

**Soft-x-ray-emission studies of bulk  $\text{Fe}_3\text{Si}$ ,  $\text{FeSi}$ , and  $\text{FeSi}_2$ , and implanted iron silicides**

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Bulk iron silicides and implanted iron silicides have been studied by soft-x-ray emission (SXE) spectroscopy. The Si  $L_{2,3}$  emission spectra of these materials are measured. For bulk silicides, these spectra provide a measure of  $s$ - and  $d$ -type partial density of states (PDOS) localized on the Si sites. We compare them with available band-structure calculations and also with photoemission measurements. For implanted systems, the Si  $L_{2,3}$  emission spectra provide useful information about the silicide formation process with the variation of implant doses.

**I. INTRODUCTION**

In a great number of studies<sup>1-4</sup> conducted on the transition-metal (TM) silicides and metal-silicon interfaces, iron silicides have received far less attention than cobalt and nickel silicides. Only a small number of electronic structure studies have been performed on iron silicides. Partly, this is due to the lower technological potential of iron silicides at present compared with either Co or Ni silicides, and partly it is due to the complex crystal structure of these materials. Yet iron silicides have very interesting electronic and magnetic properties. A more comprehensive understanding of their electronic structures certainly will help to explore these properties.

One of the three pure phase bulk Fe silicides,  $\text{FeSi}_2$  is a good semiconductor<sup>5</sup> and shows potential use in combining silicon-based digital technology with new optoelectronic devices.<sup>6</sup> Another,  $\text{Fe}_3\text{Si}$ , has drawn considerable interest due to the site occupation preference of substitutional transition-metal impurities in this material. But it has been studied mostly by nuclear magnetic resonance (NMR) and neutron scattering techniques.<sup>7</sup> The magnetic properties and structural stability of the third,  $\text{FeSi}$ , are also very interesting. A clear picture of its electronic structure and chemical bonding is needed to fully understand these properties. However, our knowledge of these materials is still incomplete as far as the electronic structure and chemical bonding are concerned. We have made soft-x-ray-emission (SXE) measurements on these materials in order to gain more experimental information on the filled bands of these compounds. SXE spectroscopy is a proven method in investigating the bulk electronic structures of solid materials. Our previous studies<sup>8,9</sup> have demonstrated the usefulness of SXE spectroscopy in studying bulk silicides and implanted silicides. In particular, the  $s$ - and  $d$ -like partial density of states of the valence electrons localized on Si sites can be effectively

studied by this method.

In this paper, we will present the Si  $L_{2,3}$  emission spectra of these bulk Fe silicides and also of some iron-implanted silicon samples. In SXE spectroscopy, energetic 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 these photons are detected and analyzed, which provides information about the filled valence or conduction bands of the materials studied. Because the spectra are generated in radiative transitions to a localized core hole, the spectroscopy is chemically selective and provides a local density of states (LDOS) for each element of a complex solid. In addition, the radiative transitions obey the dipole selection rule for angular momentum so that SXE spectra formally represent angular-momentum-selected partial density of states (PDOS). Also, 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.

By measuring the Si  $L_{2,3}$  emission spectra of iron silicides, the local  $s$  and  $d$  LPDOS's for the Si sites can be effectively probed by this method. This information is not available from photoemission measurements due to the dominance of the Fe  $d$  electrons in photoemission spectra. We will discuss the involvement of silicon  $s$  electrons in bonding and compare our results with available calculations and photoemission results. General agreement is found between our spectrum on  $\text{FeSi}_2$  and theoretical calculations as well as previous experimental results. Some comparisons can also be made with less detailed calculations available for  $\text{Fe}_3\text{Si}$ . No detailed band-structure calculations with projected LPDOS exist in the literature for  $\text{FeSi}$ . However, some clear trends can be identified in going from iron-poor to iron-rich com-

pounds that give information about the evolution of bonding in these materials.

## II. EXPERIMENT

The bulk  $\text{FeSi}$  and  $\text{FeSi}_2$  samples were prepared by compressing commercially obtained powders into pellets. The powders have crystallites visibly large enough to represent the bulk properties. The  $\text{Fe}_3\text{Si}$  sample is a single crystal prepared by arc melting. Its composition and crystal structure were checked by x-ray scattering. The iron-implanted samples were prepared by uniformly implanting polished silicon (100) wafers. A scanning beam of 150-keV  $\text{Fe}^+$  ions was used for implantation with substrate temperature maintained at about 350°C in a vacuum of  $10^{-6}$  Torr. The sample holder was surrounded by a liquid-nitrogen trap and warmed by a heater with temperatures monitored and stabilized during the implantation. The samples we studied here have implantation doses of  $5 \times 10^{17}$ ,  $7 \times 10^{17}$ , and  $1 \times 10^{18}$   $\text{Fe}/\text{cm}^2$ .

