

Hydrogen adsorption on $\text{ErSi}_{1.7}(0001)$

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The adsorption of hydrogen atoms on $\text{ErSi}_{1.7}(0001)$ thin films, epitaxially grown on Si(111), has been studied *in situ* by low-energy electron-diffraction, photoemission, temperature programmed desorption (TPD), and work-function measurements. The results obtained with these techniques indicate that, at low hydrogen exposures, the adsorption sites on the silicide surface are very similar to those on Si(111), confirming the structural model of a silicide terminated by a buckled silicon plane without Si vacancies. At larger exposures, a second state is observed by TPD at higher desorption temperature. This state is not observed by TPD on Si(111) and is attributed to hydrogen chemisorbed in the subsurface region of the silicide.

I. INTRODUCTION

Erbium silicide, $\text{ErSi}_{1.7}(0001)$, thin films grown on Si(111) by the evaporation or coevaporation techniques¹ are perhaps the best epitaxial silicide films, as ascertained by the sharp low-energy electron-diffraction (LEED) patterns and the richly structured angle-resolved photoemission spectroscopy (ARUPS) spectra.² The crystalline structure of the bulk silicide is of a defective AlB_2 type, with one out of six Si atoms in the (0001) plane missing. These vacancies appear to have a significant influence on the electronic structure³ although the energy location of the features related to the vacancies is still ambiguous.^{4,5} Ordering of the Si vacancies on the surface is commonly invoked in order to explain the $(\sqrt{3} \times \sqrt{3})R 30^\circ (R 3)$ LEED pattern, characteristic of the $\text{ErSi}_{1.7}(0001)$ surface, but some authors have recently proposed, on the basis of ARUPS experiments combined with band-structure calculations, that there are no vacancies on the surface.⁶ With an aim to obtain additional information on the atomic and electronic structure of the $\text{ErSi}_{1.7}(0001)$ surface, we have studied its interaction with hydrogen by means of LEED, photoemission (ARUPS, Auger electron spectroscopy, and x-ray photoemission spectroscopy), temperature-programmed desorption (TPD), and work-function (WF) measurements. The adsorption of atomic hydrogen on Si(111) has been the subject of both experimental and theoretical studies⁷⁻⁹ and offers a good basis for comparison with the silicide surface.

II. EXPERIMENT

The silicide layers, about 100 Å thick, were prepared *in situ* by solid-phase epitaxy, that is evaporation of Er on a clean Si(111) (7×7) surface followed by annealing at 750°C. Their crystalline quality was routinely controlled by the presence of the characteristic R3 LEED pattern

and/or the silicide-type Si *KLL* Auger spectrum.^{1,2} Atomic hydrogen adsorption near room temperature on the silicide surface was achieved by exposure to 1×10^{-6} mbar of H_2 in front of hot tungsten filament located about 5 cm from the sample. The exact flux of atomic hydrogen was not calibrated therefore exposures are reported in terms of molecular hydrogen. Atomic hydrogen exposures should be lower by a factor of the order of 10^{-3} , similar to previous work.⁷

Measurements were made in two different ESCA systems. The first one was additionally equipped with LEED and ARUPS,¹ whereas the second one with a quadrupole mass spectrometer for TPD and a Kelvin probe for WF measurements.¹⁰

III. RESULTS AND DISCUSSION

Before examining the experimental results, we briefly review the atomic and electronic structure of the erbium silicide epilayers. The silicide has a defective AlB_2 crystallographic structure, and is formed by alternate Er and Si planes with hexagonal symmetry. One out of six Si atoms is missing, giving the approximate composition $\text{ErSi}_{1.7}$. Vacancy ordering is thought to take place in the bulk material, and various superstructures have been reported.¹¹⁻¹³ The amount of these Si vacancies and their positions are found to influence greatly the electronic structure of the silicide.³ Several band-structure calculations have been performed for both stoichiometric ErSi_2 and nonstoichiometric $\text{ErSi}_{1.7}$,^{4,5} but the comparison between calculations and experiments remains inconclusive.

