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Temperature-dependent two-dimensional plasmons at clean and hydrogenated Ge(001) surfaces

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High-resolution electron-energy-loss spectroscopy has been used to investigate the behavior of the quasielastic peak in low-energy electron scattering from clean and hydrogen-covered Ge(001) surfaces. A marked dependence of the quasielastic peak shape on both temperature and incident electron energy was found, and these peak shapes were successfully reproduced using dielectric theory simulations. The simulations provide strong evidence for the existence of a thin metallic surface layer supporting two-dimensional plasmons. The variation of peak shape with temperature arises from both changes in the Bose-Einstein spectrum of plasmon excitations and variation in the sheet electron density with temperature. The temperature dependence of the sheet electron density differs for the clean and hydrogen-covered surfaces.

I. INTRODUCTION

High-resolution electron-energy-loss spectroscopy (HREELS) is now a well-established technique for probing the electronic properties of semiconductor surfaces.[1–7] It is also ideal for examining the interaction of atomic hydrogen with Si and Ge surfaces by measurement of the vibrational losses associated with adsorbed hydrogen.[8–10] This system has significant technological impact, in particular because of the importance of epitaxial growth of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ using gaseous precursors such as disilane and germane.[8,11,12] In the majority of HREELS studies of near-surface electronic excitations in semiconductors, the excitations of primary interest involve three-dimensional (3D) surface plasmons due to oscillations of free charge in the valence or conduction bands. However, it is also possible to observe two-dimensional (2D) plasmon excitations of electrons in the conduction band of a III-V semiconductor material. Systems studied by HREELS include near-surface δ-doped layers in GaAs (Ref. 7) and the inversion layer at the surface of p-type InAs(001).[13] The reduced dimensionality of the plasmon excitation is a consequence of the plasma-active region being much thinner than the plasmon wavelength. This alters the plasmon dispersion relation so that the plasmon energy increases as the square root of the wave vector, rather than having a nonzero energy at zero wave vector as for a 3D excitation.[14] In the long-wavelength regime of specular HREELS, this 2D dispersion relation gives rise to multiple excitations of very low energy which broaden the elastic peak.[3,4,7,13]

In the cases of InAs and GaAs mentioned above, the oscillating electrons lie in the bulk conduction band, which is distorted over a short length scale by surface donors or δ-doping, respectively. However, on Ge and Si surfaces it has been possible to observe the effects of charge trapped in a true surface band rather than distorted bulk bands.[1–4] The reduced dimensionality of the plasmon excitations in such cases arises from the strong localization of the surface-state electron density within a few atomic layers of the surface plane. For example, the temperature-dependent quasielastic peak shape for HREELS on Si(111) has been analyzed in terms of multiple 2D plasmon excitations in a very narrow, partially filled surface band.[1,4] Surface states can be investigated more directly by photoelectron spectroscopy (PES) and inverse photoemission. Several studies have been performed on Ge(001) surfaces,[15–18] showing the presence of a surface state at the Fermi level, localized at the center of the surface Brillouin zone. A number of interpretations have been offered regarding the nature and origin of this surface state, and its apparent temperature sensitivity. The model of Kevan and Stoffel[16] involves a defect dangling-bond state, related to disorder in the dimers forming the (2×1) reconstruction, which can be quenched on cooling via a (2×1)-$c(4\times2)$ transition. Alternative interpretations include thermal excitation to a normally empty dangling-bond band just above the Fermi level[15,18] and thermal population of π^* antibonding surface states derived from bulk states near the Brillouin-zone center.[17] It appears that the precise surface reconstruction,[15,16] bulk doping level,[15,17] surface preparation method,[18] degree of surface contamination,[18] and surface hydrogen content[2,15] all influence the characteristics of the surface states at the Fermi level. However, the clean Ge(001) surface clearly shows metallic character at room temperature, in contrast to the semiconducting surface of Si(001). This leads to a composition-dependent metal-semiconductor transition which has been observed in recent HREELS studies of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy surfaces.[2]