SXE measurements were carried out on our high-efficiency SXE spectrometer installed at the National Synchrotron Light Source, Brookhaven National Laboratory. Spectrometer and detector have been described elsewhere.<sup>10,11</sup> Our measurements were conducted with a 600-lines/mm grating and a 100- $\mu\text{m}$  input slit. Instrumental resolution is estimated to be better than 0.2 eV at a photon energy of 100 eV. Measurements were made in an UHV chamber at a pressure of  $5 \times 10^{-9}$  Torr. Emission was excited by a 100- $\mu\text{A}$ , 3-keV electron beam focused to a 1-mm<sup>2</sup> 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 take-off 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. Bremsstrahlung background induced in electron excitation is fitted as a straight line and subtracted from the spectra. For the 3-keV electron excitation, we estimate the penetration depth to be about 1000 Å for pure Si and to be reduced to about 300 Å for the most Fe-rich samples.

Self-adsorption effects sometimes seriously distort SXE spectra. In these studies, self-absorption effects are believed to be small and are not corrected. We confirmed this assumption by varying both the excitation energy of exciting electrons and the takeoff angle of emitted x rays, and observing that no significant changes were found in the measured spectral features.

## II. RESULTS AND DISCUSSION

### A. The Si $L_{2,3}$ emission of bulk Fe silicides

Figure 1 shows the Si  $L_{2,3}$  emission spectra from  $\text{Fe}_3\text{Si}$ ,  $\text{FeSi}$ , and  $\text{FeSi}_2$ . In most Si compounds these spectra can be divided into two regions. There is a peak region at

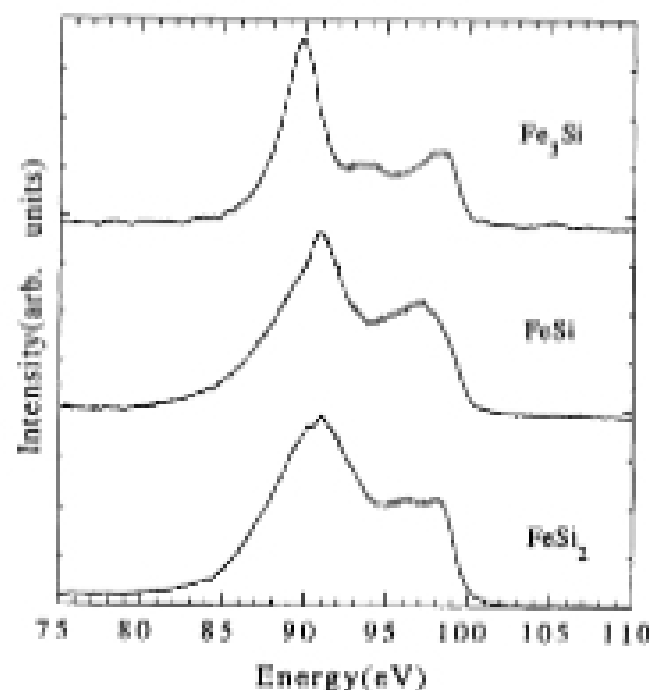


FIG. 1. The Si  $L_{2,3}$  emission spectra of  $\text{Fe}_3\text{Si}$ ,  $\text{FeSi}$ , and  $\text{FeSi}_2$ .

lower photon energies near 90 eV associated with non-bonding Si 3s orbitals and a shoulder region above this peak extending up to the top of the filled valence states at about 100 eV. In the peak region, the spectrum for  $\text{Fe}_3\text{Si}$  has a narrow and symmetric peak centered just below 90 eV. The major peak of the spectrum for the  $\text{FeSi}$  is asymmetric with its maximum at roughly 91 eV and a shoulder superimposed on its low-energy flank. The major feature of the spectrum for  $\text{FeSi}_2$  is a nearly symmetric peak with its top flattened. The centroid of this peak is at 91 eV and it is wider than the analogous peaks from  $\text{FeSi}$  and  $\text{Fe}_3\text{Si}$ . In the shoulder region,  $\text{Fe}_3\text{Si}$  has a wide peak near the Fermi level with its maximum at approximately 98 eV and another small hump located at roughly 94 eV. The shoulder region for  $\text{FeSi}$  is a broad hump between 93.5 and 100 eV, which peaks at 97 eV. For  $\text{FeSi}_2$ , the shoulder is a rather flat one with two small features on top of it. One of the features is at 96.4 eV and another one is at 98 eV.

