

Ion-beam-induced modification of Ni silicides investigated by Auger-electron spectroscopy

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Surface modifications induced by Ar bombardment on Ni silicides have been investigated with the use of Auger-electron spectroscopy. The compounds considered are all the six predicted in the Ni-Si equilibrium phase diagram. The relative Si to Ni concentration varies between the surface and at a depth of a few tens of angstroms; the surface region is richer in Si than the near-surface region. Changes in the ion-beam energy in the range 0.5–5 keV also significantly affect the compositional and electronic properties of the surface and near-surface regions. By changing the ion-beam energies, the silicide surface can be modified in a controlled and reversible way, leading in some cases to the formation of a surface layer with composition and chemical properties characteristic of higher-Si-content Si-rich silicides. Surface segregation seems the dominant mechanism in the observed Si enrichment, and in the final product the chemical bonding plays an important role.

INTRODUCTION

The effect of ion bombardment on alloy composition has been the subject of recent investigations because of the use of ion mixing to produce new materials and of the possibility of modifying the near-surface composition by sputtering.^{1,2}

Surface compositional changes due to preferential sputtering have been observed in many alloys. From a collisional point of view, ion sputtering results from particle-solid interactions. The phenomenon becomes more complex when thermodynamical forces are involved and forces are sometimes modified by the presence of high-defect concentrations in the system.

To investigate the role of thermodynamic forces and the effect of defects, the near-noble-metal silicides are suitable systems to study. Ion-beam mixing on silicon and near-noble-metal structures promotes the formation of compounds of fixed stoichiometry, suggesting that the main driving force is the compound formation.

Only few and sometimes contradictory data are available on the compositional, structural, and chemical modification of silicide surfaces under ion-beam bombardment.^{3–6} The disagreement mainly concerns the nature and the intensity of the enrichment and the amount of change in short-range order, and often comes from different sample treatments and different capabilities of the experimental techniques or procedures involved.

Auger-electron spectroscopy (AES) is an ideal method for simultaneous determination of surface and “in-depth” composition: In fact, it provides for some elements (in particular, those involved in near-noble silicide formation) low- and high-energy peaks with different escape depths; the high-energy peaks can be used to determine the near-surface composition (escape depth between 10 and 20 Å) while the low-energy peaks provide information on the surface composition (escape depth of about 4 Å).⁷

In addition, the sensitivity of the Si *L*VV Auger-peak shape to the valence-electron distribution provides a powerful method to study the local chemical environment of the Si atom at the surface. This sensitivity arises from the involvement of two valence electrons in the *L*VV transition; the formation of a Si-metal bond (and any change in it) affects the Si *L*VV peak shape,^{3,8} although the Si *L*VV Auger spectrum does not directly reflect the density of states in the Si-valence band, owing to the effects of the matrix elements.⁹

Owing to the possibility of following separately the Si and metal contribution to the full spectrum, AES appears as a unique probe for a detailed study of the compositional and chemical behavior of Si in compound surfaces, especially in systems such as Ni silicides. Photoemission spectra do not provide information on Si-valence electrons, since the photoionization cross section of Si states is considerably lower than the cross section of metal *d* orbitals. For silicides of transition metals belonging to the second and third series, such an effect can be reduced by working at the Cooper minimum.^{10,11} This is not possible for Ni compounds, since Ni does not show any minimum in the photoionization cross section for *d* states. We report here on AES investigation of six Ni-silicon compounds at the surface, and their compositional and chemical modification due to Ar⁺-ion bombardment.

EXPERIMENTAL

The Ni-Si equilibrium phase diagram predicts six stable compounds (Ni₃Si, Ni₅Si₂, Ni₂Si, Ni₃Si₂, NiSi, and NiSi₂). They were prepared by evaporating a Si film followed by a Ni film of appropriate thickness onto a SiO₂ substrate and processing the system in a vacuum furnace (10⁻⁸ Torr) at suitable temperatures and times, 200–500 °C and 120–180 min, respectively.

