High Temperature Surface Metallization of Ge(111) Detected by Electron Energy Loss Spectroscopy

S. Modesti,[1] V. R. Dhanak,[1,2] M. Sancrotti,[1] A. Santoni,[3] B. N. J. Persson,[4] and E. Tosatti[5]

[1]*Laboratorio Tecnologie Avanzate, Superfici e Catalisi–Istituto Nazionale per la Fisica della Materia, Padriciano 99, I-34012 Trieste, Italy*

[2]*Interdisciplinary Research Center in Surface Science, Liverpool University, P.O. Box 147, Liverpool L69 3BX, United Kingdom*

[3]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France*

[4]*Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany*

[5]*International School for Advanced Studies (SISSA), Via Beirut 2, I-34014 Trieste, Italy and International Center for Theoretical Physics (ICTP), P.O. Box 586, I-34014 Trieste, Italy*

(Received 31 May 1994)

Using electron energy loss spectroscopy (EELS) we show that the Ge(111) surface is metallic for $T > 600$ K. The surface conductivity increases almost linearly with temperature for $600 < T < 1040$ K but exhibits a steplike increase at $T = T_c \approx 1040$ K after which it stays constant up to the bulk melting temperature $T_m = 1210$ K. The data support a picture where at $T \approx 1040$ K incomplete surface melting takes place. The surface free carrier concentration deduced from the EELS intensity is consistent with the assumption that only the top surface bilayer has melted, in agreement with recent theoretical work.

PACS numbers: 68.35.Rh, 68.35.Ja, 73.20.–r, 79.20.Kz

The Ge(111) surface exhibits a number of phase transitions as a function of temperature. The stable low-temperature phase has a $c(2 \times 8)$ adatom structure [1]. At $T \approx 600$ K the surface structure changes to (1×1) where the adatom lattice melts [2]. This state persists up to $T = T_c \approx 1050$ K. At this temperature, which is only 160 K below the bulk melting temperature $T_m = 1210$ K, different types of spectroscopies have detected a new structural phase transition. However, conflicting pictures have been offered for the state of the surface between T_c and T_m [3].

Recently, Takeuchi, Selloni, and Tosatti [4] performed a first-principles molecular dynamics study of the Ge(111) surface close to (but below) the bulk melting temperature T_m. The simulations show that the first bilayer of this surface becomes dynamically disordered, with liquidlike hopping diffusion. At the same time, the surface electronic structure acquires a metallic character, as in liquid Ge. Remarkably, however, this state does not propagate onto the second and deeper bilayers, which remain solid, semiconducting, and nondiffusive.

In this Letter we present high-resolution electron energy loss spectroscopy (EELS) data which show that massive surface metallization takes place at $T_c < T < T_m$, providing strong additional support to the incomplete melting hypothesis. The basic idea is the following: at high temperature, say, $T \sim 1100$ K, the concentration of thermally excited carriers in the bulk Ge is so high that, if the Ge surface were insulating, an intense surface plasmon excitation should be visible in the EELS spectrum at $\hbar\omega \approx 0.1$ eV. In contrast, if the first bilayer of Ge is instead in a melted metallic state characterized by a conductivity similar to that of bulk liquid Ge, then the plasmon will be completely screened out and invisible in dipole EELS, while an intense broadband EELS background should appear.