In this paper we report on HREELS measurements of 2D plasmon excitations propagating at clean and hydrogen-covered Ge(001) surfaces. The emphasis is on the shape and width of the quasielastic peak, essentially in the energy-loss range ±60 meV. The observed quasielastic peak broadening depends on the surface termination, temperature, and incident electron energy, and has been modeled in terms of a thin plasma-active layer on top of an inert bulk. From the model parameters it is possible to derive the temperature dependence of the sheet electron density in the plasma active layer. This is found to decrease with temperature (in the available range) for the monohydride surface, but saturates at

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high temperatures for the clean surface, only dropping away at the lowest temperatures. The different temperature dependence of the surface electron densities in the two cases suggests a more complex surface-state behavior than previously thought.

II. EXPERIMENTAL DETAILS

Experiments were carried out in an ultrahigh vacuum chamber (base pressure 3×10^{-10} mbar) equipped with HREELS and low-energy electron diffraction (LEED). The HREEL spectrometer is based on a design by Ibach,[19] comprising a double-pass cylindrical monochromator and analyzer assembly, with the former rotatable. The spectrometer resolution was better than 3 meV when tuned ''straight through'' with no sample, with an electron energy range of 1–15 eV. Higher electron energies up to 60 eV were also employed in some cases, although with a somewhat degraded resolution. The specular scattering geometry was fixed for all experiments with an incident and scattered polar angle of 45°.

The Ge(001) samples were very lightly doped with antimony ($\sim1\times10^{14}\,\mathrm{cm}^{-3}$) and were introduced to the chamber with no chemical pretreatment. The substrate temperature could be measured by means of a thermocouple in close proximity to the sample, calibrated by an optical pyrometer. Experiments at various sample temperatures were performed by cooling the sample with a remote liquid-nitrogen reservoir and by radiative heating from a tungsten filament (temperature range 200–450 K). Substrate preparation began with thorough outgassing at 600 K, followed by argon-ion bombardment (600 eV, 2 μA) and annealing to 800 K. A final rapid anneal to 900 K resulted in a clean and well-ordered two-domain (2×1)-reconstructed surface. Hydrogen dosing was achieved by introducing molecular hydrogen to the chamber while heating a tungsten cracking filament positioned ~5 cm from the sample. Molecular hydrogen doses were recorded and the overall cracking efficiency of the filament was unknown, although the latter should be constant throughout the experiments. Experiments were carried out primarily on clean and monohydride surfaces, the latter showing a sharp (2×1) two-domain LEED pattern. Pure monohydride surfaces were prepared by exposure of the clean surface to 500 L H_2 at a substrate temperature of 500 K, and were characterized by Ge-H bending and stretching modes at 68.8 and 246.7 meV, respectively.[9] The Ge-H_2 scissor mode at 102.9 meV was not present on the pure monohydride surface.

