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Ni on Si: Interfacial compound formation and electronic structure

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Photoemission and Auger electron spectroscopic measurements are done on Ni-Si interfaces prepared by Ni deposition onto cleaved Si(111) surfaces with the use of synchrotron radiation as a light source. Results show that an interfacial reaction takes place even at room temperature. The resultant compound formed at room temperature contains higher Ni concentration than for compounds formed at high temperatures. A simple rigid-band model for these interfacial compounds explains the change in valence-band spectrum near the Fermi level that occurs with increasing Ni content.

Many transition metals are expected to react immediately after deposition onto clean Si surfaces at ambient temperatures due to strong chemical reactivity. This phenomenon has recently been observed in several systems, including Pd-Si (Refs. 1,2) and Pt-Si.[3] Very recent ion-channeling[4] and ultraviolet photoemission spectroscopy (UPS)[5] experiments show that a low-temperature interfacial reaction also takes place in a Ni-Si system.

This letter reports a study of the valence-band-structure change during compound formation at Ni-Si(111) interfaces. The UPS and Auger electron spectroscopy (AES), which have been shown to be very sensitive to valence-band change,[2,6] were exploited for this purpose. The experimental results are successfully interpreted by a simple rigid-band model. The experiments were made utilizing photoemission facilities at Beam Line 2 of the SOR-RING of the University of Tokyo.

The Ni-Si interfaces were prepared by depositing Ni onto clean Si(111)-cleaved surfaces in an ultrahigh vacuum chamber. Ni deposition was achieved by direct sublimation from a resistively heated Ni wire. The evaporation rate was determined by measuring the thickness of Ni film deposited onto glass plates during a fixed period of time. Synchrotron light was monochromated by a modified Roland-type monochromator. Emitted photoelectrons were analyzed by a double-path cylindrical mirror analyzer (CMA). Total-energy resolution for the measurements was about 1 eV. Pressure was kept below 5×10^{-10} Torr during measurements.

Examples of photoelectron energy distribution curves (EDC's) in the valence-band region are shown in Fig. 1(a). The clean surface spectrum (a) shows a characteristic three-band structure at 2.5, 7, and 11 eV below the Fermi level. These bands are assigned as $3p$, $3s$-$3p$, and $3s$-like band structures. In addition to these structures, a shoulder due to the intrinsic surface state is seen at the top of the $3p$-band structure. The topmost band intensity increases as Ni exposure is increased. To show this change clearly, the clean surface spectrum (dotted curve) is superimposed on this Ni-covered spectrum. This increment is a Ni $3d$ contribution. The Si valence-band feature, i.e., the three peak structures, remains until Ni exposure exceeds 0.67 $\times$ 10^{15} cm^{-2}.

When Ni exposure reaches 2×10^{15} cm^{-2}, the 11 eV structure almost disappears and the 7 eV structure becomes weaker (d). On the other hand, the d-like character of the topmost band is enhanced. That is, as the topmost band intensity increases, the bandwidth decreases with the peak shifting towards the Fermi level. This tendency monotonically continues until the highest Ni exposure of 1.6×10^{16} cm^{-2} in the present experiments.

At a 1.6×10^{16} cm^{-2} Ni exposure, the EDC of the surface (f) is very similar to that for metallic Ni.[7] That is, the d-band peaks just below the Fermi level (within the energy resolution) and falls steeply on the higher-energy side. The line shape near the Fermi level suggests the Fermi-edge existence. A weak broad band that ranges between 4 and 12 eV is seen in this Ni-Si surface EDC. The reported