It is clear that the *s*-orbital peak narrows in going from Si-rich silicide to Fe-rich silicides. As we mentioned earlier, these Si *s* states are not involved in the bonding with the metal atoms. The width of this peak is essentially determined by the wave-function overlap of the neighboring silicon atoms. In metal-rich silicides, the Si-Si interatomic distances are increased due to the introduction of large numbers of metal atoms and the lowering of the Si concentration, which reduce the wave-function overlap between different silicon atoms.<sup>12</sup> The broadening is most dramatic between  $\text{Fe}_3\text{Si}$ , which has no Si nearest neighbors (Si-Si distance = 3.999 Å, Ref. 7) and  $\text{FeSi}_2$ , which has an average Si-Si distance of 2.708 Å.<sup>13</sup> The detailed shape of this major feature, however, is related to the long-range order in the crystals. We recall that in elemental silicon the major feature has a very different appearance depending on whether it is crystalline or amorphous. In crystalline silicon, the *s*-orbital peak is splitted. In amorphous Si, the splitting is removed by filling in the region between the twin *c*-Si peaks, but the

overall width of the feature is essentially unchanged.<sup>9</sup> The basic tetrahedral local symmetry and the nearest-neighbor distances are the same in these two materials so that the width remains the same, while the long-range order in the crystalline phase splits the peak. The asymmetric shape of the major feature in the spectrum for FeSi is probably due to the irregular number and distances of Si neighbors as a result of complex cubic *B20* crystal structure of FeSi.<sup>14</sup>

The broad peak centered at 98 eV, about 2 eV below the Fermi edge in the shoulder region of Fe<sub>3</sub>Si, can be identified as the overlap of Fe *d* orbitals onto the Si sites, consistent with observations in our previous study on Co and Ni silicides.<sup>8</sup> A band-structure calculation by Switendick<sup>15</sup> gives the Fe *d* LPDOS for the two inequivalent Fe sites in this structure. In the unit cell of Fe<sub>3</sub>Si, there are 8 Fe *A,C* sites at 2.449 Å from each Si and 6 Fe *B* sites at 2.828 Å from each Si.<sup>7</sup> From a comparison with this calculation, we conclude that the peak in our spectrum at 98 eV derives mostly from the *A,C* site LPDOS which peaks 2 eV below the Fermi edge. The *B* site LPDOS makes no contribution at this energy, but peaks 2 eV deeper in the band. The photoemission study by Egert and Panzner<sup>16</sup> also yields a broad Fe *d* feature close to the Fermi level.

The weak hump observed at approximately 94 eV is either due to the Si *s* and *p* hybridization or due to the Si *s* and Fe *d* bonding formation. Switendick's calculation has Si *p* states at this particular energy. Though transitions from *p* states will not contribute to our spectra, we do pick up intensity from *s-p* hybridizations. Thus we tentatively identify this feature with Si *s-p* hybridized states. We remind the reader that *sp*<sup>3</sup> hybridization is responsible for all of the intensity seen in the shoulder region in pure Si samples.

The broad feature centered at 97 eV in the shoulder region of the spectrum for FeSi is difficult to interpret at the present time. There is no detailed band-structure calculation with projected LPDOS's available for this compound. Hence our analysis is limited. Some extra intensity near the Fermi edge in the shoulder region for FeSi probably results from the *d* overlap from the Fe atoms surrounding the silicon sites. Photoemission measurements of FeSi (Refs. 16–18) locate the maximum of the *d* band very close to the Fermi level (–1 eV), so that it is unlikely that the intensity peaking 3 eV below the edge results primarily from Fe *d* overlap. A recent cluster calculation<sup>19</sup> on FeSi found that the strongest bond between Fe and Si is the Si *sp*-Fe *sp* orbital interactions (if this is true here, it is probably also true for CoSi, since it has the same crystal structure as FeSi). The same calculation also points out that although Fe *d* orbitals contribute to bonding significantly, they do so through electrostatic diatomic interactions. This suggests to us that the majority of the intensity of the hump centered at 97 eV in our spectrum is probably due to the Si *sp* hybridized states. However, the validity of cluster calculation on complex crystals such as FeSi remains questionable.