All six phases expected from the Ni-Si phase diagram,

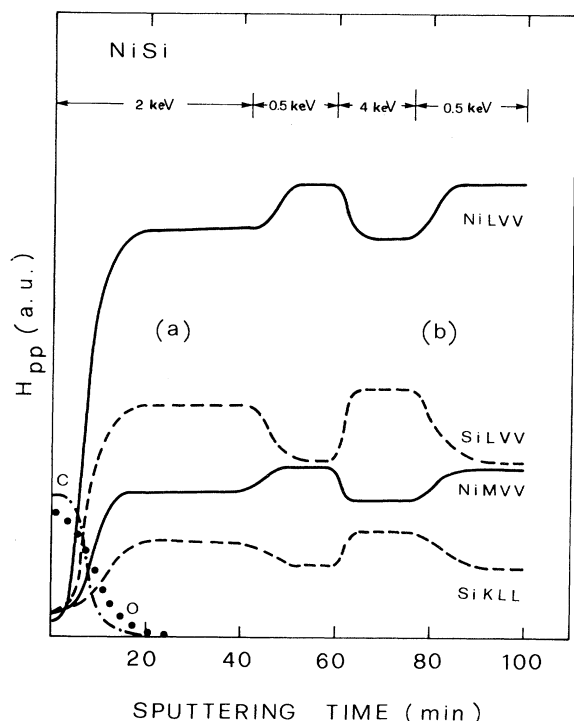


FIG. 1. (a) Peak-to-peak heights (H_{pp}) of the Si *LVV* (92 eV), Si *KLL* (1619 eV), Ni *MVV* (61 eV), Ni *LVV* (848 eV), C (273 eV), and O (511 eV) lines under Ar^+ bombardment at 2 keV. (b) Ar^+ -beam-energy effect on the H_{pp} of the Si and Ni low- and high-energy lines.

in films several thousand angstroms thick, were obtained. The annealing of Ni films on a Si wafer is known to give only Ni_2Si , NiSi , and NiSi_2 .^{12,13}

For comparison, NiSi and NiSi_2 samples were also grown in this more conventional way on a Si(110) substrate, and a Ni_2Si compound was grown by e^- beam heating a calibrated amount of Ni and Si powder to obtain a very thick (~ 1 cm) sample. All the samples were characterized in bulk composition and homogeneity by Rutherford back scattering (RBS), x-ray diffraction, and x-ray fluorescence. The deviations from the nominal stoichiometry were less than the sensitivity of the techniques used (1%).

For AES investigation, a PHI scanning Auger microprobe 590A was used; a single-pass cylindrical mirror analyzer (CMA) (0.3% resolution) was employed to discriminate the electron kinetic energy, with a modulation amplitude of 1 or 6 V peak to peak, leading to the measurement of the derivative form of the energy spectrum. The coaxial electron gun was used to excite the samples with a primary beam of $2 \mu\text{A}$ at 5 keV in a $1\text{-}\mu\text{m}$ -diam spot.

The cleaning and ion-beam processing of the surfaces were achieved with a differential ion gun at 55° . An Ar^+ beam with energy between 0.5 and 5 keV and current density of about $10 \mu\text{A cm}^{-2}$ was used over a rastered area of $3 \times 3 \text{ mm}^2$. The basic pressure was 1×10^{-10} Torr and during sputtering the Ar^+ partial pressure was increased

to about 4×10^{-7} Torr.

The peak-to-peak heights, H_{pp} , of the Si *LVV* (92 eV), Si *KLL* (1619 eV), Ni *MVV* (60 eV), Ni *LVV* (848 eV), C (273 eV), and O (511 eV) peaks were monitored under ion bombardment until all surface contaminants were removed (below 0.5 at. %) and a steady state was reached, as shown in Fig. 1(a). At this point the ion gun was turned off and the Si and Ni low- and high-energy peaks were recorded at the following peak-to-peak amplitude modulation: 1 V for Ni *MVV*, Ni *LVV*, and Si *LVV*; 6 V for Si *KLL*. These peaks provide, with their different escape depths ($\sim 4 \text{ \AA}$ for Ni *MVV* and Si *LVV*, $\sim 10 \text{ \AA}$ for Ni *LVV* and $\sim 18 \text{ \AA}$ for Si *KLL*),¹⁴ information from the surface and the near-surface region.

