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2002 J. Phys.: Condens. Matter 14 6833

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Electronic structure of rhenium disilicides

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Received 20 December 2001

Published 28 June 2002

Online at stacks.iop.org/JPhysCM/14/6833

Abstract

The valence band structure of amorphous and crystalline films of rhenium silicides has been studied by ultrasoft x-ray spectroscopy. A theoretical calculation of the electronic structure of bulk crystals and thin films of ReSi_2 and $\text{ReSi}_{1.75}$ was carried out. The experimental $L_{2,3}$ -spectra of silicon show the best correlation with the theoretical calculation for $\text{ReSi}_{1.75}$. The decrease in the density of states at the Fermi level in $\text{ReSi}_{1.75}$ in comparison with ReSi_2 testifies that the phase with lack of silicon is more stable than the stoichiometric composition.

1. Introduction

As a rule, transition metal silicides have metallic properties. Only a very small group of silicides of iron, chromium, iridium, rhenium, osmium and ruthenium exhibit features of semiconductors. These compounds are mostly indirect narrow bandgap semiconductors. The best known and most extensively studied of these are CrSi_2 - and $\beta\text{-FeSi}_2$ disilicides. For many decades these materials have been used in the technology of Si-based digital devices, optoelectronics, fibre-optic communications, and IR photodetectors [1–3]. However, in recent years, attention has been mostly paid to rhenium silicide, which is caused by several factors. First, it has been found that, of all the semiconducting silicides, rhenium silicide is best matched with silicon, the basic material of microelectronics [4, 5]. Second, the manufacture and processing of rhenium silicide is rather simple [6]. Third, this material can be grown with both n- and p-types of conduction, depending on technological parameters (annealing temperature and argon/hydrogen ratio) [7], without any dopants.

Furthermore, it has been found that rhenium disilicide may exist in several stable modifications: the stoichiometric composition ReSi_2 [6, 8, 9], or compositions with lack of silicon: $\text{ReSi}_{1.8}$ [4, 7] and $\text{ReSi}_{1.75}$ [4, 5, 7, 10]. The probability of $\text{ReSi}_{1.8}$ [4, 7] or $\text{ReSi}_{1.75}$ [7] formation is much higher than that for ReSi_2 . According to [11, 12], ReSi_2 has a body-centred orthorhombic lattice with $a = 3.11 \text{ \AA}$, $b = 3.14 \text{ \AA}$ and $c = 7.67 \text{ \AA}$. This crystal structure

is very close to the well-known structure of CaC_2 (MoSi_2). Since the difference between lattice constants a and b is only about 0.5%, it is often assumed that the crystal lattice of rhenium disilicide is body-centred tetragonal with $a = b = 3.13 \text{ \AA}$ and $c = 7.67 \text{ \AA}$ [9] or $a = b = 3.212 \text{ \AA}$ and $c = 7.858 \text{ \AA}$ [13, 14]. $\text{ReSi}_{1.75}$ has a similar structure characterized by small deviation of the angle between the axis c and the plane ab from 90° : $a = 3.138 \text{ \AA}$, $b = 3.120 \text{ \AA}$, $c = 7.67 \text{ \AA}$, $\alpha = 89.90^\circ$ [10].

Much attention has been paid to studying the methods for production of rhenium silicides [4, 10] and the crystal [5, 10–12], optical [4, 6, 7], electrical [7, 8, 10] and some other properties of these materials. However, the electronic structure of their valence band has not been properly investigated, despite the considerable opportunities and abundant information furnished by modern spectroscopic techniques. Theoretical studies in this field have also been limited. We are only aware of two attempts to study the electronic structure of rhenium silicide: photoemission spectroscopy of core levels of a thin $\text{ReSi}_{1.75}$ film [4] and calculation of the band structure and density of states for the ReSi_2 bulk crystal [13].

In this work we report the results obtained in studying the valence band by x-ray emission spectroscopy, and also densities of electronic states and x-ray emission spectra calculated for bulk crystals and thin films of rhenium silicides.

2. Experimental details

Crystal thin-film rhenium silicide $c\text{-ReSi}_2$ was obtained by electron-beam evaporation and condensation of the metal onto heated silicon substrates in a vacuum (residual pressure $5 \times 10^3 \text{ Pa}$). Single-crystal Si(100) wafers heated to 850°C were used as substrates. The deposition rate and film thickness were $0.8\text{--}1.3 \text{ nm s}^{-1}$ and $40\text{--}60 \text{ nm}$, respectively. After the deposition process was complete, thin-film structures were immediately cooled to room temperature in a vacuum.

