Local partial densities of states in Ni and Co silicides studied by soft-x-ray-emission spectroscopy

J. J. Jia, T. A. Callcott, W. L. O'Brien, and Q. Y. Dong

Department of Physics, University of Tennessee, Knoxville, Tennessee 37996

J.-E. Rubensson, D. R. Mueller, and D. L. Ederer

Photon Physics Group, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. E. Rowe

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 18 July 1990; revised manuscript received 8 November 1990)

The Ni and Co monosilicides and disilicides are studied by soft-x-ray-emission spectroscopy. The Si $L_{2,3}$ spectra, which provide a measure of the partial densities of states of s and d angular momentum symmetry ([$s + d$] PDOS) localized on the Si site, are compared with available theoretical calculations, and discussed in terms of the contribution of s electrons to the bonding. The Ni and Co $M_{2,3}$ emission spectra are also obtained, and analyzed to provide information about the d PDOS localized at the metal site. These spectra are discussed in terms of p-d bonding in the silicides.

I. INTRODUCTION

The transition-metal (TM) silicides have generated great interest due to their metallic conductivity and compatibility with Si. These features make them of great potential value for device applications ranging from simple ohmic contacts to Schottky barriers and other multilayer geometrics which require high-quality, stable, metal-semiconductor interfaces.

The bulk electronic properties of TM silicides (T-Si) have been studied both theoretically and experimentally. Stable T-Si compounds with a wide range of stoichiometries may be formed (e.g., TSi_3, TSi_2, TSi, T_2Si, T_3Si, etc.), most of which have quite complex crystal structures. Bonding in these materials has generally been discussed in terms of bonding between TM d orbitals and Si p orbitals. Pettifor and Podloucky, using a tight-binding model, discussed the stability of these compounds in terms of p-d bonding, and concluded that p-d interactions dominate the bonding in the binary TM-metalloid compounds.[1] The importance of p-d bonding in these compounds has been confirmed by photoemission studies.[2-4] More detailed theoretical studies of the disilicides have recently been carried out using band-structure techniques.[5,6] Very recently, and after our own measurements had been completed, two studies of the TM disilicides have appeared utilizing soft-x-ray-emission techniques similar to those used in these studies.[7,8]

In their discussion of p-d bonding Pettifor and Podloucky asserted that Si s electrons form a local orbital with energy well below the TM d bands and do not contribute significantly to the bonding of the compounds. Several factors suggest, however, that s electrons play a much more significant role. We recall that hybridized sp^3 orbitals provide the primary bonding of elemental Si, and that tetrahedral local symmetry is the signature of such bonding. In the Si-rich compounds $CoSi_2$ and $NiSi_2$, Si occupies sites surrounded by four nearest-neighbor TM atoms in tetrahedral sites,[9] which suggests that hybridized sp^3 orbitals also play an important role in stabilizing their structure. More recently, band-structure calculations of $CoSi_2$ and $NiSi_2$ have suggested a significant role for the s electrons in these compounds.[6]

Photoemission spectroscopy (PES) measurements, which provide a measure of the total density of states (TDOS) of a solid, have confirmed the importance of p-d interactions in the TM silicides. In PES spectra, the TM d bands, which dominate the spectra, develop characteristic sidebands produced by the p-d interactions. PES spectra are unable to probe the s-electron density effectively because d electrons have higher photoionization cross sections and completely dominate the measured spectra.[2]

Soft-x-ray-emission (SXE) spectroscopy provides a useful complementary tool to investigate the valence-band structure. In SXE spectroscopy, electrons or photons are used to generate vacancies in the core levels of atoms within the specimen. Soft x rays are emitted as valence electrons radiatively recombine with the core-level vacancies. The energy distribution of SXE photons thus provide electronic-structure information about the material. Because the spectra are generated in transitions to a localized core state, the spectroscopy is chemically selective and provides a local density of states (LDOS) for each element of complex solids. Because the radiative transitions obey dipole selection rules, the spectra provide a measure of the angular-momentum-selected partial density of states (LPDOS). Finally, for most operating conditions, both excitation and escape distances are sufficiently great so that SXE spectroscopy is a bulk probe which is relatively insensitive to surface conditions.

Here we report Si $L_{2,3}$ and TM $M_{2,3}$ emission spectra of ~ 1000-Å films of polycrystalline NiSi, $NiSi_2$, CoSi, and $CoSi_2$ samples grown on Si(111) wafers. Formally,

the spectra provide $[s+d]$ LPDOS's for the Si and TM atoms in these materials. For Si, the spectra are dominated by s electrons, but have a significant contribution from d electrons. For Ni and Co, the spectra measure primarily the d LPDOS.

Using the Si spectra, we discuss the role of silicon s electrons in the bonding of the silicides and compare our spectra with available calculations. We find excellent agreement between our data and theoretical calculations for both Co and Ni disilicides, and believe that a thorough understanding of these two materials has been obtained. Due to the complexity of the crystal structure of the monosilicides, there are no detailed theoretical calculations with projected LPDOS's with which to compare our data. However, certain features of the Si spectra, which we identify as being due to overlap of d electrons from nearest-neighbor TM atoms onto the Si site, are observed to increase in the monosilicides with its higher concentration of TM atoms. From the Ni and Co M spectra, we obtain information about the d LPDOS on the TM-atom sites, which is compared with both theoretical calculations and the results of PES investigations.

