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Brief Reports

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Ultraviolet inverse-photoemission spectroscopy of Gd silicides

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Empty electronic states of gadolinium silicides (Gd_3Si_5 and Gd_5Si_3) are investigated by means of inverse photoemission in the ultraviolet photon range. Isochromat spectra taken at different photon energies (11–25 eV) are presented. The results are discussed in terms of bond formation between metal and silicon orbitals, in analogy with silicides of other low-*d*-occupancy metals (Ca silicides).

The valence electronic states and the chemical bond in transition-metal silicides have been widely studied in recent years;[1–3] these studies have been largely motivated by the interest in connecting silicides properties with those of reactive silicon-metal interfaces. More recently rare-earth–silicon interfaces have attracted increasing attention because of their peculiar properties.[4] However, up to now only few spectroscopic investigations on the rare-earth bulk silicides have been reported.[5–7] This is due to the difficulty in the investigation of valence states because of the overlap with strong spectral features of the 4*f* states. This problem is common both to direct photoemission (PE) and to inverse-photoemission (IPE) spectroscopy.

However, Gd is a favorable case since the 4*f* signal in PE is about 7 eV below the Fermi level E_F,[8] thus leaving an energy window to observe valence states near E_F. This attractive situation has been already exploited to investigate occupied valence states via PE spectroscopy for the whole Gd-silicide family[7] as well as for the Gd/Si interface.[9]

The purpose of the present work is to give an insight into the empty valence counterpart of these systems by means of inverse photoemission in the ultraviolet (uv) region. This is done by measuring isochromat spectra for the two extreme stoichiometries of Gd-Si phase diagram (Gd_3Si_5 and Gd_5Si_3) at low enough energies so that the 4*f* signal is negligible.

In studying chemical bonds in silicides, a simple picture based on a two-level model (Si *p* and metal *d* states) has been developed.[1] Though very useful at a first approach, at least for near-noble-metal silicides, this model is subject to some criticism.[10] In particular it is expected to fail in the case of alkaline-earth and rare-earth silicides, where the metal atoms have a *d*-atomic occupancy close to zero. Detailed calculations as well as experimental results on the occupied[11] and empty[12] electronic states in Ca silicides confirming this expectation have been presented recently. To some extent the results on the Si-Ca system can be used as a guideline to interpret the related data on Gd silicides. Auger line-shape analysis has indeed been performed on both Ca and Gd silicides,[13,14] using the same interpretation scheme. In this connection the present investigation can also be considered an extension of the already presented study on Ca silicides.[12] The fact that Gd presents an atomic configuration d^1 is also interesting. The average *d* population is in fact higher than in Ca, so that the study of Gd silicides adds information on trends associated to *d* occupancy in the family of low-*d*-occupancy silicides.

Polycrystalline samples were prepared by melting stoichiometric amounts of the pure elements in tantalum crucibles in an inert-gas atmosphere and were characterized by x-ray diffraction. Clean surfaces were obtained by scraping the samples with a diamond file in ultrahigh vacuum (base pressure below 1×10^{-10} mbar).

The IPE data were acquired with an apparatus described in detail elsewhere.[12] A thoriated tungsten hairpin filament is used as an electron source. The diffused nature of the source and the polycrystalline nature of the samples ensure the averaging over the whole **k** space. The emitted photons are dispersed by a uv spherical grating on a flat field and are detected by a movable channeltron. Spectra are collected in the isochromat mode by sweeping the incident electron energy at a fixed photon energy (i.e., fixed channeltron position). The isochromat energy is varied in the 11–25-eV range by moving the channeltron. The total resolution is given by a full width at half maximum (FWHM) of 0.45 eV at $h\nu=14.5$ eV.

An overview of the measured isochromat spectra of Gd_5Si_3 and Gd_3Si_5 is given in Fig. 1; the spectra are normalized to the same height of the main feature (labeled

A). The main results can be summarized as follows:

(i) The position of the peak A (about 4.5 eV above E_F) is independent of isochromat energy and is the same in the two silicides, within the experimental uncertainties. Also the intensity of A with respect to the total area under the spectrum is basically independent of isochromat energy.

(ii) At low energy a shoulder (labeled B) is clearly present in the first 2 eV above E_F in the Gd-rich silicide. The intensity of this feature strongly depends upon the isochromat energy: it decreases very rapidly going from 11 to 14.5 eV and disappears at higher energies.

