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A Study of Al/Si Interface by Photoemission, Auger Electron Yield and Auger Electron Spectroscopies

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Abstract

Photoemission, Auger electron yield and Auger electron spectra were observed for Al/Si(111) interfaces with various Al coverage prepared by successive deposition using a molecular beam source. The Al 3p derived states are introduced at around the top of the valence band by the Al coverage of less than one monolayer. The Al surface layer behaves as a "metal" and the Fermi level is stabilized in the Al 3p derived states at about 0.3 eV above the top of the valence band of Si. The Schottky barrier height in this stage is about 0.8 eV and further increase in Al coverage does not change the barrier height. A covalent bonding model of the Al/Si interface based on the experimental results is proposed. The present result favors the on-top geometry of Al atoms on Si(111) surface among the geometries used in the pseudopotential calculation by Zhang and Schlüter.

Schottky barrier (SB) formation in semiconductors has been of particular interest since Bardeen[1)] proposed that the intrinsic surface states of semiconductors are responsible for the pinning of the Fermi level. Relevant surface sensitive spectroscopies have been developed for the investigation of the electronic structures of various metal-semiconductor interfaces[2-5)]. The pseudopotential method[6-8)] has recently been applied to the calculation of the local density of states (LDOS) as well as the charge distribution in the interface region of metal-semiconductor junctions. Nevertheless, there appears to be no sufficient understanding of SB formation from the microscopic point of view even in the simplest interface, that of Al and Si.

In this letter, we report photoemission, Auger electron yield and Auger electron experiments on SB formation of the Al/Si(111) system and propose a chemical bonding model in which Al atoms are covalently bonded to the Si surface atoms based on the present results.

Measurements of LDOS are most desirable to identify the chemical bonding states at the interface. Ultraviolet photoemission spectroscopy, which is applied for that purpose, only gives a weighted average of the LDOS of several layers near the surface. Surface sensitivity is expected to be improved if the photon energy is increased to 50 - 100 eV, owing to the smaller escape depth (2 - 5 Å) in this energy region than that in the lower photon energy region.

Auger electron spectroscopy (AES) has not been as widely used as photoemission spectroscopy for the study of valence band structure. Recently, Al and Si $L_{2,3}$ VV Auger spectra have been shown to be a very sensitive probe for the chemical bonding states at Al/Si interfaces[9)]. According to the recent theory[10, 11)], the Auger current is proportional to the square of the atomic charge (in LCAO terms) which is very sensitive to the chemical bonding states. Since the p-like states predominantly contribute to the atomic charge in non-ionic s-p band materials, the $L_{2,3}$ VV Auger line shape in these materials is approximately determined by the self convoluted p-like partial density of states (PDOS)[12].

For the investigation of interface regions yield spectroscopy, as a probe for empty states, can be modified by setting the final energy of the analyzer to the Auger electron energy of the different atoms in the interface ("Auger yield spectroscopy AYS").
The $L_{2,3}$ VV AYS spectra of Al and Si correspond to the optical absorption spectra in the surface region from 2p core to empty states localized at Al and Si, respectively. Because 2p core levels have no dispersion, the AYS spectra are essentially determined by the density of unoccupied states.

Clean Si(111) surfaces were prepared by cleaving blocks of high resistive (∿130Ω cm) phosphorus doped n-type Si. These surfaces were exposed to an Al molecular beam of 10^{13} - 10^{14} cm^{-2} sec^{-1} generated by a conventional molecular beam source. The base pressure of the system was below $2x10^{-10}$ Torr. During the evaporation, the pressure was below $5x10^{-10}$ Torr. Measurements of EDC's (Energy Distribution Curve of photoelectrons) and AYS spectra were made using synchrotron radiation of the storage ring DORIS and the FLIPPER monochromator[13] at DESY. The AES spectra were taken in the second derivative mode with modulation widths of 0.3 - 0.6 eV using an electron beam of 3 keV as excitation source. Typical energy resolutions were 0.7 eV for valence band EDC's, 0.1-0.25 eV for core levels, 0.1 eV for AYS spectra and 0.5 eV for AES spectra.