II. EXPERIMENTAL PROCEDURES

The TM silicide samples were prepared at AT&T Bell Laboratories as thin-film polycrystalline layers on Si(111) substrates by the solid-phase reaction of evaporated layers of either Ni or Co. The composition was determined by Rutherford backscattering spectroscopy. The disilicides $NiSi_2$ and $CoSi_2$ are lattice matched to Si and thus grew epitaxially on the Si(111) substrates. The monosilicides typically had polycrystalline grain sizes of 600–1000 Å as determined by electron microscopy.

SXE measurements were carried out on our high-efficiency SXE spectrometer installed at the National Synchrotron Light Source, Upton, NY. The spectrometer is a 5-m Rowland circle design employing interchangeable toroidal gratings that focus the spectrum in the plane of dispersion. A 40-mm-diam position-sensitive detector made of microchannel plates and a resistive anode readout plate is used to record spectra. A Macintosh II computer interfaced with a computer automated measurements and control crate is employed for data acquisition and analysis. Using a 600-line/mm grating and a 200-μm input slit, instrumental resolution is estimated to be better than 0.4 eV at photon energies of 90 eV. Measurements were made in an UHV chamber at a pressure of 1×10^{-8} Torr. Emission was excited by a 100-μA, 2keV electron beam focused to a 1-mm^2 spot. The samples were placed on a holder located 3 or 4 mm away from the entrance slit of the spectrometer. Electrons were incident on the sample at an angle of 30° from the sample normal, and the takeoff angle for x rays was 50°. The spectra were corrected for the nonuniform detector response and astigmatic deformation in the nondispersion direction. Complete spectra were assembled from segments taken at successive positions along the Rowland circle. Each segment covers roughly 15 Å in the silicon L emission range.

Self-absorption effects sometimes seriously distort SXE

spectra. In these studies, self-absorption effects are believed to be small and no explicit corrections have been made for these effects. For the Si L spectra we confirmed this assumption by varying both the excitation energy of exciting electrons and takeoff angle of emitted x rays and observing that no significant changes were found in the measured spectral features. In the M spectra of Ni and Co metals, self-absorption effects are expected to affect the upper edge of the spectra due to the overlap of emission and absorption edges in metals. In the TM silicides, the d bands narrow and shift to higher binding energies with respect to the Fermi level. Moreover, in the case of the disilicides a quasigap opens in the vicinity of the Fermi level. Both of these effects make self-absorption less of a problem in the silicides than in the pure metal. Therefore no corrections were made to correct for self-absorption in the Ni and Co M spectra, though small effects may remain at the upper edge of the spectra.

III. RESULTS AND DISCUSSION

A. The Si $L_{2,3}$ emission spectra of $NiSi_2$ and $CoSi_2$

In Fig. 1, the Si $L_{2,3}$ emission spectra of $NiSi_2$ and $CoSi_2$ are shown and compared with the spectra of crystalline and amorphous Si. The spectra of the disilicides show a strong resemblance to that of amorphous Si. For each of the spectra, the splitting of the low energy peak of c-Si is absent and there is a broad peak associated with a Si s orbital centered at about 90.5 eV with a broad shoulder extending to the Fermi edge. Other features of the spectra include a small peak located at about 97.5 eV (approximately 2 eV below the Fermi edge) in $CoSi_2$ and a sharp, prominent peak located at about 99.5 eV (0.4 eV below the Fermi edge) in $NiSi_2$. The nickel disilicide also has a small peak superimposed on the high-energy shoulder at about 96.5 eV that will be discussed further below. Separate photoemission experiments[11] established the
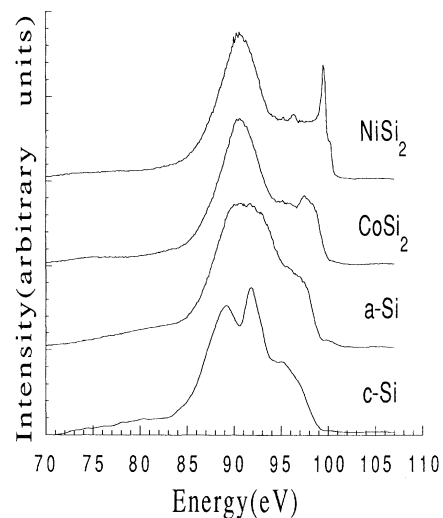

FIG. 1. The Si $L_{2,3}$ emission spectra of $CoSi_2$, $NiSi_2$, and crystalline and amorphous Si.

binding energy of the Si $2p_{3/2}$ line as 99.9 and 99.4 eV for the $NiSi_2$ and $CoSi_2$, respectively. This small shift appears to be evident in the high energy threshold of our x-ray-emission spectra (see Figs. 1 and 2).