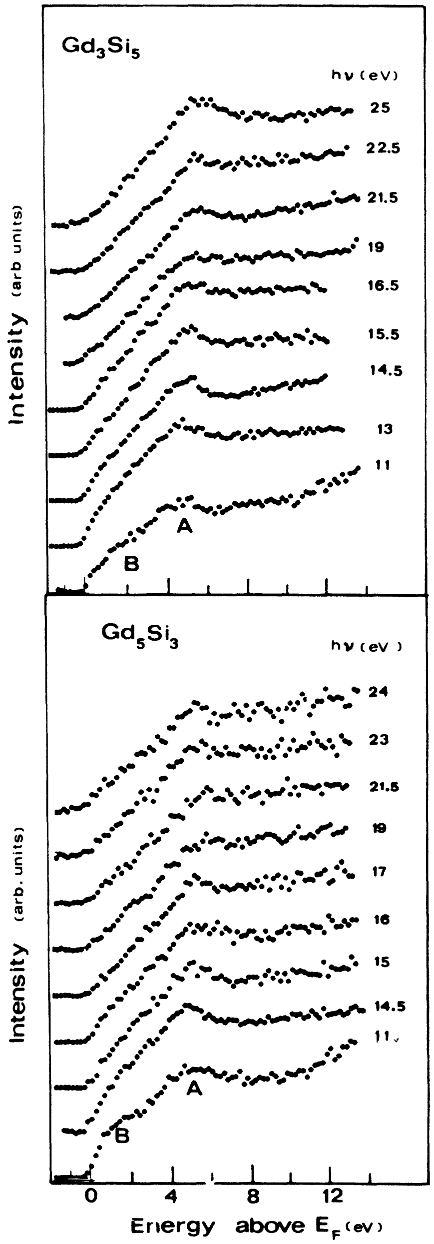

FIG. 1. Inverse photoemission spectra normalized to the same height for Gd_3Si_5 (upper panel) and Gd_5Si_3 (lower panel). The spectra have been taken in the isochromat mode, at the photon energy indicated.

(iii) In the Si-rich compound a feature analogous to B is, if present at all, much weaker: It is hardly seen at 11 eV and disappears at 11.7 eV (not shown).

We begin the discussion by commenting the gross features of the spectra.

The stabilities of both the shape and the relative intensity of peak A above 15 eV are remarkable. In particular, no resonance effects at the crossing of the Gd 5p core level occur. This is consistent with recent findings showing that in rare earths such resonances are considerably delayed in the energy scale.[15] Comparison with measurements taken in the same conditions on a Pt sample confirms this point. Thus resonant effects are not relevant in the present case.

Another important issue is the orbital origin of peak A. This can be addressed on the basis of the stability of the spectral shape and of direct photoemission cross sections by using the time-reversal connection between direct and inverse photoemission.[16] The main points are the following:

(i) In electron addition spectra, the 4f peak of Gd is just at the same energy as structure A and is very sharp in the x-ray range.[17] However, this does not imply that the structure A in the present uv measurements is dominated by a 4f contribution. As a matter of fact, the 4f cross section is very low in our photon-energy range. Indeed, it has been found in PE spectroscopy that the emission from 4f states is unimportant, at least up to 21 eV. This has been first demonstrated for GdS,[18] and later also in an extensive photoemission study on rare earths by Broden *et al.*[19] Moreover, no photoemission from 4f states has been observed below 30 eV in recent work on reacted Si-Gd interfaces.[20]

(ii) While the 4f cross section rapidly increases with energy,[21,22] the peak A does not show any evident increase (at least up to 23 eV) with respect to the remaining part of the spectrum.

(iii) A line-shape analysis of IPE spectra taken from metallic Gd (Ref. 22) in comparable resolution conditions shows that the 4f peak should be much narrower than structure A in our spectra.

We can therefore conclude that most of our spectra are free from 4f contribution, which could perhaps be present with a modest weight only in the upper part of our photon-energy range. Thus, to a good approximation, the shape of the spectra can be interpreted by disregarding the existence of the 4f states.

