# Valence-band electronic structure of $NiSi_2$ and $CoSi_2$: Evidence of the Si *s* electronic state at the Fermi edge

H. Nakamura
*Osaka Electro-Communication University, Hatsu-cho, Neyagawa, Osaka 572, Japan*

M. Iwami, M. Hirai, and M. Kusaka
*Research Laboratory for Surface Science, Faculty of Science, Okayama University, Tsushima-naka, Okayama 700, Japan*

F. Akao
*Department of Electronic Engineering, Okayama University of Science, 1-1 Ridai-cho, Okayama 700, Japan*

H. Watabe
*Matsushita Electric Industrial Company, Ltd., Higashi-ku, Osaka 590, Japan*
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It is found that the Si $L_{2,3}$ soft-x-ray emission band of a $NiSi_2$ single crystal has two main peaks at $h\nu \simeq 91$ and 100 eV, where the Si $L_{2,3}$ spectrum is expected to reflect the density of states of the valence band with *s* and *d* symmetry. The sharp peaks at the top of the valence band are concluded to be due to the *s* band that mainly originated from the Si *s* state and are not due to the *d* band that originated from the Ni *d* state, which is a clear departure from the existing widely accepted explanation of the valence-band density of states. A similar result may be true for $CoSi_2$.

## I. INTRODUCTION

In semiconductor devices, metal-semiconductor junctions play an important role as a Schottky barrier or an Ohmic contact. Among many metals, transition-metal silicides have attracted attention for their characteristics, e.g., their stability for heating, etc. $NiSi_2$ is one of the most interesting silicides because of its possible epitaxial growth on a Si single-crystal substrate with appropriate Schottky-barrier height.[1,2]

In order to clarify the electric properties of silicide-Si contact systems, the study of the electronic structure of a silicide itself has been carried out experimentally and theoretically.[3–10]

It is well known that photoelectron spectroscopies (PES) such as UPS (ultraviolet photoelectron spectroscopy) and/or XPS (x-ray photoelectron spectroscopy) provide useful information on the valence-band density of states (DOS). Soft-x-ray–emission spectroscopy (SXS) is also a powerful means to elucidate the valence-electronic structure of solids. The PES measurement is sensitive to the surface layer and the observed spectra reflect the DOS of the surface region of a specimen under study. In contrast, x-ray spectroscopy has mainly been applied to the study of bulk DOS due to the fact that photons have a rather large mean free path in a solid compared with electrons. This is also the case for soft x rays that have a mean free path less than conventional hard x rays, although a new application of the SXS method to the surface and interface study has been proposed.[11] An important point is that PES provides information on the total DOS of the valence band of a material, while the SXS provides information on the partial DOS of the valence electronic state due to the dipole selection rule for electron transitions.

In this study we intend to characterize the valence electronic state of $NiSi_2$ and $CoSi_2$ single crystals through the study of the soft-x-ray Si $L_{2,3}$ valence-band emission spectra of $NiSi_2$ and $CoSi_2$ single crystals.

## II. EXPERIMENT

Specimens were prepared as follows. A Ni film with thickness of $>100$ nm was evaporated on a Si(111) substrate in a vacuum of about $10^{-6}$ Pa and then the specimen was heat treated in an electric furnace at 800°C for 30 min in a $N_2+H_2$ atmosphere. $H_2$ was used for preventing oxidation of the specimen during the heat treatment. In this heat treatment a $NiSi_2$ single crystal was epitaxially grown on a Si(111) substrate. The growth of a $NiSi_2$ single crystal was confirmed by a combination of x-ray diffraction, electron-probe microanalysis, and Auger depth profiling. Similar was the case for $CoSi_2$. SXS experiments were caried out with energetic electron excitation, where the energy of primary electrons, $E_p$, was 4.0 keV. A grazing incidence vacuum spectrometer equipped with a concave grating with a radius of 2 m and 1200 grooves/mm was used for the measurement of soft-x-ray–emission spectra. Specimens were pasted on a Cu plate by a conducting resin compatible with ultrahigh vacuum and were put in a Henke-type x-ray tube, where specimens were kept at room temperature by water cooling. The directions of the incident electrons and exiting photons were normal to the specimen surface. A photomultiplier was used for the detection of emitted x rays. The energy resolution of the present spectrometer is