III. RESULTS AND DISCUSSION

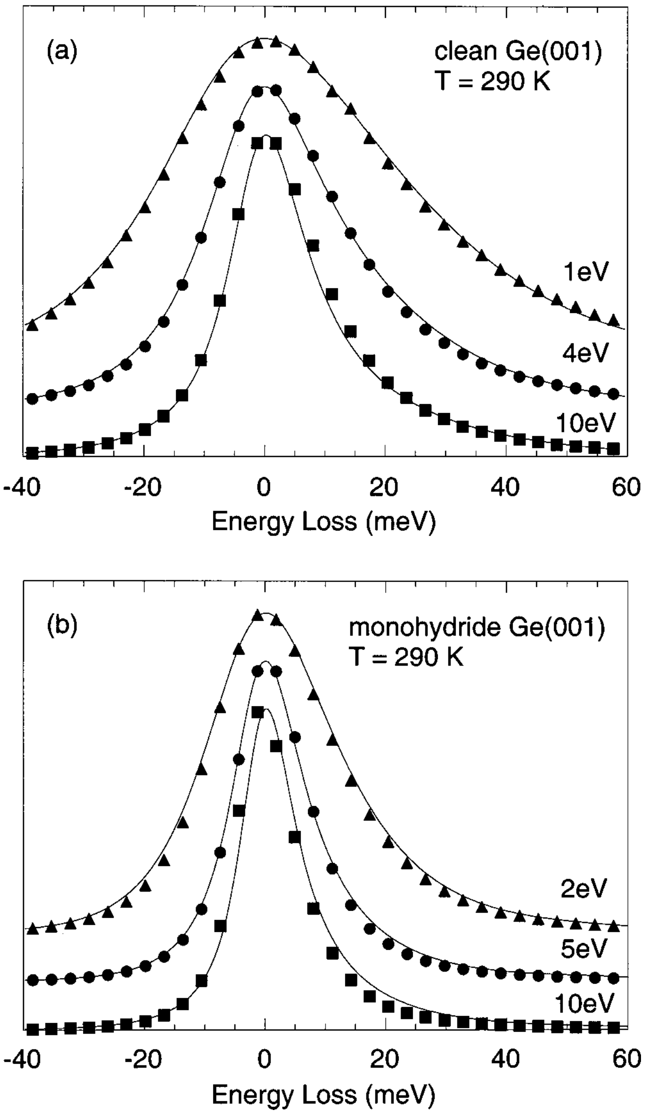

FIG. 1. HREEL spectra obtained from Ge(001) at room temperature and different electron energies for (a) the clean surface, and (b) the monohydride surface. For each electron energy, every fifth experimental point is shown along with solid curves generated by dielectric simulations. The curves are vertically offset for clarity.

Figure 1(a) shows a series of three HREEL spectra recorded at electron energies of 1, 4, and 10 eV from clean Ge(001) at room temperature. The quasielastic peak is much broader than the instrumental width (~4 meV) in all cases. There is a pronounced asymmetry between the energy loss and gain sides, and the full width at half maximum (FWHM) increases dramatically with decreasing electron energy. The tail of the quasielastic peak shows considerable intensity out to energy losses greater than 60 meV, particularly at lower electron energies. The solid curves are generated by dielectric theory simulations which will be discussed later. Very similar quasielastic peak shapes are observed for the monohydride Ge(001) surfaces, and three typical spectra are shown in Fig. 1(b). Again, the FHWM increases for decreasing electron energy, although the values are lower than for corresponding clean surface spectra.

A complete set of FWHM values (ΔE) for clean Ge(001) at room temperature and different electron energies is shown in Fig. 2. The plot shows the strong reduction of FWHM with increasing electron energy, and is fitted by a function of the following form (solid line):

$$\Delta E=\Delta E_0+\frac{A}{\sqrt{E_i}}, \tag{1}$$

where ΔE_0 is the instrumental broadening of 4 meV, A is the sole fitting parameter, and E_i is the electron incidence en-

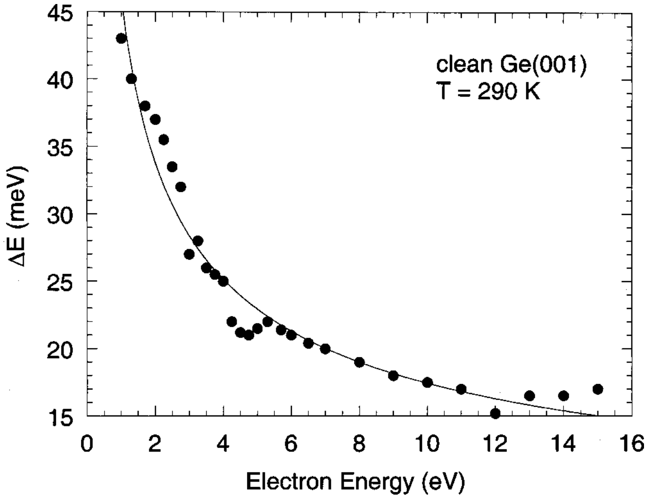

FIG. 2. The energy dependence of the quasielastic peak FWHM at room temperature for clean Ge(001). The experimental data are shown as solid circles, while the solid line is a fit according to Eq. (1).

ergy. Very similar energy-dependent behavior is observed for the monohydride surface and for both surfaces at other temperatures.

