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THE ELECTRONIC PROPERTIES OF THE Si(111) - TRANSITION METAL INTERFACES

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We present the results of a joint experimental and theoretical investigation of the electronic properties of Silicon - transition metal interfaces. We carried out ultraviolet photoemission (UPS) experiments on Si-Pt, Si-Ni and Si-Pd interfaces at different coverages. Our results indicate that these interfaces are reactive. Comparison with semi-empirical LCAO calculations allows to understand the main features of the observed spectra.

The electronic properties of transition metal silicides have received increasing attention in the last few years for the importance of these materials in device applications. We have previously carried out UPS measurements on silicon-transition metal interfaces at increasing coverages, thus providing the spectroscopic evidence that these interfaces are reactive both at room and at low temperature [1]. We have also done measurements on bulk transition metal silicides and compared them with theoretical band structure and density of states (DOS) [2].

In this paper we present a complete set of photoemission spectra for some of these interfaces (Si-Ni, Si-Pd and Si-Pt) as well as data for bulk silicides, and we compare them with theoretical results of semi-empirical LCAO calculations for bulk silicides. Such a comparison allows us to elucidate some important aspects of the electronic properties of both bulk silicides and interface phases, as well as to specify the chemical interactions between Silicon sp-orbitals and metal d-states, which are responsible of the main features of the electronic structure.

The UPS results presented here are angle integrated energy distribution curves (EDCs) measured with He I ($h\nu = 21.2$ eV) radiation incident normally onto the sample in ultra-high vacuum (10^{-10} torr range). The samples were prepared in situ by depositing the metal onto cleaved Si (111) surfaces. The temperature of the sample could be varied, in order to change the growth conditions in a controlled way.

When the metal is evaporated onto the silicon substrate held at room temperature an interfacial reaction takes place, which causes the electron density of states seen by photoemission to be drammatically different from the one of the pure metal. This effect is evident in Fig.(1) which presents the interface EDCs for the systems under consideration at two metal coverages together with the pure metals EDCs. It is seen that the interface EDCs for low coverage show a considerable loss of structure near the Fermi energy E_f, when compared with those for pure metals. The d-band is shifted toward higher binding energy and is less structured, giving rise to a single wide peak with a maximum -1.5 and -3 ev from E_f. These features are retained in the EDCs for ten monolayers cover-

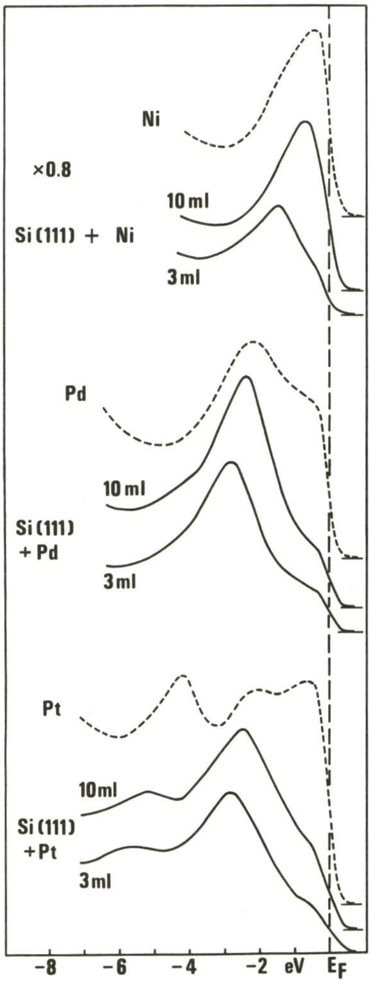

Fig.1 EDCs of Ni,Pd and Pt deposited onto Si(111) at 3 and 10 monolayers coverage: The EDCs for pure metals are also given

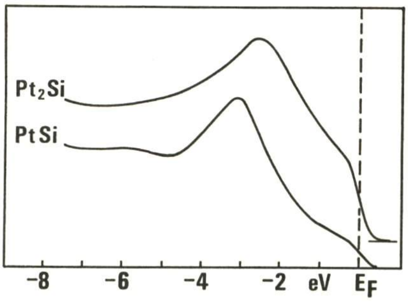

Fig.2 EDCs for bulk Pt_2Si and PtSi

age in the Si-Pd and Si-Pt case, while in Si-Ni the experimental curve is close to the one of pure nickel.

To better understand these spectra it is useful to compare the interface data with those for bulk silicides. Figure (2) shows UPS spectra for bulk Pt_2Si and PtSi compounds prepared in situ by interdiffusing about 100 monolayers of Platinum onto Si(111) at high temperature. The crystal structures of these materials were checked by X-ray diffraction after the photoemission measurements. The EDCs from silicides show that the main d-peak has increasing binding energy, when the metal concentration decreases: this trend agrees with the one seen for Pd/Si glassy metals [3] and can be used to discuss the interface results. In this case the d-peak position depends on the coverage and it is closer to E_f at higher coverages i.e. when the metal concentration in the region explored by photoemission increases. This fact provides experimental evidence that a concentration gradient is present in the interface region from the Si-rich to the metal-rich side. The concentration gradient seems to be considerably higher in Si-Ni, a point still under investigation.