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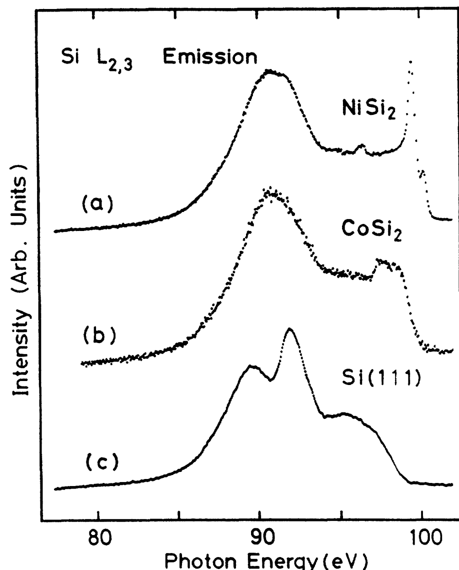


FIG. 1. Si $L_{2,3}$ valence-band–emission spectra of (a) a $NiSi_2$, (b) a $CoSi_2$ and (c) a Si single crystal. These spectra are obtained with an electron beam energy of 4.0 keV. The intensity is normalized at the highest peak.

better than 0.6 eV, which will be shown later in relation to the Si $L_{2,3}$ soft-x-ray–emission spectrum of a $NiSi_2$ single crystal [Fig. 1(a)]. Details of the measurement of soft-x-ray spectra were reported elsewhere.[12] An XPS measurement was carried out with either a VG ESCALAB 5 or a SHIMAZU ESCA 850, where Mg $K\alpha$ x rays were used.

## III. RESULTS AND DISCUSSION

Si $L_{2,3}$ valence-band–emission spectra are shown in Fig. 1. Figure 1(a) is the spectrum of a $NiSi_2$ single crystal, Fig. 1(b) is that of a $CoSi_2$ single crystal, and Fig. 1(c) is that of a Si single crystal. The intensity of the spectra is normalized to the highest peak. It must be noted that these two spectra of silicides show very different features from the spectrum of a Si single crystal. The spectrum of a Si single crystal has two peaks at $h\nu \simeq 89.5$ and 92.0 eV with a broad shoulder at $h\nu \simeq 94-98$ eV. On the other hand, the spectrum of a $NiSi_2$ single crystal has a broad peak at $h\nu \simeq 91$ eV, a terrace at $h\nu \simeq 94-9\eta$ eV, and a strong and sharp peak at $h\nu \simeq 100$ eV. The case for $CoSi_2$ is similar, although the peak at $\simeq 100$ eV is not as clear as that for $NiSi_2$. These soft-x-ray–emission spectra are caused by the radiative transitions of electrons from the valence band to the Si $L \rightarrow L_{2,3}$ core level. If one looks at the strong and sharp peak at $h\nu \simeq 100$ eV for $NiSi_2$ carefully, he will find that the spectrum is composed of two lines peaked at 99.6 and 100.2 eV, where the energy separation is 0.6 eV. Since the amount of the energy separation is close to the spin-orbit splitting of the Si $L_{2,3}$ level, the most probable explanation of the double peaks at $h\nu \simeq 100$ eV for $NiSi_2$ is that the two peaks are the result of the spin-orbit splitting of the $2p$ core level of Si atoms, i.e., $Si(2p_{3/2})$ and $Si(2p_{1/2})$ levels. Therefore these two sharp peaks originate from the same initial state. Consequently the large widths of the other broad peak at $h\nu \simeq 91$ eV and of the terrace of $h\nu \simeq 94-97$ eV are not due to the window function of the spectrometer, because the energy resolution of the present spectrometer is better than 0.6 eV.