The sharp peak just below the Fermi edge of the $NiSi_2$ spectrum has a well-defined shoulder produced by the spin-orbit splitting of the $2p_{1/2}$ and $2p_{3/2}$ core level. Analysis of the edge indicates a splitting of 0.6 eV and a ratio of approximately 2:1 for the intensity of the L_3 and L_2 spectra, consistent with the known splitting and 2:1 relative degeneracies of the $2p$ core levels. In many L spectra of light elemental metals, L_2 intensity is reduced below the expected value by an L-LV Coster-Kronig process that fills this level in competition with the radiative and L-VV Auger processes. The observation of the 2:1 ratio indicates that the Coster-Kronig process is not significant in this material. We note that the width of the Fermi edge of this spectrum is determined by core hole, Fermi edge, and instrumental broadening effects, but not by lifetime broadening of the valence-band hole in the final state that significantly broadens the spectra at lower energies. Very nearly the same broadening parameters should apply to all of the Si L spectra at the Fermi edge (or VB maximum in the case of pure Si). Thus the extra width observed at the Fermi edges of our other spectra can be associated with added broadening present in the valence-band density of states or possibly due to the inhomogeneous broadening in the polycrystalline monosilicides.

Using a one-electron model and neglecting dynamical effects, the x-ray-emission intensity is proportional to the partial density of states localized on a particular constituent of a system, multiplied by the square of transition matrix elements and also multiplied by the cube of the transition energy. By assuming constant matrix elements and
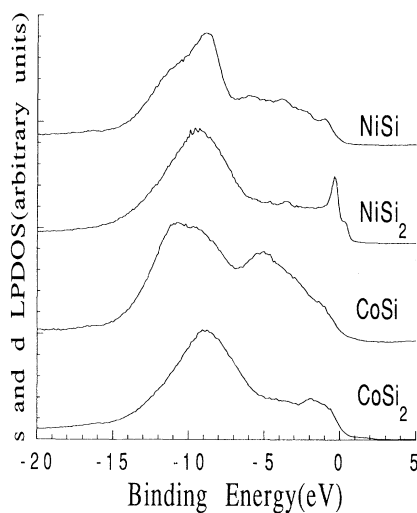

FIG. 2. The $[s+d]$ LPDOS for Si sites in Ni and Co silicides derived from the Si $L_{2,3}$ spectra. The zeros of energy scale are taken to be 99.8 eV for NiSi and CoSi, 99.9 eV for $NiSi_2$, and 99.4 eV for $CoSi_2$.

dividing by the cube of the photon energy, we can obtain a LPDOS for comparison with theoretical calculations. The qualitative effect is largely to reduce the intensity of the high-energy emission in the spectra relative to the low-energy emission, without significantly shifting spectral features. In the process of obtaining these LPDOS's we ignored the low-energy tailing of our emission spectra, which happens in all soft-x-ray-emission spectra.[12] This broadening effect is due to the finite lifetime of the final states (a hole in the valence or conduction band). Its magnitude is dependent on the final-state energy. While vanishing at the Fermi energy, it becomes larger toward the bottom of the conduction band (or valence band for semiconductor and insulator), which produces a tailing extending below the band minimum. This effect will broaden the low-energy portion of our spectra without changing the characteristic spectral features which we are going to discuss below. These measured $[s+d]$ LPDOS of the cobalt and nickel silicides are plotted in Fig. 2. The zero of the energy scale for NiSi and CoSi spectra is taken at 99.8 eV, the crystalline Si $2p_{3/2}$ binding energy relative to the conduction band, while the zeros are taken to be 99.9 and 99.4 eV, respectively, for $NiSi_2$ and $CoSi_2$. The fact that the spectra show no large "chemical shifts" is evidence that the electronic environment of the Si atoms is similar for all of the spectra. Calculated s and d LPDOS's are available for the disilicides which will be compared with the spectra in Figs. 1 and 2 in later paragraphs. Less detailed information is available for the monosilicides.

The L spectra of elemental silicon (amorphous or crystalline) give typical representations of the s PDOS of covalently bonded material with local tetrahedral symmetry. It is well known that the local effects for tetrahedral covalent bonds can be described by sp^3 orbitals directed towards the four nearest neighbors of each atom. In amorphous silicon, the removal of the splitting of the low-energy peak is related to the loss of long-range order rather than to any significant change in the local tetrahedral bonding. This point is explicitly made by silicon cluster calculations[13] where the s orbital corresponding to the peak is not split in 5-atom clusters, where only nearest neighbors are present, but appears in 17-atom clusters when second-nearest-neighbor interactions are present. Both $CoSi_2$ and $NiSi_2$ crystallize in the calcium fluoride structure in which each silicon atom is surrounded by four Co or Ni atoms in tetrahedral nearest-neighbor sites, while more remote neighbors have entirely different symmetries than in elemental silicon. However, since one of the two Si sublattices in $NiSi_2$ and $CoSi_2$ is identical to one of the Si sublattices in elemental Si, some of the second neighbors are the same for all three materials. The tetrahedral local symmetry and the similarity of the spectra of disilicides to that of pure silicon provide clear qualitative evidence that covalent bonding involving sp^3 hybrids contribute in a significant fashion to the bonding in the disilicides.

Calculations of charge density in these disilicides indicate that the charge distribution around the Si atom is very similar to that in bulk silicon.[4] In addition, Bylander et al. have calculated s,p and d LPDOS's for both

Ni and Si in NiSi$_2$,[5] and Tersoff and Hamann have published somewhat more limited data for CoSi$_2$.[6] Some of these results that are relevant to the interpretation of our data are reproduced in Fig. 3.

