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Valence photoelectron spectroscopy of Gd silicides

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Gd_3Si_5, GdSi, and Gd_5Si_3 were investigated with photoemission spectroscopy in the photon-energy range 40.8–149 eV by exploiting the energy dependence of the photoemission cross sections and the valence resonance at the crossing of the Gd $4d$-$4f$ threshold. The modification of the spectra versus photon energy, along with their stoichiometry dependence, show the relevance of covalent mixed Gd $5d$–Si $3sp$ states in the formation of the chemical bond. In the region close to the Fermi level an increase of the d contribution is observed. These points are discussed in connection with the existing models of the silicide bond.

I. INTRODUCTION

The electron spectroscopy of silicides is receiving increasing attention since the problem has fundamental and technological interest and silicides are connected with reactive silicon-metal interfaces.[1,2] In this context the silicides of rare earths (RE's) are particularly relevant since they are connected with an important class of reactive interfaces such as silicon-RE interfaces.[2] These silicides are characterized by a low value of the d occupancy and therefore the traditional model of the chemical bond,[1] based on the metal d–silicon p mixing, cannot be taken *a priori* for granted. In the field of RE silicides very little information is available on photoemission from the valence states[3] since in most cases the $4f$ signal dominates the spectra and the valence states are not directly accessible. In this connection the purpose of the present paper is twofold.

(i) To present for the first time photoemission results from the valence states of a family of RE silicides covering a broad range of stoichiometries; this is possible because we have chosen Gd silicides (Gd_5Si_3, GdSi, Gd_3Si_5) where the $4f$ emission leaves a window of about 6 eV below E_F totally available to the observation of the valence states.

(ii) To take advantage of the photon-energy dependence of the photoemission cross sections to understand the main aspects of the chemical bond and to recognize the most relevant orbital contributions to the density of occupied states. This is possible because we cover the energy range between 40.8 and 149 eV in which the relative Gd and Si contributions to the spectra change very strongly. These results, therefore, constitute a good database for future theoretical investigations.

The paper is organized as follows. The experimental techniques are summarized in Sec. II A while Sec. II B briefly presents how the photon-energy dependence of the photoemission cross section has been used in the present work; results and discussion are given in Sec. III, and conclusions are summarized in Sec. IV.

II. EXPERIMENTAL

A. Techniques

Polycrystalline samples were prepared by melting pure elements in Ta crucibles after degassing, flushing with inert gas, pumping, and sealing. The samples were characterized with x-ray diffraction; undesired phases containing oxygen were less than 5%. Moreover, these impurities are concentrated in small regions of the sample surface (occupying a few percent of the surface) as shown by scanning Auger microscopy. Thus, photoemission spectra give information on clean silicide electron states.

The experiment has been performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 1-I. Technical reasons allowed satisfactory valence photoemission between 65 and 200 eV; at lower photon energies we used a conventional He discharge lamp. The base pressure was 7×10^{-11} Torr and the spectra were taken with a double-pass cylindrical mirror analyzer. The surfaces were cleaned *in situ* with a diamond file with fully reproducible results and with core line intensities consistent with stoichiometry.

B. The method

In the present work we exploit the energy dependence of photoemission by comparing valence spectra taken at different photon energies; in order to make the paper more transparent we summarize here the necessary information. In this connection we must distinguish between resonant valence photoemission at the crossing of the core $4d$-$4f$ threshold and photoemission far from resonance (hereafter called ordinary photoemission). The main points are the following.

(i) The boundary between resonant and ordinary photoemission can be placed immediately before the $4d$-$4f$ threshold as suggested by the shape of the resonance measured in the constant initial state (CIS) and in the constant final state (CFS) mode. In Fig. 1 we report, as an example, the data for Gd_5Si_3 (final state 2 eV in CFS and initial state 2 eV below E_F in CIS). The data for the other compounds are analogous and are not reported. The weak features below threshold are identical to those observed in Gd metal and are due to the Auger decay of the $4d^9 4f^{n+1}$ configuration;[4] these features, being atomiclike, are not useful to the present investigation. In spite of the presence of these features it is quite clear that the antiresonance below threshold is rather weak; thus we will interpret, to a first approximation, the 137-eV spectrum in terms of ordinary photoemission.