Measurements were carried out on thick and thin samples in different experimental conditions, at different electron beam powers (from $0.5 \mu\text{A}$, 2 kV to $5 \mu\text{A}$, 8 kV), and after sputtering at different ion-beam energies (0.5–5 keV) or ion-current densities ($0.5\text{--}15 \mu\text{A}$, changing the rastered area or defocusing the ion beam) with the purpose of elucidating the role of the experimental parameters. It has been found that the only parameter affecting in a significant way the intensity ratio or the line shape of Ni and Si peaks is the ion-beam energy, as shown in Fig. 1(b).

DATA ANALYSIS

Figure 2 shows low- and high-energy Auger lines for Si and Ni in Ni_3Si and NiSi_2 after sputtering at two different ion-beam energies: 0.5 keV (continuous lines) and 4 keV (dashed lines). At 4 keV the $I_{\text{Si}}/I_{\text{Ni}}$ line intensity ratio increases with respect to 0.5 keV, for both low- and high-energy peaks; this effect is more evident in NiSi_2 but is already present in Ni_3Si .

To gain quantitative information from these measurements we had to determine the relationship between the Auger signal intensity and atomic concentration; the simplest quantitative approach is the use of experimentally determined elemental standards. However, there are several sources of error in this procedure, namely, surface topography, matrix effects on the backscattering factors, chemical effects on the peak shapes, etc.¹⁵

Previous work^{16,17} has established that under ion bombardment the surface topography evolves, changing the surface area and orientation: There is a strong correlation between these modifications and the Auger intensities. To reduce this effect we measured the spectra of pure elements in identical experimental conditions after the cosputtering of adjacent spots of evaporated Ni and Si.

The backscattering factor r , which reflects the increase in the primary beam intensity due to the electron backscattering from the underlayers, depends on the energy of the considered transition and on the nature of the substrate.¹⁵ Using the expression given in Ref. 18 for the Z and E_b/E_p dependence of r (where E_b is the binding energy), we found that $r_{\text{Ni}}^{\text{st}}/r_{\text{Si}}^{\text{st}}$ for the Ni *MVV* and Si *LVV* in Ni and Si standard samples, respectively, is 1.18, while for the high-energy lines the same ratio is 1.25. For the corresponding Auger lines in silicides, because the electrons involved in all the transitions experience the same matrix, the Z dependence of the backscattering factors ratio is re-