On Si(111) substrates, the silicide has the (0001) orientation. Its R3 LEED pattern is generally attributed to an ordering of the Si vacancies in the outermost plane, similar to a previous LEED and x-ray photoelectron diffraction study on the isostructural silicide $\text{YSi}_{1.7}$ by Baptist *et al.*¹⁴ These authors have shown that the sili-

side surface is terminated by a buckled Si plane the geometric structure of which is quite similar to that of an ideal Si(111) surface but studded with ordered vacancies. The existence of Si vacancies on the surface plane has been questioned.¹⁵ Recently, on the basis of ARUPS experiments combined with band-structure calculations, Wetzal *et al.* have concluded that there are no vacancies on the outermost Si plane.⁶ This point is relevant for adsorption experiments since the presence of vacancies greatly increases the number of dangling bonds (DB) on the Si atoms in the surface plane, and thus the number of available adsorption sites. On the contrary, without vacancies in the buckled Si top layer there are only 3 DB per $R3$ surface unit cell, perpendicular to the surface plane and pointing to the vacuum, as for an ideal Si(111) surface.

A. LEED and photoemission results

Hydrogen adsorption modifies very slightly the LEED patterns. Up to 400 L (langmuir, $1 \text{ L} = 10^{-6} \text{ Torr s}$), the characteristic $R3$ diagram of the clean $\text{ErSi}_{1.7}(0001)$ remains unaffected. Afterwards, very weak changes are observed. The $R3$ diagram is still preserved up to more than 10000 L. For such long exposures the only difference with the clean surface is in the relative intensity of the (1×1) and the superstructure ($R3$) spots, which shows a dependence on the primary energy. For instance, the intensity of the $R3$ spots relative to the (1×1) spots increases at 65 eV and decreases at 73 eV. The stability of the diffraction pattern, in the surface sensitive energy range (40–90 eV), indicates that the geometrical configuration of the surface is not strongly affected by hydrogen adsorption.

ARUPS spectra, on the contrary, show drastic modifications. This is illustrated in Fig. 1 for the two critical points K and M of the surface Brillouin zone (SBZ). Similar effects are also observed at the other critical points of the SBZ. The sharp and intense structures that are characteristic of the clean silicide surface in the 0–2-eV binding energy range, are found to become strongly attenuated at 400 L and even to disappear at higher exposures. These structures, located respectively near the Fermi level (at the M point) and about 1.4 eV below it (at the K point) have been attributed to surface states.^{2,6,15} The later state, furthermore, corresponds to the dangling bonds of the Si atoms of the outermost plane.⁶ The broad structures centered at 2.5 eV (M point) and at 3 eV (K point) seem to be less sensitive to H adsorption, at least for small exposures, in agreement with previous adsorption studies using oxygen² and silicon.^{6,16} The origin, probably bulk, of these broad structures is not firmly established. The ARUPS experiments basically show that the well-known surface states disappear upon exposure to hydrogen, that is, hydrogen atoms are adsorbed on the silicide surface. Since the silicide is terminated by a double layer of silicon atoms, one can conjecture that at least part of the H atoms are bonded to the Si surface atoms, saturating the dangling bonds and forming a monohydride phase, as in the case of the Si(111) surface.^{7–9} This hypothesis is consistent with the disappear-

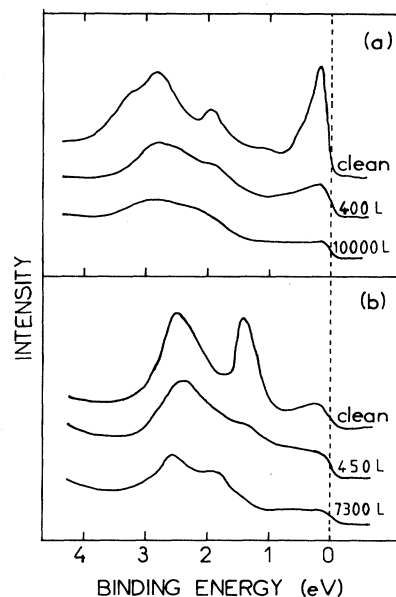


FIG. 1. ARUPS (He I) spectra close to the M point (a) and the K point (b) of the SBZ, taken on clean $\text{ErSi}_{1.7}(0001)$ surface and upon hydrogen exposures, in Langmuir.

