PHYSICAL REVIEW B VOLUME 41, NUMBER 14 15 MAY 1990-I

Surface phase transitions on clean Ge(111) studied by spectroscopic ellipsometry

M. Abraham,* G. Le Lay, and J. Hila
Centre de Recherche sur les Mécanismes de la Croissance Cristalline (CRMC2) du Centre National de la Recherche Scientifique, Case Postale 913, F-13288 Marseille CEDEX 09, France

(Received 6 November 1989)

We have studied by ellipsometry the surface optical response of clean reconstructed Ge between room temperature and up to a temperature very close to the melting point. In monochromatic temperature scans, three reversible phase transitions are detected. The first is the well-known transition $c(2\times 8)\leftrightarrow(1\times 1)$ around 250 °C. A second one occurs between 700 and 750 °C and is probably related to the order-disorder transition reported by McRae and Malic [Phys. Rev. Lett. **58**, 1437 (1987)]. The third transition, at about 70 °C below the bulk melting point, is found for the first time. The changes of the electronic properties of the surface transition layer during these phase transitions are investigated with use of spectroscopic ellipsometry. The transition $c(2\times 8)\leftrightarrow(1\times 1)$ is also studied by photoemission spectroscopy. On Ge(100) surfaces in the high-temperature range, no surface phase transitions could be detected.

I. INTRODUCTION

To understand surface reconstructions and surface phase transitions of homopolar semiconductors is a very formidable task. In contrast to simple physisorbed systems, there is a strong interaction between the reconstructed surface region and the underlying bulk caused by important strain fields. Furthermore, the homopolar bonding of a semiconductor leads to a strong coupling between the electronic system and the actual surface order which allows the detection of phase transitions via techniques which are especially sensitive to the electronic properties.

The Ge(111) surface undergoes a number of phase transitions.[1] After cleavage at room temperature a metastable (2×1) surface structure is obtained which converts irreversibly to a stable $c(2\times 8)$ reconstruction between 70° and 200 °C. This reconstruction is also obtained after sputtering and/or annealing cycles of polished Ge wafers.

The (2×1) and the $c(2\times 8)$ structures as well as the phase transitions have been widely studied by different techniques. As a consequence, namely, the electronic and atomic structure of the $c(2\times 8)$ reconstruction seems to be well understood in the framework of an ordered-adatom mode.[2–5] This reconstruction undergoes a reversible transition to a (1×1) structure between 200 and 300 °C.[1] The nature of this transition and the electronic and atomic structure of this disordered high-temperature phase are not completely understood.[5,6]

Recently a further reversible surface phase transition has been detected at 750 °C by low-energy electron diffraction (LEED) intensity measurements.[7,8] In this transition the surface becomes highly disordered, which has been initially attributed to a surface fusion process.[7] Especially in this case further studies using complementary techniques are necessary to clarify the situation.

Optical spectroscopy—especially ellipsometry[9]—is a well-established tool to study the electronic bulk properties of semiconductors. Main features of the band structure, such as critical-point behavior, have been obtained by the analysis of the measured complex dielectric function and its derivatives. The use of optical spectroscopy for surface electronic properties requires more care because of the large penetration depth of the electromagnetic wave. The main problem is, therefore, the separation of the bulk and surface electromagnetic response. Nevertheless important contributions to the understanding of semiconductor surfaces have been obtained by optical techniques, such as photodisplacement spectroscopy[10] or differential reflectivity.[11] To separate bulk and surface response the gas-adsorption technique was used.[12] This means that a given reconstruction is surpressed by adsorption of a reactive gas (mostly oxygen) and the surface electromagnetic response is compared before and after the reaction.

By ellipsometry it is possible to directly measure the dielectric functions for a given photon energy. This is provided by measuring the change of the polarization of the incident monochromatic polarized light beam. Usually one determines the two independent ellipsometric parameters Ψ and Δ related to the ratio of complex Fresnel reflection coefficients r_p and r_s:

$$\tan(\Psi)\, e^{i\Delta}=r_p/r_s \ . \qquad (1)$$

By use of the standard Fesnel optics it is possible to calculate dielectric functions. The determination of the surface dielectric function can be provided by assuming a film substrate model as proposed by McIntyre and Aspnes.[13] The imaginary part of the surface dielectric function can be related to photoemission and inverse photoemission experiments. The real part gives information about the dynamical screening. Semiconducting or metallic behavior of the surface can easily be deduced.

The first measurements of the surface dielectric functions of clean group-IV elemental semiconductors using ellipsometry have been done by Meyer.[12] In a recent study[14] the dielectric function of the reconstructed Ge(111)-$c(2\times8)$ surface has been published. But there are only a few papers on the surface phase transitions. Quentel *et al.*[15] studied the irreversible Ge(111)-$(2\times1)\leftrightarrow$Ge(111)-$c(2\times8)$ transition and Pchelyakov *et al.*[16] studied the reversible Si(111)-$(7\times7)\leftrightarrow$Si(111)$(1\times1)$ transition. However, these authors used monochromatic light; therefore although the transition was detected, spectroscopic information about the surface electronic properties could not be obtained.

