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Use of $L_1L_{2,3}V$ Auger transitions for an electronic-structure study of the Al—Si(111)-(2 × 1) interface

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Al and Si $L_1L_{2,3}V$ Auger transitions are used as a local probe for an Al—Si(111)-(2 × 1) interface electronic structure. Two interface state structures, which are Al 3*s*- and Si 3*s*-like in character, are newly observed in addition to the Al 3*p*-Si 3*p* interface states at the Fermi level. The present results provide further support for the on-top-site chemisorption which was proposed for this Al—Si(111)-(2 × 1) interface, based on previous electron spectroscopic experiments.

Interface electronic structure is one of the most important subjects in present surface physics. Metal-semiconductor (*M*-*S*) interfaces have been especially studied to gain a microscopic understanding of Schottky-barrier formation and interface chemical reactions.

Photoemission spectroscopy, with thin metal overlayer preparation techniques, has been a very powerful experimental method to study interface electronic structure evolution.[1] In spite of various studies by this method, a thorough understanding has yet to be established. The use of combinations of different surface-sensitive spectroscopies is needed to produce more detailed information.

This paper reports the first successful application of $L_1L_{2,3}V$ Auger electron spectroscopy to Al—Si(111) cleaved interface. Two interface state structures that have not been observable by photoemission spectroscopy[2-4] are clearly resolved in the present Auger spectrum measurements.

The $L_1L_{2,3}V$ Auger transition has already been used to derive the Si valence-band density state of (DOS) by Ferrer *et al.*[5] They showed that integration of the Si $L_1L_{2,3}V$ first-derivative spectrum produces a crude valence-band DOS. As the L_1 and $L_{2,3}$ core-level wave-function extent is small, the $L_1L_{2,3}V$ Auger transition is expected to involve essentially localized information on valence-band DOS. Thus, $L_1L_{2,3}V$ spectra of metal and semiconductor atoms at an *M*-*S* interface are thought to give local densities of states (LDOS's) in the metal and semiconductor layers, respectively. This is a potential advantage in Auger electron spectroscopy.

A double cylindrical mirror analyzer (CMA) was used for Auger measurements. To improve resolution and reduce background signal, the second derivative mode was chosen with the smallest possible modulation width of about 0.3 eV peak to peak. Total resolution is estimated at about 0.5 eV. This permits observation of valence-band structures separately, as seen later. Clean Si(111) surfaces were prepared by cleaving blocks of *n*-type single-crystal Si under a pressure of 1×10^{-10} Torr. It is well established that they show 2×1 surface reconstruction.[6] The Al molecular beam deposition onto these clean surfaces was done to prepare Al-Si surfaces with various Al coverage. The Si $L_{2,3}VV$ Auger intensity versus Al exposure plot was used to determine Al coverage. This plot fits well a predicted line based on the layer growth mode, until about 1.5-monolayer coverage is reached.[3]

Examples of second-derivative spectra for clean and Al-covered surfaces are shown in Figs. 1—3 by solid curves. The clean-surface spectrum shown in Fig. 1 resembles Si valence-band DOS in the structure that peaks at 40.5, 37.5, and 32 eV. Those labeled *a*, *b*, and *c* are considered to come from 3*p*, 3*p*-3*s*, and 3*s* bands, respectively.

The 0.2-monolayer coverage considerably reduces intensity and changes the spectrum line shape as shown in Fig. 2. Two additional peaks, labeled *d* and *e*, appear at 38 and 32 eV. Peaks *a*, *b*, and *c* are slightly shifted.

A monolayer covered surface shows a drastically

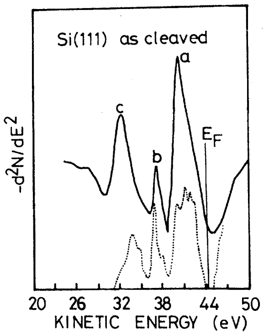

FIG. 1. Solid curves, second-derivative spectrum of Si(111)-(2×1) surface. Dotted curve, LDOS of bulk Si layer.