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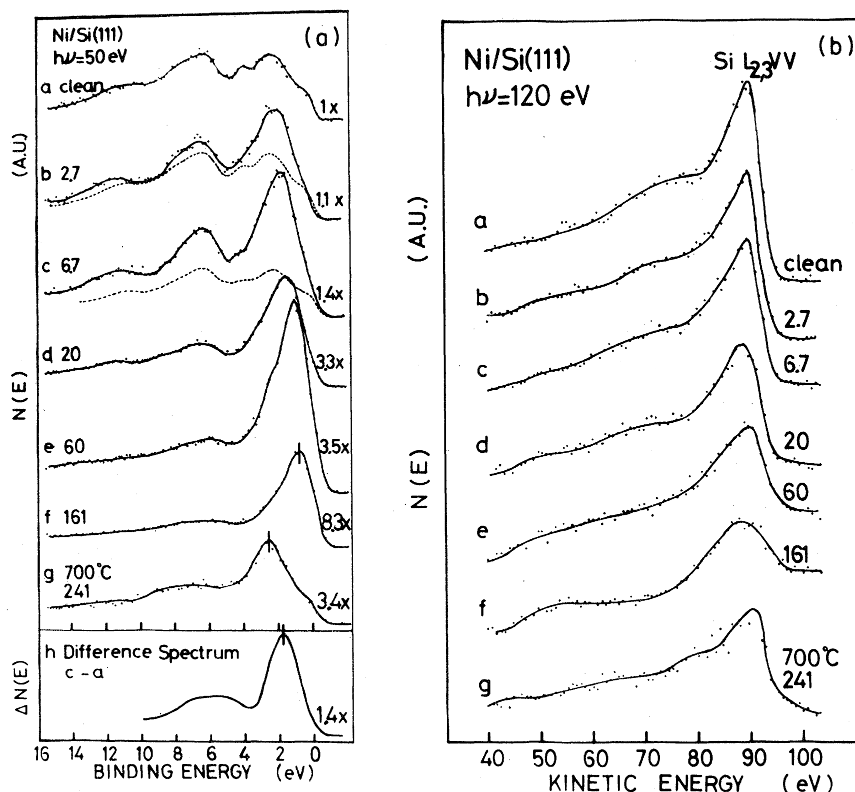

FIG. 1. (a) Examples of EDC's in the valence-band region for the Ni-Si system. The left-hand side figures are Ni exposure in units of $1\times10^{14}/\mathrm{cm}^2$. Dotted curves show clean surface EDC's. The bottom figure is incremental EDC resulting from $0.67\times10^{15}/\mathrm{cm}^2$ Ni exposure. (b) Examples of Si $L_{2,3}VV$ Auger spectra. Excitation photon energy is 120 eV. Figures are Ni exposure in $1\times10^{14}/\mathrm{cm}^2$.

metallic Ni valence-band EDC (Ref. 7) also shows a weak structure in approximately the same energy region. In spite of these similarities, this Ni-Si surface layer is identified as a Ni-Si compound as will be discussed later.

Curve (g) in Fig. 1(a) is the EDC for a Ni-Si surface prepared by 2.4×10^{16} cm^{-2} Ni exposure at about 700 °C.[8] In this spectrum the dominant peak, which may be d-like, appears about 2.7 eV below the Fermi level. A shoulder is seen at the Fermi level. A broad band, with a shape similar to the structure appearing in (f), is seen in the deeper binding-energy region.

The Si $L_{2,3}VV$ Auger electron spectra for various Ni exposed surfaces are shown in Fig. 1(b). The Si $L_{2,3}VV$ Auger line shows a sharp edge at about a 92 eV kinetic-energy position for clean and low Ni exposure surfaces. This edge gradually becomes round with increasing exposure after exposure exceeds 2×10^{15} cm^{-2}. Intensity of the Si $L_{2,3}VV$ structure decreases with increasing exposure. However, this structure can still be observed at the highest exposure of 1.6×10^{16} cm^{-2}. The Si $L_{2,3}VV$ line shape is almost symmetric at this exposure.

