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The role of the Si 3s3d states in the bonding of iridium silicides (IrSi, Ir₃Si₅ and IrSi₃)

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Abstract

Si L_{2,3} soft-x-ray emission spectra of IrSi, Ir₃Si₅ and IrSi₃ compounds have been taken and the valence band densities of states associated with them have been analysed as functions of the concentration of Si atoms, the coordination number of Si–Ir in the iridium silicide compounds and the average distances of the Si–Si bonds in those compounds. The role of silicon 3s3d states in the bonding of the different iridium silicides is discussed. All the spectra show two regions, one associated with the low-energy Si 3s states and another one associated with high-energy Si 3s3d states. The effects of the interaction between the Si and Ir atoms in the silicides are: (a) the distribution of silicon states, even those associated with the least energetic s electrons, are modified, suggesting that the s electrons play a role in the formation of the iridium silicides; (b) the energy bandwidth corresponding to the Si 3s3d states increases up to 2.5 eV as the number of Si atoms that interact with the Ir atoms increases; and (c) there is a significant contribution from the d electrons, the fraction of the states associated with them being at least 20% of the total of states associated with the 3s3d states.

1. Introduction

X-ray photoelectron spectroscopy (XPS) of the iridium silicides provides a measure of the total-density-of-states (DOS) distribution in the valence band—mainly those associated with the transition metal 5d states. The valence states of s symmetry show up weakly because of their small photoionization cross sections, around two orders of magnitude lower than those corresponding to the 5d states.

Soft x-rays are emitted as valence electrons radiatively recombine with the core-level vacancies. X-ray emission spectroscopy (XES) is chemically selective and provides information related to the DOS distribution for each element of the complex solid, so Si L_{2,3} XES spectroscopy, in accordance with the dipole selection rules, probes the silicon 3s3d partial

DOS distribution in the valence band. Therefore, Si $L_{2,3}$ soft-XES is a very appropriate method for analysing the role of the Si 3s3d electrons in the formation of the iridium silicides.

The DOS distribution, $N(E)$, and the x-ray emission intensity, $I(E)$, are related by [1]

$$N(E) \propto \frac{I(E)}{E^2 P(E)} \quad (1)$$

where E is the energy of the transition between the 3s3d states and the Si 2p core level ionized by primary-electron excitation and $P(E)$ the probability of this transition.

Transition metal (TM) silicide bonding has generally been discussed either in terms of bonding between TM d orbitals and Si p orbitals [2], neglecting the contribution of the s electrons, or taking into account the contribution of the s and d electrons [3]. In the first case, the Si 3p electrons interact with the metal d ones, while in the second case there is a significant contribution from Si d electrons. The Si d DOS distribution results from the overlap of the metal d orbital with the Si sites [3, 4].

In this paper we analyse in depth the $L_{2,3}$ XES spectra of different iridium silicides, IrSi, Ir_3Si_5 and $IrSi_3$, and the distribution of the valence band DOSs associated with silicon 3s3d electrons as a function of the density of silicon atoms, the Si–Ir coordination number and the average distances of the Si–Si bonds in those compounds.

2. Experimental details

Iridium films 160 nm thick were deposited on Si substrates by electron-beam evaporation. Further details on the deposition process are available elsewhere [5]. After deposition, the specimens were annealed in vacuum using a rapid-thermal-processing (RTP) system.

The composition and thickness of the layers formed were determined by Rutherford backscattering spectrometry (RBS) using a 1.6 MeV $^4He^+$ beam. The detector resolution was 14 keV, corresponding to a thickness resolution of 2–3 nm for iridium. The compounds were also identified by means of x-ray diffraction.