The aim of this paper is to provide a complete study of the different surface structures of clean Ge(111) and their reversible transition using monochromatic and spectroscopic ellipsometry. The measurements are extended over a large temperature range from room temperature to 70 °C below the bulk melting point. After a short description of experimental detail results concerning the Ge(111)-$c(2\times8)\leftrightarrow$Ge(111)$(1\times1)$ reversible transitions will be presented. This transition has, to our knowledge, not been studied up to now by any optical technique. In a second part we detect in a monochromatic scan two reversible transitions of the surface properties in the range between 700 and 850 °C. While the first one is probably related to te phenomenon reported by McRae and Malic,[7] the second one has never been mentioned. Information about the change of the electronic properties were obtained by the determination of the surface dielectric function. For comparison the surface properties of Ge(100) have been studied also.

II. EXPERIMENT

The experiments were realized in a ultrahigh vacuum chamber (base pressure $\sim5\times10^{-10}$ Torr) equipped with a four-grid LEED system and Auger-electron spectroscopy. An ion gun (Ar) was used for surface cleaning. The optical measurements were done using two windows allowing for ellipsometric measurements at 70° incidence. The automatic ellipsometer (SOPRA) is of the rotating polarizer-sample-analyzer type. A 150 W halogen lamp was used as source and a simple grid monochromator provides an energy selection between 1.5 and 3.8 eV. The modulation of the light before reaching the sample enables measurements of surfaces at high temperatures while they are emitting light.

This type of ellipsometer is very sensitive to residual polarizations of the light source. Furthermore, it is quite difficult to determine the actual angle of incidence inside the UHV chamber with high precision as required for ellipsometry. Therefore, we provided a correction of these systematic errors. The correction procedure consists of a simulation of the effects of residual source polarizations and window birefrengence by an apparent compensator. The influence of the compensator (assumed to be achromatic) on the transfer function of the ellipsometer is known.[17] Thus the parameters of this compensator (azimut and phase shift), as well as the actual angle of incidence, are calculated by a nonlinear regression. The known optical bulk constants over the whole spectral region of Ge (Ref. 9) were used as a standard. In Fig. 1 we show the dielectric functions of a clean Ge(111) sample before and after the correction of systematic errors in comparison to the values of Aspnes.[9] The accuracy in the determination of the ellipsometric parameters was about 0.02° for Ψ and 0.2° for Δ. Usually ten values were accumulated to improve the accuracy.

The experiments were made on Ge crystal samples ($23\times7\times0.4$ mm^3). It was heated Ohmically. The surface temperature was measured by a pyrometer. The obtained temperature scale was checked by ellipsometric monitoring of the melting of a thick lead overlayer ($T_m=327$ °C) evaporated at the end of the experiments and by the observation of the melting of the Ge sample itself ($T_m=937$ °C). The surface of the Ge samples were

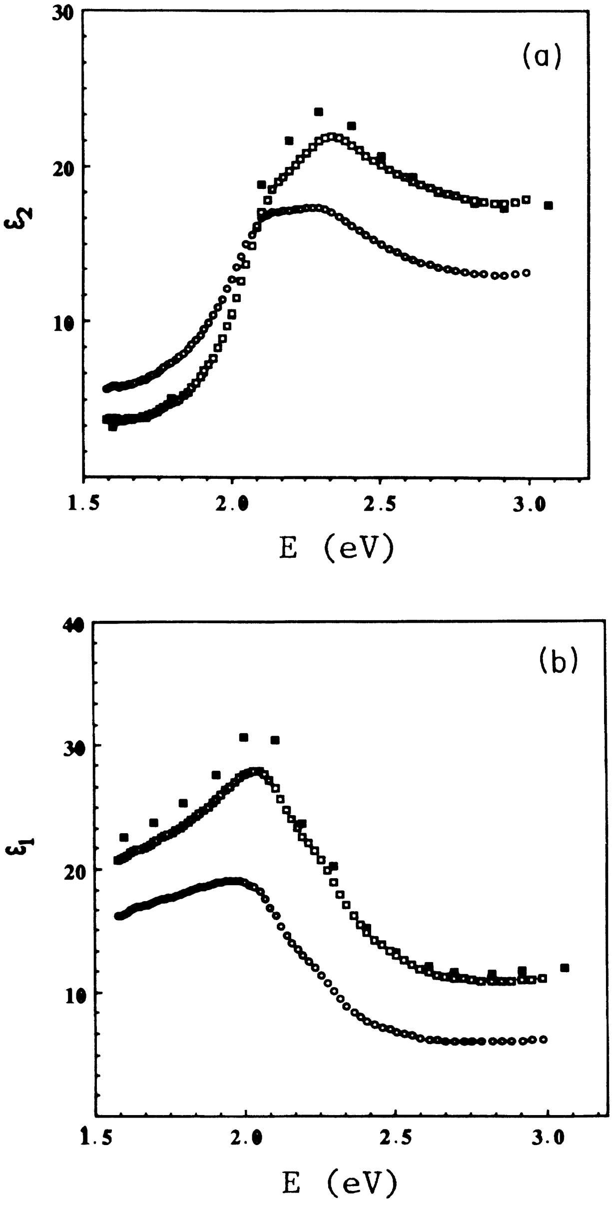

FIG. 1. Imaginary part and real part of the dielectric function of Ge. Open circles noncorrected from systematic errors; open squares, after correction of window imperfections, residual polarization, and angle of incidence; solid squares, values given by Aspnes *et al.* (Ref. 9).