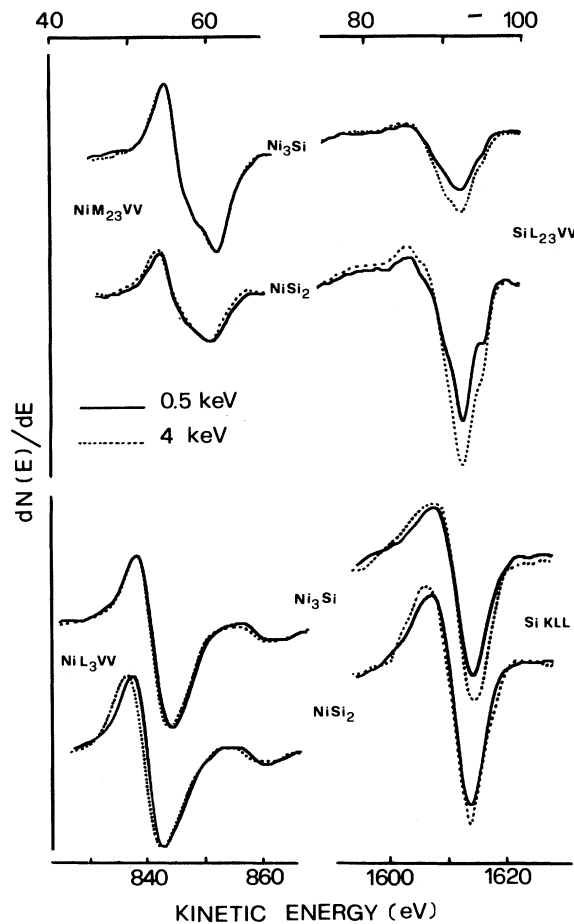


FIG. 2. Ni MVV , Si LVV , Ni LVV , and Si KLL , Auger peaks of Ni_3Si and $NiSi_2$ samples, sputtered at 0.5 keV (continuous lines) and 4 keV (dashed lines), the low- and high-energy part of the spectra of each sample at different sputtering energies were normalized to the Ni MVV and Ni LVV lines intensity, respectively, to put in evidence the Si enrichment.

moved and the E_b/E_p dependence is very low with respect to the Z dependence so that we can assume that in silicides the r_{Ni}/r_{Si} ratio, for both low- and high-energy transitions to be 1.

The chemical effects on the peak shapes, which can affect the H_{pp} -derived intensity measurements, are not so strong in Ni silicides as in Pt and Pd silicides³ but for a more correct quantitative approach we refer to the peak areas in the integral form of the Auger spectrum. We integrated the measured $dN(E)/dE$ form of the spectra to obtain the $N(E)$ form, and we subtracted the background with a spline method.¹⁹ Figure 3 shows the results of this data handling on the low-energy lines of Ni and Si for $NiSi_2$ and Ni_3Si signals already given in differential form in Fig. 2.

In taking care of the main source of error, the elemental standards method can be a good quantitative approach for determination of the relative constituent concentration in compounds from AES spectra. For a Si-Ni compound, the Si concentration (in at. %) is given by

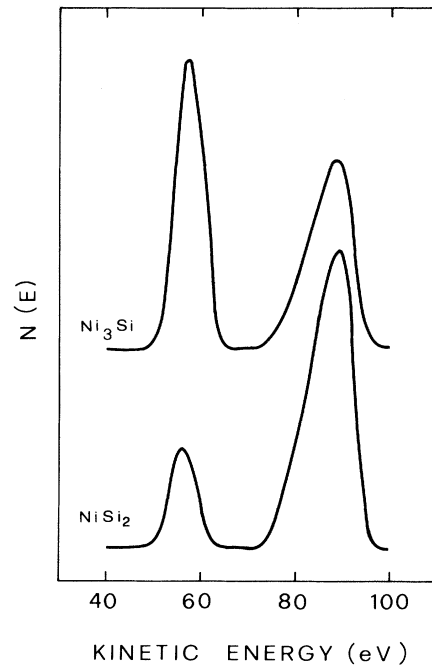


FIG. 3. $N(E)$ form of low-energy peaks of Ni and Si in Ni_3Si and $NiSi_2$ samples, sputtered at 0.5 keV, obtained by integration and background subtraction on the corresponding derivative form of Fig. 2.

$$C_{Si} = \frac{A_{Si}}{A_{Si} + \alpha_{Si/Ni} A_{Ni}}, \quad (1)$$

where

$$\alpha_{Si/Ni} = \frac{A_{Si}^{st} r_{Ni}^{st}}{A_{Ni}^{st} r_{Si}^{st}}, \quad (2)$$

and A_{Si}, A_{Ni} and A_{Si}^{st}, A_{Ni}^{st} are the areas of the two selected Auger peaks in silicides and standards, respectively.

RESULTS

The Si concentration calculated using Eq. (1) from low-energy lines ("surface concentration," Si_{SC}) and high-energy lines ("near-surface concentration," Si_{NSC}) are reported in Table I for all the Ni silicides after sputtering at 0.5 and 4 keV; for comparison, the nominal "bulk concentration" Si_{BC} , checked by RBS, is also reported. The percent error is estimated to be $\pm 2\%$ resulting essentially from the approximations involved in the determination of the peak areas, from the reproducibility of the experimental conditions in the measurement of standards and samples, and also from the scatter of the experimental data.

The modifications in the surface composition given in Table I, induced by changing the ion-beam energy, are reproducible and do not depend on the previous sputtering treatment of the sample.

