Published in Surface Science 566-568, issue 2, 1047-1051, 2004
which should be used for any reference to this work

Use of angle-resolved photoemission and density functional theory for surface structural analysis of YSi_2

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Abstract

The atomic structure of two-dimensional yttrium silicide epitaxially grown on Si(1 1 1) was investigated by means of density functional theory calculations and angle-resolved photoemission experiments. The obtained accuracy of the calculations allowed to discriminate different surface arrangements in a quantitative way via comparing their theoretical band structure to the experimental result. Theoretically we find significant changes in the dispersion of a surface localized band upon varying the thickness of the topmost silicon bilayer. For a thickness of 0.4 Å of the topmost silicon bilayer a strong asymmetry of the surface localized band with respect to $\overline{\Gamma}$ is found, while a thickness of 0.8 Å yields a more symmetric dispersion of the band. By comparison with the experimental photoemission results, which show a rather symmetric band around $\overline{\Gamma}$, we can conclude that the topmost bilayer has a thickness of 0.8 Å.

Keywords: Density functional calculations; Angle resolved photoemission; Surface electronic phenomena (work function, surface potential, surface states, etc.); Surface structure, morphology, roughness, and topography; Metal–semiconductor interfaces; Yttrium; Silicon

1. Introduction

For almost two decades the electronic structure of heavy rare earth (RE) silicides has attracted considerable interest due to potential applications in silicon based devices as a metallization layer. Very low Schottky barrier heights on n-type Si(1 1 1) [1] were determined. On a fundamental level, the very initial stages of silicide formation, e.g. the formation of the first monolayer (ML) are of special interest. It has been shown for YSi_2, $GdSi_2$ [2], $ErSi_2$ [3], $DySi_2$ [4] and $HoSi_2$ [5] that a solid state reaction at elevated temperatures takes place, which transforms the initially deposited monolayer into a structure commonly denoted as a two-dimensional (2D) surface silicide. Fig. 1 shows a graphical representation of this model, together with the resulting surface Brillouin zone. An intermixing of the two initial constituents (metal, silicon) leads to a buckled silicon-bilayer terminated surface (Si1–Si2), with a planar, hexagonal metal atom sheet (Y) underneath. Below, the silicon bulk follows (Si3 to Si11), which is rotated 180°

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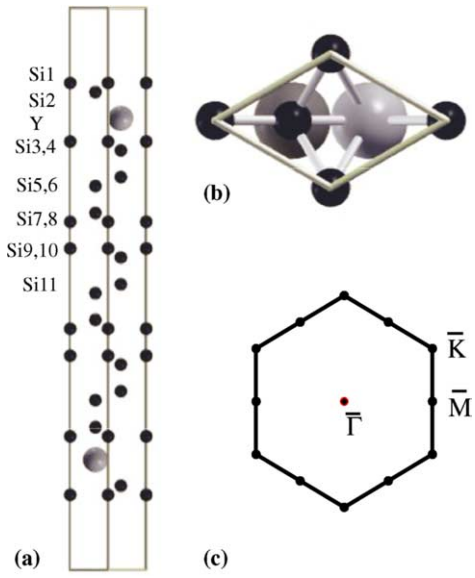

Fig. 1. (a) Side view of supercell, (b) top view of supercell, and (c) hexagonal surface Brillouin zone of the same supercell.

around the surface normal with respect to the orientation of the surface terminating bilayer (Si1–Si2). The depicted supercell (slab) is inversion symmetric in order to simplify electronic structure calculations (see below). A generalization of this structural model to other rare earths seems feasible.