The measured $[s+d]$ LPDOS of NiSi$_2$ is in excellent agreement with the calculations of the s and d LPDOS's in this material. The major peak centered at -9 eV and the sharp peak at the Fermi edge are associated with structure in the Si s LPDOS [Fig. 3(a)]. The Fermi-edge peak is clearly associated with antibonding orbitals lying above a quasigap in the s-like LPDOS. An analysis of this structure by Tersoff and Hamann identify these states as s-d antibonding states.[6] The Si spectrum of CoSi$_2$ is similar to that of NiSi$_2$ except that the sharp peak at the Fermi edge is absent. This results from a shift of the Fermi edge downward into the quasigap region below the s-d antibonding states. To the extent that the two silicides may be described in terms of a rigid band model, this shift of the Fermi level may be understood to result from the fact that Co contributes one less

electron than Ni to the filling of the band states. In contrast to elemental Si, which has negligible contribution from states of d symmetry, Si d states [Fig. 3(b)] contribute significantly to the measured spectrum of Si in nickel disilicide in the shoulder region between 94 (-6) and 99 (-1 eV), and are responsible for the small peak feature at 96.5 (-3.5 eV). Here the numbers in parentheses indicate approximate energy positions in Figs. 2 and 3. A comparison with the calculated Ni d LPDOS's [Fig. 3(c)] clearly indicates that the Si d LPDOS results from overlap of the Ni d orbitals onto the Si sites. This is an important observation because this feature of the Si spectrum might be expected to persist in other silicides and to increase in intensity in silicides with increasing Ni or Co content. In CoSi$_2$, d states are also expected to make a significant contribution to the measured $[s+d]$ LPDOS in the region of the high-energy shoulder, with the major contribution being a few eV below the Fermi edge at the energy position of the Co d-band states. Tersoff and Hamann[6] locate the maximum of the d band in this ma-
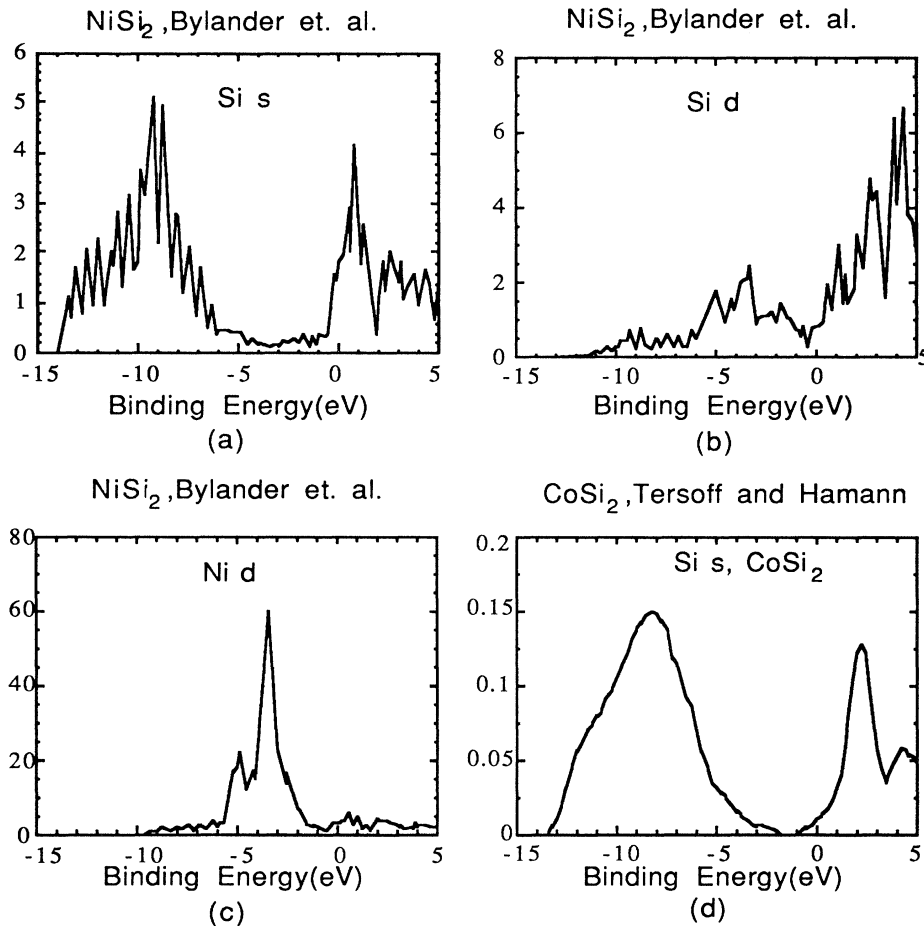

FIG. 3. The projected LPDOS's for NiSi$_2$ and CoSi$_2$ from published calculations. (a) s LPDOS on Si sites for NiSi$_2$. (b) d LPDOS on Si sites for NiSi$_2$. (c) d LPDOS on Ni sites for NiSi$_2$. (d) s LPDOS on Si sites for CoSi$_2$. The LPDOS's are in units of tenths of an electron per unit cell per eV for (a)–(c) from Ref. 5. The LPDOS is in units of electrons per atom per eV for (d) from Ref. 6.

terial at an energy about 2 eV below the Fermi edge, so that it coincides with the peak at about 97.5 (-2 eV) in the Si spectrum of this material. Comparing the s-like gap calculated in Figs. 3(a) and 3(d) to the corresponding data for $NiSi_2$ in Figs. 1 and 2, we see that measured sharp peak near the Fermi level is somewhat stronger than the calculated peak, perhaps indicating a slightly smaller measured s gap than the calculation would indicate. However, the lifetime broadening of the final states on the lower energy peak at 90 eV may have caused the peak near the Fermi level to look higher than what it actually is. In Fig. 4 we align the experimental s and d PDOS of $NiSi_2$ with the Lorentzian convoluted Si s and d calculations of Bylander et al. Here we use a Lorentzian corresponding to the intrinsic width of $2p$ core level in elemental Si, which is 200 meV.[14] The low energy peak in the experimental curve is clearly broadened compared with theoretical calculations.