Ir metal, IrSi and Ir_3Si_5 compounds can coexist in samples processed at temperatures below 950 °C [6]. The thickness of each phase depends on the thickness of the as-deposited Ir, and the temperature and processing time. For temperatures higher than 950 °C, and enough processing time, $IrSi_3$ is the only compound present. Some samples were annealed at 675 °C for 710 s in order to ensure that the only phase present was Ir_3Si_5 . The thickness of the $IrSi_{1.75}$ layer formed was 540 nm. A single layer of $IrSi_3$, 640 nm thick, was formed by annealing the samples at 675 °C for 15 s, and then processing further at 1000 °C for 5 s. Due to the coexistence of the Ir_3Si_5 and IrSi compounds, even for very thin layers of IrSi, it is not possible to guarantee, with the experimental set-up and procedures described above, the formation of a single layer of IrSi. Therefore IrSi samples were prepared by arc melting of iridium and silicon in an argon atmosphere, and further annealed at 1000 °C [7].

Si $L_{2,3}$ (3s3d \rightarrow 2p transition) x-ray emission valence spectra were measured using an ultrasoft-x-ray spectrometer with high spatial ($\Delta S \approx 4\text{--}5 \mu\text{m}$) and energy resolution ($\Delta E \approx 0.4 \text{ eV}$). A focused electron beam was used for excitation of x-ray emission spectra and the radiation was analysed using a curved diffraction grating ($N = 600 \text{ lines mm}^{-1}$, $R = 2 \text{ m}$). A soft regime of operation ($V = 10 \text{ kV}$, $i = 300 \text{ nA}$) was used.

3. Results and discussion

In order to obtain the $P(E)N(E)$ distributions, the measured x-ray emission intensities, $I(E)$, were divided by the square of the transition energy value. Since the transition probabilities are

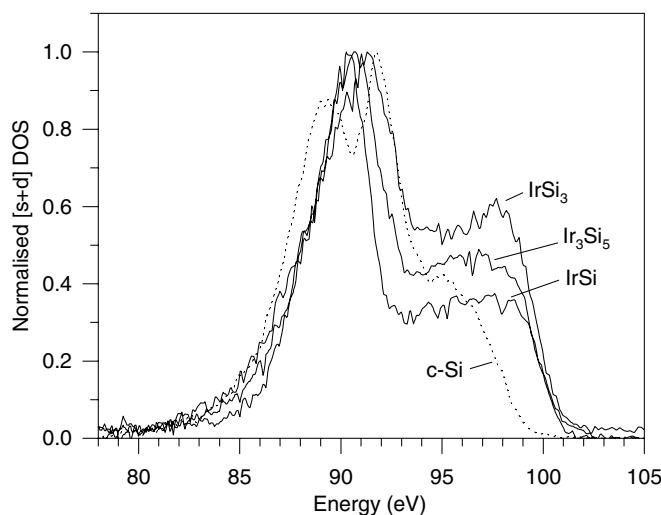


Figure 1. Normalized [s + d] DOS spectra of c-Si, IrSi, Ir₃Si₅ and IrSi₃.

undetermined, $N(E)$ cannot be derived from equation (1). In order to compare, in a qualitative way, the distribution of the silicon 3s and 3d DOSs of the different iridium silicides, we have normalized the $P(E)N(E)$ distributions to their peak values and have assumed that the value of $P(E)$ is constant. However, we are able to calculate a lower limit for the fraction of the states associated with the highest-energy ones, the 3d states, taking into account the fact that $P(E)$ decreases as the energy difference between the initial and final states increases [8]. The normalized [s+d] DOS spectra of crystalline pure Si (c-Si) and the IrSi, Ir₃Si₅, IrSi₃ compounds are shown in figure 1.

The spectrum of c-Si presents two peaks and one shoulder. The low-energy peak is attributed to low-lying 3s states, the 92 eV peak is associated with a DOS maximum with s-p hybridization and the shoulder is associated with a DOS maximum, which has a dominant 3p contribution [9].

The partial DOS distributions for the three iridium silicides associated with the silicon 3s3d states have similar appearance. The double-peak feature found in the low-energy part of the c-Si spectrum is not observable; similar results have been reported for other silicides [10, 11]. Those changes in the spectra are due to the reduction of the peak associated with the pure s states in relation to that associated with the s-p states, in comparison with the c-Si.

