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Photoemission spectroscopy of Yb_3Si_5 and its connection with Si-Yb interfaces

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Angle-integrated photoemission results are presented for Yb_3Si_5 taken with synchrotron radiation in the interval 80—450 eV and with Mg $K\alpha$ radiation. The spectra give evidence of mixed-valence behavior of Yb in the bulk (a valence of 2.52 ± 0.02), while the Yb atoms at the surface and just below the surface are in the divalent state. This is consistent with the $4f$ compound formation shift which is 1.05 eV for bulk Yb and with the surface compound formation shift which is reduced by a factor of 0.76. The results are compared with those from Si(111)-Yb interfaces annealed at 300 °C and at 450 °C. The valence of the mixed-valence Yb in the interface does not depend on the annealing conditions and its value (2.37 ± 0.02) is lower than in Yb_3Si_5. The results are briefly discussed in connection with interface growth problems.

I. INTRODUCTION

The binary silicides of rare earths (RE's) in which valence fluctuations take place are interesting not only because of the growing interest for mixed valence[1,2] but also in connection with interface physics.

In fact silicon-RE interfaces are in general reactive[3–5] so that silicidelike reaction products are formed whose discussion calls for information also on the bulk silicides. This motivation is relevant for fundamental interface physics and also for technological interest; part of this interest stems from the very low Schottky barrier height observed for (RE silicide)/silicon junctions.[6]

In this context we present here the results on photoemission from Yb_3Si_5 which is the only stoichiometric Si rich Yb silicide;[7] we discuss the Yb valence and we compare the results with Si(111)-Yb interfaces which are among the most important Si-RE interfaces. We have used both synchrotron radiation and a conventional x-ray source. This is the first extensive presentation of photoemission results from a bulk Yb silicide and it is the first analysis of the mixed valence in a Si-Yb interface.

The paper is organized as follows. The experimental details are given in Sec. II and the results in Sec. III. The discussion of Sec. IV is organized in two subsections; in the first the results on Yb_3Si_5 are discussed and in the second the comparison with Si (111)-Yb interfaces is done. The conclusions are summarized in Sec. V.

II. EXPERIMENTAL

The angle-integrated photoemission spectra were measured with a double pass cylindrical mirror analyzer (CMA, Physical Electronics) in a UHV chamber at a pressure below 1×10^{-10} Torr. The angle of incidence of the light on the sample was about 70° and the sample surface was near normal to the CMA axis. The light source was the "grasshopper" monochromator on the beam line *I*-1 at Stanford Synchrotron Radiation Laboratory. Also a Mg $K\alpha$ x-ray source was available. Three Yb_3Si_5 samples were used in two synchrotron runs and were cleaned *in situ* by mechanical scraping with an alumina file. This is the only possible procedure, since samples were small and brittle. Also sputtering cannot be used because of the very different sputtering yields for Yb and Si. We have also checked in a separate Auger experiment that no surface segregation takes place at temperature up to $\simeq$100 °C where Yb begins to be accumulated at the surface.

The Yb_3Si_5 samples were prepared by direct reaction of the right amounts of Yb and Si in a Ta crucible sealed under argon as explained in Ref. 8. The samples after annealing at 850 °C for 4 days were examined microscopically and with x-rays; the amount of undesirable phases was negligible in connection with the present research (surely lower than 1%).

The results on the interfaces were taken in the same experimental run in strictly comparable conditions. The interfaces were obtained by depositing Yb by thermal evaporation onto Si(111) cleaved *in situ*. The Yb evaporators were accurately degassed to avoid the contamination of the interfaces; the absence of contamination was checked with photoemission.

III. EXPERIMENTAL RESULTS

An overview of the $4f$ states of Yb_3Si_5 is given by photoemission at increasing photon energies. This is done in Fig. 1(a) where the synchrotron radiation data are given together with the spectrum taken with Mg $K\alpha$ radiation (1253.6 eV). Due to counting time problems this $h\nu$ scanning was done with rather high luminosity (25 eV pass energy). The Mg $K\alpha$ spectrum (25 eV pass energy) was counted for 10 hours. The results were found perfectly reproducible in the different runs with all samples.

The photoemission results are final-state spectra and show the well-known contributions coming from the Yb in the 2 + configuration (from -3.5 eV to E_F) and from the Yb in the 3 + configuration (from -12 eV to -4 eV). The relative weight of the 3 + component increases when $h\nu$ increases, i.e., at higher escape depths. This is the consequence, as it will show below, of the fact that the bulk Yb is mixed valence while the remaining Yb is divalent. The enhancement of the 3 + component at 181.5 eV is the well-known Fano resonance at the crossing of the $4d-4f$ threshold and will not be discussed.

