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VACANCY-INDUCED ELECTRONIC STATES IN $ErSi_{1.7}$(0001)

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Abstract—The physical origin of bulk related features observed by angle-resolved photoelectron spectroscopy for an ordered 2ML $\sqrt{3} \times \sqrt{3}$R30° $ErSi_{1.7}$ silicide on Si(111) has been investigated by means of band structure calculations. The photoemission data are well explained with the defected Er silicide model, i.e. the prominent peaks related to bulk states are consistent with the presence of a defected Si graphite-like plane. More specifically, the calculations clearly predict a nearly flat non-bonding π band near the Fermi level that is observed experimentally and directly reflects the ordered $\sqrt{3}$ array of Si vacancies. © 1997 Elsevier Science Ltd. All rights reserved

Keywords: A. thin films, B. epitaxial growth, C. photoelectron spectroscopy, D. electronic structure.

$ErSi_{1.7}$ silicide films epitaxially grown on Si(111) have been investigated extensively in both experimental and theoretical studies. These silicides are thought to form a defected AlB_2-type structure resulting from the presence of vacancy networks in the Si sublattice [1–3]. The silicide atomic structure is made up of alternated hexagonal Er planes and defected Si graphite-like planes which are piled up along the [0001] direction. A $\sqrt{3} \times \sqrt{3}$R30° superstructure is induced by the ordered array of Si vacancies. The $ErSi_{1.7}$ silicide surface electronic structure is now well established [4–7]. It has greatly benefited from the successful determination of the atomic structure of an ultrathin (≤ 1 Er monolayer (ML)) stoichiometric two-dimensional p(1 × 1) $ErSi_2$ silicide [7–9]. This surface silicide can be considered as a prototype for experimental and theoretical studies because of its inherent simplicity since its structure does not involve Si vacancies in contrast to bulk-like $ErSi_{1.7}$. Yet, both $ErSi_2$ and $ErSi_{1.7}$ silicide layers exhibit very similar surface atomic structures made of a buckled Si layer without vacancies similar to a (1 × 1) Si(111) surface in spite of the different $p(1 \times 1)$ and $\sqrt{3}$ periodicities [4, 10, 11]. As far as the $ErSi_{1.7}$ surface electronic structure is concerned specific surface bands mainly derived from dangling bonds of the topmost Si layer have been identified [4, 5]. In contrast, much less is known about the bulk electronic structure of $ErSi_{1.7}$ silicide layers where the presence of defected Si graphite-like planes is expected to reflect in the electronic structure. The creation of Si vacancies, one atom out of six missing, involves the breaking of covalent bonds and thus the creation of dangling bonds pointing parallel to the graphite-like plane. These dangling bonds are quite reactive and they are directly involved in rebonding in bulk [12, 13]. Up to now, the identification of specific vacancy related electronic states in photoemission data has been suggested but it is not yet firmly established [7, 13–16].

The purpose of the present paper is to provide theoretical information on $ErSi_{1.7}$ silicide bulk related electronic bands and to compare them with experimental photoemission data. In contrast with previous attempts [14, 16] we concentrate here mainly on a 2 ML $ErSi_{1.7}$ slab (Fig. 1) which involves only a single defected Si plane and results in a much simpler band structure than thicker silicide layers. In this way we obtain good insight into their physical origin as well as a definite assignment of the main features observed by photoemission. In order to clearly identify bands related to bulk states originating in the Si graphite-like plane and investigate their physical origin we have first calculated the energy bands pertaining to a single Si(0001) honeycomb plane with and without an ordered array of Si vacancies. The calculations definitely demonstrate that an occupied nearly flat π band reflecting p_z-like states appears near the Fermi level (E_F) which is induced by the periodic $\sqrt{3}$ arrangement of vacancies in the Si graphite-like plane. These states can be viewed as non-bonding defect-induced states near the middle of the π band. They indeed reflect as a sharp peak in photoemission with correct symmetry and energy position.

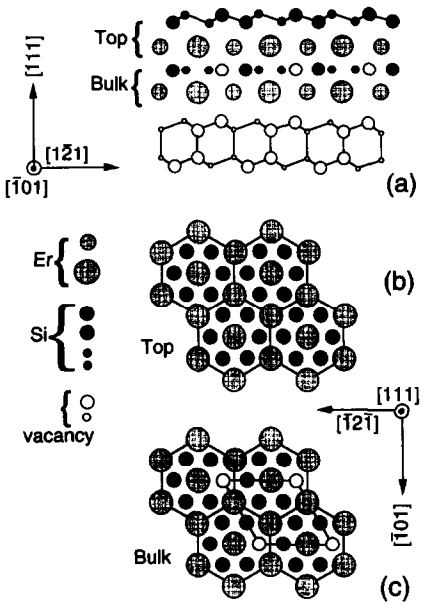

Fig. 1. Slab used in the band calculations for a 2 ML Er silicide: (a) side view, the smaller circles indicate atoms lying out of the plane of the paper; (b) sketch of the reconstructed silicide top layer; (c) underlying bulk-like silicide layer.