The observed energy dependence arises from changes in the momentum transfer from the electron to surface excitations in specular dipole scattering.[1] It can be explained by assuming the presence of low-energy 2D excitations whose wave vector is determined by the momentum transfer. In this model the quasielastic peak broadening arises from 2D plasmons propagating in a thin surface layer. The expected energy loss $\hbar\omega_{2D}$ due to 2D plasmons can be derived as[13]

$$\hbar\omega_{2D}=\frac{n_{2D}}{m^*}\frac{\hbar e^2\sin\theta_i}{\varepsilon_0\varepsilon(\infty)}\sqrt{\frac{m_e}{E_i}}. \tag{2}$$

In the above equation n_{2D} is the sheet electron density in the surface layer and θ_i is the incident polar angle of the electrons relative to the surface normal. Assuming that only single-plasmon losses are observed, and that the plasma frequency is not significantly larger than ΔE_0, then the following approximation can be made:

$$\Delta E\approx\hbar\omega_{2D}+\Delta E_0. \tag{3}$$

The quasielastic peak broadening should then behave in a manner described by Eq. (1), as observed in the experiments. This simple treatment neglects possible effects due to the changes of effective probing depth in specular HREELS, which is approximately the inverse of the plasmon wave vector.[1] However, for a 2D excitation confined sufficiently close to the surface, such effects should be minimal. Potentially more serious is the multiple excitation of low-energy plasmons as well as quasielastic peak broadening on the energy gain side due to thermally activated plasmon excitations.[1,4] In particular, the validity of Eq. (3) is suspect for thermal energies ~25 meV and $\Delta E_0 \sim 4$ meV. Although the effects on elastic peak broadening of multiple plasmon excitations can be treated analytically,[4] in the present paper we use dielectric theory simulations.[20] In these calculations, single-loss spectra are convoluted with a bosonlike distribution of multiple losses and gains.[21] This proves to be a crucial correction to the single-loss approach of Eq. (3), and allows investigation of the effects of temperature in a robust way. However, 2D plasmons, as described by Eq. (2), remain the source of the broadening.

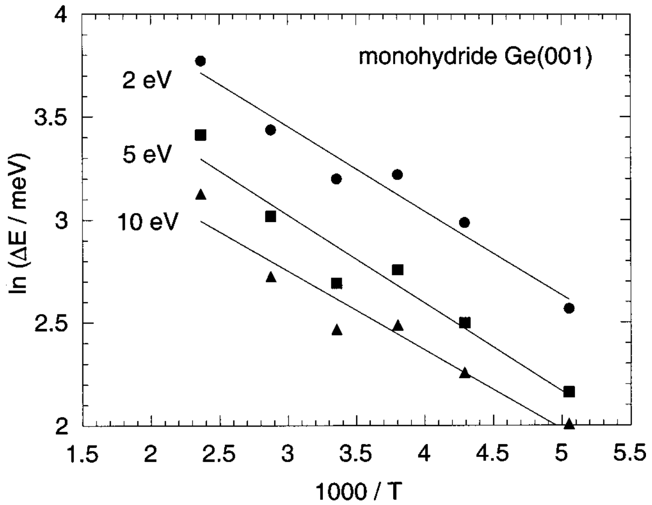

FIG. 3. The temperature dependence of the quasielastic peak FWHM for monohydride Ge(001)-H at room temperature and for three different electron energies (2, 5, and 10 eV). The activation energy derived is 35 meV. For clean Ge(001), a value of 24 meV is obtained.

The temperature dependence of the FWHM for the monohydride surface is shown in Fig. 3 for three different electron energies. The plot clearly shows that the peak widths follow an exponential dependence, with a very similar activation energy for all three energies. For the monohydride surface, this energy is 35±3 meV, while the clean surface shows similar behavior and yields an activation energy of 24 ±3 meV. These results, together with Eq. (2), *suggest* that the sheet electron density arises from a thermally activated process. Such a process could be the thermal promotion of bulk electrons into a band of 2D localized surface states lying just above the Fermi level.[15,17,18] However, this interpretation of the HREELS results again neglects the possible contribution of multiple plasmon excitations. The temperature-dependent behavior was also modeled using dielectric theory and three spectra from the clean surface at fixed electron energy are shown in Fig. 4, both experimental data and dielectric theory fits. There is a marked increase of the FWHM with increasing temperature as observed for the monohydride surface.