(ii) The range of ordinary photoemission (40.8–137 eV) has been chosen in order to change drastically the relative weight of the Gd $5d$ and the Si $3sp$ contributions to the spectra. This is clearly demonstrated by atomic-cross-section calculations[5] and by the experimental work on solid-state effects on the photoemission cross section.[6] In the atomic case the ratio of the Gd $5d$ to the Si $3s$ and Si $3p$ cross sections decrease very rapidly with increasing photon energy (about a factor of 30 in the whole range). The stronger solid-state effects act on the d-orbital cross section and attenuate this trend. In $4d$ and $5d$ states the solid-state effect (see Ref. 6 for a detailed discussion) does not change appreciably the photon-energy dependence of the cross section below the Cooper minimum[7] while it removes to a considerable extent the Cooper effect in the low-d-occupancy case. The Gd $5d$ cross section has a broad Cooper minimum above 130 eV; in this case, therefore, the rapid decrease of the atomic-cross-section ratio up to 80–100 eV is retained (the decrease is at least a factor of 6), while the further decrease up to 137 eV is certainly less pronounced. In conclusion, our range covers the transition from 40.8 eV, where the photoemission spectra are dominated by Gd $5d$, to a region dominated by Si sp. It must be observed that the Gd s contribution is negligible in the whole energy range. These well-established qualitative arguments are definitely sufficient for the purpose of the present paper. Of course, future calculations might open the possibility of a more detailed analysis.

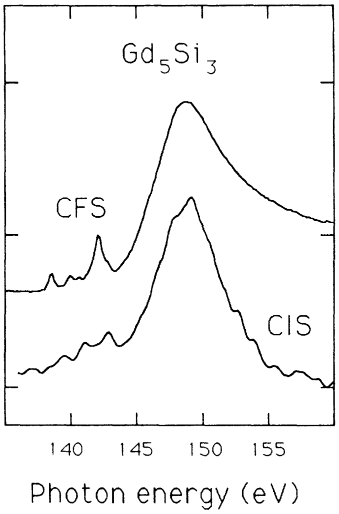

FIG. 1. Constant final state and constant initial state spectra of Gd_5Si_3. The CFS spectrum was taken by collecting photoelectron with kinetic energy of 2 eV whereas the CIS spectrum was taken from states located 2 eV below E_F. The same spectra from the other silicides (GdSi and Gd_3Si_5) are not reported because they do not show significant differences.

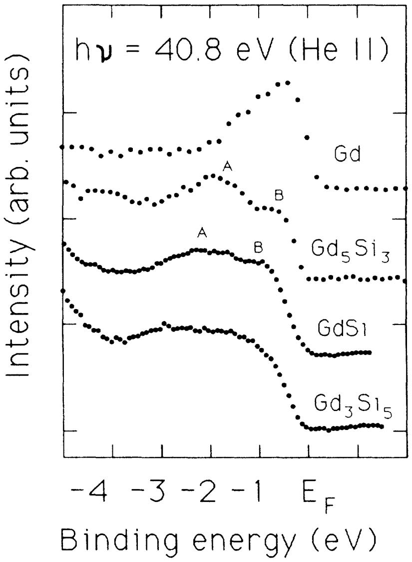

FIG. 2. EDC's taken with He II light (40.8 eV). The upper spectrum from metallic Gd, given for reference, was taken with 30-eV photon energy.

(iii) Resonant valence photoemission enhances the contribution from Gd $5d$ states; the resonant contribution is obtained, as usual, from the difference between the spectra at resonance (149 eV) and off resonance (137 eV). The difference spectra give very local information since the resonance[8] projects on to the virtual core hole of the Gd $4d$ orbital, which is very localized. In fact, the amplitude of the $4d$ wave function is reduced by a factor of 10 with respect to its maximum already at 0.75 Å from the nucleus, whereas the typical interatomic distance in these compounds is of the order of 3 Å.