The sample used in this study was an n-type Ge(111) wafer with a donor (Sb) concentration of 7×10^{15} cm^{-3}. The $c(2 \times 8)$ surface was prepared by repeated cycles of Ne^+ sputtering and annealing at 1100 K in UHV. The cleanliness of the sample was periodically monitored by Auger spectroscopy. During the EELS data acquisition the sample was directly Ohmically heated by a current pulsed at a few Hz. Data acquisition was suspended during the part of the cycle where the current was on. The temperature was measured by an infrared pyrometer for $T > 880$ K and by a thermocouple placed on the sample holder close to the sample for $100 < T < 880$ K. The temperature readings were calibrated against the Ge melting point, determined by final melting of the sample. Because of the pulsed Ohmic heating, the temperature over the sample was not uniform and constant, but the maximum temperature difference between points of the sampled surface was less than 20 K, and the peak to peak temperature fluctuations were less than 20 K. The vapor pressure in the chamber rose to a maximum of 3×10^{-8} Pa when the sample was at $\sim$1200 K. The EELS spectra were taken by a Leybold-Heraeus ELS22 spectrometer in the specular geometry with a primary energy of $E_0 = 21$ eV and an incidence angle of $\alpha = 65°$. The LEED pattern of the sample was a well defined $c(2 \times 8)$ for $T < 600$ K and (1×1) with broad intensity maxima in the vicinity of the $(0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2})$ reflections between $\sim$600 and $\sim$1000 K. Above this temperature only weak integer order spots were visible.

Figure 1 shows the raw EELS spectra as a function of increasing temperature. At low temperatures ($T = 110$ and 170 K) the loss background is very weak and the

0031-9007/94/73(14)/1951(4)$06.00

quasielastic peak is sharp [full width at half maximum (FWHM) $\Gamma_0 = 15$ meV]. As the temperature increases the quasielastic peak broadens [5]. This is most likely caused by multiple excitation of surface plasmons associated with the bulk thermally excited free carriers. This type of broadening has been observed earlier for Si [6] and GaAs [7] crystals and can be quantitatively analyzed using dipole scattering theory. The linewidth (FWHM) Γ depends on the surface plasmon energy which can be calculated from the known bulk free carrier concentration. At T = 550 K we get $\hbar\omega_{sp} \approx 4.5$ meV and, from the theory presented in Ref. [7], $\Gamma = 26$ meV. The linewidth of the quasielastic peak at this temperature is (see Fig. 1) 31 meV. Accounting for the finite experimental resolution (15 meV from the low-temperature spectra in Fig. 1) gives the experimental linewidth $\Gamma_{exp} = 27$ meV in excellent agreement with theory. Hence, the EELS spectra in Fig. 1 for temperatures up to about 550 K behave just as expected for an *insulating Ge surface*.

An insulating surface is indeed expected so long as the $c(2 \times 8)$ adatom-restatom reconstruction is stable. Electron transfer from the adatom to the restatom, which is the basic stabilizing mechanism of this reconstruction [8], naturally provides a sizable surface-state gap [9].

As the temperature is increased to ~750 K the frequency of the plasmon resonance grows high enough to become visible as a shoulder in the loss spectrum. For example, at $T = 900$ K the carrier concentration in the bulk is about 4×10^{18} cm^{-3} (see Ref. [10]) so that

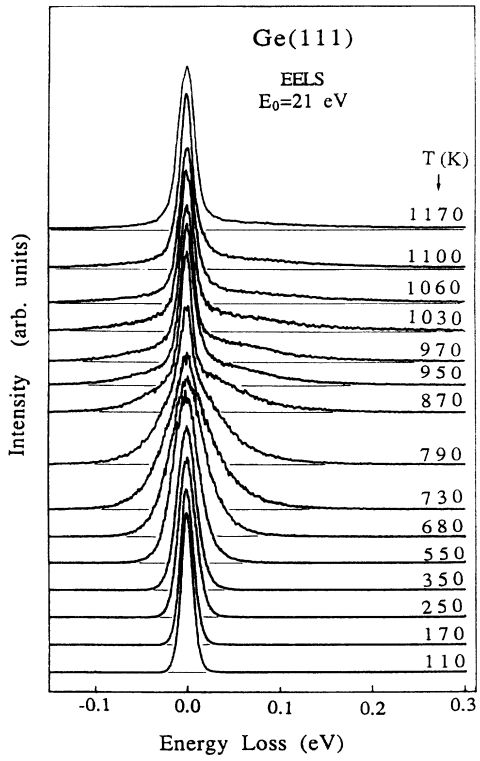

FIG. 1. Sequence of EELS spectra as a function of temperature, for $E_0 = 21$ eV and $\alpha = 65°$.