At the sputtering energy of 0.5 keV, $Si_{SC} \approx Si_{BC}$, indicating that no surface stoichiometry modification occurs (ex-

TABLE I. Si "surface concentration" Si_{SC} and "near-surface concentration" Si_{NSC} of Ni silicides after sputtering at 0.5 and 4 keV. Nominal "bulk" Si concentration Si_{BC} , checked by RBS, is also reported. All the concentrations are expressed in at. % of Si.

Silicide		Ni_3Si	Ni_5Si_2	Ni_2Si	Ni_3Si_2	$NiSi$	$NiSi_2$
	Si_{BC}	25	29	33	40	50	67
0.5 keV	Si_{SC}	25	30	34	41	48	59
	Si_{NSC}	17	22	26	29	31	42
4 keV	Si_{SC}	33	39	44	48	58	72
	Si_{NSC}	19	22	27	30	34	44

cept for the $NiSi_2$ sample in which $Si_{SC} < Si_{BC}$, suggesting a Ni surface enrichment). At the same energy, $Si_{NSC} < Si_{BC}$, indicating a Si depletion in the region immediately below the surface.

At 4 keV the Si-surface concentration Si_{SC} equals the Si_{BC} value characteristic of the Si-rich compounds. At this sputtering energy, for example, Ni_3Si shows a Si-

surface concentration near that of stoichiometric Ni_2Si . Also $NiSi_2$ shows, at 4 keV, a strong surface Si enrichment.

At 4 keV, Si_{NSC} also increases with respect to the 0.5-keV case, but only slightly; it does not exceed the nominal value Si_{BC} and for the Si-rich silicides it remains considerably lower. The absolute variation between 0.5 and 4 keV is $+ (8-12)\%$ in Si_{SC} and $+ (1-3)\%$ in Si_{NSC} for all the silicides.

The difference between Si_{SC} and Si_{NSC} in each silicide (i.e., the Si-concentration gradient along z in the surface layer) is greater at 4 keV than at 0.5 keV and increases with the nominal Si content.

To show in more detail the ion-beam energy effect on

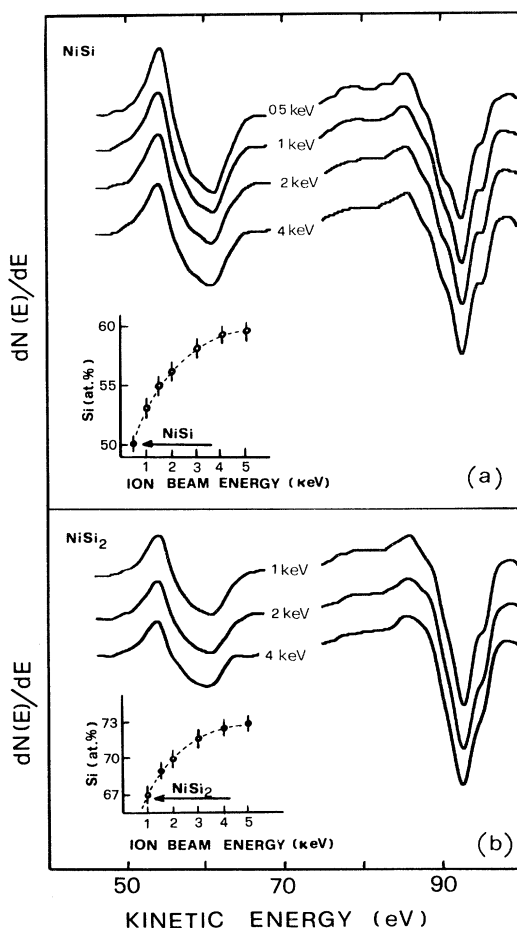


FIG. 4. Ni MVV and Si LVV line shapes in (a) $NiSi$ and (b) $NiSi_2$ after sputtering at different ion energies; the spectra are normalized to the Si LVV line intensity. The inset shows the Si concentration increase vs ion energy.