prepared by sputtering (10^{17}Ar$^+$ ions/cm^2, 2 keV) at room temperature, followed by a flash to 750 °C to desorb GeO$_x$. Thereafter no carbon and oxygen contamination were observed in the limit of Auger sensibility. The sample was then cooled down to 500 °C and held at this temperature for 10 h. Thereafter a $c(2\times8)$ reconstruction was obtained at room temperature as checked by LEED. The described procedure leads to a minimum amount of defects as recently revealed by scanning tunneling microscopy (STM).[4]

III. THE $c(2\times8)\leftrightarrow1\times1$ TRANSITION

A. Optical evidence

To detect the reversible Ge(111)-$c(2\times8)\leftrightarrow$Ge(111)-$(1\times1)$ surface phase transition by ellipsometry a temperature scan at constant wavelength (600 mn) was done. This is the region of the E_1 interband transition in Ge.[18]

The measurements have been realized in a quasistatic regime. This means after stabilization of the temperature which can be well controlled by monitoring the ellipsometric parameters. In Fig. 2 we show the ellipsometric rough data of a freshly prepared Ge(111) sample as a function of the temperature. For comparison the corresponding data for an evaporated polycrystalline Ge film calculated from the optical constants of Ref. 19 are presented. The general slope of the curves is connected to the temperature behavior of the electronic and hence the optical properties of Ge.[18] Between 200 and 250 °C, however, we notice a change of the slope in the case of the Ge(111) sample. It is exactly the temperature range, where the surface phase transition $c(2\times8)\leftrightarrow(1\times1)$ was detected by LEED. The transition is not seen for the polycrystalline film which is obviously not reconstructed. Therefore we attribute the feature in the slope of the optical response of the Ge(111) wafer to a change of the surface electronic properties due to a rearrangement of surface atoms during the $c(2\times8)\leftrightarrow(1\times1)$ phase transition.

It is interesting to compare the behavior of the real and imaginary part of the pseudoelectric function of the Ge sample (bulk and surface response not separated) to the available data from LEED (Ref. 5) and core-level photoemission experiments.[20] In Fig. 3 we show ϵ_1 obtained by inversion of the ellipsometric relation and the intensity of the quarter-order LEED reflection peak normalized to the low-temperature Debye-Weber factor (after Ref. 5). It is important to emphasize that LEED probes the structure of the outermost surface layer with the characteristic correlation length of several hundred Å, whereas optical methods probe the electronic structure which is mainly determined by local order. Subsurface modifications of the electronic structure are also monitored. First we notice that the transition as monitored by ellipsometry spreads over a temperature range between 200 and 300 °C. On the other hand, the LEED intensity of the quarter-order peak drops abruptly at ~300 °C. Because of the sharp drop of the LEED signal and a slight hysteresis the author of Ref. 5 concludes a first-order transition towards an incommensurate surface structure at 300 °C. We observe a more sluggish transition.

We can try to understand this quite complicated phase transition in connection to the important strain fields built up in the surface region during heating at the crystal. Indeed, there is a strong correlation between lateral stress and surface reconstruction as shown by Miller *et al.*[21] The stress yields an additional term in the surface free energy and can spread the typically abrupt phase transition over a certain temperature region. When the new high-temperature phase begins to nucleate at a critical temperature, this will immediately relax a part of the stress. The modified elastic state will then shift the actual critical temperature to a higher value. The process is terminated when the surface has completely transformed to the high-temperature (1×1) phase and

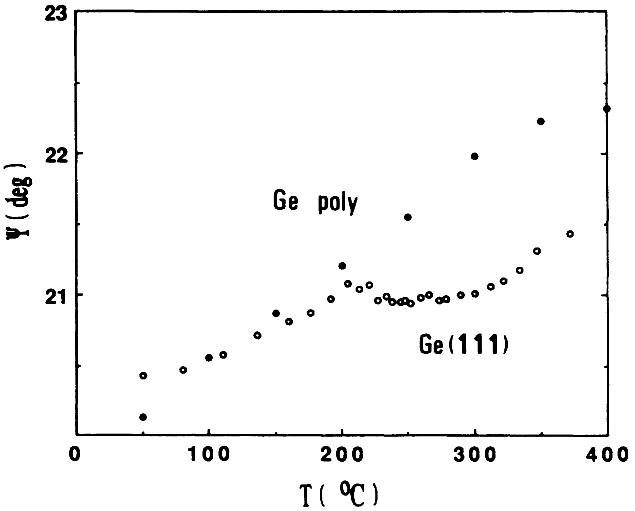

FIG. 2. Ellipsometric data Ψ as a function of the temperature at $\lambda=600$ nm for a clean Ge(111) surface (open circles) and a polycrystalline film after Algazin *et al.* (Ref. 19).