Examples of EDC's of clean and Al covered Si(111) surfaces are shown in Fig.1(a). All the spectra are normalized to the photon flux. In this figure, θ denotes the fraction of saturation coverage of Al. The Fermi level position which is experimentally determined from bulk metal spectra is indicated by the vertical line. The intensity decreases and the line

shape near the Fermi level changes with increasing coverage θ . The general feature of the EDC, i.e. the three peaks at ∿3 eV, ∿7 eV and ∿11 eV below the Fermi level, is conserved even after the Al coverage of θ = 1. The shoulder (indicated by i in the figure) of the clean surface EDC is assigned to the intrinsic filled surface state[14]. When the surface is covered by 0.4 monolayers of Al, the intrinsic surface state structure (i) is replaced by a new structure (e). The extrinsic surface state (e) is absent in the EDC for θ ∿ 0.8, and a shoulder (indicated by a) is seen about 0.5 eV below the Fermi level in the EDC for ∿ 1.5. The rise at the Fermi level is almost the same for the clean surface and the surface with θ ∿ 0.4, and becomes slightly steeper when θ increases to around unity. In order to show this change in the rise at the Fermi level, EDC's of clean, θ ∿ 0.4, and θ ∿ 1.5 surfaces are normalized at the maximum of the clean surface EDC as shown in the insert of Fig. 1(a). The Fermi level is located just at the mid point of the rise of the EDC of the θ ∿ 1.5 surface.

The evolution of Al and Si $L_{2,3}$ VV Auger structures is shown in Fig. 1(b). The Si Auger intensity decreases with increasing θ, however, the line shape stays almost the same. The Al Auger structure shows two line shape changes during the overlayer formation. Two peaks at 64 eV and 66 eV are observed at the coverage of θ ∿ 0.12. The 66 eV peak becomes weaker when θ increases to 0.2 and diminishes between θ ∿ 0.2 and θ ∿ 0.4. A dip remains at the energy position of the diminished peak. For θ ∿ 1, the second line shape change is observed. The dip (D) at 67 eV becomes sharper and a new sharp structure (A) appears at 66 eV as seen in the spectrum of the θ ∿ 1.5 surface in Fig. (b).

The work function change during overlayer formation was measured from the shift in the low energy cut off of the EDC. Changing the coverage θ from 0 to 0.4 results in a decrease of the work function by 0.5 eV. Further increase of θ does not change the work function any more. The band bending at the surface is measured by monitoring the Si 2p core level for different mean escape depths of the photoelectrons. We find that the band bending increases with increasing θ until monolayer coverage is completed. The increase in electrostatic potential ΔV at the surface compared with the clean surface is estimated as 0.2 eV when θ exceeds unity. From these results, SB formation at the Al/Si(111) interface is considered to be completed at around monolayer coverage. The SB height was determined in the present measurements as follows:

$$\Phi_{SB} = \Delta V - \Delta\Phi + \Phi_{Al} - \chi_{Si} = 0.8 \text{ eV}$$

Here the values for work function and electron affinity of the Al/Si surface were determined as $\Phi_{Al} = 4.6$ eV and $\chi_{Si} = 4.5$ eV from the present EDC and AYS results, respectively. Subtracting this SB height from the band gap value of 1.1 eV, the Fermi level position is determined to be 0.3 eV above the top of the valence band. This spectroscopically determined value of the Al/Si(111) SB height is slightly larger than the reported value of 0.5 - 0.77 eV[15].