ance of the surface DB states after hydrogen dosing and also with the stability of the LEED pattern. Further evidence for an interaction between H and Si atoms in the near surface region can be obtained from Auger electron spectroscopy, namely, from the Si $L_{23}VV$ spectra shown in Fig. 2. Due to the low kinetic energy (90 eV) of the Si $L_{23}VV$ Auger electrons, their mean free path λ is of the order of magnitude of the distance between Si planes normal to the surface (4 Å), which makes this Auger line surface sensitive (about 50% of the total signal would originate from the terminal Si plane for $\lambda = 6 \text{ Å}$). One can see from Fig. 2 that the Si $L_{23}VV$ line shape becomes significantly different after H adsorption, which is indicative of a modification of the Si partial density of states in the surface region. We interpret this as another indication of Si-H bonding in the surface silicon plane.

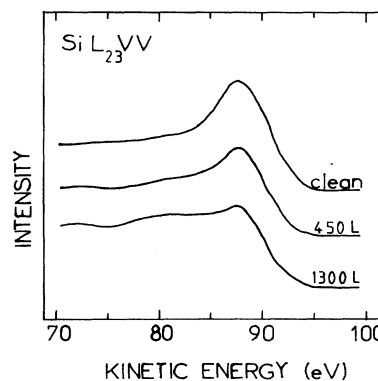


FIG. 2. $\text{Si}L_{23}VV$ spectra on clean $\text{ErSi}_{1.7}(0001)$ and upon hydrogen exposures, in Langmuir.

The possibility that H atoms diffuse in the volume of the silicide needs further consideration. Due to the existence of vacancies in the bulk Si planes, H trapping in these sites is conceivable. ARUPS is too surface sensitive to provide information on this point. The Si $2p$ and Er $4f$ and $4d$ XPS core levels, as well as the Si KLL Auger line have been recorded before and after large exposures (> 1000 L). The corresponding photoelectrons have a kinetic energy larger than 1000 eV, and thus should originate mainly from the bulk. The only difference observed after H adsorption is a slight broadening of the Si lines by ~ 0.2 eV. This, however, could also be a surface effect, due to changes in the electronic structure of the surface silicon plane. Evidence for hydrogen incorporation in the subsurface region of the silicide is offered by the TPD results.

B. Thermal desorption and work-function results

Figure 3 shows the hydrogen TPD spectra from the erbium silicide surface following a series of increasing exposures and using a heating rate of about 1.5 K/s. Only molecular hydrogen was obtained upon desorption. The spectra have been background subtracted and displaced along the vertical axis for clarity.

The desorption spectra in Fig. 3 exhibit two desorption states, β_1 around 800 K and β_0 around 880 K. It is remarkable that the low-temperature state β_1 begins to fill first, followed by state β_0 above 1200 L. State β_1 should be attributed to hydrogen atoms chemisorbed on top of silicon atoms of the outermost surface layer in a monohydride configuration thus corresponding to the β_1 state for hydrogen desorption from Si(111). This state desorbs around 800 K for Si(111) (Ref. 7) as well as for other single-crystal silicon planes.⁸ The above assignment is consistent with the close resemblance of the $\text{ErSi}_x(0001)$ surface to the outermost surface layers of unreconstruct-