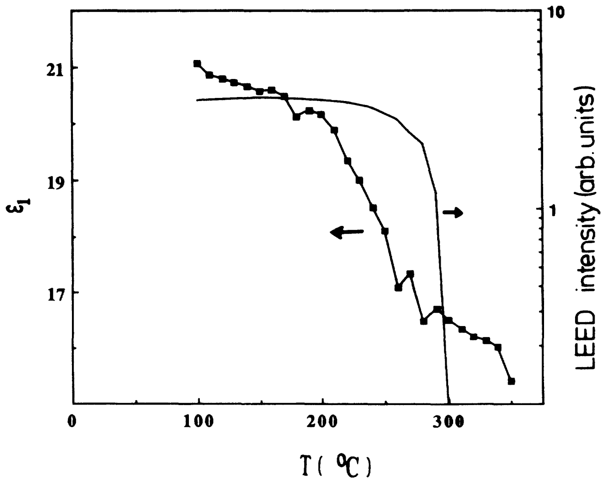

FIG. 3. Temperature behavior of the real part of the dielectric function (solid squares) and the intensity of a quarter-order LEED spot normalized to the low-temperature Debye-Waller factor from Phaneuf *et al.* (Ref. 5).

the LEED quarter-order peak drops to zero. The behavior of the surface and bulk sensitive ellipsometric response is indicative for the participation of subsurface regions in the transition which are not detected by LEED.

We now compare our results to the ellipsometric study of the Ge(111)-(2×1)↔Ge(111)-$c(2\times8)$ transition.[15] This is interesting because it was pointed out by several authors (e.g., Ref. 5) that the (1×1) phase could be an incommensurate partner of the low-temperature metastable (2×1) structure. Actually we find for Ge(111)

$$\Psi(c(2\times8))-\Psi(1\times1)>0^\circ$$

and

$$\Delta(c(2\times8))-\Delta((1\times1))>0^\circ\ ,$$

and from Ref. 15

$$\Psi(c(2\times8))-\Psi((2\times1))>0^\circ$$

and

$$\Delta(c(2\times8))-\Delta((2\times1))<0^\circ\ .$$

The discrepancy in the sign of the Δ change is not in favor of the former hypothesis. On the other hand, the behavior of the ellipsometric parameters for the transition Si(111)-(7×7)↔Si(111)-(1×1) is very similar to our results.

The formation of the (1×1) phase over a temperature range of 20–30° has been demonstrated by low-energy electron microscopy.[22]

B. Electronic properties

To study the change of the electronic properties during the transition, we have measured the spectral dependence for fixed temperatures before (135 °C) and after (266 °C) the $c(2\times8)$↔(1×1) transition.

To compare these spectra we have to take into account the effect of the temperature on the electronic properties. Actually the electron-phonon interaction and lattice expansion leads to a red shift and a damping of the critical points.[18] In a first approximation we correct the temperature-induced spectral shift E of the main peak (E_1 and $E_1+\Delta_1$) in our spectrum by using the empirical formula $E=E(T=0\text{K})-\alpha T^2/(\beta+T)$ [with $\alpha=4.510^{-4}$ eV/K and $\beta=210$ K (Ref. 18)]. We shift the whole measured spectrum at the lower temperature towards lower photon energy by the energy difference corresponding to the temperature difference of the two spectra.

To calculate the surface optical response we follow the classical film-substrate model.[13] The optical properties of the reconstructed surface region are considered as a thin homogeneous and isotropic layer on a substrate with bulk optical properties. Of course this is a rough approximation. Actually this surface region is neither homogeneous nor isotropic. The optical surface response can be described as a sum of a local bulk and a nonlocal surface contribution, which is different for an electric field parallel and perpendicular to the surface.[10]

What we are measuring in ellipsometry is a mixture of these parameters: at 70° incidence the parallel (to the plane of incidence) polarized light observes mainly the perpendicular component of the surface dielectric function. Since the thickness of the surface layer is very small compared to the wavelength a linearized formula can be used to calculate the surface dielectric function from the measured ellipsometric angles.[23] To apply this formula it is necessary to know the bulk properties, the thickness, and the difference spectrum

$$\Psi,\Delta(\text{surface}+\text{bulk})-\Psi,\Delta(\text{bulk})\ . \tag{2}$$

Our aim is to calculate the surface dielectric function of the (1×1) surface and to compare it to that of the $c(2\times8)$ surface. As the latter has been determined by the gas-adsorption technique,[14] we can subtract the corresponding $\delta\Psi,\delta\Delta$ spectrum from our Ψ,Δ spectrum of the sample before the transition. The obtained spectrum is corrected by the temperature effect and used as substrate reference with respect to the sample response after transition. Assuming a surface layer thickness of 5 Å (one double layer), we calculate the dielectric function of the (1×1) surface. In Fig. 4 we compare the imaginary parts of the surface dielectric functions of the (1×1) and the $c(2\times8)$ reconstruction, the bulk contribution being subtracted according to

$$\text{Im}(\epsilon_{SS})=\text{Im}(\epsilon_S-\epsilon_B)\ , \tag{3}$$

ϵ_{SS} being the contribution from surface states, ϵ_S the surface, and ϵ_B the bulk dielectric functions. The function ϵ_{SS} reflects mainly the transitions between filled and unfilled surface states.