In order to investigate the electronic structure of the interface just after the completion of the SB formation, we examined EDC's, AYS and AES spectra of the $\theta \sim 1.5$ Al/Si(111) surface in detail. The second derivative $L_{2,3}$ VV AES spectra of Al and Si are compared with the corresponding EDC in Fig. 2. The energy for AES is taken as $E_v = (E_c - E_k)/2$ to compare the AES spectra and the EDC on the same energy scale. Here E_v, E_c and E_k represent energies of two final holes in the valence band, the binding energy of the 2p core

level and the kinetic energy of the Auger electrons measured from the analyzer vacuum level, respectively[16]. In this figure, dip (D) and peak (A) in the Al AES spectrum appear near the Fermi level where the Si AES spectrum shows no remarkable structure. These two structures suggest that the Al 3p derived state yields an edge and a shoulder at lower energy near the Fermi level. Although the inflection point between (A) and (D) is about 0.5 eV below the energy of the steepest gradient position in the rise of the EDC, we assume that this edge-like structure in the Al derived state corresponds to the rise of the EDC at the Fermi level. The discrepancy in energy position is within the experimental errors. The broad maximum (b) in the EDC about 2.5 eV below the Fermi level appears to originate from both Al and Si 3p states.

The Al and Si $L_{2,3}$ VV AYS spectra are compared with the EDC in Fig. 2. The energy scale for AYS is taken as $h\nu - E_c$. Both the Al and Si AYS spectra show a two-step structure at threshold due to the spin-orbit splitting of the 2p core levels. The Al AYS spectrum, which reflects the density of the unoccupied states localized in the Al layer, is seen to rise steeply at the Fermi level. This fact and the edge-like structure in the Al derived occupied states at the Fermi level discussed above suggest the existence of a Fermi edge in the interface state originating from Al. The Al layers on the Si(111) surface with $\theta \sim 1.5$ are considered to behave as a "metal". Comparison of the EDC and Si AYS spectrum shows a gap of about 1 eV between the filled and empty states of Si in the interface region.

The Al $L_{2,3}$ VV AES spectrum of the $\theta \sim 1.5$ Al/Si(111) surface and a thick Al film are compared in Fig. 3. The absence of peak (A) in the thick film AES spectrum shows the difference between the Al 3p PDOS of the Al layers on a Si(111) surface and that of the bulk metallic Al. The Al $L_{2,3}$ VV AYS spectrum in Fig. 2 can be compared with the $L_{2,3}$ core absorption spectrum of bulk Al and also of surfaces of the single crystal Al[17,18]. Both the bulk and surface of metallic Al show sharp spike structures just above the absorption edge[17,18]. These spike structures are absent in the Al/Si(111) surface spectrum. The Al/Si(111) spectrum shows a broad peak which is not seen in the metallic spectra[17,18] at around 2 eV above the Fermi level. Thus, we conclude that for the "metallic" Al overlayer on a Si(111) surface the valence and conduction band structures are different from those of the Al bulk and the Al surface.

Now we discuss the present results in comparison with the pseudopotential calculation of an Al/Si(111) monolayer chemisorption system by Zhang and Schlüter[8]. They calculated the band structure and charge distribution for the four different geometries of Al atoms arranged on the Si(111) surface, i.e. the one fold (on-top) covalent geometry, two different three fold ionic geometries with different Al-Si distances, and Lander's substitutional geometry which had already been used in the calculation of Chelikowsky[7]. All these geometries give the work function decrease of 0.5 eV which is consistent with the present result. The Fermi level is pinned at about 0.4 eV above the top of the valence band for the one-fold covalent geometry, and 0.8 – 0.9 eV for the ionic three-fold geometry. The Lander substitutional geometry gives a Fermi level position of 0.9 eV above the top of the valence band. The wave function character of the interface state near the Fermi level is Al p_z-like in one-fold geometry, a mixture of Al s-like and Si p_z-like in three-fold geometries, and Si p_{xy}-like in Lander's substitutional geometry[8]. The Fermi level position of 0.3 eV above the top of the valence band in the present results, which show that the Al derived state near the Fermi level is of Al 3p character, agree fairly well with the calculation for the one-fold geometry. In this geometry, Al atoms sit on top of the Si surface atoms with the Al p_z

orbital forming a covalent bonding with the Si dangling bonds. This bond formation results in semimetallic Al p-like interface bands in the band gap region. An Al s-like band is located about 4.3 eV below the top of the valence band[8].