ed Si(111) as pointed out in the previous paragraph. State β_0 has no counterpart on Si(111) and should be related to a distinct feature of the silicide, such as the presence of Er atoms or the silicon vacancies in the subsurface region. Although state β_0 eventually desorbs at higher temperature, the adsorption probability for filling it appears to be vanishingly low as long as β_1 is not substantially filled. On Si(111) state β_1 is filled with a sticking probability close to one and additional hydrogen populates multiple adsorption states, like β_2 and β_3 , dihydride or trihydride type, with lower desorption temperature.⁷ It is clear that state β_0 cannot be assigned to such multiple adsorption states since it desorbs at higher temperature. The possibility of another surface site special for the silicide, like silicon vacancies with extra dangling bonds, is not likely because it is difficult to explain why such an energetically favorable surface site would be kinetically excluded in the early stages of adsorption. Thus the existence of surface vacancies is not necessary for explaining the TPD results. On the other hand, the presence of vacancies in the subsurface is consistent with state β_0 since incorporation of an adsorbing species into the subsurface, although energetically favorable, can be kinetically hindered. Quantification of this hindering effect, that is, determination of a possible activation barrier for interconversion of β_1 and β_0 states calls for additional kinetic measurements beyond the scope of this work.

The work-function measurements using a Kelvin probe support the above picture. The clean silicide has a WF value of 5.4 eV, referenced to the Si(111)- 7×7 surface with a WF value of 4.5 eV.¹⁷ The higher WF of the silicide is consistent with the more closely packed, unreconstructed surface layer compared to the open 7×7 surface. Upon atomic hydrogen adsorption the WF increases and saturates at around +120 meV for an exposure of 1800 L when the β_1 state is filled and the β_0 state has begun to populate. The sign of the WF change is indicative of charge transfer from the silicide to hydrogen, which is consistent with the drastic attenuation of the surface states upon hydrogen adsorption. Further growth of the β_0 state does not affect the WF value, within an experimental uncertainty ± 10 meV, consistent with the assignment of this state to subsurface adsorption. The absence of any measurable bulk electronic effects in XPS associated with state β_0 suggests that there is no substantial charge transfer between hydrogen atoms and the substrate in this state. However, state β_0 could be associated, at least in part, with the attenuation of the higher binding energy (1.5–3 eV) features in the ARUPS spectra, thus supporting their subsurface origin.

IV. CONCLUSION

The adsorption of hydrogen on $\text{ErSi}_{1.7}(0001)$ was studied by means of LEED, photoemission, TPD, and WF measurements. The main conclusions are the following: (1) The electronic features attributed to surface states in previous studies are rapidly attenuated upon adsorption confirming their surface nature. (2) Initial hydrogen ad-

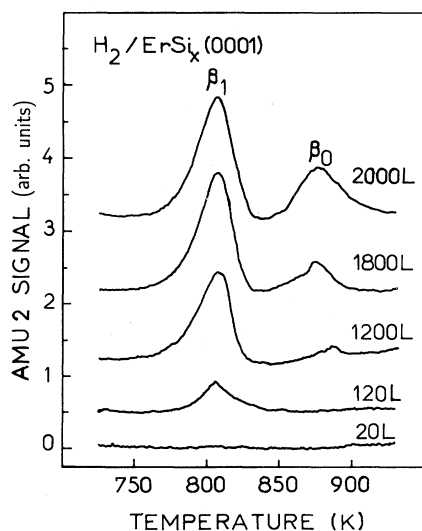


FIG. 3. Temperature programmed desorption (TPD) spectra upon increasing exposures to H_2 , in Langmuir.

sorption proceeds in the same manner as on Si(111), supporting the picture that $\text{ErSi}_{1.7}(0001)$ is terminated by a buckled Si plane the geometric structure of which is very similar to that of an ideal Si(111) surface. Moreover, as only one type of surface adsorption site is detected on the surface, the Si atoms should have the same atomic environment, supporting the surface model proposed by Wetzel *et al.*⁶ (buckled Si layer without Si vacancies). (3)

Large exposure to hydrogen leads to hydrogen incorporation in the subsurface, possibly at Si vacancies.

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