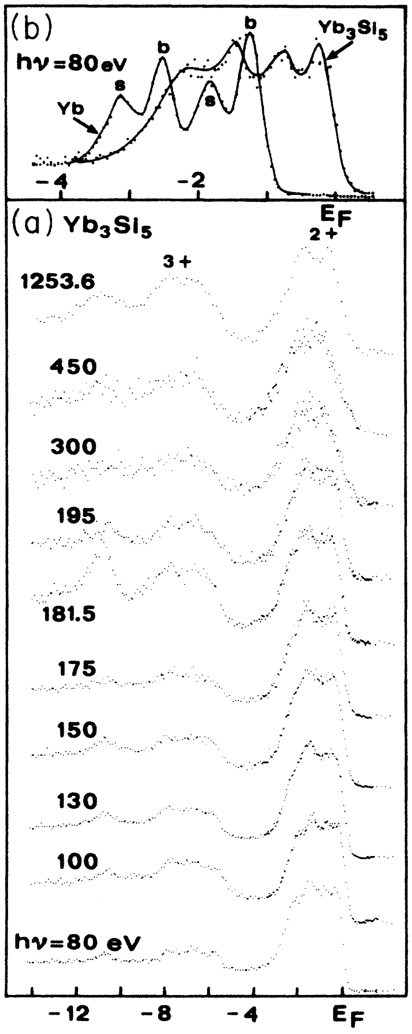

FIG. 1. (a): angle-integrated photoemission spectra from Yb_3Si_5 at increasing photon energies. The 2 + and 3 + $4f$ components from Yb are clearly seen. (b): the 2 + component measured with better resolution in Yb_3Si_5 and in Yb metal (label *b* means bulk and *s* means surface).

For the discussion of the Yb valence it is very convenient to have also better resolved $4f$ photoemission. This is given in Fig. 1(b) for the 2 + contribution in Yb_3Si_5 and in pure Yb obtained by evaporation *in situ* onto a stainless-steel substrate. These measurements were taken with 15-eV pass energy. The comparison of the $4f$ spectra in the metal and in the silicide is fully significant since the measurements were done in the same run without breaking the vacuum. The spin-orbit doublets due to bulk and surface atoms in Yb metal are seen very well and are in excellent agreement with the literature.[9,10]

IV. DISCUSSION

A. Yb_3Si_5 properties

The main comments to the above results can be summarized as follows.

(i) Yb_3Si_5 has the Th_3Pd_5 structure given in the z projection of Fig. 2. The structure consists of alternate Si and Yb planes and all Yb sites are equivalent. The distances can be found in Ref. 8. Thus in the measurements the only inequivalent sites are in the surface region (grain boundaries give a negligible contribution) and the presence of a 3 + and of a 2 + components in the spectra at higher escape depths (higher $h\nu$) cannot be attributed to inequivalent bulk Yb sites. This is a strong support for the homogeneous mixed valence behavior discussed below. We note that Yb_3Si_5 is the only stoichiometric compound in the Si-rich side of the phase diagram. The other compounds are defect disilicides ($YbSi_{2-x}$) with a statistical distribution of vacant sites in the AlB_2 structure.[8]

(ii) A more detailed discussion can be done by separating the $4f^{2+}$ spectra measured at higher resolution [Fig. 1(b)] in the subcomponents coming from Yb in different environments. This is done in Fig. 3 for Yb and Yb_3Si_5, with the standard procedures used in RE spectroscopy after having subtracted a small secondary electrons background which has been assumed proportional, at the energy E, to the area of the spectrum between E and the end point.[11] The best decomposition of Yb metal which fits also the left side of the spectrum is obtained with a slightly asymmetric line shape; we have ascertained with extensive computer work that small modifications of the line

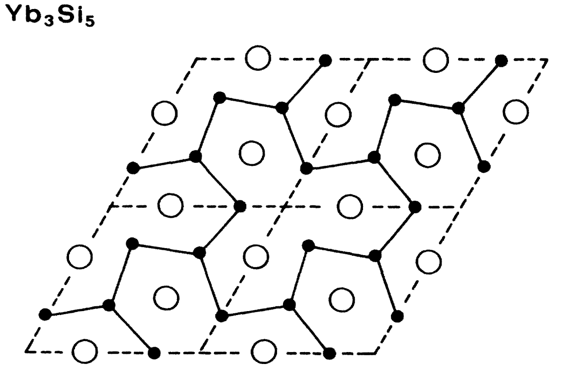

FIG. 2. A z projection of the structure of Yb_3Si_5 (black dots: Si; open dots: Yb).