The principal conclusion from Fig. 4 is that the main features of the surface density of states are not changed by the transition, confirming the finding of core-level photoemission studies.[6,20] We find a strong peak around

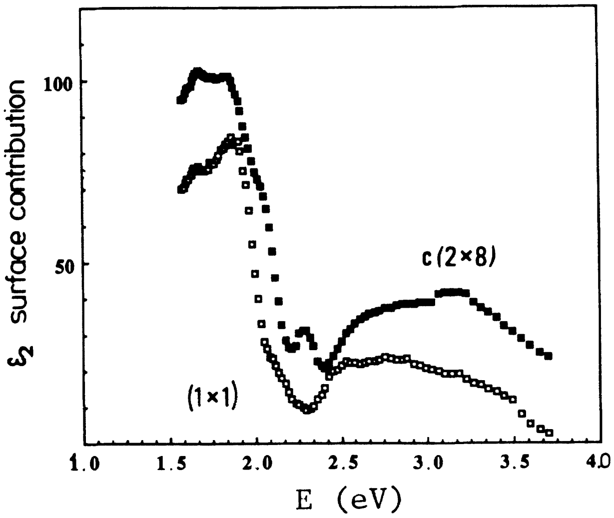

FIG. 4. Imaginary part of the surface dielectric function of the Ge(111) surface (open squares) just above the $c(2\times8)$↔(1×1) transition and the corresponding function of the $c(2\times8)$ surface calculated from data given by Zandvlieth *et al.* (Ref. 14) (solid squares, values multiplied by 5). The thickness of the transition layer is supposed to be 5 Å.

1.8 eV and a weaker and larger one around 2 eV. To identify the peaks, one needs information about the density of filled and unfilled surface states. While there are only inverse photoemission experiments on cleaved Ge(111)-(2×1) but not on the Ge(111)-(2×8) and Ge(111)-(1×1) surfaces to our knowledge, the surface valence-band structure of the Ge(111)-*c*(2×8) is well known.[3] Furthermore the surface density of states (filled and empty) has been measured recently by STM spectroscopy.[4] A rather structureless empty surface density of states has been attributed to the four adatom dangling bonds on *c*(2×8) unit cells. The respective charges are transferred to the four restatoms which are responsible for the intense surface peak at 0.7 eV below the valence-band maximum seen in photoemission.[3] At (1.2–1.4) eV, there is a weaker and larger band attributed to the ensemble of backbonds. From a photothermal displacement study of the Ge(111)-(2×1)↔Ge(111)-*c*(2×8) transition it is known that the surface state in the band gap (0.4 eV) disappears during the transition.[10] Thus there are no transitions from surface states in the gap of the *c*(2×8) structure. Therefore we attribute the strong peak around 1.8 eV to a transition from the filled restatom dangling-bond surface state to the empty adatom dangling-bond band. This hypothesis can be supported by application of the sum rule to this peak (integration interval: 1.5–2.5 eV)

$$\int \epsilon_2(\omega)d\omega=\pi\omega^2/2 \; . \tag{4}$$

For the *c*(2×8) spectrum, this leads to about 1/4*e* per atom (within 10%) or four electrons per *c*(2×8) unit cell. This is just the number of restatoms.

The conservation of this peak after the transition to the (1×1) structure agrees with the corresponding valence-band photoemission measurements (Fig. 5).[24]

The most important difference between the ϵ_2 spectra of the *c*(2×8) and the (1×1) structure is the difference in the peak amplitude. But we cannot exclude *a priori* that the amplitude of the peaks is affected by the fact that the temperature-induced broadening of the critical points is not included in our calculation. Therefore we do not discuss this fact further.

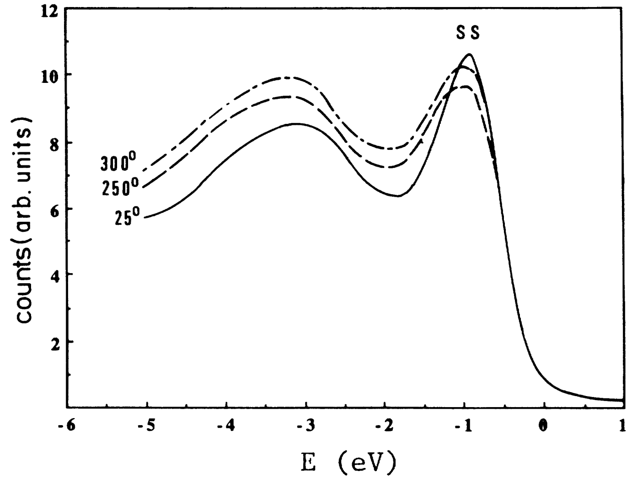

FIG. 5. Angle-resolved photoemission spectra from the Ge(111) surface valence band ($\hbar\omega=45$ eV) for different temperatures below (25 °C), during (250 °C) and above the *c*(2×8)↔(1×1) phase transition. Energy scale is referred to the Fermi level (Ref. 24).

What can be concluded from the surface dielectric function about the nature of the (1×1) structure?

The conservation of the strong surface-state peak at 1.8 eV is an important argument for the conservation of restatoms and adatoms of the same short-range order than in the *c*(2×8) surface. The corresponding domains should be smaller than the LEED correlation length in order to produce a (1×1) pattern. A total disorder (without short-range order) is incompatible with the existence of a relatively strong surface-state peak. However, the small and sharp structure at 2.3 eV in the *c*(2×8) surface disappears in the (1×1) case. Although this peak is not yet identified it could be related to a long-range-order effect destroyed by the transition to (1×1) symmetry.