$\hbar\omega_{sp} \approx 40$ meV which is roughly the center position of the shoulder in Fig. 1 [11]. The center position of the surface plasmon structures in the loss spectra in Fig. 1 for $700 < T < 1000$ K scales with the temperature roughly as expected based on the temperature dependence [10] for the carrier concentration in the bulk. However, the observed plasmon loss intensity is weaker than predicted by dipole scattering theory under the assumption of a fully insulating surface. As we will see below, this is most likely connected with weak surface metallization, above the $c(2 \times 8)$ deconstruction transition, but still well below T_c. It has recently been shown [12] that the jump of an adatom on a semiconductor (111) surface implies a corresponding electron "backflow" from the former restatom, which is being mounted to the new one which is freed behind. If this process is followed adiabatically, the backflow is seen to originate from an electronic level crossing, which corresponds to a closing of the surface-state gap, taking place while the adatom is negotiating the barrier between a T_4 and an H_3 site. It is therefore natural that a fast and generalized jumping of adatoms, such as that which is believed to take place between 600 and 1000 K, should produce a nonzero average concentration of surface free carriers, as well as the progressive washing out of the surface-state gap.

Finally, for $T > 1050$ K no plasmon loss can be seen anymore. Here, the surface conductivity seems to have grown so large as to screen out the bulk completely, exactly as expected [4] for incomplete surface melting.

If the surface metallization hypothesis is indeed correct, then it should be possible to cross-check it with other independent features in the EELS spectrum. In particular associated with surface metallicity there should be a broadband EELS background intensity, which would be totally absent for an insulating surface. The quantity $I(T)$ in Fig. 2(a) is the temperature dependence of the loss intensity integrated from 0.15 to 0.3 eV, normalized to the total EELS intensity between −0.15 and 0.3 eV. For $T < 500$ K, I is practically zero, while for $T > 550$ K it increases monotonically with temperature. This loss intensity is directly related to the surface conductivity (see below), thus confirming that the surface becomes increasingly metallic as the temperature rises above the $c(2 \times 8)$ deconstruction temperature.

We can analyze the data in Fig. 2(a) quantitatively. In dipole scattering, the probability for an electron to scatter inelastically is given by [13] the product of a "kinematic prefactor" and the "loss function" Img which contains all the information of the substrate. The function $g(q, \omega)$ depends on the momentum transfer $\hbar\mathbf{q}$ parallel to the surface and on the energy transfer $\hbar\omega$ [13]. We assume that the Ge(111) surface is covered by an infinitely thin conducting layer of Ge. In this case Img is given by [14,15]

$$\mathrm{Im}g = -2\mathrm{Im}\left[\epsilon(\omega) + 1 - \frac{4\pi n_s e^2 q}{m_s \omega(\omega + i/\tau_s)}\right]^{-1}, \quad (1)$$

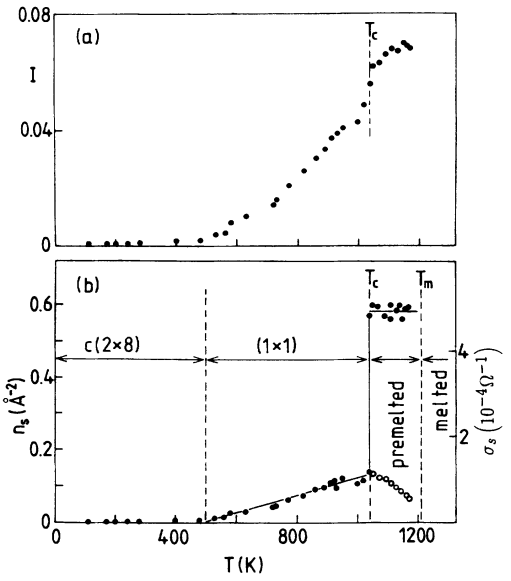

FIG. 2. (a) Temperature dependence of the integrated loss intensity I. This is the ratio between the EELS background intensity integrated from 0.15 to 0.3 eV and normalized by the total integrated intensity between −0.15 and 0.3 eV. (b) The surface conductivity σ_s as a function of temperature as deduced from (a) using dipole scattering theory.