A recent detailed structural investigation of the YSi_2 surface silicide based on low energy electron diffraction (LEED), demonstrated that this technique might show ambiguities due to the existence of different local *R* factor minima [2]. In this case the ambiguities arose for a bilayer thickness (Si1–Si2) of 0.33 and 0.79 Å, where the *R* factor was similarly low. By choosing different measurement geometries and with the support of ab initio total energy calculations Rogero et al. [2] were able to circumvent this problem and proposed a structural model with bilayer thickness (Si1–Si2) of 0.8 Å. In this paper we present additional experimental evidence for the proposed model, by comparing the experimental electronic structure to theoretical results obtained for different bilayer thicknesses (Si1–Si2). For this purpose we calculated the band structure for surfaces, which deviated from the proposed structure and compare the calculations to photoemission results. We used structural parameters closely derived from the aforementioned LEED study with one free parameter, namely the uppermost bilayer thickness (Si1–Si2), where the ambiguities in LEED arose [2]. With regard to slight deviations for (Y–Si3) and (Si3–Si4) (see Table 1), it is assumed that they do not affect the employed surface state dispersion due to its localized nature (see below). The band structure was calculated ab initio for different thicknesses of the topmost bilayer (Si1–Si2). The different parameters for structures "α" to "δ" and the LEED derived results are shown in Table 1.

2. Experimental and computational details

The YSi_2:Si(1 1 1) silicide was prepared by depositing 1 ML of Y on a clean Si(1 1 1)-7×7 reconstructed substrate at room temperature and a subsequent anneal to 400 °C for 15 min. The pres-

Table 1
Interplanar distances (in Å) between atomic planes along the (1 1 1) direction, derived from a LEED study (2) and the values employed in the present investigation

Atoms	LEED	DFT–LDA (Wien2k)			
		Slab "α"	Slab "β"	Slab "γ"	Slab "δ"
Si1–Si2	0.79	0.2	0.4	0.8	1.13
Si2–Y	1.85			1.88	
Y–Si3	2.08			2.04	
Si3–Si4	0.90			0.78	
Si4–Si5	2.35			2.35	
Si5–Si6	0.78			0.78	

(Si1–Si2) is varied between 0.2 and 1.13 Å.
Both LEED and this study use a lateral lattice constant of 3.83 Å.

sure during evaporation and anneal was in the low 10^{-10} mbar range. The formation of the 2D yttrium silicide was confirmed by the presence of a sharp (1×1) LEED pattern with traces neither of the (7×7) nor the $(\sqrt{3}\times\sqrt{3})$ reconstructions, which would have been indicative for the reconstructed thicker silicide (for more details see Ref. [2]).

The photoemission experiments were performed in situ in a modified VG ESCALAB Mk II spectrometer with a base pressure lower than 10^{-10} mbar. All measurements were obtained using monochromatized He I radiation. The combined angular resolution of sample manipulator and energy analyzer was approximately 1° and the energy resolution 50 meV [6,7].

For the electronic structure calculations the ab initio code Wien2k [8] was used. A muffin tin radius for Y and Si of 2 and 2.1 Å, respectively, was assumed. The calculations are based on a slab as depicted in Fig. 1a and b. The hexagonal unit cell with 12 inequivalent atoms has an in-plane lattice constant of 3.83 Å, a value based on the aforementioned LEED study [2]. The lattice vector perpendicular to the surface has a length of 49.3 Å and includes a vacuum region of more than 12 Å. The unit cell is inversion symmetric and is comprised of an YSi_2 terminated top and bottom of the slab. In principle, such a construction is valid, if a standing wave formation due to the limited extension in z-direction is omitted. The supercell was constructed such that, the interaction of the two surfaces through the slab and through the vacuum region was minimized and the calculation was still feasible on a Linux PC with an Athlon processor. Self-consistency was achieved, when the total energy change was less than 0.1 mRy in subsequent cycles.

3. Results

The resulting band structure for slab "γ" with a, bilayer thickness of 0.8 Å is plotted in Fig. 2a in an energy window from −10 to 1.6 eV along $\overline{M}\,\overline{\Gamma}\,\overline{K}\,\overline{M}$ in the surface Brillouin zone (Fig. 1b). Additionally the surface projected band structure for Si(1 1 1) is shown in grey as an overlay.

