Metallic properties of the Ge(001) surface

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dc-field-effect studies of the Ge(001) surface are reported which clearly indicate the existence of a metallic or nearly metallic surface state, in agreement with high-resolution angle-resolved photoemission measurements by Kevan and Stoffel [Phys. Rev. Lett. **53**, 702 (1984)]. Furthermore, we will give an estimate of the density of such "metallic" surface states.

The Ge(001) surface has been the subject of recent experimental¹⁻⁹ and theoretical¹⁰⁻¹³ investigations. The (001) surface of Ge is generally thought to reconstruct to form a nominal (2×1) surface unit cell by asymmetric dimerization of nearest-neighbor surface atoms. However, higher-order reconstructions $[c(4 \times 2)$ and $p(2 \times 2)]$,¹ generated by various ordered arrangements of asymmetric dimers, are observed on the Ge(001) surface. First-principles electronic-structure calculations by Krüger and co-workers^{10,11} assuming an asymmetrical dimerization are in very good agreement with scanning tunneling microscopy (STM) measurements,¹ ellipsometrical measurements,⁹ and angle-resolved ultraviolet photoemission spectroscopy (ARUPS).³⁻⁵ We must therefore conclude that asymmetric dimers are the main building blocks of the Ge(001) 2×1 surface. STM measurements^{2,14} of the Ge(001) 2×1 surface indicate that besides asymmetric dimers, symmetric dimers also exist at this surface. Symmetrical dimerization results in an odd number of unpaired electrons per surface atom, forming a half-filled band corresponding to a metallic surface. High-resolution ARUPS studies of the Ge(001) surface show the existence of a metallic surface state near the center of the surface Brillouin zone.⁶⁻⁸ This state slowly disappears as the temperature is lowered from room temperature to 77 K. This metal-insulator transition is coincident with a recently predicted and observed transition from a disordered to an ordered $c(4 \times 2)$ structure.⁶ Mårtensson, Cricenti, and Hansson¹⁵ observed on a heavily *n*-doped Si(001) 2×1 surface a new surface state at the Fermi level. Since the state is observed only at the Γ and the J' points in the 2×1 surface Brillouin zone, they conclude that the Si(001) 2×1 surface has an almost empty surface-state band with minima at these points. Mårtensson, Cricenti, and Hansson¹⁵ also suggest that the peak observed near E_F on the Ge(001) 2×1 surface is not due to emission from localized defects, but to emission from the bottom of an almost empty dispersing surface-state band. It is the aim of the present paper to investigate whether this Ge(001) surface is metallic or not. And, if the Ge(001) surface has a metallic character, we will give an estimate of the minimum density of such "metallic" surface states.

The Ge sample ($30 \times 10 \times 0.52$ mm³) was made out of a 20 Ω cm, *n*-type crystal in the (001) orientation. Prior to mounting the crystal was cleaned ultrasonically in ethanol. For the field-effect measurements four titanium con-

tacts were evaporated through a tantalum mask.¹⁶ A current was sent through the outer pair of contacts of the sample, while the resulting potential was measured between the inner pair of contacts. In this way nonlinear behavior of the metal-semiconductor contact is eliminated.¹⁶ Use of an ac current averages out thermic or photovoltage effects resulting from a nonuniform sample temperature or illumination.¹⁶ The field electrode consisted of a Si plate (8×8 mm²) with a SiO₂ toplayer, which could be placed in front of the sample. Typical values for the capacitance between sample and field electrode are about 10 pF cm⁻². The parallelism of this assembly with respect to the sample surface was adjusted by three springs located at positions around the sample. The ellipsometric measurements were performed with a rotating analyzer in the photon energy range from 1.5–4 eV.

The experiments were performed in a stainless steel UHV system described previously,^{9,16,17} the base pressure of this system was below 1.10^{-10} Torr. A clean surface was obtained by cycles of sputtering (800-eV Ar⁺ ions, 2 μ A cm⁻², 30 min, angle of incidence 45°) and annealing (850 K, 30 min).^{3,5,6,8,9} Also during sputtering the crystal was heated to 700 K for about 15 min, followed by slow cooling.

