function for this layer model is given by[4]

$$\epsilon(q_{\parallel},\omega) = \epsilon_s\left[\frac{1+\Delta\exp(-2q_{\parallel}d)}{1-\Delta\exp(-2q_{\parallel}d)}\right], \tag{4}$$

where $\Delta = (\epsilon_b - \epsilon_s)/(\epsilon_b + \epsilon_s)$. Inside the substrate we use a simple Drude model for the dielectric constant,[1]

$$\epsilon_b(\omega) = \epsilon_\infty - \left(\frac{\omega_p}{\omega}\right)^2 \frac{1}{1-1/i\omega\tau}, \tag{5}$$

where the plasmon frequency $\omega_p = (4\pi ne^2/m^*)^{1/2}$. Values for the effective mass m^* and relaxation time τ are chosen to represent silicon at carrier densities of $\sim 10^{16}$ cm^3. For the surface depletion layer we take the carrier density equal to zero with $\epsilon_s = \epsilon_\infty$. The quasielastic linewidth is then calculated by use of Eq. (2) with the depletion layer thickness d as the only parameter. The result is finally convoluted with the surface-state broadening and an 8-meV Gaussian transmission function and is plotted in Fig. 3 for $n = 5.6\times10^{16}$ cm^{-3} and $T = 300$ K. Here the linewidth decreases exponentially with a rate approximately proportional to $(\hbar\omega_{sp}/2E)kd$, where $\omega_{sp} = \omega_p/(1+\epsilon_\infty)^{1/2}$. The measured linewidth is seen to be significantly reduced from the $d=0$ value. A comparison of these calculations with the measured linewidths yields values of $d = 1050 \pm 150$ and 1900 ± 400 Å for $n = 5.6\times10^{16}$ and 8.9×10^{15} cm^{-3}, respectively. These values compare favorably with the space-charge depth estimated from the band bending at this surface as shown in the inset in Fig. 3 for $n = 5.6\times10^{16}$ cm^{-3}. The derived depletion region is shown by a step function at $d = 1050$ Å and is compared with the charge density obtained from solving Poisson's equation[12] for the band bending at the surface with the position of the Fermi level at 0.53 eV below the conduction-band minimum.

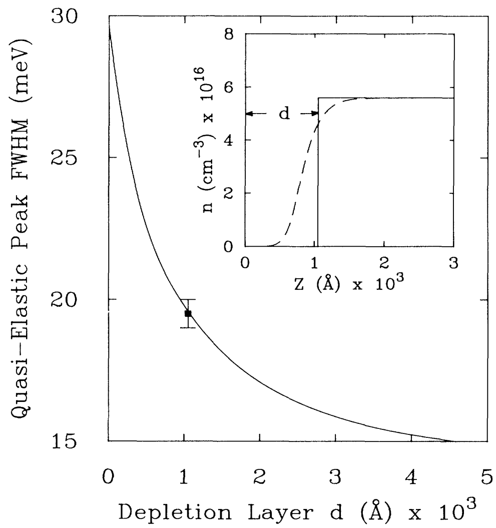

FIG. 3. The calculated quasielastic-peak width as a function of depletion layer depth for $n = 5.6\times10^{16}$ cm^{-3} and $T = 300$ K compared with the measured value (square). The inset shows the derived depletion layer profile (solid line) and is compared with the charge density obtained from solution of Poisson's equation for the surface band bending (dashed line).

For fixed d and n, the calculated linewidth as a function of temperature is shown by the solid lines in Fig. 1. A test of the above analysis is to account correctly for the measured temperature-dependent quasielastic scattering during thermal activation of free carriers across the silicon band gap. Figure 2 shows the calculated linewidth for various functional forms of d and n. For n and d constant, the calculated temperature-dependent linewidth increases monotonically which results from the Bose-Einstein factor in Eq. (2) and does not reproduce the measured results. Similarly, with d constant and the appropriate expression for n activated to produce the transition from extrinsic to intrinsic conduction, the calculated linewidth does not account for the measured data. This results from the exponential decrease in the linewidth with increasing n (or ω_p) for fixed d which was described above in Fig. 3. The experimental observations can be reproduced, however, with n activated and $d \propto n^{-1/2}$ as shown by the solid line in Fig. 2. The only parameters here are the initial depletion layer depth, which was found to be equal to 1900 Å, and the band-gap energy E_g. From our data we obtain a best fit with $E_g = 1.07 \pm 0.05$ eV which is in good agreement with the measured band gap of 1.1 eV for silicon. As seen in Fig. 2 the agreement with the measured linewidth is very good and the deduced functional form for $d \propto n^{-1/2}$ is exactly what is expected from consideration of the electrostatics of the band bending at the surface.[12]

In conclusion, conduction-band surface plasmon excitations are seen to contribute to the quasielastic scattering from the Si(111)7×7 surface in contrast to the well-defined losses observed on compound semiconductors. An analysis of this quasielastic scattering shows that these excitations are localized below the semiconductor surface space-charge layer as a result of band bending.

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