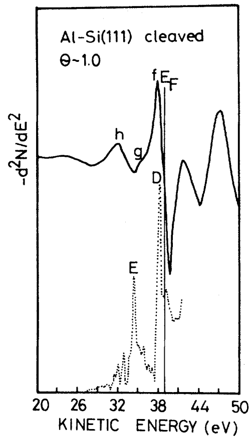

FIG. 3. Solid curve, second-derivative spectrum of one monolayer Al covered surface. Dotted curve, interface Al layer LDOS of on-top geometry.

different line shape from clean and lower-coverage surfaces as shown in Fig. 3. A narrow peak *f* accompanied by a sharp dip, a shoulder *g*, and a broad peak *h* are recognized at 42.5, 35.5, and 32 eV, respectively.

Intensity variations of these structures are plotted as a function of Al coverage in Fig. 4. The intensity of *a*, *b*, and *c* decreases, while that of *f* increases with increasing coverage. The *f* structure suddenly becomes strong at monolayer coverage, and gradually continues its increase with further increase in Al coverage. Peaks *d* and *e* are clearly recognized only in the region below about 0.4-monolayer coverage. On the other hand, structure *h* is seen in the region between 0.8- and 1.6-monolayer coverage.

Based upon intensity variation described above, observed structures are classified as follows:

(i) *a*, *b*, and *c* are related to bulk Si states because they are diminished by Al coverage.

(ii) *d* and *e* are related to Si interacting with Al because they are induced by Al coverage and screened by further Al coverage.

(iii) *f* and *g* are related to Al because they are prominent after monolayer coverage completion.

(iv) *h* is related to Al interacting with Si because it appears at around monolayer coverage and is screened by further Al coverage.

The 0.2-monolayer covered surface spectrum (Fig. 2) consists of bulk and interface Si state structures. Meanwhile, one monolayer covered surface spectrum (Fig. 3) consists of Al related structures. Thus they are considered to correspond to LDOS's of Si bulk, interfaced Si, and interface Al layers, respectively.

Three different chemisorption geometries were adopted for Al-monolayer covered Si(111) surface

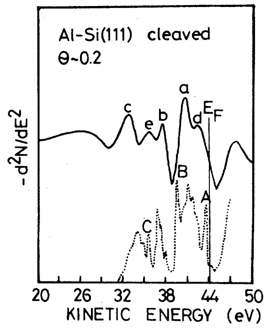

FIG. 2. Solid curve, second-derivative spectrum of 0.2-monolayer Al covered surface. Dotted curve, interface Si layer LDOS of on-top geometry.

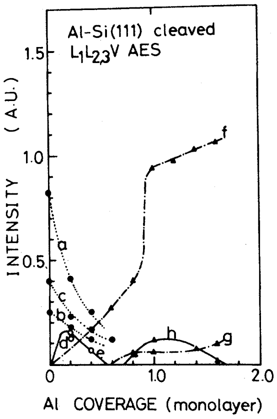

FIG. 4. Si and Al related $L_1L_{2,3}V$ Auger structure intensities as functions of Al coverage.

electronic structure calculations using the pseudopotential method.[7-9] These are substitutional, on-top, and hollow-site geometries. Among them, the on-top covalent geometry calculation provides the most consistent explanation for recent photoemission and Auger electron spectroscopic experiments on Al-Si(111)-(2×1) surface.[3,4] Thus calculated LDOS's of the on-top geometry[8] by Zhang and Schlüter should be compared with observed spectra in Figs. 1–3.

To do so, the Fermi-level position is calculated by the relation

$$E_F(k) = E_{2s} - E_{2p} - \phi_D \ .$$

Here, $\phi_D = 5.0 \pm 0.1$ eV is an analyzer work function, and E_{2s} and E_{2p} are $2s$ and $2p$ core binding energies. The Fermi-level position is indicated by a vertical line in Figs. 1–3.

With clean surfaces, peaks a and b coincide well with $3p$ and $3p$-$3s$ bands at about 2.5 and 7 eV below the Fermi level in the calculated LDOS's (dotted curve) of the bulk region as seen in Fig. 1. However, peak c is at about 2 eV below the calculated $3s$ band peak. Comparison of photoemission energy distribution curves[3] with the pseudopotential calculation shows that the calculation produces about 1 eV shallower binding energy. The remaining 1-eV energy discrepancy may be related to a non-negligible relaxation effect for $3s$-like states.[10]