Coming back to the comparison with the (2×1) surface, it is interesting to note the similarity between our (1×1) spectrum, the *c*(2×8) spectrum, and the spectrum of the (2×1) surface obtained by differential reflectometry.[11] The only remarkable difference is the strong surface state in the gap in the case of the (2×1) surface: a spectral region which we have not explored due to spectral limitations of our apparatus.

Obviously the electronic structure does not change significantly during the phase transition. But how can we explain the rather strong variation of the ellipsometric signal. A plausible explication could be a relaxation of the stress accumulated in the surface region during heating due to the different expansion coefficient of the bulk and the dense Ge(111)-*c*(2×8) surface. The corresponding lattice deformation acts on the electronic properties not only of the surface but also on the subsurface region which is seen by ellipsometry, but not by surface sensitive core-level photoelectron spectroscopy nor by LEED. The reason why the range in the ellipsometric signal is much weaker for the Si(111)-(7×7)↔Si(111)-(1×1) transition is explained as follows: the Ge lattice is much more softer than the silicon one. E.g., the logarithmic pressure derivative of the infrared optical constant ϵ_∞ is about 12 times greater for Ge than for Si.[25] The important influence of strain on the electronic properties of Ge has been demonstrated by a strain-induced metal insulator transition of the Ge(111) surface.[21]

IV. HIGH-TEMPERATURE PHASE TRANSITIONS

A. Optical evidence

Now we address the study of the high-temperature behavior of the Ge(111) surface. To our knowledge the dielectric function of Ge has not been studied up to now in a temperature region above 550 °C. With our ellipsometer we were able to perform measurements at light emitting surfaces. The study of bulk optical properties up to 850 °C will be published elsewhere.[26] In the present paper we focus on surface properties.

Figure 6 shows the temperature behavior of the ellipsometric rough data $\Psi(T)$ for Ge(111) and Ge(100) samples. In this temperature range both surfaces show a (1×1) LEED pattern. The Ge(100) surface was, at room temperature, (2×1) reconstructed.

There appears two reversible high-temperature phase transitions of the Ge(111) surface. The first one (A) occurring between 700 and 750 °C, the second (B) between 800 and 850 °C. The absence of any feature in the case of the Ge(100) surface prove that the observed changes are surface induced.

To learn about the electronic properties we have carried out spectroellipsometric measurements before the transition A (at 660 °C), at the plateau between the transitions A and B (750° C) and after the transition C (800 °C). Then we calculate the difference in the optical properties of the surface properties at these temperatures following the ideas explained in Sec. III B. The only difference is that we do not separate the optical responses of the surface layers before and after the respective transitions. Therefore the surface dielectric function in Figs. 7 and 8 describes the change of the surface optical properties. For the calculations we have to assume a certain thickness of the transition region. It was interesting to note that for a thickness < 10 Å, it was not possible to obtain physically relevant solutions. This means that the subsurface region involved in the transitions is at least 10 Å thick.

B. Discussion

There are only a few papers in the literature which report on high-temperature phase transitions on Ge(111) surfaces.

The first one[27] shows an anomalous reversible drop of the sticking coefficient of oxygen at about 720 °C followed by a plateau. This effect was not observed on Ge(100) and Ge(110) surfaces. The authors of Ref. 27 discuss a temperature-dependent rearrangement of the surface structure specific of the (111) surface.

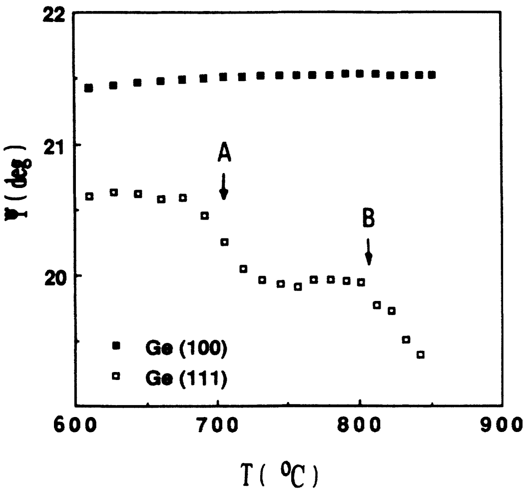

FIG. 6. Temperature behavior of the ellipsometric angle Ψ for Ge(111) and a Ge(100) sample. Evidence for two transitions: around 700 °C (A) and around 800 °C (B).

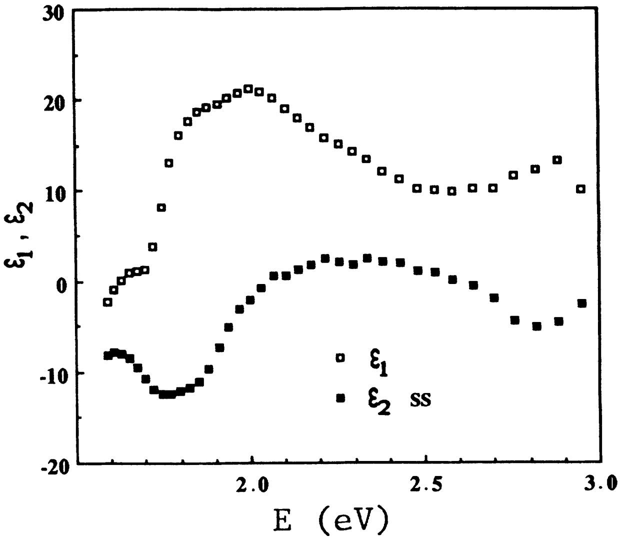

FIG. 7. Dielectric function corresponding to the change of the surface electronic properties on a 10-Å transition layer during the phase transition A at clean Ge(111) surfaces around 700 °C. In the case of the imaginary part the bulk contribution is subtracted.