shape and of the background subtraction have little influence, if any, on the present discussion. The best decomposition of Yb_3Si_5 spectrum is also given in Fig. 3. It is absolutely clear that the spectrum cannot be fitted with two components; a third component must be used and the deepest component is much broader than the others. The need of three components is analogous to what was found in Ref. 12 for $YbAl_2$, a system related to the present one. In analogy to this case[12] the deepest component is that from surface atoms and the intermediate one is the subsurface component due to Yb atoms beneath the surface which are influenced by the proximity of the surface as suggested theoretically in Ref. 13. The higher broadening of the surface component is reasonable since the surface prepared by scraping must contain inequivalent sites. Obviously some extra broadening could be attributed to the subsurface component by reducing the broadening of the surface component but this is immaterial to the mixed valence evaluation which depends only on the relative weight of the bulk component.

(iii) The above decomposition shows that the bulk component extends in the photoemission spectrum up to E_F as it must be in the case of mixed valence. The weight of this $2+$ component with respect to the total $2+$ emission and the $2+/3+$ ratio from the wide scan at the same $h\nu$, given in Fig. 1, gives (taking into account the occupation numbers) the valency $v=2.52\pm0.02$ for the bulk Yb while the surface and subsurface Yb is divalent. An independent evaluation of the valence can be done without the $4f^{2+}$ decomposition by fitting the evolution of the $3+$ and $2+$ components in the whole $h\nu$ range of Fig. 1(a), i.e., in conditions of variable surface to bulk sensitivity.[14] This method gives $v=2.55-2.60$ in excellent agreement with the present analysis in consideration of the numerous approximations involved. Thus we shall quote the value 2.52 ± 0.02 as the mixed valence in Yb_3Si_5.

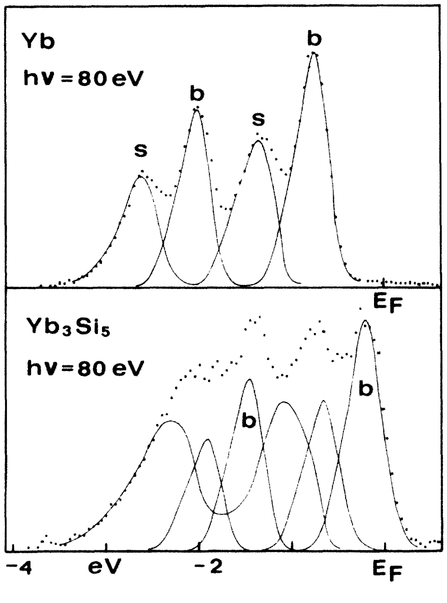

FIG. 3. Decomposition of the $4f$ doublets in Yb metal (upper panel) and in Yb_3Si_5 (lower panel). (Label *b* means bulk and *s* means surface.)

(iv) As shown in Fig. 3 the so-called compound formation shift of the $4f$ states as seen with photoemission is 1.05 eV for the bulk Yb atoms. On the other hand the compound formation shift of the surface atoms is 0.8 eV, i.e., 76% of that in the bulk. The lower sensitivity of the surface atoms to compound formation, which preserves the Yb divalency, is due to the lower surface coordination and is in agreement with the behavior of other mixed valence Yb compounds.[15]

B. Yb_3Si_5 vs interface reaction products

As mentioned in the Introduction one of the main motivations of the study of bulk Yb silicides is the con-