Films of $a\text{-Re}_{30}\text{Si}_{70}$ amorphous alloy with composition close to that of the higher rhenium silicide were obtained by three-electrode ion-plasma sputtering of composite targets at argon pressure of $4 \times 10^{-1} \text{ Pa}$. Polycrystalline aluminium plates mounted on a sample holder cooled with running water were used as substrates. The film thickness was $\sim 10 \mu\text{m}$.

The phase composition and the structural state of the objects of study were investigated by the x-ray diffraction method. Diffraction patterns were recorded with an RCD x-ray diffraction camera in accordance with the microsection technique or using DRON-2 or DRON-4-07 diffractometers with Bragg–Brentano focussing. In the case of the RCD camera, the grazing angle of the primary beam with respect to the sample surface was 14° . K_α -radiation was used in both cases. The elemental composition was only monitored for the $a\text{-Re}_{30}\text{Si}_{70}$ alloy by means of microanalysis on a CamScan instrument.

Ultrasoft x-ray spectra of Si $L_{2,3}$ emission were obtained using an RSM-500 spectrometer-monochromator. The investigations were carried out with emission excitation by an electron beam with energy of 3 keV and current of $1\text{--}2 \text{ mA}$. The irradiated sample area was $\sim 5 \text{ mm}^2$. The working vacuum in the spectrometer tube was maintained by oil-free facilities at a residual pressure of $2 \times 10^{-4} \text{ Pa}$. The instrumental broadening in recording the spectrum did not exceed 0.3 eV , and the sample thickness analysed was about 60 nm .

3. Calculation procedure

The electronic structure of bulk crystals was calculated using the bulk method of linearized augmented plane-waves (LAPW) [15], and that of film structures, by means of the film LAPW [16] method. A brief description of the calculation procedures is given in [17–19].

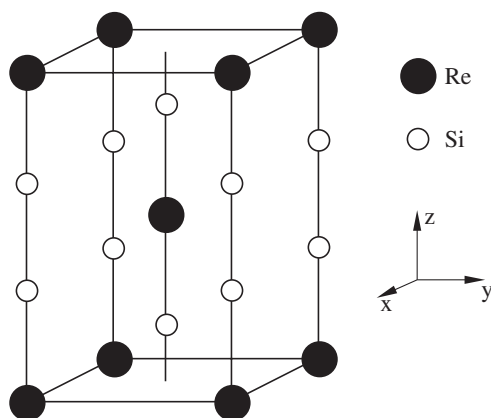


Figure 1. Crystal structure of ReSi_2 .

Spectral characteristics were calculated for a bulk sample of stoichiometric rhenium silicide with lattice constants $a = b = 3.212 \text{ \AA}$ and $c = 7.858 \text{ \AA}$ [13, 14]. The unit cell of ReSi_2 is shown in figure 1. To simulate the structure of $\text{ReSi}_{1.75}$, we doubled the lattice constants along directions a and b , so that they were equal to 6.424 \AA , and created in the lattice two vacancies at silicon atom sites symmetric with respect to the cell centre. Thus, $\text{ReSi}_{1.75}$ actually has in our calculation a chemical formula $\text{Re}_8\text{Si}_{14}$.

For films, the calculation was carried out in two variants: with excess and lack of silicon (henceforth designated as film-1 and film-2, respectively). In the first case, the unit cell of the film comprises two conventional unit cells of bulk crystal with two additional layers of silicon atoms on each side. The thickness of such a film, with the vacuum regions disregarded, is 20.97 \AA . The thickness of the rhenium silicide film of type two, with unit cell comprising two conventional cells of bulk crystal, is 15.72 \AA . The chemical formulas of such films are $\text{Re}_5\text{Si}_{12}$ and Re_5Si_8 .