In the spectral region from 103 to 119 eV, a weak satellite structure with an intensity of about 2% of the primary peak is observed in the silicides. It is produced by transitions to $2p$ core levels with two vacancies. The satellite is observed when excitation energy exceeds the threshold energy for removing an electron from the $1s$ core state. The double core hole states are produced primarily by a *KLL* Auger process that fills the $1s$ (k) core hole and removes two electrons from the $2p$ levels (LL). This satellite spectrum thus provides a measure of the ($s+d$) LPDOS of a Si atom that retains a core hole in its final state, and is believed to closely approximate the local LPDOS that would be calculated for an "impurity" atom with a hole in its core. The satellite spectrum for $NiSi_2$ is plotted in Fig. 5. The primary spectrum for $NiSi_2$ is also plotted after being shifted by 17.58 eV to bring the sharp peaks at the Fermi threshold into alignment.

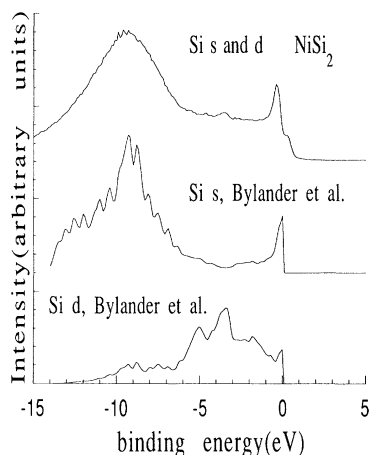Several features of the satellite spectrum are significant. Two of these features are consistent with re-
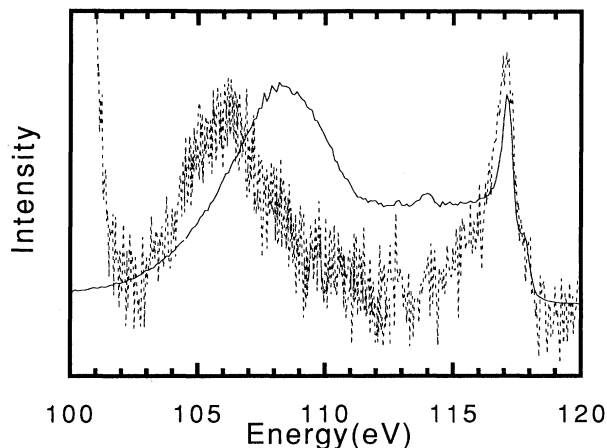
FIG. 5. The double-core-hole satellite spectrum of Si in $NiSi_2$. For comparison, the primary spectrum is also shown shifted to higher energy by 17.58 eV. (Dashed line, satellite spectrum; solid line, primary spectrum.)

sults obtained in previous studies of double-hole satellites.[15] Extrapolation of the low-energy edges of the primary and satellite peaks to the base line indicates that both spectra are about 15 eV wide. And the prominent low energy peak of the satellite spectrum is enhanced and displaced to the extreme lower edge of the spectrum. These are features expected for a $Z+1$ impurity atom in a Z host, for which the bandwidth is set by the bandwidth of the host, and the extra core hole is screened by a localized charge which provides s-like LPDOS near the bottom of the band. Two other features are more surprising. The s-like peak at the Fermi threshold is as strongly enhanced as the low energy peak. And the intensity in the plateau region below the threshold peak, which we believe to consist mostly of d-like LPDOS, is strongly suppressed in relative magnitude. While we do not yet have a detailed understanding of this behavior, it seems safe to conclude that the strongly enhanced peaks are associated with local orbitals that are modified and strengthened by the accumulation of screening charge.

The satellite spectrum of $CoSi_2$ has also been measured and is found to have the enhanced low energy peak observed in $NiSi_2$, but the prominent peak at the Fermi edge is absent. This provides additional evidence that the peak lying about 2 eV below the Fermi edge in the primary spectrum of cobalt disilicide is associated with a feature in the d LPDOS rather than with s-like states.