It has been well established, experimentally and theoretically,[9] that the Si $L_{2,3}VV$ Auger structure is essentially determined by the self-convoluted Si $3p$ partial density of states. Thus, the line-shape change by a 1.6×10^{16} cm^{-2} exposure eliminates the possibility of the pure Ni crystallet formation and indicates that the Si $3p$ states are modified by Si-Ni interaction. Auger electron escape depth is as shallow as 5 Å. Layer thickness is estimated to be about 24 Å. Therefore, the observed Si $L_{2,3}VV$ structure suggests that Si atoms diffuse into the Ni-deposited layer, and that a Ni-Si chemical reaction takes place.

The Si $L_{2,3}VV$ Auger structure intensity, the EDC topmost band intensity, and its peak position are plotted as functions of Ni exposure in Fig. 3. On the right-hand side of the figure, these quantities for the hot substrate deposited surface are also shown by closed symbols. All three plots show

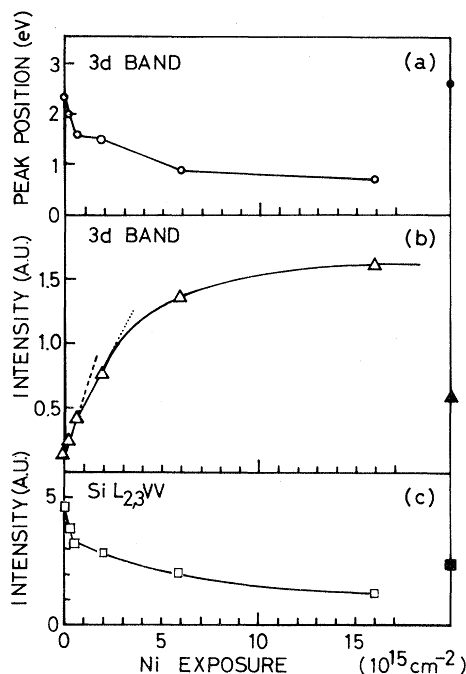

FIG. 2. The 3*d*-like band peak position (a), its intensity (b), and Si $L_{2,3}VV$ Auger intensity (c) as functions of Ni exposure. Solid symbols are for deposition onto hot substrate.

discontinuity near a 0.67×10^{15} cm^{-2} exposure, where the first monolayer is to be finalized when the sticking coefficient is unity.

Recently, Oura and co-workers[10] observed that low-energy electron diffraction (LEED) patterns gradually change from 7×7 to 1×1 during Ni deposition onto Si(111) 7×7 surfaces at room temperature. This strongly suggests that the first monolayer is an epitaxial layer in which Ni atoms

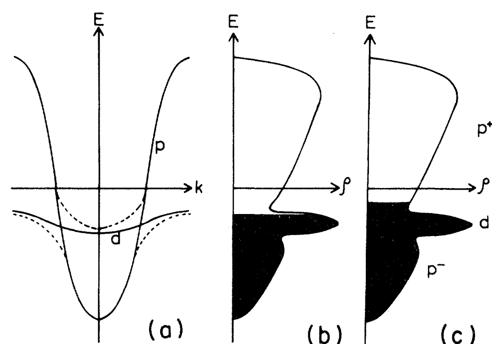

FIG. 3. Schematic energy-band diagram and state densities for Ni-Si interfacial compounds. (a) is the *p-d* hybridized band scheme, (b) is the low-temperature phase, and (c) is the high-temperature phase.

are arranged on Si surface atoms. Incremental EDC due to Ni coverage on this first stage, an example of which is shown by *h* in Fig. 1(a), is markedly dissimilar to second stage and metallic Ni EDC's. This indicates that a sort of Ni–Si chemical bonding different from that in the second-stage compound is formed in the first monolayer.

In the second stage, where Ni exposure exceeds 0.67×10^{15} cm^{-2}, the Si $L_{2,3}VV$ intensity monotonically decreases and approaches a constant value with increasing exposure. The EDC topmost band intensity also tends to saturate in the high-exposure region. The solid curve in Fig. 3(b) is a calculated Ni 3*d* contribution increase from

$$I=I_0+I_1[1-\exp(-d/\lambda)] , \quad (1)$$

with an apparent electron escape depth of λ = 5.5 Å, $I_0=0.4$, and $I_1=1.2$. This calculation matches experimental data quite well. It suggests that the intensity increase is due to layer thickness change during constant composition, rather than with composition change. The fact that the topmost band peak position is nearly independent from of Ni exposure, except at the beginning of the second stage where the first monolayer affects the spectrum, confirms this postulate.