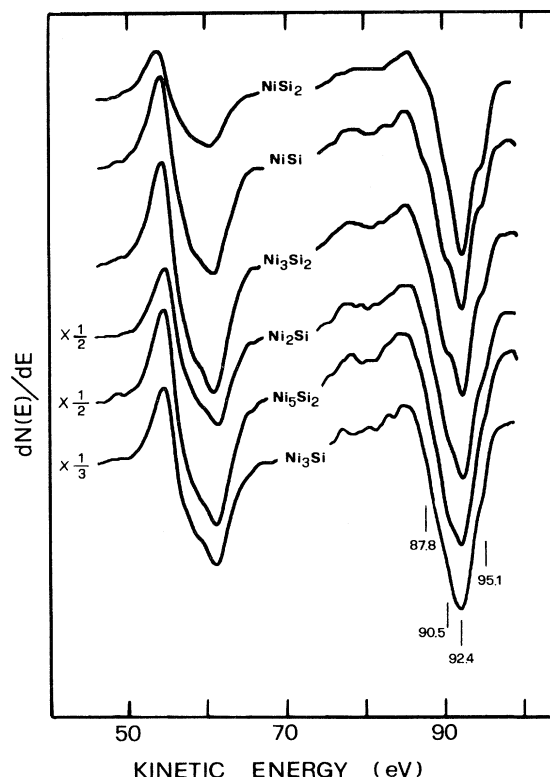


FIG. 5. Ni MVV and Si LVV line shapes of Ni silicides after sputtering at the ion energies which preserve the nominal Si and Ni surface concentration. The spectra are normalized to the Si LVV line intensity.

the silicide surface, we report in Figs. 4(a) and 4(b) the low-energy Ni and Si peaks in NiSi and NiSi₂ after sputtering at different energies, starting from the energy giving the "correct" Si-surface concentration, i.e., $Si_{SC} = Si_{BC}$ (0.5 keV for NiSi and 1 keV for NiSi₂) to that giving the highest Si enrichment. The insets in Figs. 4(a) and 4(b) show the Si_{SC} values in the whole range of ion-beam energy we explored. The Si-surface enrichment is not linear with the energy of the ion beam, but reaches a saturation at about 4 keV.

It seems clear from Figs. 4(a) and 4(b) that not only the surface stoichiometry changes with the sputtering, as reported in Table I, but also the surface chemical state changes; in fact the Si *L*VV line is strongly modified, and in NiSi also the Ni *M*VV line shows some changes. This is in agreement with previous results indicating that the strongest chemical effect in AES spectra of near noble silicide occurs in the Si *L*VV transition but is also present in the low-energy metal peak.^{3,20}

Figure 5 shows the low-energy Ni and Si peak shapes at the nominal, bulklike Si-surface concentration for all the investigated Ni silicides. The Si *L*VV line assumes a characteristic shape in which four predominant peaks can be identified at 87.8, 90.5, 92.4, and 95.1 eV, respectively. The energy positions of these peaks are weakly sensitive to variations in Si content (either by changing silicide or by sputtering at different ion-beam energies) within the uncertainty in the assignment of the energies, and is in good agreement with that found for NiSi.²⁰ The changes in Si *L*VV spectrum are mainly due to variation in the relative intensity of the peaks.

DISCUSSION

The results shown in Table I refer to the stoichiometry, and indicate that in Ni silicides a Si-surface enrichment occurs by sputtering at ion energies higher than 0.5 keV. A Ni-enriched undersurface region is already present at 0.5 keV while the Si content increases in both regions by increasing the sputtering energy.

A question arises about the kind of Si enrichment which occurs at the surface. In fact, as a consequence of different treatments, three possible situations have been observed: (i) a "pure," covalently bonded Si layer may segregate at the silicide surface,²¹⁻²⁴ (ii) the silicide may evolve toward an amorphous Si-enriched structure,²⁵ (iii) a new Si-rich phase, with a well-characterized structure may form.²⁶

To elucidate the nature of the Si-surface enrichment we can follow the line-shape evolution under ion bombardment. To this end we assume as "standard" for each silicide the Ni *M*VV and Si *L*VV line shape obtained after sputtering at the ion-beam energy which preserves the nominal Si and Ni relative concentration at the surface (see Fig. 5). The possible effect of the surface layer amorphization on the line shapes should be negligible and may only consist in a little increase of the intensity in the high-energy region of the spectra.²⁷