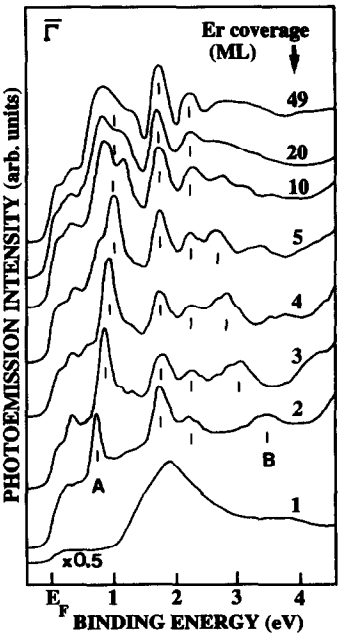

Fig. 2. Normal emission angle-resolved photoelectron spectra for various epitaxial Er silicide film thicknesses taken with He_I photon energy.

The experimental procedure and apparatus has been described previously [5]. All photoemission data were obtained using a hemispherical analyzer with overall energy and angular resolutions of less than 40 meV and ±1° at He_I, respectively. To produce the $ErSi_{1.7}$ silicide layer, Er and Si are codeposited on the clean 7 × 7 Si(111) sample at room temperature and then annealed in the 500–700°C range. Upon cooling to room temperature, a $\sqrt{3} \times \sqrt{3}$R30° low-energy electron diffraction (LEED) pattern is observed. The silicide layer obtained in this way presents a nearly layer-by-layer growth mode [17].

Calculations are performed using the crystalline extension of the extended Hückel method. These are essentially 'tight binding calculations' including the usual approximations of the extended Hückel method for the wave functions and Hamiltonian matrix elements [18–20]. This method and the parameters adopted for the simulations have been described in detail in previous publications [4]. We consider a slab of two (or more) silicide layers and five Si(111) double layers in order to simulate the Si(111) substrate. Orbital analysis allows us to identify bulk-related states which are the subject of the present investigation.

First let us consider the available experimental data. Fig. 2 shows highly structured angular resolved photoemission spectra of $ErSi_{1.7}$ silicides for different Er coverages. All spectra were collected at normal emission and excited with 21.2 eV photons. Surface states located at 1.8 and 2.2 eV binding energy (BE) have been identified in previous works [14, 21]. According to their dependence on the polarization of the exciting light [15] we have assigned the peak at 1.8 eV to $\bar{\Gamma}3$ initial states reflecting back-bond surface states of the buckled Si layer terminating the silicide. Bulk related features are located around 1.0 eV and in the 2.5–4.0 eV BE range. They show a marked dependence on film thickness, display $\bar{\Gamma}1$ symmetry and were tentatively assigned in previous work to Si p_z-states, i.e. states that reflect the graphite-like Si π band [15]. For 2ML Er a well-defined and sharp peak (denoted A) can be seen at ~0.7 eV below E_F. This peak with $\bar{\Gamma}1$ symmetry appears only for Er coverages above 1 Er ML in connection with the formation of a graphite-like Si plane expected at this coverage and is fully developed upon completion of the second Er monolayer. For higher Er coverages the shape of this feature evolves into a broader structure centered around 1 eV BE. In previous studies [15] this feature was proposed to reflect defect-induced π states due to the presence of vacancies in the graphite-like Si plane. As shown below, the present theoretical analysis definitely confirms this assignment as well as the interpretation of the feature at ~3.5 eV BE for 2 ML (denoted B) in term of bonding Si π bands. Experimental data show that the latter shift towards lower BE with increasing the Er coverage.