The dc-field effect consists of the steady-state changes in surface conductance induced by electrostatic fields. For each applied field the system is allowed to reach equilibrium and the sample conductance is measured when no further change in its value is detectable.^{16,18} In our experiments a transverse field is applied to the semiconductor surface by placing an electrode parallel to the semiconductor surface and using this system as a flat-plate condenser. The semiconductor sample is connected to ground and after the application of a potential difference $\Delta V \equiv V_{\text{electrode}} - V_{\text{semiconductor}}$, the charge per unit area Q_{ind} on the semiconductor surface is equal to $-C\Delta V$, where C is the capacitance per unit area. The induced charge is distributed between the space-charge region and the surface states, giving rise to changes ΔQ_{sc} and ΔQ_{ss} in the free and trapped charge densities, respectively,

$$Q_{\text{ind}} = -C\Delta V = \Delta Q_{\text{ss}} + \Delta Q_{\text{sc}}, \quad (1)$$

where Q_{ss} is the amount of charge located in surface states, and Q_{sc} is that located in the space charge. The contribution to the surface conductance by the charge car-

TABLE I. dc-field-effect results, $C=6.4$ pF/cm². Band bending of the clean Ge(001) surface is about -340 mV (σ_s is about $4 \times 10^{-4} \Omega^{-1}$).

Q_{ind} (C/cm ²)	$\Delta\sigma_s$ (Ω^{-1})	ΔQ_{sc} (C/cm ²)	ΔQ_{ss} (C/cm ²)	ΔV_s (mV)	$\sum_i N_{\text{sai}} + \sum_j N_{\text{sdj}}$ (cm ⁻²)
1.6×10^{-8}	1.1×10^{-6}	6×10^{-10}	1.54×10^{-8}	-0.15	7×10^{13}
8×10^{-9}	5.7×10^{-7}	3×10^{-10}	7.7×10^{-9}	-0.07	7×10^{13}
-8×10^{-9}	-5.7×10^{-7}	-3×10^{-10}	-7.7×10^{-9}	0.07	7×10^{13}
-1.6×10^{-8}	-1.1×10^{-6}	-6×10^{-10}	-1.54×10^{-8}	0.15	7×10^{13}

riers in the surface states can, at least for Ge and Si surfaces, be ignored.¹⁸ Variations of σ_s , brought about by the applications of a transverse electric field can be ascribed to a first approximation to variations of the band bending V_s . The band bending for the clean Ge(001) 2×1 surface has a value of about -340 mV.^{9,18} For intrinsic crystals with a p -type surface we have

$$\Delta\sigma_s/\Delta V_s \approx -\frac{e}{2kT}\sigma_s \quad (\text{for } V_s < 0 \text{ and } |V_s| \gg kT/e). \quad (2)$$

The value of V_s itself determines the absolute value of the surface conductance.¹⁶ Once $\Delta\sigma_s$ is measured and σ_s is known the change in band bending due to the induced charge can be calculated. The field effect not only determines the change in band bending, but also a lower limit of the surface-state density near the Fermi level.

Assuming k types of acceptor states, a density of the i th state N_{sai} , Fermi factor F_{sai} , and r types of donor states, a density of the j th state N_{sdj} with Fermi factor F_{sdj} , then ΔQ_{ss} , the change of the charge in the surface states, as a result of the application of the transverse field, is given by

$$\Delta Q_{\text{ss}} = -e^2 \Delta V_s / (kT) \left[\sum_i N_{\text{sai}} F_{\text{sai}} (1 - F_{\text{sai}}) + \sum_j N_{\text{sdj}} F_{\text{sdj}} (1 - F_{\text{sdj}}) \right], \quad (3)$$