The energy ranges of the $L_{2,3}$ transitions in the iridium silicides are larger than the ones corresponding to the c-Si. In order to compare them, we have defined the energy bandwidth of the DOS distributions associated with the $L_{2,3}$ transitions as the energy difference between energies corresponding to 10% of the maximum of the partial DOS distributions [1]. The increments of the energy bandwidth values for IrSi, Ir₃Si₅ and IrSi₃ are 0.5, 1.5 and 2.5 eV respectively.

The increase in the energy bandwidth associated with the 3s3d electrons is due to the interaction of the Si atoms with the Ir atoms in the silicides; more precisely it is due to the hybridization of the Si 3d states with the transition metal 5d states [4]. The concentration of Si atoms that interact with the Ir atoms is proportional to the product of the concentration of the Ir atoms in the silicide (1.79 , 2.55 and 3.42×10^{22} atoms cm^{-3} for IrSi₃, Ir₃Si₅ and IrSi respectively) with the Ir-Si coordination number in the silicide (6 for IrSi₃ and 2 for IrSi) [4].

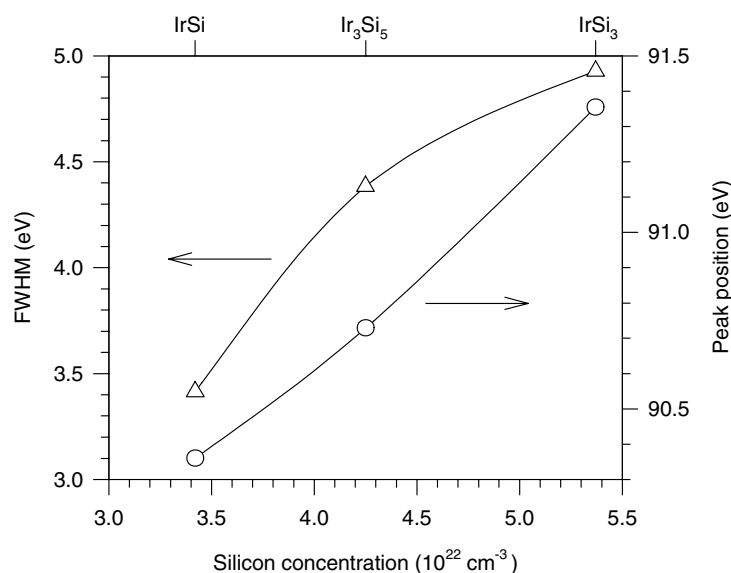


Figure 2. The energy position (circles) and FWHM (triangles) of the mean peak of the low-energy region as functions of Si concentration in the iridium silicides.

Therefore the number of Si atoms that interact with Ir atoms increases as the Ir fraction in the silicide increases and therefore more electrons occupy higher-energy states.

To study the distribution of the partial DOS valence band associated with the $[s + d]$ states, we have divided each spectrum into two regions: a low-energy one, that corresponds to the less energetic 3s electron states, fitted with two Lorentzian functions, and a high-energy one, that gives information about more energetic 3s3d states.

The energy position and the full width at half-maximum (FWHM) of the mean peak of the low-energy region as functions of the Si concentration in the silicide are shown in figure 2. The FWHM increases with silicon concentration in the silicide. This increase is in accordance with the fact that the energy band associated with one isolated-atom state increases as the density of atoms increases [12]. The energy peak position shifts towards higher energies with increasing Si concentration, approaching the energy value of the maximum of the partial DOS of c-Si associated with the $s-p$ hybridization. Its dependence on the Si concentration is not linear. This behaviour can be explained by taking into account, in addition to the different concentrations of the Si s electrons in the silicides, the different intensities of the Si-Si interactions due to the different bond lengths in the silicides (the Si-Si bond length decreases as the concentration of the Si in the silicide increases). The shift in the energy peak position is about 1 eV. This low-energy peak corresponds to the -8.9 eV peak found in IrSi and Ir₃Si₅ by XPS. This peak is not observable by XPS in the IrSi₃ compound [13].