McRae and Malic[7,8] followed the LEED intensity of the nonspecular spots. They found up to 700 °C a typical Debye-Waller decrease, the Debye-Waller factor being that of a well-ordered surface. Then the intensity drops more rapidly at the apparent critical temperature of 780 °C followed by a plateau. These authors discuss a surface disordering process but they exclude surface melting and surface roughening as classical surface disordering phenomena. The proposed mechanism is probably a strain-induced transition from an ordered (1×1) surface to strained domain structure with liquidlike boundaries. The model is supported by a molecular-dynamics simulation.[28]

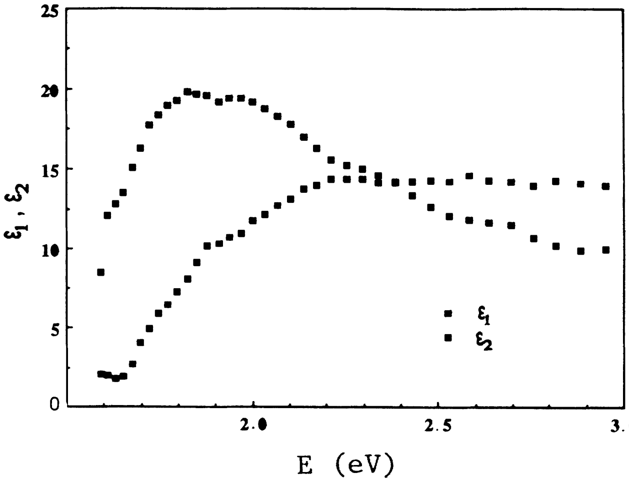

FIG. 8. Dielectric function corresponding to the change of the surface electronic properties in a 15-Å transition layer during the phase transition B at clean Ge(111) surfaces around 800 °C.

The first transition (A) we have detected by ellipsometry falls in the region of the transition, detected by Refs. 7 and 27, and displays the same sluggish shape followed by a plateau (Fig. 6). In Fig. 7 we show the change of the electronic properties during the transition A. The negative part in the surface state difference spectrum (ϵ_{2SS}) signifies the bleaching of the surface-state peak between 1.5–1.9 eV which is characteristic for the $c(2\times 8)$ and the (1×1) surface dielectric function (Fig. 4). This must be associated with a perturbation of the atomic structure in a short-range scale. We agree with Ref. 8 that a premelting process is not the reason of the observed phenomena. Our argument is the positive sign of the real part of the surface dielectric response. It is known that liquid Ge has a negative real part of the dielectric function.[29] This is due to a dehybridization, a change of the open diamond structure to a close-packed liquid one, and hence to a metallic behavior.

We emphasize that from our measurements we conclude that transition A involves at least a subsurface region of 10 Å thickness, which is certainly connected to stress relaxation. So our observation is compatible with the model proposed by McRae and Malic, but on the other hand, we cannot exclude from the optical point of view a roughening transition.

The second transition occurs just at the limit of the LEED measurements of McRae and Malic in the electronic properties, we see a more structureless behavior of the difference spectra (Fig. 8). This is indicative for a less drastic change of the electronic surface properties. In the limits of our measurements ($T_m - 70°$), we have not observed a saturation of the behavior of the ellipsometric parameters (Fig. 6). As the change in ϵ_1 of the surface is positive, the formation of a liquid layer (in the bulk liquid sense) does not take place. It is very difficult to understand this phase transition only in the framework of optical measurements. A simple explication in the sense of the model of Ref. 28 may be the following. After formation of the strained domains during transition A, the completely disordered regions continue their growth (plateau) until the surface is completely disordered. Then during the second transition deeper-lying layers undergo this disordering process.

V. SUMMARY

In summary, we have provided the first systematic study of the optical properties of Ge(111) surfaces by spectroscopic ellipsometry between room temperature and temperatures very close to the bulk melting point. In monochromatic temperature scans we detected three reversible surface phase transitions by abrupt changes in the slope of the ellipsometric data. Then we studied the change of the electronic properties during the phase transition by spectroscopic measurements at temperatures around the transitions. Before the comparison of the spectra, the effect of thermally induced shift of the critical points was corrected.

First, we studied the $c(2\times 8)\leftrightarrow(1\times 1)$ transition at around 250 °C. In contrast to LEED measurements, which are surface sensitive to the first atomic double layer only, we detect by ellipsometry changes of the electronic properties deeper in the bulk with an onset at 200 °C. We attribute both the sluggish behavior of the transition and the amplitude in the change of the optical properties to a contribution of important strain fields.[30] On the other hand, we find that the electronic properties of the surface do not change significantly confirming photoemission measurements of core levels and the valence band. Especially when a strong surface-state-induced peak, which we attribute to an optical transition from filled restatoms to empty adatom sites, is conserved. Therefore the (1×1) structure must be ordered in a scale below the LEED correlation length with a short-range order of restatoms and adatoms very close to the $c(2\times 8)$ structure.