B. The Si $L_{2,3}$ spectra of CoSi and NiSi

The Si L spectra of NiSi and CoSi are displayed in Fig. 6, and in Fig. 2, after the removal of the frequency cubed factor. The major changes from the spectra of the disilicides are that the major peaks associated with the s orbital centered at 90.5 eV in the disilicides are split and that additional emission intensity is observed in the high-energy shoulder region between about 92.5 and 98 eV. In NiSi, the splitting of the low energy peak produces a peak at 90.5 eV and a shoulder at about 88.5 eV. In CoSi, a

FIG. 4. The experimental Si s and d LPDOS with Lorentzian broadened Si s and d calculations by Bylander et al. The Lorentzian corresponds to the intrinsic width of 200 meV of elemental Si $2p$ core level.
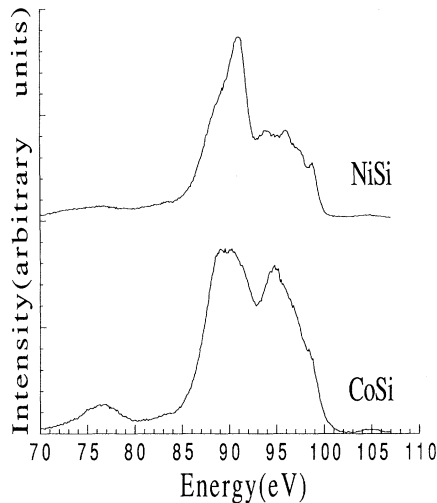
FIG. 6. The Si $L_{2,3}$ spectra of NiSi and CoSi.

double-peaked structure composed of peaks of nearly equal magnitude centered at about the same two energies is observed. In CoSi, the additional structure in the shoulder region has a maximum at 95 eV and a weaker shoulder at about 97 eV. In NiSi, the additional structure has three small maxima at about 94, 96, and 97.5 eV. In addition to the above changes, the prominant peak at the Fermi edge in $NiSi_2$ has disappeared, and a weak and broad peak centered at 77 eV is observed in the CoSi spectrum. We currently have no explanation for the weak peak at 77 eV, but suspect that it is associated with some impurity in the system rather than the valence-band structure of the silicide.

CoSi crystallizes in the $B20$ cubic structure like FeSi,[16] and NiSi in the cubic $B31$ of MnP.[17] For NiSi, one band-structure calculation employing the Haydock recursion method, which is a relatively simple theoretical tool, exists with projected partial densities of states.[18] However, this calculation lacks fine structures as compared to more rigorous band-structure calculations and its projected s LPDOS shows little resemblance to our L emission spectrum of NiSi. To our knowledge, no band-structure calculations with projected LPDOS's are available for CoSi, so that our analysis of the monosilicide structure is necessarily incomplete. A few observations may be made, however. In both structures, the tetrahedral symmetry of the TM nearest neighbors to the Si atom breaks down, which will result in dehybridization of the sp^3 bonding orbitals. For example, in the nickel silicides, the four nearest-neighbor (NN) Ni atoms in $NiSi_2$ at a distance of 2.34 Å are replaced in NiSi by four Ni atoms at 2.31 Å and two Ni atoms at 2.32 Å to give a formal coordination number of 6. Similarly, in going from $CoSi_2$ (coordination number 4) to CoSi (coordination number 7), the number of nearest-neighbor Co atoms increases, and the NN interatomic spacing decreases. In the absence of calculations to guide our analysis, we speculate that the splitting of the major low energy peak results from dehybridization of the sp^3 orbitals and the

reduction in the symmetry of the surroundings of the Si atoms. We also suggest that the buildup in intensity in the spectral region between 93 and 98 eV may be associated primarily with overlap of the TM d orbitals onto the Si site, which increases as the TM content of the material increases. In a study of ion implanted Co in Si to be reported elsewhere, we observe that the high-energy shoulder of the Si spectrum increases in relative magnitude as the Co content is increased, and that this evolution of the Si spectrum may be used to monitor the Co content and qualtitative features of the bonding in the Co in Si system.[19]

C. Metal $M_{2,3}$ emission spectra of the silicides

The $M_{2,3}$ emission spectra for both Ni and Co silicides are shown in Figs. 7(a) and 7(b). Formally, these spectra provide a measure of the $[s+d]$ LPDOS of these materials. However, the oscillator strengths of the $3d$-$3p$ transitions are known to greatly exceed that of the $4s$-$3p$ transitions, so that the observed spectra represent primarily the transition-metal d bands, with a negligible contribution for the s states. The measured spectra represent a sum of radiation produced by transitions to the $3p_{1/2}$ and $3p_{3/2}$ core levels.

A deconvolution of the M_2 and M_3 spectra can be readily achieved if it is assumed that the spectra have the same shape and if both the spin-orbit splitting of the core levels and the relative intensities of the spectra are known. It is known that the M_2 to M_3 intensity ratio is not proportional to the 1:2 degeneracy of the core levels for the transition metals, because the intensity of radiation to the lower M_2 level is suppressed by a competing MMV Coster-Kronig process. For the nickel silicides, we have used the spin-orbit splitting (1.80 eV) and 0.2 intensity ratio determined from studies of Ni-metal spectra[20] to deconvolute the spectra for the materials. These values are found to give consistent spectra when the deconvolutions are performed from either end of the spectra, while deconvolutions which assume a larger M_2 component do not give consistent results. The deconvoluted M_3 spectra of the nickel silicides are displayed in Fig. 7(c). To our knowledge, the spin-orbit splitting of the $3p$ levels and the relative intensities of the M spectra are not known for cobalt, so that we have not been able to deconvolute these spectra.