A 0.2-monolayer covered surface spectrum is compared with the LDOS of the Si layer just behind the Al layers. Peaks A, B, and C in the LDOS are due to interface states induced by Al–Si bond formation. Peak d in the observed spectrum coincides well with peak A, which is an interface state of mainly Si $3p_z$-like character. No peak corresponding to peak B is seen in the observation. This is reasonable since peak B is Al $3s$-like and contains few Si originated states. Peak e, that has never been observed by photoemission experiments,[2-4] coincides with peak C. This is a Si $3s$-like interface state that appears in the energy gap in M–K direction of the surface Brillouin zone.[11]

Peak f coincides with peak D of the surface Al layer LDOS as seen in Fig. 3. This state D is dominantly Al $3p_z$-like. Calculation shows that the Fermi level is pinned in this state. The observed shape of structure f is naturally interpreted as the second derivative of the Fermi edge. The sudden intensity increase and line-shape change of structure f at around monolayer coverage is thus thought to be a metallization of the Al overlayer.[3,4]

The Al $L_{2,3}VV$ Auger line also shows a sudden shape change at monolayer coverage.[3,4] Namely, a sharp peak and dip structure, which is interpreted to come from the Fermi edge, appears at monolayer coverage. Moreover, a broad peak is seen in the lower energy side of this Fermi edge originated structure. This structure is assigned to the Al $3p$-like state from its energy position. The structure g in Al $L_1L_{2,3}V$ spectrum in Fig. 3 is thought to come from the same $3p$-like state that the broad peak structure in the Al $L_{2,3}VV$ spectrum comes from. Meanwhile, the calculated[8] LDOS shows no corresponding structure to this broad peak. This suggests that the Al $3p$-like band exhibits larger dispersion in the interface Brillouin zone than the pseudopotential calculation[8] predicts.

Peak h appears at about 2.5 eV below the calculated peak E position. This peak E is Al $3s$-like. This energy discrepancy may again be explained as follows:

(i) Theoretical calculation tends to give shallower binding energy for the $3s$-like state.

(ii) Relaxation effect is not negligible for the $3s$ state due to its localized nature.

Aluminum chemisorption onto the Si(111)-(2×1) surfaces is shown to take place in quite a different manner from that onto Si(111)-(7×7) surfaces.[12] In the case of the Al–Si(111)-(7×7) system, chemisorption results are most consistently interpreted by threefold hollow-site geometry. This is also consistent with the theoretical analysis[8] of photoemission and electron energy loss measurements. On the other hand, Al–Si covalent bond formation at on-top sites has recently been postulated for the Al–Si(111)-(2×1) system by the present authors[3,4] as mentioned in the text. The present $L_1L_{2,3}V$ Auger results provide further support for this postulate with respect to energy positions and characters of the observed interface states as well as appearance of the metallic edge in the Al $3p$-like state at monolayer coverage.

In conclusion, Auger transitions of the $L_1L_{2,3}V$-type were found to be useful in probing the Al–Si interface electronic structure. Aluminum and silicon $3s$-like interface states, which have never been observed by other spectroscopic methods, are detected. This type of Auger transition is thought to have potential in application to interface systems.

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[1] P. Skeath, I. Lindau, P. W. Chye, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. 16, 1143 (1979).

[2] G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B 14, 5396 (1976).

[3] K. L. I. Kobayashi, F. Gerken, J. Barth, and C. Kunz, Solid State Commun. (in press).

[4] K. L. I. Kobayashi, F. Gerken, J. Barth, and C. Kunz, *Proceedings of the Fifteenth International Conference on Physics of Semiconductors, Kyoto, Japan, 1980,* edited by S. Tanaka [J. Phys. Soc. Jpn. 49, Suppl. A, 1063 (1980)].

[5] S. Ferrer, A. M. Baro', and M. Salmeron, Solid State Commun. 16, 651 (1975).

[6] W. Monch, in *Festkorperprobleme* (Advances in Solid State Physics), edited by J. H. Queisser (Pergamon, New York, 1973), Vol. XIII, p. 241.

[7] J. Chericovsky, Phys. Rev. B 16, 3618 (1977).

[8] H. I. Zhang and M. Schlüter, Phys. Rev. B 18, 1928 (1978).

[9] M. Nishida, Phys. Status Solidi B 95, 263 (1979).

[10] M. A. Smith and L. L. Levenson, Phys. Rev. B 16, 2973 (1977).

[11] S. G. Louie and M. L. Cohen, Phys. Rev. B 13, 2461 (1976).

[12] K. L. I. Kobayashi and Y. Shiraki (unpublished).