The shape of the interface EDCs is similar, but not equal to that of the EDCs of bulk silicides. This is clear for Pt silicides from Fig.(2) and for the other cases from the results of other authors [4]. It is interesting to note that a thermal treatment of the interface above 150 °C promotes the chemical reaction, so that the interface EDCs become closer to those from silicides. Thus the intermixing occurring at the interface at room temperature can be thought as the result of a reaction, which cannot proceed up to the final point due to bottleneck of the mass transport.

To understand the chemical interactions responsible of the above mentioned features in the valence band, we performed semi-empirical LCAO calculations of the DOS in silicides using the Extended Huckel Theory (EHT). Details of this approach are given elsewhere [2,5]. Suffice it to say that the method allows to calculate the electronic structure of materials with many atoms per unit cell. Although some aspects, as the charge transfer or the behaviour of the excited states, are not treated very accurately, the description of the filled states is satisfactory and permitts to draw conclusions about the contribution of the metal and non-metal atomic orbitals to the valence states.

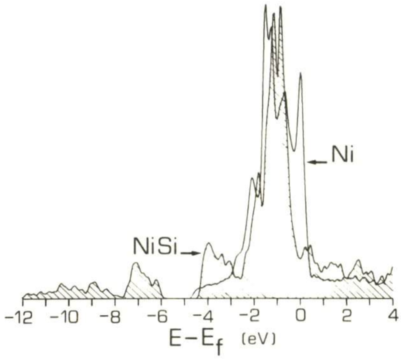

Fig.3 Theoretical DOS for NiSi and pure Ni

Figure (3) shows the theoretical DOS for NiSi. For sake of comparison we give also the DOS of pure nickel as obtained from an EHT calculation. It is seen that the Ni d-band in the silicide is narrowed and less structured than in the pure metal. It lies almost entirely below E_f and contains nearly ten electrons.

The most prominent Si-derived features in the silicide DOS are:

i) the band lying between -6 and -12 eV from E_f, well separated from the rest of the valence band: it arises from silicon s-orbitals with a small contribution of Nickel sp-states;

ii) the structure at -4.5 eV near the upper edge of the internal gap, which is essentially Si p-derived.

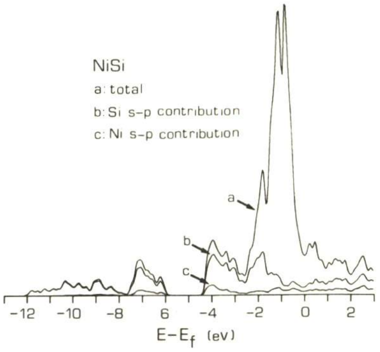

Fig.4 Orbital contributions to the DOS of NiSi

These features are clearly illustrated in Fig.(4), which displays the contribution of metal and silicon atomic orbitals to the DOS. It is interesting to note that the structure near E_f, just above the main d-peak, is mainly d-derived. This suggests that, in spite of the narrowing of the d-band, a significant contribution to the electron states near E_f from d-orbitals is still present. This is in contrast with the conclusions of Weare et al. [6], who claim that the silicide electronic structure is essentially similar to that of the noble metals.

We have performed similar calculations for platinum silicides. A comparison between the theoretical DOS for these compounds and the experimental spectra is given in Fig.(5). It is seen that, although the Pt d-band is larger than in Ni silicides, some of the basic features, as the narrowing of the d-band and the presence of a coupling between Si p-orbitals and metal d-states, are essentially the same as in NiSi.

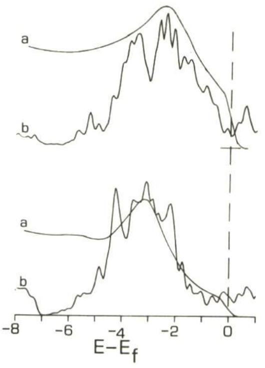

Fig.5 Experimental EDCs and theoretical DOS for Pt silicides

On the basis of the previous results for bulk silicides, we can understand the experimental findings for the interfaces: deposition at room temperature gives rise to non stoichiometric phases, whose electronic behaviour resembles that of bulk silicides. The modifications in the interface EDCs on increasing metal coverage are close to those which occur in the DOS of bulk compounds on increasing metal content.

A more detailed understanding of the differences between the interface phase and the compounds requires more theoretical and experimental work. However we believe that the present analysis provides a description of the essential features of the electron behaviour at these interfaces.

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