We now discuss the dielectric model used to fit the spectra shown in Figs. 1 and 4 (as well as many other spectra not shown). The theory is based on a layered model of the substrate and allows complete HREEL spectra to be generated.[21] The input to the general model comprises only the dielectric functions of each layer. For the present system, this comprises plasmon excitations and the background dielectric constant only. The plasmon dielectric contribution requires only a plasma frequency and a plasmon damping rate; plasmon spatial dispersion is neglected in the low wave-vector regime explored here.[5,22] To check the effects of band bending and bulk charge, we first attempted to fit the data using conventional models for a semiconducting medium affected

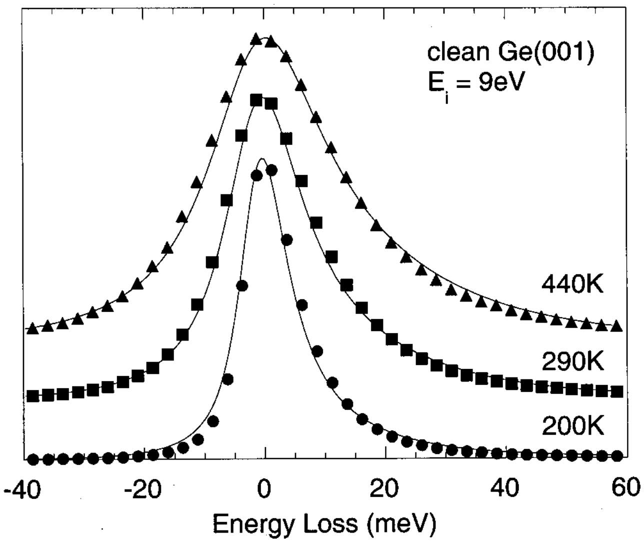

FIG. 4. Three HREEL spectra obtained at an electron energy of 9 eV from clean Ge(001) as a function of surface temperature. Solid lines are generated by dielectric theory simulations.

TABLE I. The best-fit plasma frequencies (in meV) for clean and monohydride Ge(001)-(2×1) as a function of temperature. The layer thickness was 6.5 ± 0.5 Å and the plasma damping was fixed at 20 meV.

T (K)	Clean Ge(001)	H-Ge(001)
200	75	58
230	91	67
260	104	75
290	100	73
365	102	81
440	100	103

by upward or downward band bending. However, the very low doping level of the present sample produces a negligible bulk plasma frequency (0.2 meV) and inefficient screening, leading to very wide space-charge regions (~1 μm). It proved impossible to fit the spectra with such a model. We therefore turned to an alternative two-layer system, for which there are only three parameters: the thickness d of the plasma-active layer, the plasma frequency ω_p, and the plasma damping Γ. The semi-infinite bulk region is assumed to have no frequency-dependent contribution to its dielectric function. The model is shown schematically in Fig. 5, and best-fit plasma frequencies are summarized in Table I.

The free electrons that give rise to plasma oscillations in the active surface layer occupy a discrete band of surface states localized within a few atomic layers of the surface. The plasma frequency relates to the 3D electron density in the usual way and, with the layer thickness fixed, the sheet electron density can then be calculated. There are two problems with this method. Firstly, the uniform surface layer represents what is presumably an electron density decaying smoothly into the bulk, and its precise thickness (6.5 Å in the model) is of limited physical meaning. Secondly, the effective mass m^* for electrons in the 2D surface band is unknown. An estimate of the effective mass associated with conduction within a lattice of localized surface orbitals was given by Persson and Demuth (Appendix E of Ref. 4) for Si(001), resulting in a value of $m^*\approx60$. Applying their method to Ge(001) yields a value of $m^*\approx15$. Because of the uncertainty of these values, the sheet electron density can only be considered an approximation based on the plasma frequency. It should also be pointed out that care must be taken in deriving the plasma frequency itself, which is only one of three model parameters. Unlike space-charge layer models, bulk band-structure calculations are of no help in guiding parameter choice.[5–7,22–24]