4. Results and discussion

4.1. Densities of electronic states

Figure 2(a) presents the calculated total and partial densities of electronic states, localized on the silicon and rhenium atoms of a bulk ReSi_2 crystal of stoichiometric composition. As follows from the calculation, the structures of the density of electronic states localized on atoms of the bulk samples and on atoms from inner layers of the films are virtually the same. For silicon atoms the highest density of the s states is concentrated near the valence band bottom at energies of $8\text{--}15 \text{ eV}$ below the Fermi level (E_F). At bond energies from 1.8 to 2.3 eV , a quasi-gap is observed for these states. However, the density of the s states is high enough directly at the Fermi level and in its vicinity. The p and d states of silicon are concentrated mainly at bond energies of $2.5\text{--}9 \text{ eV}$ and $2.5\text{--}6.5 \text{ eV}$, respectively. Their main peaks lie 3.8 eV below E_F . For rhenium atoms, the s states are distributed evenly across the valence band except in the range from -1 to -2.6 eV , where the quasi-gap is observed. The p and d states of rhenium lie in a rather narrow energy interval. Their peaks are situated at bond energy of 3.8 eV . As seen in figure 1, s and p states of silicon atoms and d states of rhenium atoms make the maximum contribution to valence band formation. In this case the Fermi level lies in a

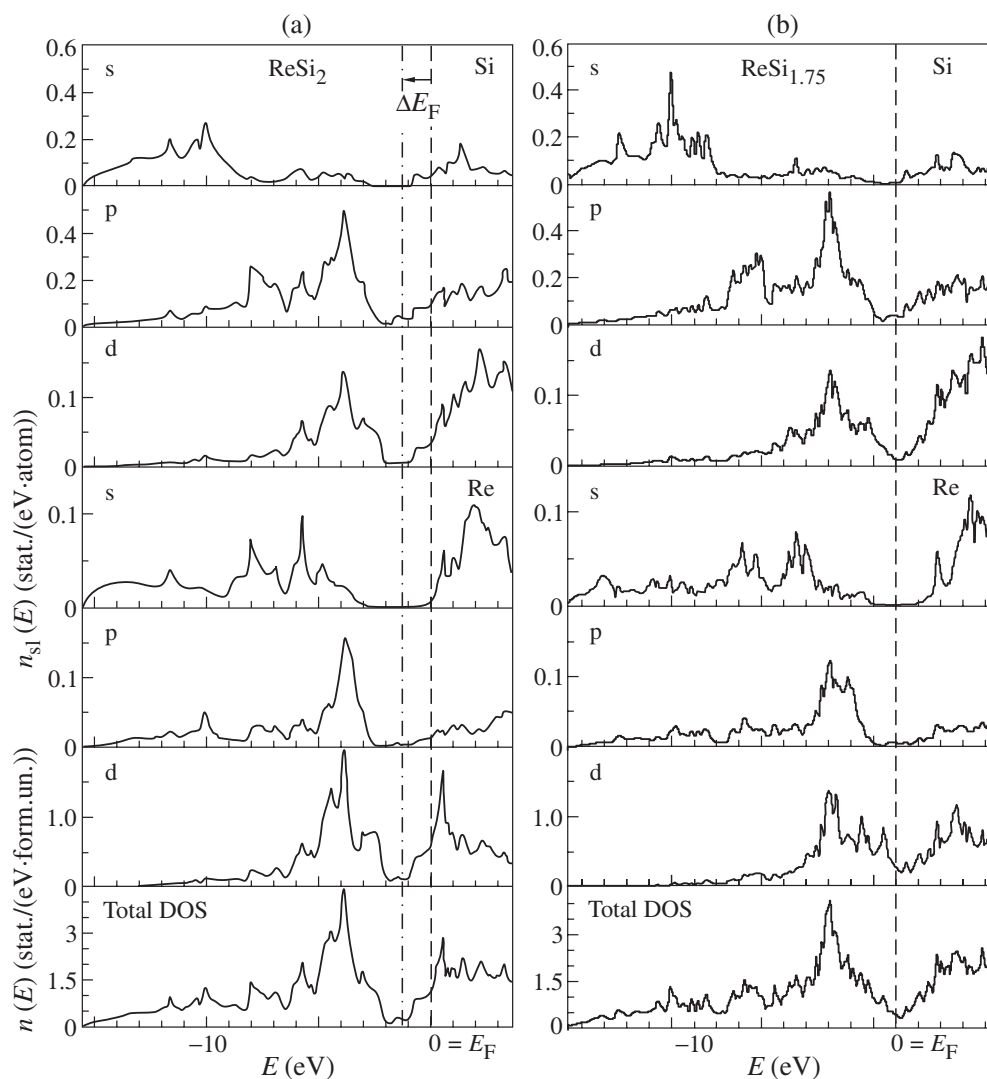


Figure 2. Total and local partial densities of electronic states of silicon and rhenium atoms in bulk (a) ReSi_2 and (b) $\text{ReSi}_{1.75}$ crystals.

region with high density of states, whereas in the energy range from -1 to -2 eV the density of states is much lower. So, according to our calculation, which is in excellent agreement with other calculations of densities of states [13], ReSi_2 is a metal with rather high density of states at the Fermi level. The width of the rhenium disilicide valence band is 15.55 eV in the bulk sample and 15.57 or 15.45 eV for films with, respectively, excess and lack of silicon.