The LDOS and charge deviation from the neutral background of the Al/Si(111) surface after the SB formation is schematically shown in Fig. 4 based on the above discussion. The covalent bond formation between Al and Si causes i) a polarization of the Al atoms ii) a polarization of the Si surface atoms and iii) a redistribution of space charge in the bulk region of Si as schematically shown on the right hand side of the figure. The Al 3p-derived state appears at around the top of the valence band of Si. The interaction between Al atoms becomes strong enough to make this Al 3p derived state form bonding and antibonding bands which overlap with each other in the band gap region when the Al coverage increases to around one monolayer. Consequently the surface Al layer behaves as a two-dimensional "metal". The Fermi level is stabilized at $\sim$ 0.3 eV above the top of the Si valence band in these Al derived bands.

The present results suggest the break down of the weak interaction models[1, 19] for the metal/semiconductor interfaces. More spectroscopic investigations are necessary to give a consistent understanding of SB formation in various metal/semiconductor systems.

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12) The $L_{2,3}$ VV Auger current is written as:

$$I(E_V) = \int_0^{\xi} |M|^2 \rho\,(E_V-\varepsilon)\,\rho\,(E_V+\varepsilon)\,d\varepsilon;$$

$$\xi = \begin{cases} E_1 - E_V & \text{for } E_1 = E_V < \frac{E_1+E_2}{2} \\ E_V - E_2 & \text{for } \frac{E_1+E_2}{2} = E_V < E_2 \end{cases}$$

with the transition energy of $E_k = E_c - 2E_V$.

Here M, ρ and E_1 and E_2 represent the Auger matrix element, density of states, and the top and the bottom of the valence band, respectively. The density of states can be written as

$$\rho = \rho_s + \rho_p$$

where ρ_s and ρ_p represent s- and p-like PDOS, respectively. As firstly

pointed out by Jennison in ref. 10) and 11), the p-p component is much greater than s-p and s-s components in the Auger current in non-ionic s-p band materials due to the matrix element effect. Thus the main structure in the $L_{2,3}$ VV Auger spectrum in Al and Si is reproduced by folding the p-like PDOS. On the other hand, the Al $L_{2,3}$ VV Auger structure is not observed in highly ionic Al_2O_3 due to the almost complete transfer of Al 3p electrons to O 2p levels (K.L.I. Kobayashi et al., Surface Sci. 77, 458 (1978)). The above mentioned facts suggest that the $L_{2,3}$ VV Auger structure in the s-p band materials can be a probe of p-like charge localized at the atom of interest.

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16) On the basis of the discussion given in 12), we estimate the energy range of the p-like PDOS from the observed AES spectrum $I(E_k)$ only by changing the energy from E_k to $E_V = (E_c - E_k)/2$ without deconvoluting the spectrum. At least the highest and the lowest energy structures in the unfolded spectrum with this reduced energy can be correlated to the structures in EDC. Comparison of EDC and AES spectra of the clean Si(111) surface shows that this simplification is valid, that is, the Si $L_{2,3}$ VV AES spectrum in the 2nd derivative mode shows a broad peak in the 3p band region, weak structures (∿ 10% of the p-p component) in the 3s-3p mixed band region and no detectable structure in the 3s band region.

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Figure Captions

Fig. 1 EDC(a) and AES spectra (b) of clean and successively Al-covered Si(111) surfaces. The Al coverage is given by θ.

Fig. 2 Comparison of EDC with (a) Al and Si $L_{2,3}$ VV AES and (b) Al and Si $L_{2,3}$ VV AYS spectra of the θ= 1.5 Al/Si(111) surface. Energy is measured as ($h\nu - E_k$) for EDC, ($E_c - E_k$)/2 for AES and ($h\nu - E_c$) for AYS, respectively. The zero energy level is the vacuum level of the energy analyzer.

Fig. 3 Comparison of the Al $L_{2,3}$ VV AES line shape of the Al/Si(111) surface with that of a thick clean Al film surface.

Fig. 4 Schematic drawing of the Al/Si(111) surface electronic structure after completion of the SB formation. The left hand side shows the LDOS in the interface region and deep in the bulk. Polarization of surface atoms and space charge distribution are shown on the right hand side. Broken lines are for the clean surface and solid lines are for the Al/Si surface.