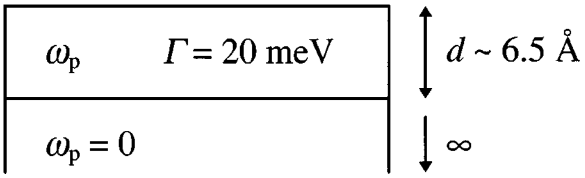

FIG. 5. A summary of the two-layer dielectric model used to fit the HREEL spectra. The main variable parameter is ω_p, the active layer plasma frequency. The semi-infinite bulk contains no plasma dielectric term.

In general, it is crucial to model several spectra at different electron energies using the same parameter set (with the possible exception of the plasma-damping term[23,24]) in order to produce reliable and unique fits in HREELS. We were able to fit the various sets of experimental spectra across the whole electron-energy range (1–15 eV) with single parameter sets, and examples are shown in Fig. 1. The value of the layer thickness d has a significant effect on the spectra. If d is too large, distinct intensity can be discerned in the 3D plasmon mode (loss energy is proportional to plasma frequency). This is particularly important when the plasma damping Γ is set too low. There is no evidence for such modes in the experimental spectra and so this sets an upper limit on d. In fact, when refining the fits, d mainly affects the intensity at higher loss energies (>25 meV). Values of d in the range 6.0–7.5 Å were found to produce the best fits, and it was generally possible to fix d at 6.5 Å.

There is a more complex relationship between the curve shapes and the values of ω_p and Γ. For 3D plasmon modes it is possible to fit the two parameters separately, with the former defining the loss energy and the latter the width and intensity of the peak.[5] However, for 2D modes which fall within the broadened quasielastic peak, it is possible to compensate for reduction of the plasma frequency by also reducing the damping. For example, it is possible to obtain a rather similar simulated spectrum if the plasma frequency is halved by also sharply reducing the damping. The reason for this is simply that multiple excitations of low-energy plasmons dominate the quasielastic peak broadening, and intense (low-damped) plasmons of lower energy give equivalent broadening to less intense (higher-damped) plasmons of higher energy. This clearly leads to potential difficulties in obtaining a unique parameter set, although certain limits can be set on the variation allowed.

We have set the plasma damping at a constant value of 20 meV or $(5\ \mathrm{ps})^{-1}$. The plasmon damping rate depends on several mechanisms: Landau damping, structural damping, and electron scattering by phonons and defects.[23,24] Landau damping is suppressed at the long wavelengths here, and

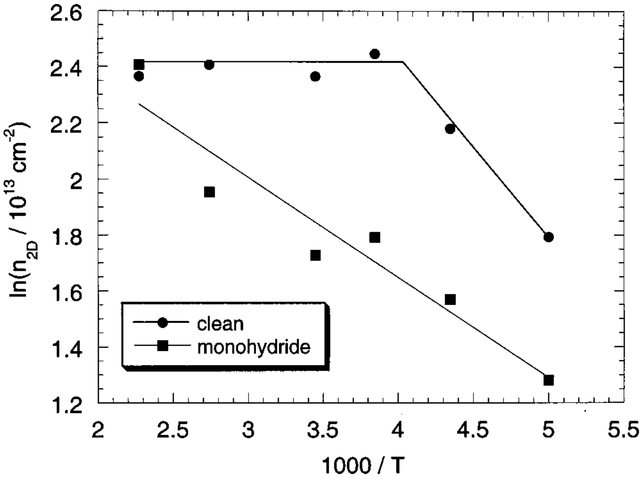

FIG. 6. The sheet electron density obtained from dielectric theory simulations of clean and monohydride Ge(001) as a function of temperature.

structural damping should be relatively unimportant for the very thin surface layer,[24] and so the damping value is expected to be independent of incident electron energy. However, because of the interdependence of simulated spectra on ω_p and Γ, it is not possible to use the temperature-dependent measurements to gauge the relative importance of phonon and surface defect scattering on the momentum scattering rates of electrons participating in the plasmon oscillations.[22–24] If the plasma damping value of 20 meV is an underestimate, then we obtain higher plasma frequencies from the fitting process, and would hence expect significantly higher sheet electron densities than shown here (the electron density varies as the square of plasma frequency).