where ΔV_s , the differential change in band bending, is immediately given by Eq. (2). The term in square brackets can be calculated and has a value of about 1.75×10^{13} /states per cm². The only statement that can be made is that, when plotting $F_{\text{sa,sd}}(1 - F_{\text{sa,sd}})$ against $(E_F - E_{\text{sa,sd}})$, there is a maximum of $\frac{1}{4}$ at $E_F = E_{\text{sa,sd}}$. Therefore, the value of the bracketed part of Eq. (3) is only an indication of the minimum value of $\sum N_{\text{sa}} + \sum N_{\text{sd}}$ around the Fermi level. This minimum has a value of about 7×10^{13} /states per cm², i.e., at least about 10% of the number of surface atoms [for Ge(001) this is 6.23×10^{14} atoms/cm²], see Table I. Higher values of the density of surface states around E_F can be found when they are located within a few kT from E_F . Therefore, we must conclude from the field-effect measurements that the Ge(001) surface has a metallic or nearly metallic surface state. This result is essentially consistent with high-resolution ARUPS measurements by Kevan and co-worker.⁶⁻⁸ They found that this metallic surface state gradually disappears as the temperature is lowered, leaving a semiconductor surface for $T \leq 100$ K. This metal-insulator transition is coincident with a recently predict-

ed¹⁹ and observed transition from a disordered to an ordered $c(4 \times 2)$ structure.⁶⁻⁸ But this "metallic" surface state can also be due to symmetric dimers^{2,14,20} or an almost empty dispersing surface-state band.¹⁵ The performance of temperature-dependent field-effect measurements is not possible at the moment due to the very high-temperature stability required for these experiments.

The changes in the ellipsometric parameters $\delta\psi$ and $\delta\Delta$ upon oxygen adsorption were recorded as a function of photon energy. The results are given in Ref. 9. The $\delta\psi$ and $\delta\Delta$ vs E curve showed a significant amount of structure, this structure interpreted as being due to a substrate change upon chemical adsorption, i.e., the saturation of the dangling bonds of the surface atoms. The substrate effect has been described phenomenologically as the effective disappearance of a transition layer present at the clean surface.²¹ This transition layer with an arbitrary chosen thickness of $5 \text{ \AA}$ (this value has no influence on the model) has optical constants ($\tilde{\epsilon}_{\text{ss}}$) different from the bulk ($\tilde{\epsilon}_b$), due to the difference in electronic structure between the surface layer (dangling bonds) and the bulk (sp^4 -type bonds). The effect of the thin oxide layer on the surface can be taken into account in both $\delta\psi$ and $\delta\Delta$.⁹ The relevant parameter for the transitions involving surface states is the difference between the imaginary part of the dielectric constant at corresponding photon energies, i.e., $\text{Im}(\tilde{\epsilon}_{\text{ss}} - \tilde{\epsilon}_b)$. The $\text{Im}(\tilde{\epsilon}_{\text{ss}} - \tilde{\epsilon}_b)$ curve for Ge(001) covered with one monolayer oxygen as a function of photon energy

FIG. 1. The imaginary part of the difference in complex dielectric constant $\text{Im}(\tilde{\epsilon}_{\text{ss}} - \tilde{\epsilon}_b)$ between the surface-state layer and the bulk substrate for the clean Ge(001) surface as a function of the photon energy.

E is given in Fig. 1, optical transitions at 1.8 and 3.3 eV are observed. These transitions are in very good agreement with STM measurements (1.9 and 3.5 eV).^{1,9} The difference in transition energy measured with the tunneling microscope and that measured by ellipsometry could arise from the difference in k space emphasized by these techniques; the transitions in ellipsometry are threshold energy differences that need not occur at the Γ point of the surface Brillouin zone, which is emphasized in the tunneling spectrum. Using a local-density-functional formalism in a self-consistent scattering theoretical method, Pollmann, Krüger, Mazur, and Wolfgarten¹⁰ determined the surface band structure for the Ge(001) surface comprised of asymmetric buckled dimers. The theoretical density of states at the Γ point is in excellent agreement

with STM measurements¹ and our ellipsometric measurements.⁹ Therefore, we must conclude that our cleaning procedure results in a surface with a considerable amount of asymmetric dimers.

In summary, we have found an additional proof for the existence of a metallic or nearly metallic surface state on the clean Ge(001) 2×1 surface at room temperature, and we have given an estimate of their density. Furthermore, we have shown that on our Ge(001) surfaces asymmetric dimers, which themselves will not give rise to a metallic surface state, dominate.⁹

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