This ordered (1×1) surface undergoes a further reversible phase transition between 700 and 750 °C, as detected in a temperature scan at a fixed wavelength. We provided the first independent confirmation of this transition detected up to now by LEED spot intensity measurements.[7] By spectroscopic measurements we find out that the intense surface peak disappears. So we conclude that the surface undergoes an order-disorder transition in a scale where surface states cannot persist. But we rule out the formation of a liquid Ge layer in the sense of bulk liquid properties: the surface properties are still semiconducting and not metallic as typical for liquid Ge.

Finally we find another transition between 800 and 850 °C. We believe that in this case the disordering process is propagating into the bulk but the surface optical properties are still semiconducting. To explain the amplitude of the optical surface response change during the observed transitions, we have to take into account the contribution of a rather thick surface layer (10–15 Å) to get physical solutions for the surface dielectric function. Therefore an important strain field must be involved in both transitions. For comparison, we provided identical experiments on Ge(100). There was no evidence of either change in the surface properties in the same temperature region.

It should be very interesting to study the detected phase transitions, especially the high temperature ones by a diffraction technique which provide information about deeper subsurface regions, such as grazing-angle-of-incidence x-ray diffraction.

ACKNOWLEDGMENTS

We thank the Université de Provence for financial support. We wish to thank the technical staff of the CRMC2 and especially J. P. Dussaulcy for assistance. We thank J. Chevrier for his fruitful discussions and M. Hahnbucken for a critical reading of the manuscript.

[*] Permanent address: Institut für Physikalische und Theoretische Chemie, Universität Tübingen, auf der Morgenstelle 8, D-7400 Tübingen 1, Germany.

[1] G. LeLay, in *Semiconductor Interfaces: Formation and Properties,* Vol. 22 of *Springer Proceedings in Physics* (Springer, New York, 1987), p. 48.

[2] R. Feidenhans'l, J. S. Pedersen, J. Bohr, A. Nielsen, F. Grey, and R. L. Johnson, Phys. Rev. B **38**, 9715 (1988).

[3] J. Aarts, A. J. Hoeven, and P. K. Larsen, Phys. Rev. B **37**, 8190 (1988).

[4] R. S. Becker, B. S. Schwartzenhuber, J. S. Vickers, and T. Klitsner, Phys. Rev. B **39**, 1633 (1989).

[5] R. J. Phaneuf and M. B. Webb, Surf. Sci. **164**, 167 (1985).

[6] J. Aarts, A. J. Hoeven, and P. K. Larsen, Phys. Rev. B **38**, 3925 (1988).

[7] E. G. McRae and R. A. Malic, Phys. Rev. Lett. **58**, 1437 (1987).

[8] E. G. McRae and R. A. Malic, Phys. Rev. B **38**, 13 163 (1988).

[9] D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).

[10] M. A. Olmstead, Surf. Sci. Rep. **6**, 159 (1986).

[11] S. Nannarone, P. Chiaradia, F. Ciccaci, R. Memeo, P. Sassarol, S. Selci, and G. Chiarotti, Solid State Commun. **33**, 593 (1980).

[12] F. Meyer, Phys. Rev. B **9**, 3622 (1974).

[13] J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **24**, 417 (1971).

[14] H. J. W. Zandvliet and A. Van Silfhout, Surf. Sci. **195**, 138 (1988).

[15] G. Quentel and R. Kern, Surf. Sci. **135**, 325 (1983).

[16] O. P. Pchelyakov, Y. A. Blyumkina, S. I. Stenin, L. V. Sokolov, A. V. Arkhipendo, and M. A. Lamin, Phys. Chem. Mech. Surfaces **1**, 291 (1982).

[17] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977), p. 260.

[18] L. Vina, S. Logothetidis, and M. Cardona, Phys. Rev. B **30**, 1979 (1983).

[19] Yu. B. Algazin, Yu. Blyumkina, N. I. Grebnev, K. K. Svitashev, L. S. Semenko, and T. M. Yablontseva, Opt. Spektrosk. **45**, 330 (1978) [Opt. Spectrosc (USSR) **45**, (2), 183 (1978).

[20] K. Hricovini, G. LeLay, M. Abraham, and J. Bonnet, Phys. Rev. B **41**, 1258 (1990).

[21] T. Miller, T. C. Hsiek, P. John, A. P. Shapiro, A. L. Wachs, and T. C. Chiang, Phys. Rev. B **33**, 4421 (1986).

[22] W. Telieps and E. Bauer, Ber. Bunsenges. Phys. Chem. **90**, 197 (1986).

[23] F. Abeles, Thin Solid Films **34**, 291 (1976).

[24] K. Hricovini, G. LeLay, M. Abraham, and J. Bonnet (unpublished).

[25] G. A. Samara, Phys. Rev. B **27**, 3494 (1983).

[26] M. Abraham (unpublished).

[27] R. F. Lever, Surf. Sci. **9**, 370 (1968).

[28] E. G. McRae, J. M. Landwehr, J. E. McRae, G. H. Gilmer, and M. H. Grabow, Phys. Rev. B **38**, 13 178 (1988).

[29] J. N. Hodgson, Philos. Mag. **6**, 509 (1961).

[30] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, England, 1988).