To get physical insight into the origin of vacancy induced electronic states, let us consider first the calculated electronic structure of an isolated Si(0001) plane, i.e. a monolayer of Si in a graphite-like arrangement (honeycomb lattice) either with or without an ordered array of Si vacancies as in bulk Er silicide. The

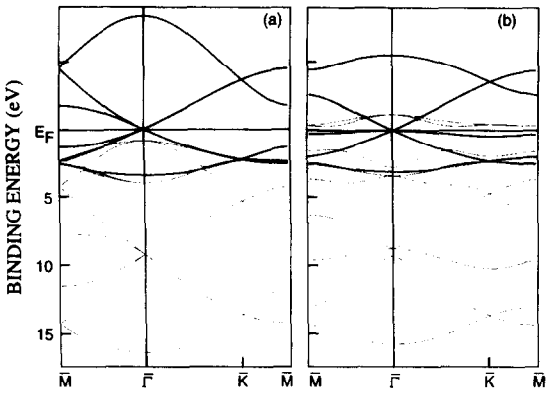

Fig. 3. Calculated energy bands: (a) for a perfect Si(0001) honeycomb monolayer; and (b) for a Si(0001) honeycomb monolayer with an ordered $\sqrt{3} \times \sqrt{3}R30°$ array of vacancies. $\sigma(\pi)$ bands are denoted by small (heavy) lines.

interaction of Si with Er has ionic character, which leads to a charge transfer from Er to Si, the Er atom being more electropositive than the Si and its valence orbitals (5d, 6s) lying at higher energies. Hence, little change in the nature of the Si derived bands is expected upon switching on the interaction with the Er and it is expected that the electronic structure of the graphite-like Si plane already displays major features of the electronic structure of the silicide. The calculated band structure and density of states (DOS) of the perfect Si(0001) honeycomb monolayer are presented in Figs 3a and 4a. The band dispersions are drawn in the reduced $\sqrt{3} \times \sqrt{3}R30°$ surface Brillouin zone (SBZ). The results reflect the well known electronic structure of graphite in which simultaneous band formation from σ as well as π bonding and anti-bonding states takes place [22]. The π bands are related to the interaction of (mainly) nearest neighbor Sip_z orbitals pointing perpendicular to the graphite-like plane. The

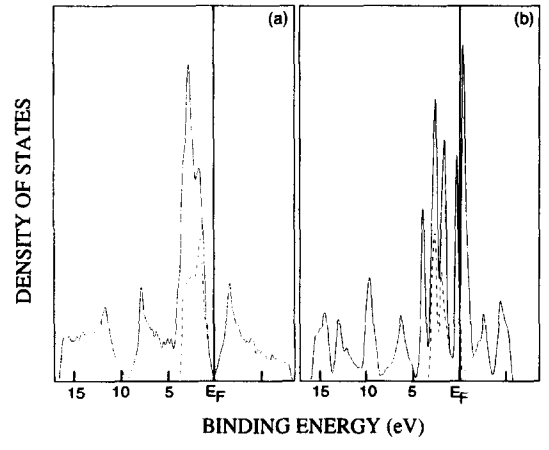

Fig. 4. Total density of states (DOS) (continuous lines): (a) for a perfect Si(0001) honeycomb monolayer; and (b) for a Si(0001) honeycomb monolayer with an ordered $\sqrt{3} \times \sqrt{3}R30°$ array of vacancies. The partial π DOS is denoted by dashed lines.

σ bonding bands are induced by the overlap of the sp_2 hybrids build from s, p_x and p_y orbitals lying in the Si graphite-like plane. The σ bands which correspond to even states never mix with π bands corresponding to odd states with respect to the Si plane. The density of π states splits into two peaks on either side of E_F. They are centered at ~ 2 and ~ -4 eV BE. The former corresponds to occupied bonding levels and the latter to unoccupied anti-bonding levels. The density of σ states shows only bonding levels in the energy range displayed in Fig. 4a. They are located lower in energy than the π bonding states since the degree of overlap in a π-bond is much less than in a σ-bond. As a result the σ bonding levels are fairly well separated in energy from σ anti-bonding states. In contrast bonding and anti-bonding π bands do not exhibit an energy gap indicating that the Si graphite-like plane is a semimetal with a zero energy gap. The system exhibits a great stability since only bonding σ and π states are occupied.