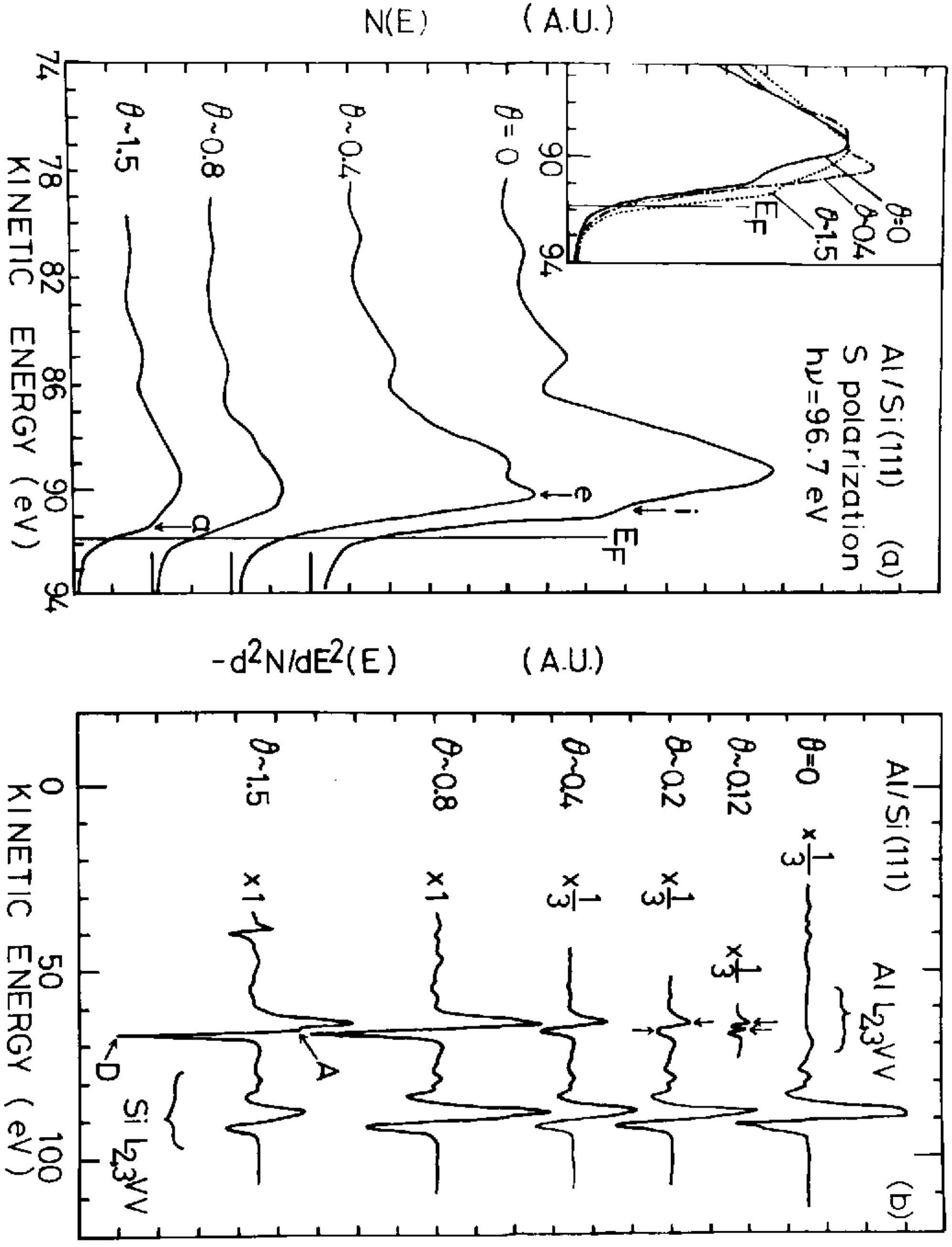