III. RESULTS AND DISCUSSION

The valence spectra at increasing photon energy are given, for the three stoichiometries, in Figs. 2–4. For comparison we also give the spectra of Gd metal measured at energies above 40.8 eV in the same experimental conditions. At 40.8 eV the spectrum of the pure metal was not available for technical reasons and therefore we use a spectrum measured at 30 eV with the same equipment in another experiment. All spectra are normalized to the same height in order to compare their shapes. The main peak in the spectra is labeled with *A* while the shoulder closer to E_F is labeled with *B*.

The photoemission spectra in the range of ordinary photoemission (40.8–137 eV) deserve the following comments.

(i) Feature A is well evident in Gd_5Si_3 and in GdSi at all energies and in Gd_3Si_5 at photon energies greater than 40.8 eV; in Gd_3Si_5 the two features merge at 40.8 eV. Moreover, features A and B do not show dispersion so that they can be regarded as a fingerprint of the total density of occupied states. With the above precautions in mind the presence of A in nearly all cases, and always at the same binding energy for a given stoichiometry, will be referred to as the "stability of feature *A*." This happens in an energy range in which the relative weight of Si and Gd change from a Gd 5*d*–dominated spectrum to a Si 3*sp*–dominated spectrum, as discussed above. For this reason it is possible to assess that feature *A* contains contributions peaked at the same energy from both components. This is very direct evidence of the importance of a covalent contribution to the chemical bond. In fact, covalent mixed orbitals due to the superposition of Si 3*sp* and of Gd 5*d* states project on the two sites with contributions almost at the same energy and labeled with different angular momenta. This argument refers to region *A* and does not tell anything about the relative Gd-Si contributions as a function of energy across the band.

(ii) The energy of feature *A* is very much dependent on stoichiometry and this shift toward higher binding energies at decreasing Gd content is consistent with the hypothesis of a strong covalent contribution to the chemical bond. Already in the earlier simplified models[1] the silicide bond was described with the mixing of metal *d* and Si *p* states originating a shift of the main bonding peak to higher binding energies at decreasing *d*-metal content, i.e., when the number of Si first neighbors to the *d* atom increases. In more complete models[9,10] it is necessary to account for a more extended basis (typically by including Si *s* states) but this trend is retained whenever the mixing of nearby orbitals is important. In the present investigation the occurrence of this trend is very significant since in this family of compounds the average Si-Gd distance is remarkably stable (3.06 Å in Gd_3Si_5, 3.0457 Å in GdSi,

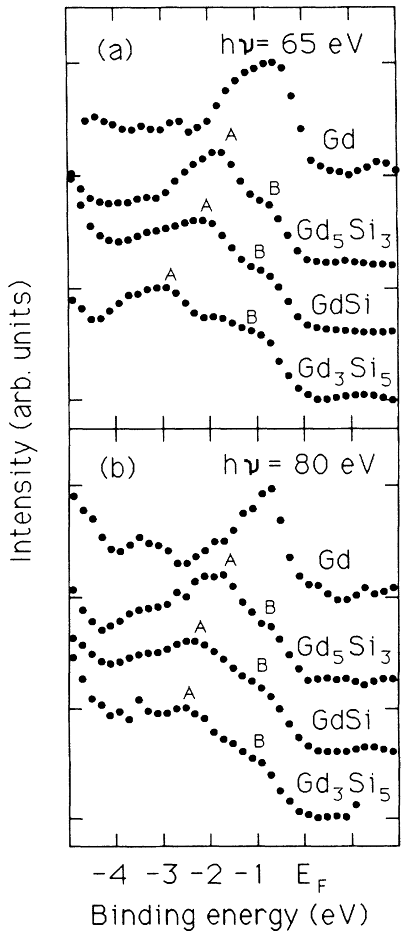

FIG. 3. EDC's from the valence-band region taken at 65-eV (upper panel) and 80-eV (lower panel) photon energy. The upper spectrum, in both panels, was taken from a metallic sample and is given for reference.