Fig. 2b shows the corresponding site resolved density of states for the first five atoms (Si1–Si4, Y) and the bulk-like atom Si11. The computed band structure (Fig. 2a) is in nice agreement with the band structure calculated by Stauffer et al. [9]. Special emphasis is drawn to band (A), which is in the fundamental gap of the underlying Si(1 1 1) substrate. It cuts the Fermi level at $k_F = 0.14$ Å^{-1} and follows an almost parabolic downward dispersion to $\overline{M}$ and $\overline{K}$ down to $E_B = -1.4$ eV. The band is then rather flat along $\overline{M}\,\overline{K}$. It is this flat region, which gives rise to a peak in the projected density of states shown in Fig. 2b and labelled as A*. This peak in the projected density of states can clearly be seen for Si1, Si2 and Y and then quickly

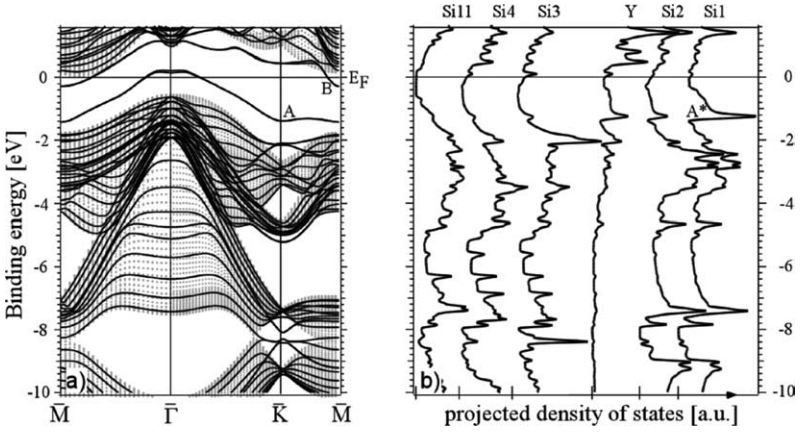

Fig. 2. (a) Band structure for slab "γ" and overlayed the surface projected band structure of Si(1 1 1) and (b) atomic site resolved density of states for slab "γ".

fades out. This confirms its localized nature and together with its position in the fundamental silicon gap we identify band (A) as surface state. A discussion of the detailed nature of bonding in this material is forthcoming [10]. In the following we compare the calculated dispersion of band (A) to the experimental spectra. The measurement and the corresponding calculated surface state dispersions are shown in Fig. 3a. We restrict the discussion to the aforementioned band (A). We note a very nice overall agreement between the measured $E(k_{\|})$ and the predicted behaviour, as an almost fully occupied band with a parabolic downwards dispersion towards $\overline{K}$ and $\overline{M}$ and a rather flat region along $\overline{K}\,\overline{M}$. Moreover if one compares to the overlayed computed surface state dispersion, we note a maximum agreement between theory and measurement for slab "γ". For the other calculated geometries the agreement is less convincing. While the dispersion is less affected in the $\overline{\Gamma}\,\overline{M}$ direction, a clear deviation from the measurement is visible in the $\overline{\Gamma}\,\overline{K}$ direction. For structure "α" and "β" we observe a notable increase of the Fermi wave vector k_F, rendering the band structure more asymmetric around $\overline{\Gamma}$. The increase in K_F is approximately 50% with respect to the value for slab "γ", which is in disagreement to the measurement, where the region of high photoemission intensity is rather symmetric around $\overline{\Gamma}$. This can be clearly seen in the symmetrized spectra of Fig. 3b, where an increased intensity at E_F is signified by the merging of the two symmetric features at E_F into one peak. This is the case for spectra (1) and (1*), which are symmetric around $\overline{\Gamma}$. With regard to a distinction between structure "γ" and "δ", we note a better agreement at $\overline{K}$ for the structure "γ".