where

$$\epsilon(\omega) = \epsilon_0 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}.$$

Here n_s is the number of conduction electrons per unit area, m_s their effective mass, and τ_s a relaxation time of the thin conducting film. The bulk dielectric function $\epsilon(\omega)$ has a contribution $\epsilon_0 \approx 16$ from interband transitions, and $\omega_p^2 = 4\pi n_0 e^2/m^*$ is the bare plasma frequency due to the (thermally excited) free carriers (concentration n_0 and effective mass m^*) and τ a Drude relaxation time. In our case $\omega \ll 1/\tau_s$ so that

$$\mathrm{Im}g \approx -2\mathrm{Im}[\epsilon(\omega) + 1 + i(4\pi n_s e^2 \tau_s/m_s)(q/\omega)]^{-1}. \quad (2)$$

In the absence of a conducting surface layer, $\mathrm{Im}g(\omega)$ has a peak at $\omega_{sp} = \omega_p/\sqrt{\epsilon_0 + 1}$ associated with the surface plasmon resonance.

Figure 2(b) shows the surface conductivity (right-hand scale) $\sigma_s = n_s \tau_s e^2/m_s$ obtained from Fig. 2(a) using dipole scattering theory. The scale on the left-hand side gives the surface free carrier concentration n_s deduced from the surface conductivity *under the assumption* that the ratio τ_s/m_s is equal to that of liquid Ge, i.e., $\tau_s \approx 3 \times 10^{-16}$ s if $m_s = m_e$. We note that the surface conductivity practically vanishes for $T < 500$ K and that it increases approximately linearly with temperature for $500 < T < 1040$ K. At $T \approx 1040$ K there is a steplike increase in n_s. Finally, for $T > 1040$ K up to the bulk melting temperature the surface conductivity is constant and the surface free carrier concentration equals $n_s \approx 0.58$ Å^{-2} under the assumption that the ratio τ_s/m_s is the same as in bulk melted Ge. This should be compared with $n_s \sim 0.3$ Å^{-2} expected if the first bilayer of Ge atoms has melted and if each Ge atom contributes roughly two "free" electrons, as suggested in the calculations of Takeuchi, Selloni, and Tosatti [16]. This value is in fact slightly lower than that extracted from EELS. However, it is likely that the relaxation time τ_s could be somewhat larger than the Drude relaxation time of bulk liquid Ge, partly because of the higher ordering of the Ge ions in the melted Ge layer as compared with bulk melted Ge and partly because of the smaller phase space into which a conduction electron in the melted bilayer can be scattered.

A comment is in order on the steplike increase in the surface conductivity at $T \approx 1040$ K. First, we note that for a given EELS intensity I there are always two corresponding solutions for the surface conductivity σ_s: a "high"-conductivity solution σ_H and a "low"-conductivity solution σ_L. Which of these two solutions is correct must be judged on physical grounds [17]. The reason why two solutions occur is physically simple, and reminiscent of optimal impedance matching in an electrical circuit. If $\sigma_s \to 0$, the system is insulating and has no low-energy excitations. On the other hand, if $\sigma_s \to \infty$ the effective electric field in the conducting layer is totally screened out. Hence, $I \to 0$ as $\sigma_s \to 0$ and as $\sigma_s \to \infty$. For any given finite I there will therefore be two solutions for σ_s.