Let us now consider the electronic structure of a similar monolayer of Si in a graphite-like arrangement but with an ordered array of Si vacancies. The creation of a vacancy involves the breaking of three covalent σ bonds and results in three Si dangling bonds. The corresponding band structure and DOS curves are depicted in Figs. 3b and 4b. As can be seen the most important changes brought about by the introduction of an ordered lattice of vacancies is the appearance of new additional bands near E_F, one occupied π band and two unoccupied σ bands. These bands are nearly flat and the π band is located between the bonding and anti-bonding π levels while the σ bands emerge just above E_F. These bands directly reflect the ordered $\sqrt{3}$ array of Si vacancies. The distance between the Si vacancies is relatively large so their interactions are small. This is why the Si vacancy induced σ and π states are essentially localized with little dispersion, reminiscent to atomic-like orbitals located near the atomic orbital energies, i.e. in between bonding and anti-bonding states. The flat π band reflects non-bonding defect-induced states near the middle of the π band. Similarly, the two unoccupied nearly flat σ bands are directly derived from a non-bonding combination of the three vacancy neighbor Si sp_2 dangling bond states. These defect-induced states reflect in two new prominent peaks in the DOS curves. Finally, it can be seen that the reduction of the number of nearest neighbors in the defected Si plane leads to an overall decrease of the σ and π bandwidth. One also observes a small change in the band topology.

We now consider the electronic structure of a 2ML thick Er silicide slab. This atomic structure can be viewed as a defected Si graphite-like layer inserted between two hexagonal Er planes and a buckled Si

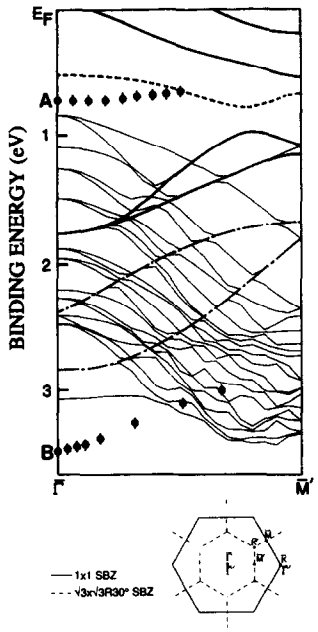

Fig. 5. Calculated band structure for a 2 ML thick Er silicide slab along the $\bar{\Gamma}\bar{M}'$ direction of the $\sqrt{3} \times \sqrt{3}$R30° SBZ together with experimental data (dots) relevant to peaks A and B.

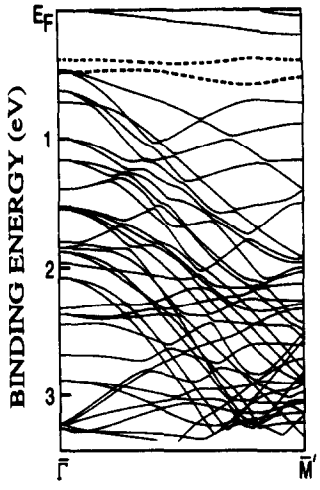

Fig. 6. Calculated band structure for a 3 ML thick Er silicide slab along $\bar{\Gamma}\bar{M}'$.

layer as top layer (see Fig. 1). The interaction of the Si with Er mainly results in a charge transfer from Er to Si. Thus, we expect that the Si graphite-like plane gets additional charge and some bands corresponding to the levels near E_F will populate. One also expects an hybridization of the higher lying σ or π bands (near E_F) with Er 5d states. In the following discussion we mainly concentrate on the π states as well as on the defect induced σ and π states expected in the 0–4 eV BE range. Bonding σ states are less sensitive to the presence of Si vacancies and are located at higher BE. They correspond to a broad feature observed in the 5–8 eV BE in the photoemission data (not shown) in fairly good agreement with theory [15].

Figure 5 displays part of the calculated band structure for a 2 ML thick Er silicide slab along the $\bar{\Gamma}\bar{M}'$ direction of the $\sqrt{3} \times \sqrt{3}$R30° SBZ together with experimental data relevant to peaks A and B [5, 6]. The calculations are performed using the crystallographic model described above and determined in Ref. [4]. A relaxation of ~ 0.25 Å of the Si vacancy neighbors towards the vacancies has been adopted [4] while the Er species are located in their ideal positions since there relaxation is expected to be very small [9]. The heavy lines found within 2 eV below E_F have been identified as surface bands and discussed elsewhere [4, 5]. On the other hand most bands dispersing downwards away from $\bar{\Gamma}$ correspond to the Sip_{xy} derived bulk bands that describe the Si substrate continuum. Of special interest here is the nearly flat band (dashed line) visible at ~ 0.5 eV BE ($\bar{\Gamma}$ point). An orbital analysis at the $\bar{\Gamma}$ point indicates that this band is mainly built up from Si3p_z on the single defected Si graphite-like plane as well as from Si3p_z on the outermost Si plane of the buckled top layer (dangling bond p_z states). There is also a sizable Er 5d contribution from the hexagonal Er planes. Off $\bar{\Gamma}$ this band acquires progressively dominant Si3p_z dangling bond character and at $\bar{M}$ it is a pure Si3p_z dangling bond state. This band is reminiscent to the defect-induced non-bonding π band obtained for the single graphite-like plane and orbital analysis confirms that this is actually the physical origin of this band around $\bar{\Gamma}$. As apparent in Fig. 5 this band fits quite well to the experimental dispersion of the conspicuous peak A. Moreover, the symmetry (p_z character) of the calculated band agrees with the polarization dependent photoemission measurements [15]. As can be seen in Fig. 5, the peak A is detected in an angular range 0–8°. With increasing emission angle the peak disappears progressively because of mixing with surface states as predicted by theory. This non-bonding π band is located at higher BE with respect to the one observed for the single defected Si honeycomb monolayer because of charge transfer from Er to Si.