The spectrum of FeSi<sub>2</sub> can be satisfactorily explained with Christensen's calculation.<sup>20</sup> The experimental *s* and *d* DOS's localized on Si sites can be obtained by dividing

the Si *L*<sub>2,3</sub> emission spectrum by the cube of the photon energy. The result is shown in Fig. 2 for FeSi<sub>2</sub>. The binding energy of the Si 2*p*<sub>3/2</sub> level was chosen at 99.8 eV, the crystalline Si 2*p*<sub>3/2</sub> level binding energy. In Fig. 3 we reproduce Christensen's projected *s*, *p*, and *d* LPDOS's for Si and *d* LPDOS for Fe for atoms in one of the two inequivalent sites available to each element. The LPDOS's for atoms in the second Si and Fe sites have almost the same characteristic structures with the first and are not shown here. The Si *s* LPDOS in Fig. 3(a) clearly supports the flattening of the top of the major peak of our experimental spectrum. Also from Figs. 3(a) and 3(b), we notice that the Si *s* LPDOS extends up to the valence-band maximum and that the Si *p* LPDOS extends all the way down to the bottom of the valence band. So the Si *s* and *p* LPDOS's overlap completely in the region of the occupied bands. The situation is very similar to that of elemental silicon and of Co and Ni disilicides. In all these materials, the *s* states in the shoulder region can be associated with the *sp*<sup>3</sup> hybridization. The *sp*<sup>3</sup> hybridization is the prototype of the covalent bonding for tetrahedral symmetry. The local tetrahedral symmetry is sustained in going from elemental silicon to Co and Ni disilicides which have the CaF<sub>2</sub> structure. Our spectrum and Christensen's calculation show that this kind of *sp*<sup>3</sup> hybridization is still largely preserved in FeSi<sub>2</sub>. This is justified by the fact that the stable structure of FeSi<sub>2</sub> deviates only slightly from the fluorite structure.

From Figs. 3(c) and 3(d), it can be seen that the Si *d* and Fe *d* LPDOS's of FeSi<sub>2</sub> peak immediately below the valence-band maximum at almost the same position. Their structures are also very similar. This probably is the origin of the peak we observed at 98 eV (–1.8 eV in Fig. 2) right below the band maximum. It is also in good agreement with the photoemission measurement of Egert and Panzner,<sup>18</sup> which locates the Fe *d* band maximum at approximately 2 eV below the Fermi level. This situation is again very similar to that of the Co and Ni disilicides where we observed features corresponding to Si *d* and Co (or Ni) *d* contributions.<sup>8</sup> We concluded that the involvement of Si *d* orbitals was due to the overlap of metal *d* orbitals onto the Si sites. Here again we observed that the same overlap is causing an observable feature in the Si

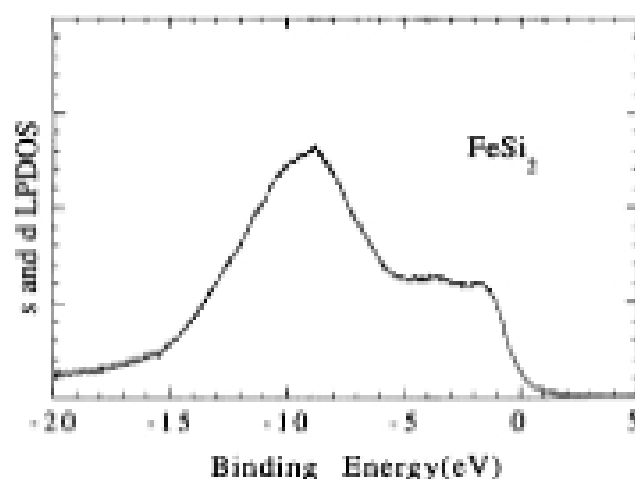


FIG. 2. The experimental *s* and *d* LPDOS's of FeSi<sub>2</sub> derived from the Si *L*<sub>2,3</sub> emission spectrum.