In the present case, it is obvious that we must start with the low-conductivity solution σ_L at low temperatures. But at $T \approx 1040$ K, where I jumps up by only about 50%, we must switch to the high-conductivity solution. If we stay with the low-conductivity solution, in fact, we would have for $T > 1040$ K that the surface conductivity decreases, as indicated by the open circles in Fig. 2(b). This seems peculiar, but it might still be the correct solution. More seriously, however, with this choice it is no longer possible to describe the frequency dependence of the electron energy loss background. That is, with the small surface conductivity σ_L which would occur at, say, 1170 K, the surface plasmon associated with the bulk free carriers would not be screened out at all, contrary to what is observed. Hence, the low conductivity is unphysical for $T > 1040$ K. The high conductivity, instead, accounts very well for the full low-energy EELS spectrum. Figure 3 shows the experimental (thin wavy line) and theoretical (thick solid line) loss intensity for $T = 1170$ K calculated from dipole scattering theory with the loss function (2). Note that there is a perfect agreement between theory and experiment in the whole frequency interval $0.05 < \hbar\omega < 0.3$ eV. This proves that $\hbar\tau_s^{-1} \gg 0.3$ eV as expected from the bulk Drude relaxation time of liquid Ge, $\hbar\tau_D^{-1} \approx 2.1$ eV. The dashed line in Fig. 3 shows the calculated loss spectra [18] *if* the Ge(111) surface were instead insulating [i.e., $n_s = 0$ in (2)]. The loss peak centered at $\hbar\omega \approx 0.1$ eV is, of course, the surface plasmon excitation associated with the thermally excited bulk free carriers. In the experimental spec-

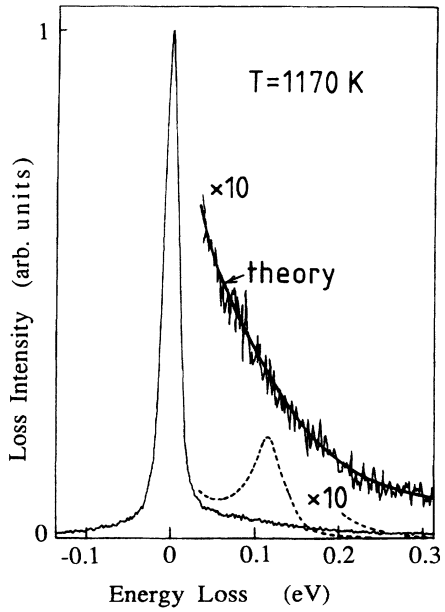

FIG. 3. Thin wavy line: experimental EELS spectra for $T = 1170$ K ($E_0 = 21$ eV, $\alpha = 65°$). Thick solid line: theory with $n_s = 0.6$ Å^{-2}. Dashed line: theory with $n_s = 0$.

tra (as well as in the complete theory, thick solid line in Fig. 3) this surface plasmon resonance has disappeared. The thin metallic layer present on the high-temperature Ge(111) surface has screened out (on the vacuum side) the electric field of the surface plasmon associated with the bulk carriers.

To summarize, we have shown that the Ge(111) surface twice changes its electronic character, in correspondence with its two thermal phase transitions. At the $c(2 \times 8) \rightarrow (1 \times 1)$ deconstruction transition near 600 K, it turns from insulating to weakly metallic. At the high-temperature transition near 1050 K, it jumps from weak to unmitigated metallicity, with at least two free carriers per surface atom. This large metallicity supports the picture of an incompletely melted surface up to the bulk melting point.

Work at SISSA is partly supported by the Istituto Nazionale Fisica della Materia (INFM), by the European Research Office, and by the EEC Human Capital and Mobility scheme under Contracts No. ERBCHBGCT92 0180, No. ERBCHRXCT92 0062, and No. ERBCHRXCT93 0342.

[1] P.W. Palmberg and W.T. Peria, Surf. Sci. **6**, 57 (1967); D.J. Chadi and C. Chiang, Phys. Rev. B **23**, 1843 (1981).

[2] R.M. Feenstra *et al.*, Phys. Rev. Lett. **66**, 3257 (1991); I. Hwang and J. Golovchenko, Science **258**, 1119 (1992).