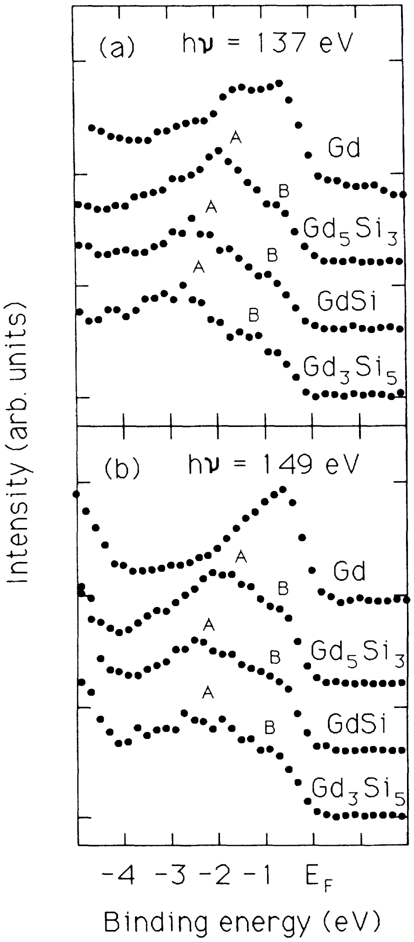

FIG. 4. EDC's from the valence-band region taken at 137-eV (upper panel) and 149-eV (lower panel) photon energy. The upper spectrum, in both panels, was taken from a metallic sample and is given for reference.

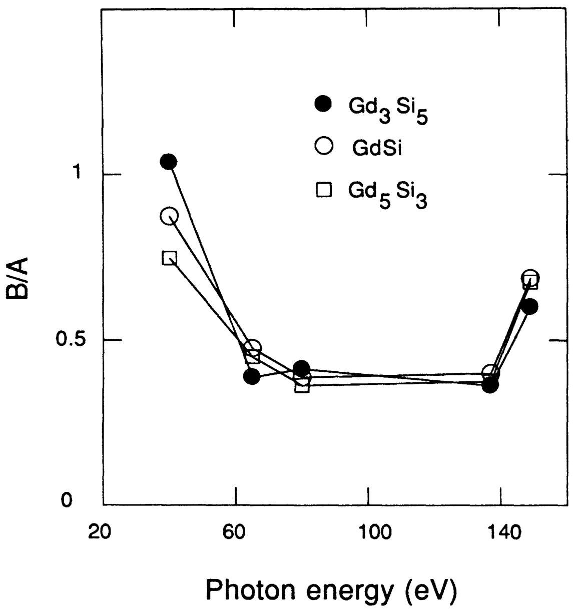

FIG. 5. Ratio of the areas of the spectral features B and A of Figs. 2–4. B is defined as the region between E_F and -1.5 eV; A as the region between -1.5 eV and the lower limit of feature A.

and 3.03 Å in Gd_5Si_3). For this reason the energy shift of feature A can be safely correlated with the average coordination number of Si atoms for each Gd site which is 10 in Gd_3Si_5 (AlB_2 structure with a stoichiometry defect[11]), 7 in GdSi (FeB structure[12]), and 4.5 in Gd_5Si_3 (Mn_5Si_3 structure with two inequivalent Gd sites[13]). Needless to say, this argument on the shift of feature A refers to the main properties of the k-integrated density of states and is appropriate for the discussion of angle-integrated results from polycrystals.

(iii) The intensity of shoulder B with respect to the main feature A is strongly dependent on the photon energy in a nonmonotonic way. This is clear already from the row data of Figs. 2–4 and is pointed out even better in Fig. 5 where we plot the ratio (B/A) of the areas of the spectra in region B (from -1.5 eV to E_F) and A (from -1.5 eV to the lower limit of feature A). This trend qualitatively reflects the Gd d resonant enhancement and the behavior of the cross-section ratio (see Sec. II B) showing that the fraction of Gd $5d$ states is greater in region B compared to region A. More precisely, this is testified by the rapid decrease of B/A up to 80 eV with a stronger effect at higher Si concentrations. Again, this fact is consistent with the importance of the Si $3sp$–Gd $5d$ mixing in the chemical bond: at greater coordination of Si to Gd the bonding states are pulled toward lower energies and are well separated from the states near E_F, which acquire an increasing d character.