Bearing in mind the above caveats, the sheet electron density has been derived from best-fit plasma frequencies for both clean and monohydride surfaces as a function of temperature. The results are shown in Fig. 6, and although the absolute error in the electron density is high, its variation with temperature should be accurate in the absence of strongly temperature-dependent plasma damping. The maximum value of the sheet electron density for both surfaces occurs at the highest temperatures and is $1.1\times10^{14}\,\text{cm}^{-2}$. For the clean surface, this value is maintained as the temperature is lowered, and only at the lowest temperatures does the electron density decrease. By contrast, for the monohydride surface, the electron density falls steadily with decreasing temperature. This behavior indicates that at the lower temperatures accessible in our system, for the clean surface, and at all available temperatures, for the monohydride surface, there is thermal activation of electrons into the 2D surface band. From Fig. 6 activation energies of 52 ± 12 meV (clean, low temperature) and 31 ± 5 meV (monohydride) are obtained. It should be noted that the former value is based on only three experimental points, and also that these results are independent of the changing Bose-Einstein spectrum of 2D plasmon losses with temperature. This factor is accounted for by the dielectric theory simulations and it is why the activation energies differ from those obtained by a direct fitting of the quasielastic peak width. Qualitatively, these results compare well with previous HREELS and PES studies, providing strong support for thermal excitation of electrons into a surface band[15,18] and for a reduction of the surface electron density with monohydride formation.[2,15]

The saturation of surface-band electron density at high temperatures has not been reported previously. The saturation electron density corresponds to 9% of the surface atoms, meaning that the surface states are not associated with regular surface dimers. However, this may be an underestimate, particularly if the plasmon damping term in the simulations is too small. Improved estimates of this parameter (as well as the effective mass for the 2D surface band) would be helpful, allowing a much better understanding of the detailed nature of the band. An approximate calculation[4] of the width of the surface band based on the effective mass and electron density yields a value of 20 meV, indicating the localized character of the states contributing to it. Our present results do not allow us to expand on the suggestion that differences in Fermi-level pinning by defect states give rise to a different thermal population of the dangling-bond band.[15] It is possible that hydrogen exposure alters the position of the surface Fermi level relative to the valence band and hence gives rise to the different activation energies for thermal population of the surface band derived here. Finally we note that the description of the Ge(001) surface as ''metallic''[2,16] is not strictly correct since thermal activation is necessary to promote electrons into the normally empty surface band whose minimum lies above the Fermi level.

IV. CONCLUSIONS

We have used HREELS to study the low-energy 2D plasmon excitations propagating at Ge(001) surfaces, both clean and hydrogen terminated. The behavior of the sheet electron density as a function of temperature has been extracted from dielectric modeling and is found to be thermally activated at lower temperatures, saturating at higher temperatures for the clean surface. The maximum sheet electron density has been found to be $1.1\times10^{14}\,\text{cm}^{-2}$, but may be higher if either the electron effective mass in the surface band is larger than the estimated value of 15 or the plasmon-damping rate is higher than the assumed value of $(5\ \text{ps})^{-1}$. The electron density is reduced on the monohydride surface compared with the clean surface, except at the highest temperatures, but the surface retains its metallic character. Activation energies to the surface band are found to be 52 ± 12 meV and 31 ± 5 meV for the clean and monohydride surface, respectively. These energies are very different from those obtained by direct fitting of the quasielastic peak width, due to the neglect of changes in the Bose-Einstein spectrum of plasmon excitations in this simpler procedure.

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