The absence of a relevant 4f contribution is very important, since it allows a qualitative comparison with the case of Ca silicides. In terms of d occupancy, the configurations of isolated Gd and Ca atoms are d^1 and d^0, respectively. Upon compound formation the d occupancy increases in Ca silicides,[11] and a similar trend is expected in Gd silicides. This yields a shift of the d band towards lower energies in Gd silicides with respect to Ca silicides, which should be visible both in direct and in inverse photoemission. IPE spectra of the two silicide families at $h\nu = 14.5$ eV are presented in Fig. 2. A close analogy between the spectra of Ca and Gd silicides is evident, with a shift of the main peak of about 1.3 eV towards lower energies in the Gd case, as expected. In the inset,

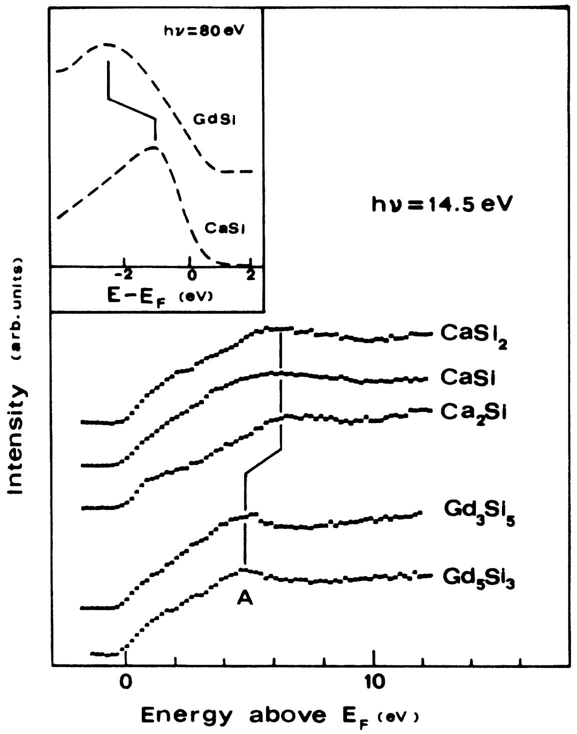

FIG. 2. Comparison of inverse photoemission spectra taken at $h\nu = 14.5$ eV for the Ca and Gd silicides. In the inset, direct photoemission spectra from CaSi and GdSi are shown (data taken from Refs. 7 and 11).

direct photoemission spectra at $h\nu = 80$ eV (from Refs. 7 and 11) are also given. Since the peak position of the occupied d states depends also on the stoichiometry, in the inset we refer to the monosilicides which are the only case of equal stoichiometry in the two families.[23] Note that the shift of the main peak in the IPE spectra is roughly the same as in direct photoemission. Thus, we conclude that the origin of peak A is the same in the two families for all stoichiometries.

By relying upon this analogy one can use the calculated electron states for Ca silicides given in Ref. 12. The calculation shows that the main peak has strong contributions from Si p and Ca d levels. Within the two-level model of silicide states,[1] this peak corresponds to the so-called antibonding state. Hereafter, we will conventionally use the terminology developed in this model for our spectroscopic data.

More precisely, from a realistic theoretical analysis,[11,12] the following qualitative picture of the silicide bond can be drawn. The states coming from the majority-type atom of given angular momentum are spread along the whole energy scale. On the contrary, the minority-type orbitals are engaged in the formation of the bonding and antibonding states, concentrated in rather narrow energy ranges. This is clearly seen for the empty states in Ref. 12. In $CaSi_2$ a rather narrow Ca d contribution at 5.5 eV above E_F is present, whereas Si p is almost uniformly distributed in the region from 2 to 12 eV above E_F. The opposite occurs in the metal-rich silicide (Ca_2Si), with the Ca d character spread over a wide energy range up to about 6 eV above E_F. Such a behavior is likely to be rather general, since in a metal-rich silicide the (metal d)-(metal d) interaction must be relatively more important, due to the lower average coordination of the metal atoms to silicon. Thus in a metal-rich silicide a relevant fraction of d character must be found in the region between the bonding and the antibonding states. This trend comes basically from the coordination number and thus to a first approximation should depend on the stoichiometry rather than on the details of the structure.[24] On the other hand, this behavior is expected to be less pronounced upon increasing the d occupation.[1,10]