[3] E.G. McRae and R.A. Malic, Phys. Rev. Lett. **58**, 1437 (1987); Phys. Rev. B **38**, 13163 (1988); S. Modesti and A. Santoni, Solid State Commun. **72**, 315 (1989); M. Abraham, G. Le Lay, and J. Hila, Phys. Rev. B **41**, 9828 (1990); A. Mak *et al.*, Phys. Rev. Lett. **66**, 2002 (1991); R.G. Silfhout, thesis, University of Leiden, 1992; A.W. Denier van der Gon *et al.*, Surf. Sci. **241**, 335 (1991); T.T. Tran *et al.*, Surf. Sci. **281**, 270 (1993); C. Meli, E.F. Greene, G. Lange, and J.P. Toennies (to be published).

[4] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. **72**, 2227 (1994).

[5] Interestingly, for the metastable (2×1) reconstructed Ge(111) surface the temperature dependence of the quasielastic peak is again very different from that of the $c(2 \times 8)$ reconstructed surface [see Phys. Rev. B **40**, 7819 (1989)]. In the (2×1), even for an intrinsic crystal, broadening of the quasieleastic peak starts already for $T \sim 100$ K and reaches a maximum around room temperature. The Fermi level at the (2×1) surface is in fact pinned close to the valence band edge giving rise to a high-density hole plasma in a thin surface layer of width ~100 Å. The decrease in the line broadening observed for $T > 300$ K is very likely related to the transition from the metastable (2×1) structure to the stable (for $T < 570$ K) $c(2 \times 8)$ phase, where the Fermi level at the surface is pinned about 0.1 eV above the valence band edge.

[6] U. Backes and H. Ibach, Solid State Commun. **40**, 575 (1981); J.A. Stroscio and W. Ho, Phys. Rev. Lett. **54**, 1573 (1985).

[7] L.H. Dubois, B.R. Zegarski, and B.N.J. Persson, Phys. Rev. B **35**, 9128 (1987).

[8] R.D. Meade and D. Vanderbilt, Phys. Rev. B **40**, 3905 (1989).

[9] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. **69**, 648 (1992).

[10] F.J. Morin and J.P. Maita, Phys. Rev. **94**, 1525 (1954).

[11] The width of the surface plasmon resonance can be estimated from the bulk Drude relaxation time τ which can be calculated form the observed conductivity (see Ref. [10]) using $\tau = m^*\sigma/n_0e^2$. For $T \approx 1000$ K, $\sigma = 500/\Omega$ cm, and $\hbar/\tau \approx 18$ meV, but the width of the surface plasmon resonance may be wider than indicated by this bulk damping because of nonlocal dielectric effects; see S.R. Streight and D.L. Mills, Phys. Rev. B **38**, 8526 (1988).

[12] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. B **49**, 10757 (1994).

[13] See, e.g., B.N.J. Persson and J.E. Demuth, Phys. Rev. B **30**, 5968 (1984); H. Ibach and D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

[14] L.H. Dubois *et al.*, Phys. Rev. B **29**, 3208 (1984).

[15] B.N.J. Persson and J.E. Demuth, Phys. Rev. B **31**, 1856 (1985).

[16] The calculations by Takeuchi, Selloni, and Tosatti (Ref. [4]) show that associated with the first melted bilayer is an ~5 eV wide density of states structure centered at the Fermi energy and containing about two electrons per Ge atom. Hence, the concentration of free electrons in the melted layer is assumed to be $n_s \approx 0.3$ Å^{-2}.

[17] B.N.J. Persson and J.E. Demuth, Phys. Rev. B **42**, 8057 (1990).

[18] In the calculation we have used the bulk Drude damping $\hbar/\tau = 45$ meV which is about twice as high as that estimated from the bulk conductivity and carrier concentration. A smaller damping would lead to an even higher surface plasmon loss peak (dashed curve in Fig. 3).