Higher Si Auger intensity and lower 3*d*-band emission intensity for the high-temperature-formed compound indicate that the high-temperature compound is Si-rich compared with the room-temperature compound.

A simple band-structure model is applied to systematically explain the differences between the valence-band EDC's . This is schematically shown in Figs. 3(a)–3(c). A half-filled broad 3*p* band, representing the Si valence band, and a partially empty narrow 3*d* band are assumed. The 3*d* band is provided somewhat below the 3*p*-band center, as shown in Fig. 3(a) by solid lines. When chemical reaction takes place, these two bands are hybridized, and bonding p^+, antibonding p^-, and *d*-like bands split, as shown by the broken lines in the figure. The Fermi level shifts downward due to electron transfer to fill holes in the Ni *d* band. If Ni concentration is sufficiently high, the Fermi level is pinned in the 3*d* band as schematically shown in Fig. 3(b).

As Ni concentration decreases, the Fermi level leaves the 3*d* band and moves towards the 3*p*-band center. Thus, the valence-band state density shows a small antibonding *p*-like state shoulder above the 3*d*-band peak, as schematically shown in Fig. 3(c).

The fact that the Fermi level lies in the antibonding state was at first thought to mean that the compound is unstable. However, the compound can be stabilized by slightly lowering the high-density 3*d* band.

Measurements of photoemission spectra for Ni, Ni_5Si_2, Ni_2Si, Ni_3Si_2, and $NiSi_2$ were performed in order to check the validity of the rigid-band model. The results, which will be reported in detail elsewhere, show that filling of the hybridized band can be crudely explained by the simple model described above. Line-shape comparison of these silicide valence-band spectra with those for interface Ni_xSi compounds yields the conclusion that the composition x is larger than 1.5 for the room-temperature phase, and smaller than 1.5 for the high-temperature phase.

The same electronic structure model can also explain the EDC increment for the first monolayer shown in Fig. 1(a). A *d*-like peak appears at about 2 eV below the Fermi level in this difference spectrum. This *d*-band binding energy is deeper than that for the second-stage compound and shallower than that of the high-temperature compound. The antibonding *p*-like structure is not discernible. These facts imply that the number of effective Ni atoms per Si atom in this first monolayer is approximately 1.5. This means that chemisorption, in which one dangling bond electron of Si is enough to fill the *d*-band hole, takes place. A similar rigid-band model[11] has been shown to work surprisingly well in describing the electronic features near the Fermi level in amorphous Si:Au alloys.

Very recently, x-ray photoemission spectroscopy (XPS)[12] and ion-channeling[13] experiments were performed to study Ni chemically cleaned interface reactions. Results of these experiments are consistent with the present results with respect to the fact that a Ni-rich silicide is formed after formation of Si-rich silicide. However, the structure and the thickness of the first-phase layer are apparently different from those of the Ni-Si(111) surface derived by the present experiments. This difference may come from the starting surface structure dependence of the initial-stage reaction, as in the case of Al-Si interfaces.[14] Existence of thin oxide film at chemically cleaned surface may also be responsible for the difference.

In summary, three different chemically reacted layers are observed in Ni-Si interfaces. That is, Ni_xSi with $x \sim 1.5$ for the first monolayer, $x \geq 1.5$ for the thicker layer formed by room-temperature deposition, and $x \leq 1.5$ for high-temperature deposition. Observed valence-band structures of these compound phases are successfully explained by a simple *p-d* hybridized rigid-band model, where the Fermi level shifts with Ni composition. Chemical trend studies of electronic structure are very desirable.

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