Fig. 1

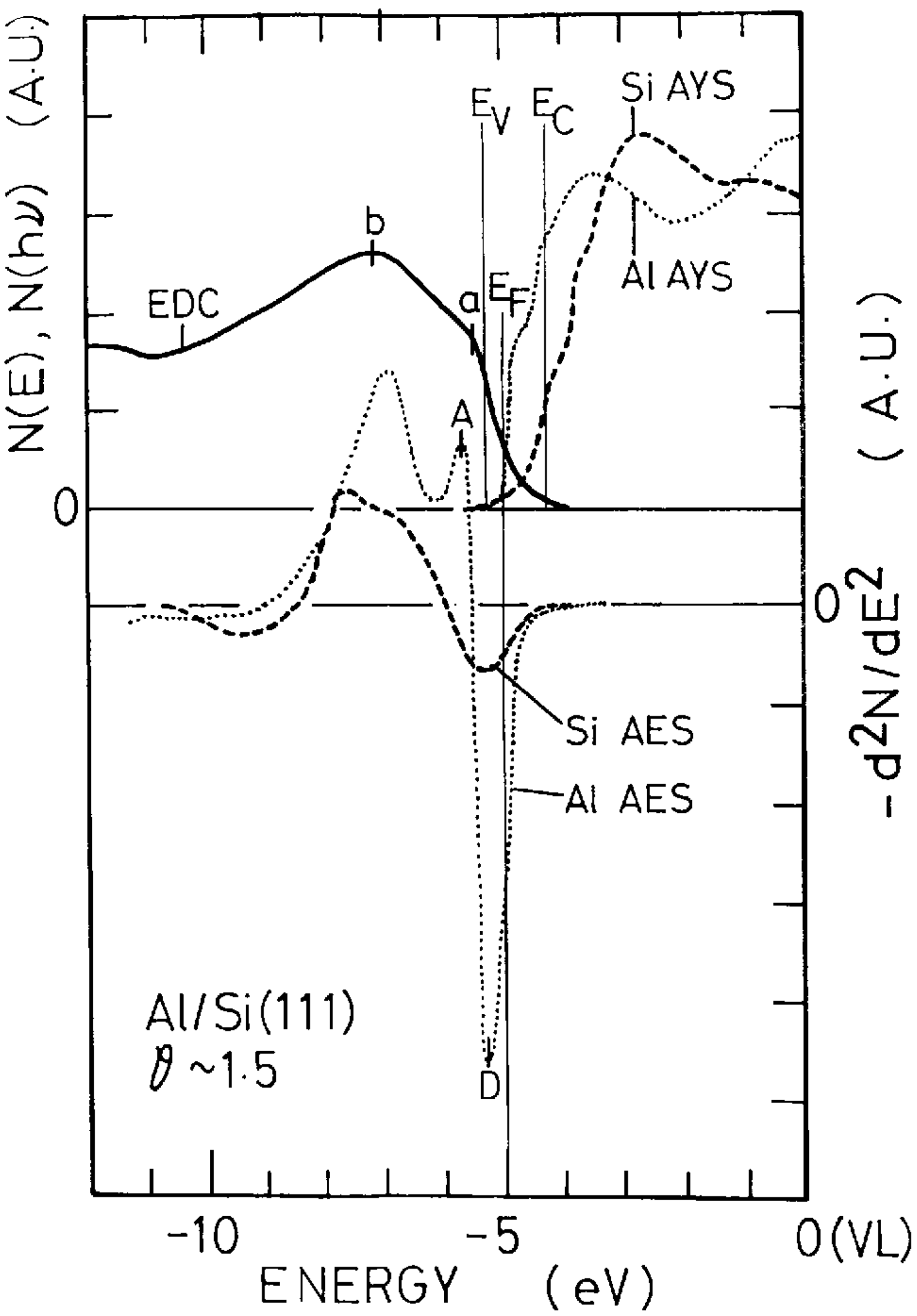