Orbital analysis shows that at $\bar{\Gamma}$ point, silicide related π bands with bonding character are predicted at ~ 2.4 and 2.8 eV BE (dash-dotted lines). They disperse upward when moving off $\bar{\Gamma}$. The π bands at $\bar{\Gamma}$ are observed experimentally at $\sim$3.5 eV BE [15]. This corresponds to the B structure in Fig. 2 and is shifted towards higher BE with respect to the calculations. Yet the agreement is quite satisfactory since the Hückel calculations are not self-consistent and photoemission measure excited states and not merely one-electron energy states. Finally, the calculations predict

defect-induced σ bands that are now populated and located at ~ 1.5 eV (at $\bar{\Gamma}$). Actually, no prominent feature is observed experimentally with He_I photons in the range where the theoretical calculations place this kind of states. More work remains to be done experimentally using different collection geometries and/or photon energies in order to identify this kind of vacancy-induced electronic states.

Having established the identification of the peak A for a 2 ML thick silicide as defect related bulk states with π symmetry, it may be instructive to consider briefly the evolution of this feature for thicker silicide layers. The effect of the interaction between the different defected graphite-like planes present in the silicide for coverage larger than 2 ML Er can be neglected for the σ bands but should be considered when dealing with bands formed from p_z orbitals, since their overlap between the different planes via Er 5d states is not negligible as they point in direction perpendicular to the planes. Thus qualitatively one expects the π derived states to show a marked dependence on thickness in contrast to the σ derived states as is indeed observed experimentally. More specifically in Fig. 2 it can be seen that the defect-induced peak A is remarkably narrow (200 meV) due to the fact that it is an atomic-like p_z state and there is only a single Si graphite-like plane. Now one observes a progressive broadening of peak A as a function of thickness in Fig. 2. By 49 ML this feature becomes a broad double-peaked structure in the 0.5–1.5 eV BE range. Clearly this is the expected behavior if the interpretation of photoemission data presented above is indeed correct. In this respect, Fig. 6 shows the calculated band structure for a 3 ML $ErSi_{1.7}$ thick silicide slab. We now clearly observe two non-bonding flat occupied π bands (dashed lines) related to the presence of two defected graphite-like planes. The coupling between the two Si planes leads to a splitting of the defect-induced π bands into two subbands. The splitting is small, of the order of 0.1 eV, indicating weak interactions between the layers. This theoretical prediction is quite consistent with photoemission where the coupling leads to a substantial broadening of the A peak by 3 ML. It also confirms the bulk related nature of these electron states.

To summarize, we have investigated the physical origin of Er silicide bulk related features observed by angular resolved photoemission using band structure calculations. We have more specifically demonstrated that for a 2 ML thick Er silicide a nearly flat non-bonding π band appears near E_F related to the ordered $\sqrt{3}$ array of Si vacancies present in the graphite-like plane. As more and more silicide layers are added, the relevant band splits because of the interaction between the adjacent defected Si graphite-like planes along the surface normal. For an N monolayer-thick silicide layer, the non-bonding π band splits into $N-1$ bands, the number of defected Si graphite-like planes. Since the splitting is small the different bands are closely spaced and form a continuous band of energy for large N, i.e. in bulk limit. Experimentally, the relevant peak becomes broader with a specific structure when more silicide layers are added as predicted by above considerations. This peak related to the π defect induced bulk states is fully developed (characteristic of thick Er silicide layer) only for layer thicknesses larger than 50 ML. This suggests some long range interaction along the surface normal, possibly related to a specific stacking of antiphase $\sqrt{3}$ vacancy networks in successive planes. In this respect a superperiod of 2c along the surface normal has been suggested for similar silicides [23].

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