4. Discussion

The idea of discriminating different surface structural models via comparing their corresponding electronic band structure to experimental photoemission results is only feasible for certain cases. Reliable band structure calculations must be possible for the system in question and the band structure, namely specific localized bands, must be sensitive to the variation of structural parameters. In this sense the YSi_2 system presents an ideal case, since it gives rise to a surface state, which is localized largely in the topmost three layers. Fur-

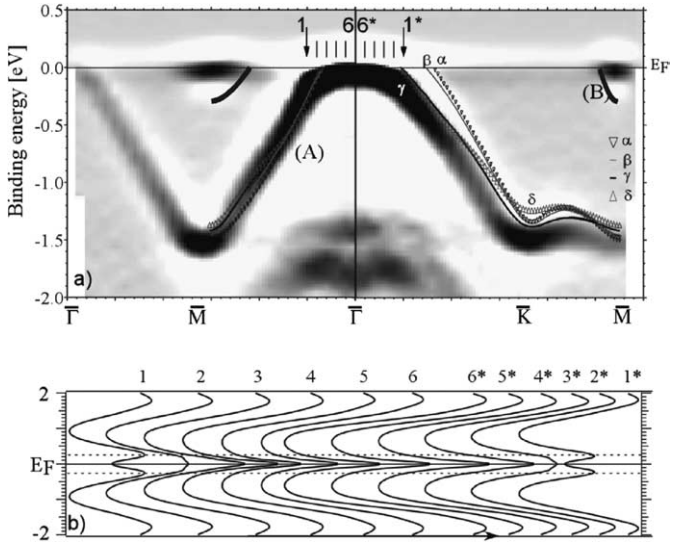

Fig. 3. (a) Experimental band structure (shown is the second derivative of the measured intensities in a grey scale, black corresponds to high intensity) for YSi_2 along $\overline{\Gamma}\,\overline{M}\,\overline{\Gamma}\,\overline{K}\,\overline{M}$ and overlayed surface state dispersion for different supercells (see text) and (b) experimental symmetrized spectra for $k_{\|}$ values around $\overline{\Gamma}$.

thermore the band dispersion is sensitive to the structural parameter that is to be optimized namely the bilayer thickness (Si1–Si2). This sensitivity allowed us to discriminate between the two different structures in question and it was possible to support the LEED derived bilayer thickness of 0.8 Å with yet another technique, a photoemission guided DFT study. Whether one can do structural analysis with this technique depends on the required accuracy. Stauffer et al. [9] have already shown for the same system that one can distinguish between vastly different surface arrangements via comparing experimental photoemission data to simple model calculations. The lack of computational accuracy though did not permit a quantitative analysis. Via using state-of-the-art ab initio calculations we successfully discriminated between a bilayer thickness for the topmost silicon layer of 0.2, 0.4, 0.8 and 1.13 Å. It is very comforting that we used rather symmetry arguments for this distinction and not so much absolute band positions. This points to the advantages of full-hemispherical photoemission, where these symmetry effects can be immediately investigated. Systematic deficiencies of e.g. the LDA approximations with its underestimation of gap sizes and bandwidths are rendered less important [11]. Despite the overall very good agreement between calculation and measurement in the case of YSi_2, we note some deviations. The minimum for the surface band (A) is too high by approximately 100 meV and the position of the minimum of the second almost empty surface band around $\overline{M}$ (band B in Figs. 2a and 3a) is calculated too low by about 150 meV. This is the case for slabs α to δ (only shown for slab γ in Fig. 3a). In this sense the LDA calculation yields a larger overlap between bands (A) and (B) (Fig. 2) than is actually present, therefore e.g. the band overlap cannot be used in the same way to determine structural parameters, as we have demonstrated for the surface band.

5. Conclusion

We demonstrated the use of DFT and angle-resolved photoemission to distinguish between different structural models. Via such a comparison it was possible to support the previously suggested structure for YSi_2 [2] via photoemission spectroscopy. We observe significant changes in the dispersion of a surface localized band upon varying the thickness of the topmost silicon bilayer, ranging from 0.2 to 1.13 Å. We find a strong asymmetry with respect to Γ of the surface band for a thickness of 0.4 Å of the topmost silicon bilayer, while a thickness of 0.8 Å yields a dispersion of the band in much better agreement to the experiment.

Acknowledgements

We are greatly indebted to our workshop and electric engineering team. Financial support by the Fonds National Suisse pour la Recherche Scientifique and by the Spanish agency 'Dirección General de Investigación' is gratefully acknowledged.

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