The structure of the density of electronic states localized on atoms of the $\text{ReSi}_{1.75}$ phase (figure 2(b)) is very close to that for ReSi_2 atoms. This, as a matter of fact, would be expected because these phases have the same crystal structure with close lattice constants. And, since the number of vacancies in $\text{ReSi}_{1.75}$ is small, the electronic structures of these phases must obviously be similar. The only significant difference is that the density of states at the Fermi level essentially decreases and the range of the maximum density of states is shifted in $\text{ReSi}_{1.75}$

Table 1. Energy positions and relative intensities of the principal peaks in $L_{2,3}$ x-ray emission spectra of silicon atoms in rhenium silicides (eV with respect to E_F)

	A	B	C	D	I_B/I_A	I_C/I_A
a-Re ₃₀ Si ₇₀ ^a	-9.0	-1.8	—	—	0.72	—
Re/Si(100) ^a	-9.4	-2.7	—	—	0.75	—
ReSi _{1.75}	-9.8	-2.9	—	—	0.81	—
ReSi ₂ (bulk)	-10.1	-4.0	-0.5	-5.8	0.85	0.43
ReSi ₂ (film-1)	-10.5	-4.0	-0.5	-5.8	0.82	0.25
ReSi ₂ (film-2)	-10.3	-4.0	-0.1	-5.3	0.78	0.30

^a Experimental data.

by approximately 1–1.5 eV towards the valence band top in comparison with the bulk and film samples of rhenium disilicide. This result is in good agreement with the so-called model of rigid bands [20, 21], according to which the shapes and positions of the energy bands do not vary appreciably between compounds with close crystal and electronic structures, with only the Fermi level shifted with respect to the valence band bottom. Just this situation takes place for rhenium silicides: two silicon atoms in ReSi₂ contribute eight electrons to the valence band, whereas ReSi_{1.75} gives only seven electrons. Having reduced by unity the number of electrons in ReSi₂ per formula unit, we found that the Fermi level is shifted in this case towards the valence band bottom by $E_F = 1.26$ eV, as shown in figure 2 by dot-dashed curve. Such a shift results in that the Fermi level comes to the region with much less density of states in comparison with the case of rhenium silicide of stoichiometric composition. Comparison of figures 2(a) and (b) shows that the shape and position of the principal peaks of the density of electronic states for ReSi₂ atoms with changed position of the Fermi level and for ReSi_{1.75} virtually coincide. The considerable decrease in the density of states at the Fermi level in ReSi_{1.75}, compared with the stoichiometric ReSi₂ composition, testifies that the structure with lack of silicon is more stable. This is also confirmed by the experimental data of [4, 7], according to which the probability of ReSi_{1.75} formation much exceeds that of ReSi₂. Nevertheless, although the density of states at the Fermi level in ReSi_{1.75} decreases essentially as compared with ReSi₂, the former remains a metal according to our calculation. Such a disagreement between the theory and experiment can be, most likely, accounted for by the fact that the commonly accepted approximation to the crystal lattice of this material by the tetragonal structure of the CaC₂ type is not quite correct. The same factor, taken together with the possible relaxation effects (e.g., atomic shifts) resulting from the appearance of vacancies and disregarded in the calculation, presumably also leads to discrepancy between the experimental data and the theoretical calculation of the electronic structure in the case of ReSi_{1.75}. Other mechanisms of band gap formation in the energy spectrum are also possible; in particular, the band gap may appear as a result of the Peierls instability [22].

4.2. X-ray emission spectra

Figure 3 compares the $L_{2,3}$ x-ray emission spectra for silicon atoms of rhenium disilicide with the results of theoretical calculations of these spectral characteristics for the ReSi_{1.75} bulk phase and for the bulk and film structures of ReSi₂. The $L_{2,3}$ -spectrum reflects, in accordance with the dipole selection rules, the distribution across the valence band of the s and d states localized on silicon atoms. The contribution from the s and d states to the $L_{2,3}$ -spectrum is represented in the figure by dotted and dot-dashed curves, respectively. The positions of the principal features of these spectra relative to the Fermi level are given in the table.