To study the distribution of the highest-energy states, we have subtracted from the DOS shown in figure 1 the low-energy region discussed above and have obtained the high-energy portion of the DOS shown in figure 3.

In the case of c-Si, these remaining states account for the shoulder observed in the high-energy edge of the partial DOS distribution, which has been fitted using a Gaussian function centred at about 95.5 eV. The states corresponding to the silicides have been fitted using two Gaussian functions: one centred at the maximum near 98.5 eV, attributed mainly to Si 3d states, that we will refer to later as region B of the high-energy portion, and another centred at about 96 eV, attributed to higher Si 3s states (region A). We are mainly interested in region B.

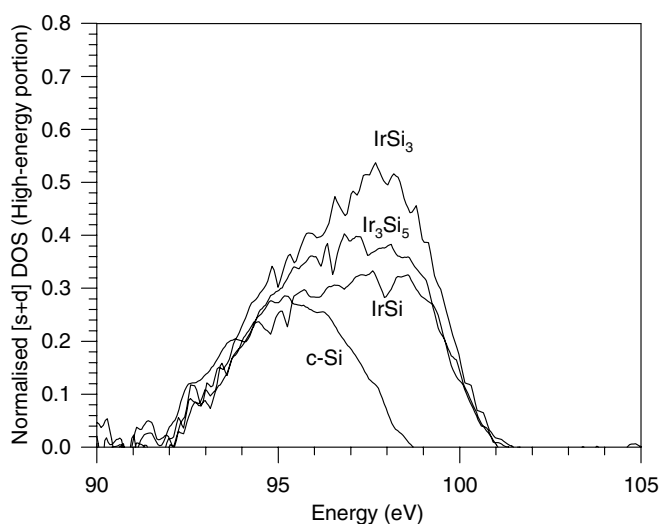


Figure 3. The high-energy portion of the [s + d] DOS for c-Si, IrSi, Ir₃Si₅ and IrSi₃.

The energy difference observed between this peak and the low-energy one is not constant but depends on the Si concentration in the silicide. This fact, together with the independence of the position of the peak, suggests that this portion of the DOS is related to the bonding of the Ir atoms with the Si ones.

In order to obtain an estimate of the fraction of the total states associated with the different regions: the low-energy portion (less energetic Si 3s states), region A (high-energy Si 3s states) and region B (Si 3d states), we have integrated these contributions and normalized them against the integral of the total 3s3d DOS distributions. The proportion of the highest-energy states associated with 3d states is larger than 20% for the three silicides. These values are lowest limits, since they have been calculated considering $P(E)$ to be independent on the transition energy, but the $P(E)$ values of the highest-energy transitions have a value which is less than that corresponding to the lowest-energy transitions. We can compare the ratio of the contributions of the regions A and B for the three silicides, taking into account that they correspond to very close energies and therefore their transition probabilities $P(E)$ would have similar values. This ratio increases with the concentration of Si atoms that interact with the Ir atoms in the silicide, showing that a larger proportion of the electrons associated with the high-energy region of the spectra occupy higher-energy states associated with d states as the concentration of the Si atoms that interact with the Ir atoms increases. It looks like there is a transfer from region A to region B. This behaviour can be explained in the same terms as were used above to describe the dependence of the energy bandwidth on the concentration of Si atoms that interact with the Ir atoms in the silicide.

4. Conclusions

The analysis of the Si L_{2,3} XES spectra of the iridium silicides gives very detailed information on the behaviour of the 3s3d electrons in their formation. The interaction between the Si and Ir atoms modifies the DOS distribution associated with silicon 3s3d electrons, even for those states associated with the less energetic s electrons. The main effect of the interaction

between the Si and Ir atoms in the silicides is that some electrons occupy higher-energy states associated with d states, increasing the energy bandwidth corresponding to the Si [s + d] states. The fraction of the states associated with Si 3d states is at least 20% of the total of Si 3s3d states.

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