In Fig. 2 are shown spectra due to XPS experiments, where (a) is a spectrum for a $NiSi_2$ crystal and (c) is that for a Ni crystal. The intensity of the spectra (a) and (c) are normalized to the highest peak. Figure 2(b) is a calculated one for $NiSi_2$ [Fig. 2(a)], where the first peak is reduced considering the difference in the photoelectron excitation cross sections at $h\nu = 1253.6$ eV, i.e., $\sigma[Si(3s)]/\sigma[Ni(3d)] = 0.16$ from Yeh and Lindau.[13] Namely, Fig. 2(b) is a rough estimate of the total DOS of the valence-band electronic state of $NiSi_2$ crystal. A comparison of the spectra of Figs. 2(a)–2(c) leads to a conclusion that the spectrum of Fig. 2(a) shows an exaggeration of the Ni $d$ DOS. Also, from a comparison of the spectrum of Fig. 1(a) with that of Fig. 2(b), it will be said that the peak at $h\nu \simeq 91$ eV of Fig. 1(a) corresponds to the one at binding energy $(E_b) \simeq 9$ eV of Fig. 2(a), because the PES signal of the bulk Ni [Fig. 2(c)] does not have a clear peak at $E_b \simeq 9$ eV. The case for $CoSi_2$ is similar. It is clear that one cannot discuss the valence electronic state of the $NiSi_2$ crystal in detail through the PES spectrum alone because the PES spectrum contains the information of the valence electronic state of a solid studied as a whole, i.e., $s$, $p$, and $d$ states of the present $NiSi_2$ and $CoSi_2$ single crystals with an enhanced contribution of the Ni $d$ or Co $d$ DOS. The SXS spectrum, on the other hand, gives the partial DOS corresponding to $(s+d)$. For $NiSi_2$ the broad peak at $h\nu \simeq 91$ eV of Fig. 1(a) is thought to originate from the Si $s$ state and the sharp one at $h\nu \simeq 100$ eV is introduced through the Si—Ni bond formation. The former is also modified in a

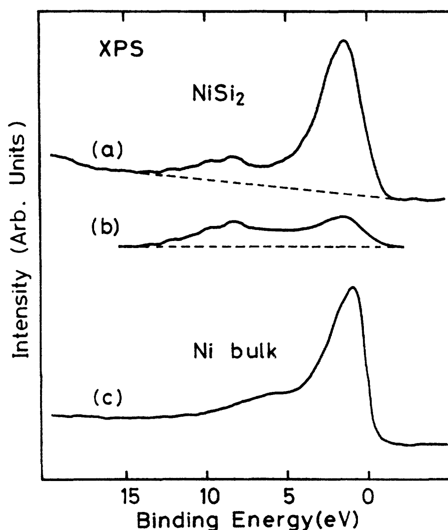


FIG. 2. XPS spectra of (a) $NiSi_2$ and (c) Ni bulk. (b) is a calculated spectrum for $NiSi_2$, i.e., (a), considering the difference in the photoelectron excitation cross sections at $h\nu = 1253.6$ eV, i.e., $\sigma[Si(3s)]/\sigma[Ni(3d)] = 0.16$ for the first peak.

$NiSi_2$ single crystal from that in a Si single crystal. However, the difference in the spectral shape between Fig. 1(a), $NiSi_2$ single crystal, and Fig. 1(c), Si single crystal, clearly shows the fact that the valence electronic structure is quite different between a $NiSi_2$ and a Si single crystal, especially in the $(s+d)$ spectrum. As for the VB-DOS for transition-metal silicides (TMSi's), it has first been claimed that the Si $s$ electronic state has significant DOS at $E_F$ by a nuclear magnetic resonance (NMR) study.[3] A theoretical calculation[4] has ensued to support the NMR observation. Strangely enough, however, it seems likely the case that the upper part of the VB-DOS of TMSi's, including $NiSi_2$ and $CoSi_2$, has been widely believed to be constructed by a Si $p$–TM $d$ hybridized electronic state only.[5–10]

For the sake of discussion we show in Fig. 3 the Si $L_{2,3}$ emission spectrum and the theoretical DOS curves obtained by Bisi *et al.*[5] as a candidate for the widely believed VB-DOS of $NiSi_2$. Figure 3(a) is the same as Fig. 1(a), and Figs. 3(b) and 3(c) are theoretical DOS spectra. Figure 3(b) shows the partial DOS for $d$ symmetry and Fig. 3(c) shows the partial DOS for $s$-$p$ symmetry. The relative energy position between the theoretical and experimental curves is chosen in the following way, i.e., the position of the Fermi energy $(E_F)$ of the experimental spectrum is placed at $h\nu=99.7$ eV considering that the observed Si($2p$) binding energy is 99.7 eV in the XPS study for $NiSi_2$.