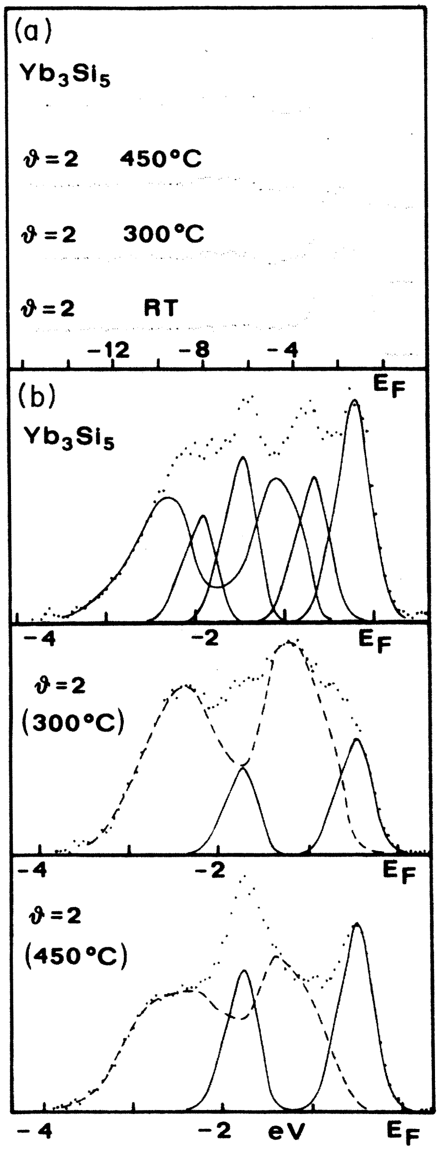

FIG. 4. (a): wide scan of the $4f$ region from a Si(111)-Yb interface at a coverage of two monolayers. The spectra at room temperature and after annealing for 5 hours and 300 °C and at 450 °C are compared with the spectrum from Yb_3Si_5. (b): decomposition of the $4f^{2+}$ region of the annealed interfaces (two monolayers) in comparison with the decomposition of Yb_3Si_5.

nection with interface physics. In particular it is known that the Si(111)-Yb interface grown at room temperature is reacted[3] with the formation of Yb-rich interfacial reaction products.[16] When the interface is annealed this reacted region becomes Si rich;[16–18] thus the natural connection is between Yb_3Si_5 and annealed Si-Yb interfaces which are potentially the most interesting for the applications.[6] The aim of this paragraph is to briefly discuss this point by presenting the first valence analysis of the annealed Yb-Si interface. The annealing temperatures were 300 °C (for 5 min) and 450 °C (for 5 min). We limit here the discussion to the Yb coverage of two monolayers which is a significant case because it is just above the coverage needed to fully develop the reaction at room temperature as seen from the Si $2p$ chemical shift.[3]

The relevant results are the spectra from the whole $4f$ region of Fig. 4(a) (interfaces at room temperature and after annealing at 300 °C and 450 °C) and of Fig. 4(b) (higher resolution $4f^{2+}$ spectra from the annealed interfaces compared with Yb_3Si_5). The analysis of the $2+$ emission is greatly simplified by the previous decomposition of Yb_3Si_5 spectrum. By using the same line shape for the doublet from the mixed valence Yb one obtains unequivocally the decomposition given in Fig. 4(b). The increase with the temperature of this component is clearly seen in the interface spectra also without decomposition and is closely parallel to the increase of the $3+$ component [Fig. 4(a)] indicating the increase of the fraction of Yb becoming the mixed valence. The $2+$ contribution coming from the remaining Yb (in the divalent state) has a complex shape and indicates the presence of several inequivalent surface and subsurface components as expected from the disordered[18] situation of the interface.

The most significant result is that the mixed valence at the interface has a value (2.37) independent of the annealing conditions, i.e., the increase in the temperature influences the amount of mixed valence Yb but not the value of the valence. Since the mixed valence is very sensitive to the environment this suggests that the annealing increases the number of Yb atoms going into a unique interface site instead of promoting a purely entropic mixing.[19] This is relevant in connection with recent suggestions indicating the tendency toward a well-defined nature of the reaction products already in the early formation stage of interfaces. These ideas have been pointed out for other systems in Ref. 20 (Si-Ni) and in Ref. 21 (Si-Ce, Ge-V, Ge-Ce).

The other point is that the interface valence $v=2.37\pm0.02$ is definitely lower than that in Yb_3Si_5. This suggests either a decompression of the site which can take place in the interface growth or a different nature of the Yb site in the annealed interface. This last possibility is not excluded by the fact that Yb_3Si_5 is the only silicon-rich bulk silicide, since the bulk-phase diagrams do not cover necessarily all situations encountered in interfaces. The assessment of these last points calls for further structural investigations; at present the main result is the well-defined value of the mixed valence at the interface after different thermal treatments.

V. CONCLUSIONS

We have presented the results of photoemission from Yb_3Si_5 with synchrotron radiation and with Mg $K\alpha$ radiation. The system is homogeneous mixed valence in the bulk (Yb valency 2.52 ± 0.02) and divalent at the surface and in the subsurface regions. The $4f$ compound formation shift in the bulk (1.05 eV) and at the surface (0.8 eV) were also measured. Moreover a comparison with the photoemission results from annealed interfaces shows that Yb goes into a preferential site having a mixed valence (2.37 ± 0.02) definitely lower than in Yb_3Si_5 which is the only silicon-rich bulk silicide. The results have been discussed in connection with interface growth problems.

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