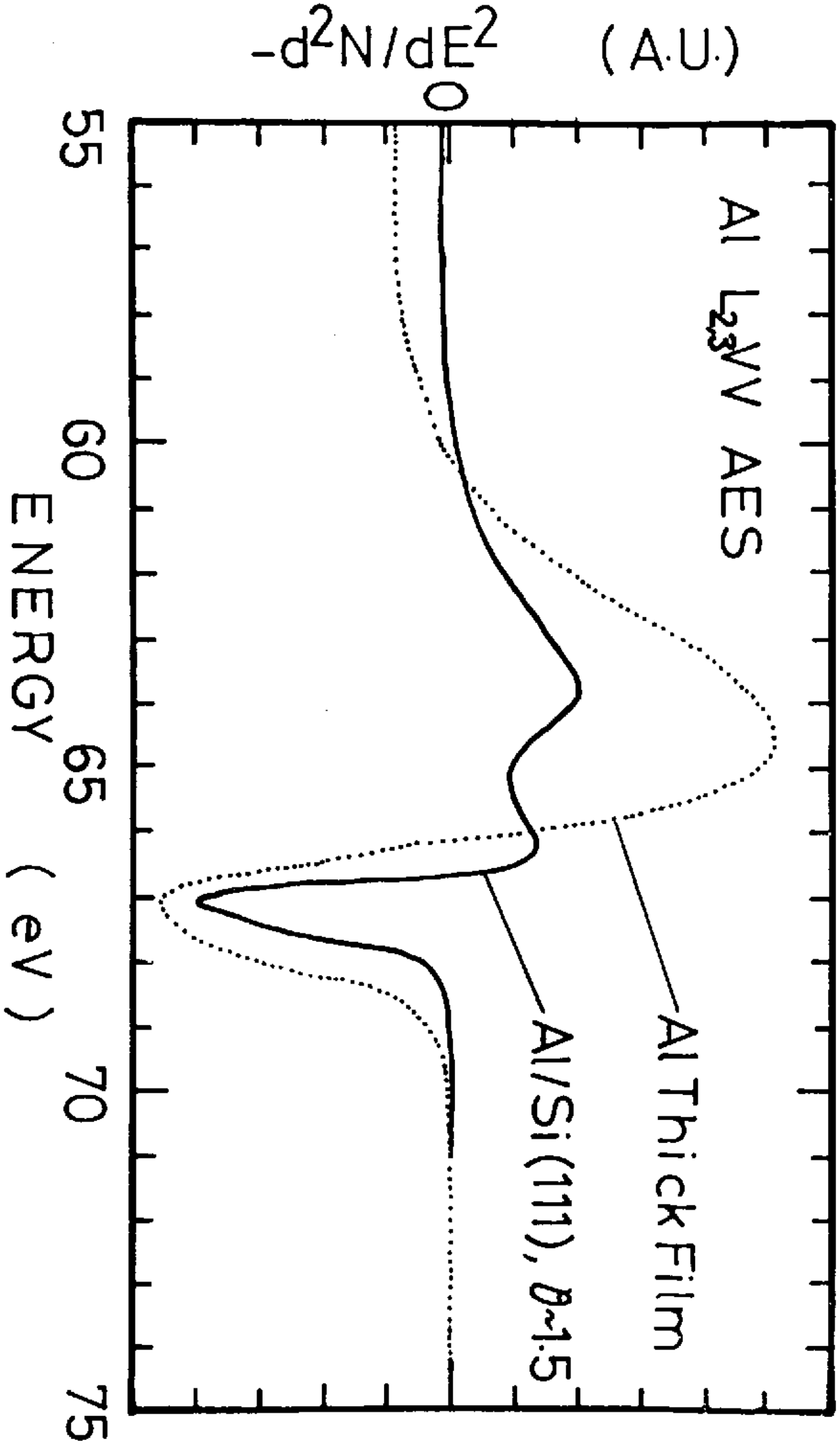