A comparison of the spectra in Fig. 3 suggests that the broad peak sitting at about 91 eV is due to the transition from the valence-band state with the $s$ symmetry, and the terrace at 94–97 eV is due to the $s$ component of the $s$-$p$ state. Previously it was concluded that the major structure which lies closer to $E_F$ (centered 2–3 eV below $E_F$) reflects Si $p$–Ni $d$–derived states[5,6] from the comparison between the theoretical DOS of a $NiSi_2$ single crystal and the experimental valence-band UPS and XPS data. A discussion similar to Refs. 5 and 6 is also given by soft-x-ray–emission experiments of Si $K\beta$ and Ni $L_3$ soft x rays.[9] In addition, they claim that the Si $s$ state does not contribute to the main valence-band DOS near $E_F$ on the basis of the Si $s$ state lying far below the Ni $d$ state, more than 10 eV according to the theoretical DOS. The sharp peaks for $NiSi_2$ at $h\nu=100$ eV of the Si $L_{2,3}$ emission band spectrum are not assigned from either the above theoretical DOS curves or considerations given above. Tersoff *et al.*[10] have claimed the Si $s$ antibonding state to appear above the Si $p$–Ni $d$–derived valence-band DOS of $NiSi_2$ and $CoSi_2$, although they have not claimed a Si $s$ DOS at $E_F$. Therefore, such a claim as the one that the upper part of the VB-DOS of TMSi's is only due to Si $p$- and TM $d$-hybridized states fails to explain the present experimental observation that the Si $L_{2,3}$ spectrum has a significant intensity at $E_F$. An exception is the one given by Okuno *et al.*,[3] where they claim a clear Si $s$ DOS at $E_F$ from a NMR study, which has been supported by a theoretical calculation.[4] Recently, a similar requirement was also given by Spier *et al.*[14] Martinage *et al.*[15] have carried out the band-structure calculation of $NiSi_2$ using the self-consistent APW method, where it is shown that the top of the valence band has a peak which originates from Si $s$ DOS above the Ni $d$ band. Therefore, the sharp peaks at $h\nu\simeq100$ eV in the present Si $L_{2,3}$ spectrum for $NiSi_2$ are considered to correspond to the $s$ band, which mainly originated from the Si $s$ electronic state. Similar consideration may be applied to the VB-DOS of $CoSi_2$, although further studies like the one by Bylander *et al.*[4] are needed.

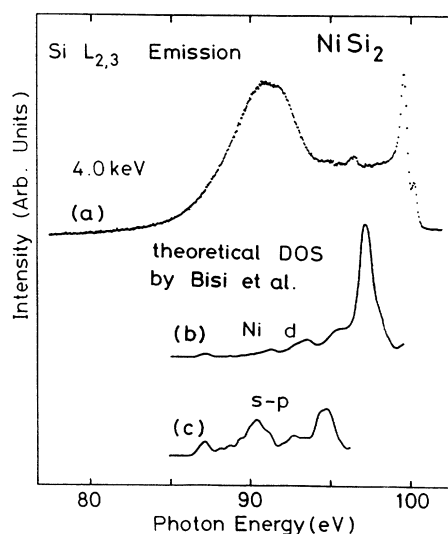


FIG. 3. A Si $L_{2,3}$ valence-band emission spectrum of $NiSi_2$ obtained in the present study is compared with the theoretical DOS curves obtained by Bisi *et al.* (Ref. 5). (a) is the same as Fig. 1(a). (b) and (c) are theoretical DOS's.

## IV. SUMMARY

We have studied the valence-band structure of $NiSi_2$ and $CoSi_2$ single crystals by measurements of either the soft-x-ray Si $L_{2,3}$ emission band spectra or XPS. The SXS spectra of $NiSi_2$ are compared with several experimental and theoretical DOS's reported. The sharp peak at $h\nu\simeq100$ eV is attributed to the $s$ band which mainly originated from the Si $s$ state and the broad peaks at $h\nu\simeq91$ eV and the terrace at 94–97 eV are attributed to the $s$ part of the $s$-$p$ band that originated from Si $s$–Si $p$ states, respectively.

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