The Ni *M*VV line-shape trends in Figs. 4(a) and 4(b) can provide a first test: No change appears for Si enrichment at the NiSi₂ surface, suggesting that it takes place without

modifying the chemical nature of the compound, i.e., via the segregation of elemental Si at the surface. In the NiSi case, on the contrary, the Ni *M*VV line shape changes, indicating that the Si enrichment occurs with some chemical modification of the compound.

A further test consists in the changes in Si *L*VV line shapes. To make this analysis more quantitative we can look at the variation in the relative intensity of the previously mentioned four peaks at increasing Si enrichment by increasing the ion-beam energy, starting from the spectra corresponding to the stoichiometrically correct surface layer. We determined the intensity of each peak as shown in the inset of Fig. 6. This is an arbitrary intensity assignment, but we will use the so determined intensities only as fingerprints of the different silicides and to compare the evolution of the different parts of the Si *L*VV spectrum in each compound.

In Fig. 6 the continuous lines show the results of this analysis for Ni₂Si, Ni₃Si₂, NiSi, and NiSi₂, where the splitting of the four peaks is more evident. The Si enrichment modifies the relative intensities in each sample in a monotonic way: In NiSi, for example, the relative intensities of the 95.1- and 92.4-eV peaks increase, while those of the 90.5- and 87.8-eV peaks decrease.

On the other hand, if we look at the same peak in dif-

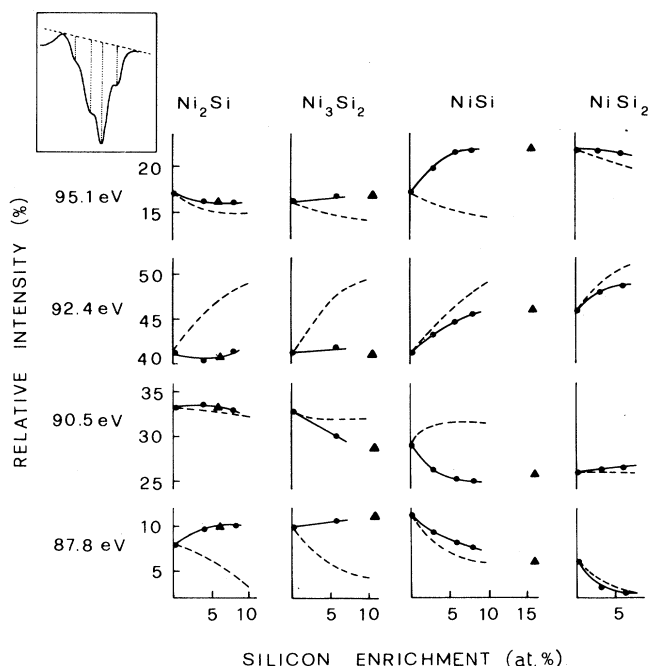


FIG. 6. Continuous lines are the relative intensity of the four contributions to the measured Si *L*VV peak in Ni₂Si, Ni₃Si₂, NiSi, and NiSi₂. Triangles indicate (at the appropriate Si enrichment) the relative intensity of the same peak in the next compound. Dashed lines are the relative intensity of the four contributions to Si *L*VV peak in computer simulated pure-Si-enriched silicides spectra, obtained as linear combination, with appropriate weights, of pure-silicon Si *L*VV peak with those stoichiometrically correct silicides (see Fig. 5). The inset shows how the intensity of each peak was determined from the Auger line.

ferent samples, its modifications show a characteristic trend as a function of the nominal Si content for Ni₂Si, Ni₃Si₂, and NiSi. For example, the 87.8-eV peak increases more slowly in Ni₃Si₂ than in Ni₂Si and it decreases in NiSi and more rapidly in NiSi₂. The other NiSi₂ peaks, however, do not follow the common trend: The 95.1-eV peak, for example, decreases with Si content in Ni₂Si, increases slowly in Ni₃Si₂ and rapidly in NiSi, but still decreases in NiSi₂. This analysis suggests a different behavior of NiSi₂ with respect to the other Ni silicides as it concerns the Si enrichment.