N(E), N(hν) (A.U.)
-d²N/dE² (A.U.)
Si AYS
Al AYS
E_V
E_C
E_F
b
a
A
D
EDC
0
0
Si AES
Al AES
Al/Si(111)
θ ~1.5
-10
-5
0(VL)
ENERGY (eV)

Fig. 2

Fig. 3


-d²N/dE² (A.U.)
0
Al L₂,₃VV AES
55
60
65
70
75
ENERGY (eV)
Al/Si(111), θ~1.5
Al Thick Film

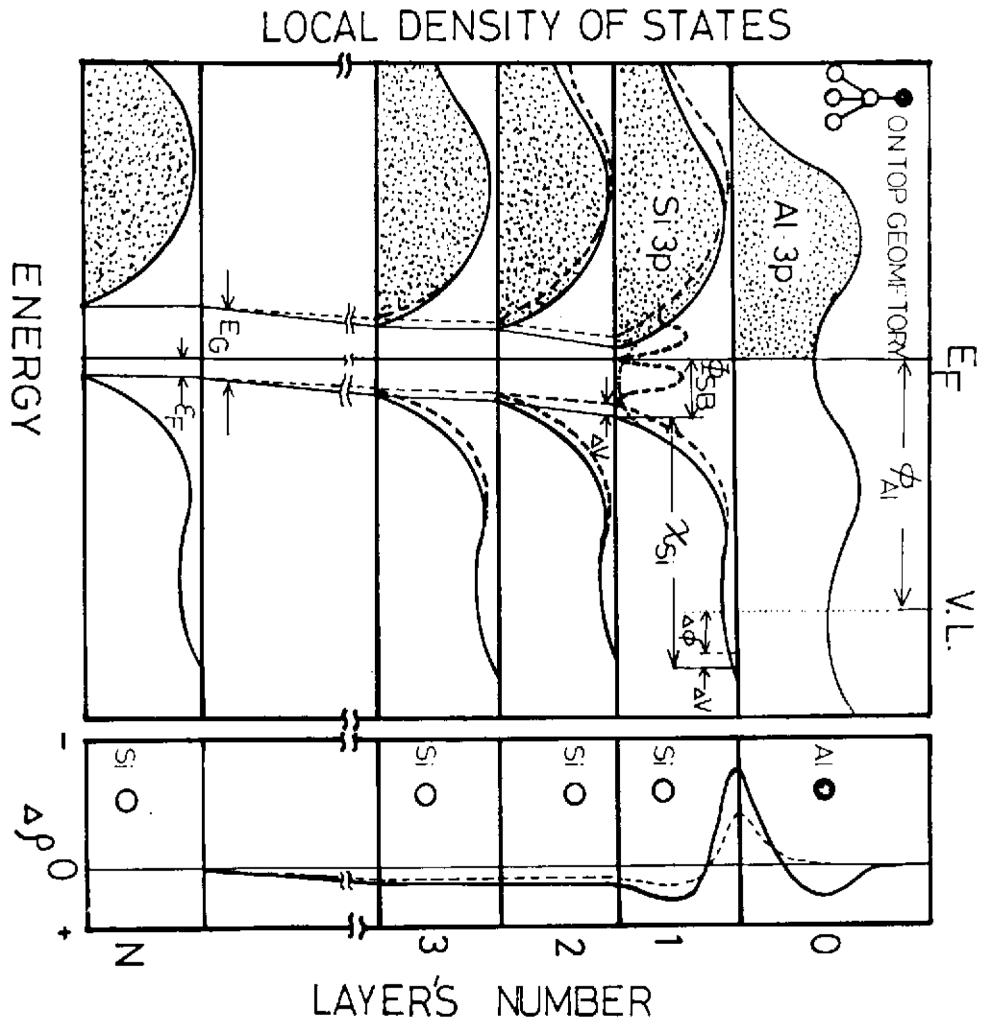

LOCAL DENSITY OF STATES
ENERGY
ONTOP GEOMETORY
Si 3p
Al 3p
E_F
V.L.
E_G
ε_F
φ_SB
ΔV
χ_Si
Δφ
ΔV
φ_Al
Δρ^0
-
0
+
Si
Si
Si
Si
Al
N
3
2
1
0
LAYER'S NUMBER

Fig. 4