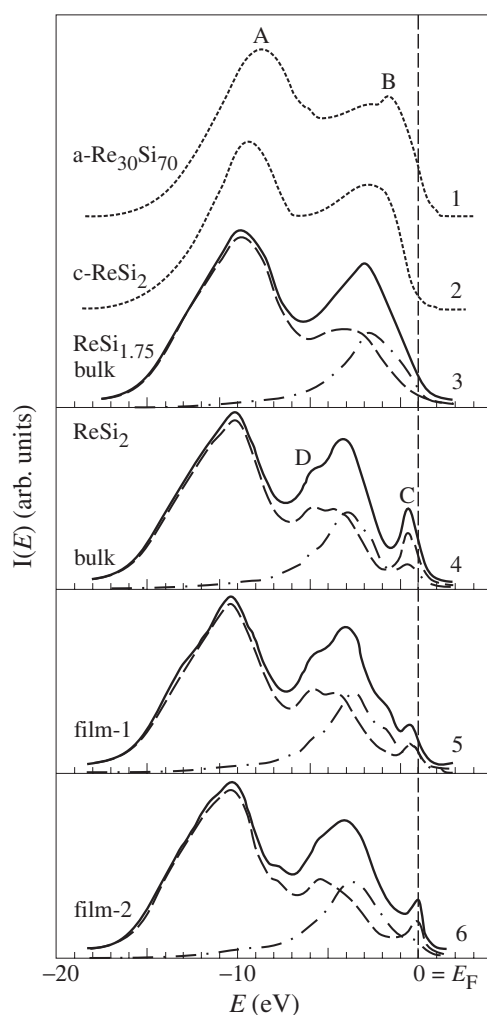


Figure 3. $L_{2,3}$ x-ray emission spectra of silicon atoms: 1 and 2, experimental data for amorphous $a\text{-Re}_{30}\text{Si}_{70}$ and crystalline $c\text{-ReSi}_2$ films; 3–6, theoretical calculations for, respectively, $\text{ReSi}_{1.75}$ and ReSi_2 bulk crystals and ReSi_2 films with excess (film-1) and lack of silicon (film-2).

As seen in figure 3 and the table, the best agreement between the calculated spectra and the experimental results is observed for $\text{ReSi}_{1.75}$: both the shapes of spectra and the energy positions of their principal features are very close. In accordance with calculations, the main peak A of these spectral characteristics is predominantly due to the s states, whereas the second peak, B, is due equally to the s and d states of silicon. The calculated $L_{2,3}$ -silicon spectra of the bulk material and rhenium disilicide films are far less consistent with experiment. First, peak B is shifted towards the valence band bottom by approximately 1.8 eV relative to the energy position of the same peak in the experiment. Second, additional features C and D, which are not observed in experiments, appear in the calculated spectra. The appearance of peak C is due to the high density of the s states of silicon in the vicinity of the Fermi level (see figure 2(a)). The appearance of a minor feature D is also mainly due to the s states of silicon, which can be explained as follows. For $\text{ReSi}_{1.75}$, the peak in the density of the s states

lies 4 eV below the Fermi level, and that of the d states, 2.8 eV below E_F . This gives rise to feature B at bond energy of 2.9 eV. In the case of ReSi_2 , the situation is somewhat different. The shift of the s and the d bands of silicon in ReSi_2 , caused by the increase in the number of valence electrons as compared with $\text{ReSi}_{1.75}$, occurs in such a way that the region of the d state localization is shifted to 3.8 eV below E_F , and a small splitting of the peak into two components at 4.8 and 5.7 eV is observed for the s states (see figure 1). The first component contributes, along with the d states, to the formation of peak B, whereas the second leads to the appearance of structure D in the Si $L_{2,3}$ -spectrum of rhenium disilicide.

5. Conclusion

Thus, we have found out that, according to the calculation, $\text{ReSi}_{1.75}$ is, indeed, a more stable phase than ReSi_2 . The fact that the experimental $L_{2,3}$ spectrum of silicon is in the best agreement with the results of calculation for $\text{ReSi}_{1.75}$, testifies that, most likely, it is this phase (and not ReSi_2 , as we originally assumed) that is formed during film formation.

Acknowledgment

This work was supported by the Russian Foundation for Basic Research (Grant 01-02-97401r98ccr).

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