The Ni and Co M spectra are very weak and are superimposed on the low-energy tail of the stronger Si spectrum and bremsstrahlung radiation generated by the exciting electrons. This background must be subtracted from the M spectrum before it is analyzed. In the transition metals the electron excited M spectrum is also often distorted by high-energy double-hole satellites associated with the presence of spectator holes in other d-band states that may occur in a significant number of atoms. In the nickel silicides, no high-energy satellites were resolved, though it is possible that weak satellite emission, comparable to the background noise, was present and subtracted with the background. In the cobalt silicide samples, a weak shoulder is observed between about 60 and 62 eV that we tentatively identify as due to double-hole satellites.
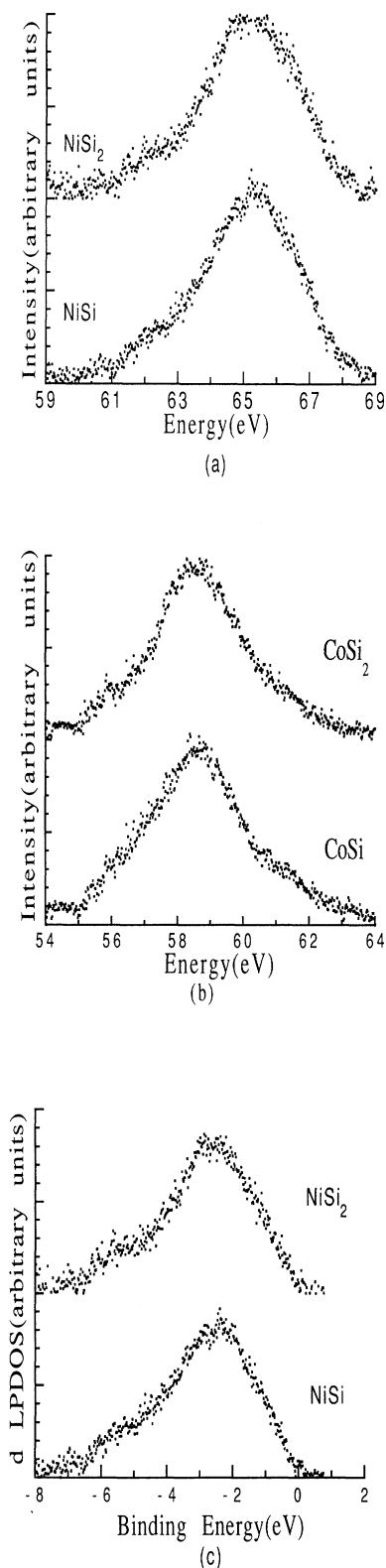
FIG. 7. The Co and Ni $M_{2,3}$ emission spectra of the Co and Ni silicides: (a) NiSi and NiSi$_2$, (b) CoSi and CoSi$_2$ and (c) the d LPDOS on Ni sites derived from the M_3 spectrum after deconvolution of the $M_{2,3}$ spectrum.

The observed spectra show no sharp spectral features, presumably due to lifetime broadening effects, which may be as large as 2.0 eV in Ni metal.[21] Photoemission measurements of the Co $3p$ level show an intrinsic width of 1.6–1.7 eV.[22] Consequently, we are able to use the spectra only to obtain rough information about the position of the transition-metal d bands with respect to the Fermi edge. From Fig. 7(c), we place the maxima of the Ni d bands at about 2.5 eV below the Fermi edge in NiSi and slightly deeper at about 2.7 eV in the disilicide. These results may be compared with photoemission results of Franciosi et al., which show d-band-derived features at 1.8 eV below the Fermi level in NiSi and at 3.15 eV below the Fermi level in NiSi$_2$.[2] We clearly do not see a comparable shift in the location of the d bands in our spectra. The results may also be compared with the calculations of Bisi and Calandra, which locate the center of gravity of the d bands on Ni sites at 3 eV binding energy for both Ni silicides,[23] as do the calculations of Bylander et al. given in Fig. 3.

For the Co silicides, if we assume that the high-energy shoulder represents a satellite structure, the Fermi edge may be taken at the break in the emission spectrum curve that occurs at 60.6 eV. The spectral maximum for both Co silicides is located at about 58.6 eV, which would place the d-band maximum in these materials at 2.0 eV below the Fermi level.

In all of the Ni and Co M spectra, a weak peak appears in the spectra at an energy of 2.5–3 eV below the main peak. In p-d bonding models of the transition metal silicides, the TM d bands are split with a peak due to p-d bonding states lying at lower energies than the main band of nonbonding states. We attribute the low-energy shoulders of our spectra to these p-d bonding states. Though the low energy peaks are not well resolved, the increased relative intensity in the low-energy shoulders of CoSi and NiSi may be evidence for stronger p-d bonding in the more metal-rich compounds.

IV. DISCUSSION AND SUMMARY OF RESULTS

The results presented here make it clear that a p-d bonding model does not provide a complete or adequate description of the Ni and Co disilicides. Both the tetravalent bonding of the Si atoms and the shape of the Si L spectra indicate that sp^3 bonding plays a role in stabilizing the structure. However, the resemblance of the spectra to that of amorphous Si is somewhat misleading, since in the disilicides, a d-like LPDOS makes a substantial contribution to the spectrum in the high-energy shoulder above the main s band. A major feature of the p-d-bonding model is the generation of a quasigap with mainly filled bonding and mainly empty antibonding states split about the TM d- band. Though a quasigap does exist in the disilicides, the states immediately above the gap are found to be s-like in nature and to be associated with s-d-antibonding states rather than p-d-antibonding states as the p-d-bonding model requires. This result implies that s-d hybridization must be included in any realistic description of the stability of these materials.