Spectra of samples of increasingly pure-Si concentrations were generated by computer and analyzed in the same way. To this end we linearly combined the spectrum of pure-Si *L*VV transitions with those of stoichiometrically correct silicides (Fig. 5) with appropriate weights. The results of this analysis are reported in Fig. 6 (dashed lines). It is clear that for NiSi₂ the agreement between dashed and continuous lines is good, while for the other silicides there is a general disagreement.

If we report for each peak of silicide the relative intensity of the corresponding peak of the next compound (at the Si enrichment corresponding to the Si increment from one silicide to the other one) we can see that the continuous lines cross (for Ni₂Si) or go toward these values (solid triangles in Fig. 6), while the dashed lines are in general far away.

We can conclude that the Si enrichment induced by sputtering seems different for NiSi₂ than for the other Ni silicides. For NiSi₂ this Si enrichment consists in surface segregation of covalently bonded unreacted Si; for the other silicides, a new Si-rich phase forms on top of the starting one. We note that this difference in behavior may be only apparent. As a matter of fact the silicide found at the surface always corresponds to one of the phases present in the Si-rich side of the phase diagram. In the case of NiSi₂ the only phase richer in Si in the phase diagram is pure Si.

An Ar⁺-beam-induced modification of the local atomic coordination was already found for some silicide surfaces.³ In particular, in a synchrotron radiation photoemission study on NiSi (Ref. 5) a modification of the electronic structure associated with large variations from the nominal stoichiometry was found. We note that in contrast with our results this variation was a metal surface enrichment. We consider the possibility, suggested by the authors themselves, that the surface of their "stoichiometric" NiSi₂ samples, annealed at 700°C, was already modified by elemental Si segregation. In addition, they determined the surface stoichiometry from the Auger intensity of the 848-eV Ni line and 92-eV Si line; the choice of the high-energy line leads to an overestimation of the Ni concentration, because of the concentration profile indicated by our results of Table I.

Changes in the compound surface composition under

ion bombardment can be due to several mechanisms.^{1,2} Silicon segregation at the surface due to simple collision processes can be excluded since either they predict a Ni enrichment, in contrast with our experimental findings, or are a second-order effect at room temperature (RT).

We believe that surface segregation⁴ assisted by radiation-enhanced diffusion is the main mechanism in determining the silicide surface composition under sputtering. The Si-concentration profile we experimentally observed (see Table I) is in agreement with the one expected according to this mechanism; (i) the segregation process enriches the surfaces and depletes the subsurface region of the segregating element²; (ii) semiquantitative evaluation of the segregating species for the Ni-Si system in the equilibrium configuration, based on the Langmuir relation,^{28,29} leads to an enrichment in Si-surface concentration.

CONCLUSIONS

We can make the following conclusions.

(a) An appropriate choice of Auger lines enable us to study the concentration profile in the surface region. For sputtered Ni silicides, strong variations in the relative Ni and Si concentration between the surface and a depth of few tens of angstroms was found, the surface region being of higher Si content than the near-surface region.

(b) By sputtering at suitable energies, the Ni-silicide surface can be modified in a controlled and reversible way (also without thermal annealing). This enables us (i) to clean the samples by ion bombardment without modifying the stoichiometric and chemical properties of the sample surface itself, and (ii) to form a surface layer with composition and chemical properties characteristics of a different silicide. In the NiSi₂ case, the surface modification occurs via covalently bonded Si segregation.

(c) In addition, we showed that different Ni silicides show different and characteristic Si-metal bonding, mainly reflected in the Si *L*VV line shape; in fact, this line shape can be used as a fingerprint for a correct phase identification.

(d) The Si-concentration depth profile we obtain under sputtering suggests that the transport occurs through radiation-enhanced diffusion.

(e) The silicide formation at the surface indicates the important role of the chemical bonding.

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