The present data confirm this picture, since they point out the importance of mixing of (metal d)-(silicon sp) states in the chemical bond. This is shown by the stability of the spectral shape in an energy range where the ratio of the Gd 5d and Si 3sp cross sections changes dramatically (in the atomic approximation the ratio of the two cross sections changes by more than 1 order of magnitude[21]). Furthermore, the degree of mixing between the d and the sp states shown by the present data is higher than that found in IPE from Ca silicides.[12]

Finally, it can be useful to consider the feature B, which is the main difference between the spectra of the two silicides at low energy, as is better seen in Fig. 3 (the shaded area puts in evidence the feature B in the Gd-rich silicide). A detailed assessment and interpretation of this difference should wait for calculations and possibly for measurements at energies lower than those allowed by our apparatus; here we present only some brief speculations. Two aspects must be considered. The decrease of feature B at increasing energy is qualitatively consistent with the decreasing trend of Gd 5d atomic cross section.[21] At present it is, however, impossible to draw quantitative information on the 5d contribution to region

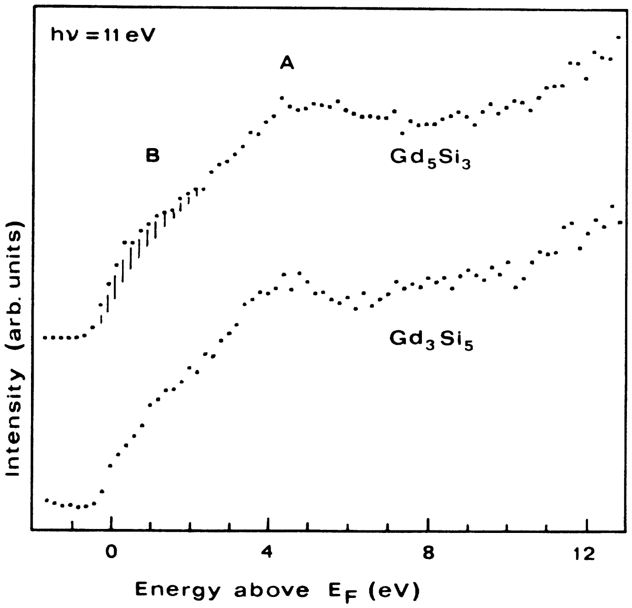

FIG. 3. Comparison of inverse photoemission spectra taken at $h\nu = 11$ eV for the two Gd silicides. The shaded area represents the difference between the two spectra in the region B, after intensity normalization at the prominent feature (A).

B from our measurements. On the other hand, a joint density of state effect might also cause the disappearance of the feature *B*. We note, regardless, that the present measurements are **k** integrated, and this greatly attenuates the effects of direct transitions at selected points of the Brillouin zone, which can cause abrupt appearance and disappearance of spectral features in angle-resolved inverse photoemission. However, such effects cannot be safely excluded. In this connection, further experimental as well as theoretical investigation are then needed.

In conclusion, we have presented extensive inverse photoemission data from Gd silicides taken in the isochromat mode in the 11–25-eV photon-energy range. We have assigned the main orbital contributions to the spectra and we have discussed the nature of the electron states on the basis of comparison with the Ca silicides. We have shown that the scheme of the chemical bond appropriate for Ca silicides can be extended to the Gd silicides, and we have stressed the importance of the (metal *d*)-(Si *sp*) interaction. We have also pointed out the usefulness of further investigations to assess in detail how much Ca silicides can be used as a paradigmatic case for the family of rare-earth silicides.

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[23] This comparison is only qualitative, since the two substances have different structures, although both are orthorhombic: CaSi is of the CrB type and GdSi is of the FeB type, and the Si-metal distance is about 3% larger in the Ca case. Nevertheless, the two situations are sufficiently close to make the comparison given in Fig. 3 significant.

[24] In Ca_2Si (orthorhombic, anti-$PbCl_2$ type) and $CaSi_2$ (rhombohedric) each Ca atom sees on the average 3.5 and 7 Si atoms, respectively, in the first coordination shell. In Gd_5Si_3 (Mn_5Si_3 hexagonal structure) and Gd_3Si_5 (defect AlB_2 structure) each Gd atom has an average number of first-neighbor Si atoms equal to 4.2 and 10, respectively.