We also note that the appearance of the sharp peak at

the Fermi edge in going from $CoSi_2$ to $NiSi_2$ may be qualitatively understood in terms of a rigid band model in which the Fermi level falls in the gap for the Co compound and moves into the antibonding states above the gap when the extra electron of Ni is added to the system. Recent calculations have shown that the structures of *p*-*d*-bonded TM compounds are destabilized when the Fermi level moves out of the quasigap into the antibonding states above the gap.[24] This result suggests that the Ni compound should be less stable than the Co compound, and that $CuSi_2$ may not be stable in this structure as have been observed.[22]

For the disilicides, the Si $(s + d)$ LPDOS's derived from the Si L spectra and the TM d LPDOS's derived from the TM M spectra are all in excellent agreement with the calculated LPDOS's, and serve to confirm those calculations as accurate theoretical representations of these systems. In every case our measurements confirm the energy positions of major features of the calculated LPDOS's which are derived from states of s and d symmetry.

In the absence of band calculations, we are unable to provide a detailed analysis of the spectra of CoSi and NiSi. We have, however, been able to draw conclusions from several features of the spectra. First, the prominent peak at about 90 eV in the Si L spectra of both compounds is split to lower energies, which we tentatively associate with dehybridization of the sp^3 orbitals as the tetrahedral symmetry of the bonding of the Si atoms is lost. Second, the Si L spectra are strongly enhanced in the spectral region between 93 and 98 eV, which we tentatively identify with increasing overlap of TM d orbitals onto the Si site. And third, the TM M spectra indicate that the energy position of the TM d bands shifts very little in going from the monosilicides to the disilicides, in agreement with calculations, but not with some published photoemission results.[2]

ACKNOWLEDGMENTS

[1]D. Pettifor, and R. Podloucky, J. Phys. C Solid State Phys. **19**, 315 (1986).

[2]A. Franciosi, J. Weaver, and F. Schmidt, Phys. Rev. B **26**, 546 (1982).

[3]J. Weaver, A. Franciosi, and V. Moruzzi, Phys. Rev. B **29**, 3293 (1984).

[4]Y. Chabal, D. Hamann, J. Rowe, and M. Schluter, Phys. Rev. B **25**, 7858 (1982).

[5]D. Bylander, L. Kleinman, K. Mednick, and W. Grise, Phys. Rev. B **26**, 6379 (1982).

[6]J. Tersoff and D. Hamann, Phys. Rev. B **28**, 1168 (1982).

[7]P. Weijs, G. Wiech, W. Zahorowski, W. Speier, J. Goedhoop, M. Czyzyk, J. van Acker, E. van Leuken, R. de Groot, G. van der Laan, D. Sarma, L. Kumar, K. Buschow, and J. Fuggle, Phys. Scr. **45**, 629 (1990).

[8]H. Nakamura, M. Iwami, M. Hirai, M. Kusaka, F. Akao, and H. Watabe, Phys. Rev. B **41**, 12 092 (1990).

[9]W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1972).

[10]T. A. Callcott, K. Tsang, C. H. Zhang, D. L. Ederer, and E. T. Arakawa, Rev. Sci. Instrum. **57**, 2680 (1986).

[11]J. E. Rowe, G. K. Wertheim, and R. T. Tung, J. Vac. Sci. Technol. A **7**, 2454 (1989); J. E. Rowe, R. S. Becker, G. K. Wertheim, and R. T. Tung (unpublished).

[12]P. Livins and S. E. Schnatterly, Phys. Rev. B **37**, 6731 (1988).

[13]V. Hietschold and G. Seifert, Phys. Status Solidi B **129**, K163 (1985).

[14]W. Eberhardt, G. Kalkoffen, C. Kunz, D. Aspnes, and M. Cardona, Phys. Status Solidi B **88**, 135 (1978).

[15]C. H. Zhang, K. L. Tsang, T. A. Callcott, D. L. Ederer, and E. T. Arakawa, Phys. Rev. B **37**, 2401 (1988), and references therin.

[16]*Structure Reports*, edited by J. Trotter (Bohn and Sohelten, Utrecht), Vol. 3, p. 14.

[17]Ref. 16, Vol. 35A, p. 86.

[18]K. Peterson, J. Hsiao, D. Chopra, and T. Dillingham, Phys. Rev. B **38**, 9511 (1988).

[19]J. J. Jia, W. O'Brien, Q. Dong, T. A. Callcott, D. R. Mueller, J.-E. Rubensson, D. L. Ederer, Z. Tan, and J. Budnick (unpublished).

[20]J. Cuthill, A. McAlister, M. Williams, and R. Watson, Phys. Rev. **164**, 1006 (1967).

[21]L. Yin, I. Adler, T. Tsang, M. Chen, D. Ringers, and B. Craseman, Phys. Rev. **9**, 1070 (1974).

[22]J. E. Rowe (unpublished data).

[23]O. Bisi and C. Calandra, J. Phys. **14**, 5479 (1981).

[24]J. H. Xu and A. J. Freeman, Bull. Am. Phys. Soc. **35**, 601 (1990).