(iv) The above arguments in favor of a dominant covalent contribution to the chemical bond cannot be used to clarify other points which, at present, remain open. In particular we cannot disentangle Si $3s$ and Si $3p$ contributions;[9,10] in this connection, x-ray emission and absorption, besides calculations, would be very useful. Moreover, one cannot exclude a certain degree of ionicity of the bond. In Ca silicides, recent works[10] suggest that this ionic contribution is relevant only in the Ca-rich compound (Ca_2Si). In Gd silicides this effect is expected to be less important than in Ca silicides, due to the smaller electronegativity difference with Si and to the higher d occupancy which favors a covalent mixing with the Si states. Our guess is that this effect is certainly reduced in Gd silicides. In any case it must be observed that a full assessment of this point will be difficult also on the basis of future theoretical research, as demonstrated by the very controversial situation in Si–alkali-metal interfaces, where extensive calculations are already available.[14]

Resonant photoemission adds important new information which can be better discussed by observing the difference spectra shown in Fig. 6. Each one of these spectra was obtained by calculating the difference between the resonance (149 eV) and off-resonance spectrum (137 eV). These spectra are correlated with the local density of states at the Gd sites and are remarkably independent of stoichiometry, in spite of the strong difference in the spectra of the three compounds at 149 eV shown in Fig. 4. This behavior show that the local contribution to the density of states in the Gd site is not influenced by the chemistry. In other words, the accumulation of the bonding charge must take place far from the Gd atoms.

Although this paper deals with valence photoemission, we give some information on core photoemission because these data could be useful in future work. The Gd $4f$ photoemission peak is observed in the same energy position in all compounds. Interestingly, there is also no shift with respect to the pure metal. On the contrary, the Si $2p$ emission linearly shifts toward lower binding energies at

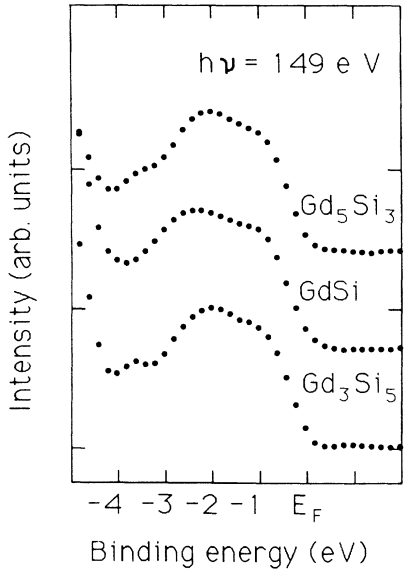

FIG. 6. Difference spectra obtained by subtracting the spectrum at 137 eV (antiresonance) from the spectrum at 149 eV (resonance). They represent the contribution to the photoemission spectra due to the resonance effect.

increasing Gd content (0.8 eV between the two extreme stoichiometries). In the Si-rich silicide the Si 2*p* shift with respect to bulk single-crystal Si is 0.4 eV. In view of the complexity of the processes involved in core spectroscopy we stress that a naive picture in terms of charge transfer must be avoided in considering these data.

IV. CONCLUSIONS

We have presented for the first time an extensive set of valence photoemission data from a family of RE silicides covering a broad range of stoichiometries (Gd_5Si_3, GdSi, Gd_3Si_5) and we have elucidated the main features of the occupied density of states by exploiting the photon energy dependence of photoemission in the range 40.8–149 eV. In particular, we have pointed out the importance of a covalent mixing between Gd 5*d* and Si 3*sp* states in the chemical bond and the increase of the *d* content near the Fermi level. Also the modification of the spectra with stoichiometry is consistent with the relevance of a strong covalent contribution to the bond.

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