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A PHOTOEMISSION STUDY OF Al/Si INTERFACE USING SYNCHROTRON RADIATION

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Photoemission EDC and Auger electron yield spectra are observed in Al/Si(111)-cleaved surface system, using synchrotron radiation. Electron beam excited Auger electron spectroscopy is also employed to probe chemical bonding state change at the surface. The Al $3p_z$ derived state which becomes metallic at monolayer coverage is introduced at around the top of the valence band. The Fermi level is stabilized in this metallic state. The present results suggest Al-Si covalent bond formation.

I. Introduction

The Electronic structure of Al/Si interfaces has been studied as a typical example of the Schottky barrier (SB), experimentally, by using various electron spectroscopic techniques [1, 2, 3], and theoretically by the pseudopotential method [4, 5, 6]. However, there seems as yet to be no thorough understanding of the SB formation mechanism. We made an experimental study of the Al/Si(111)-cleaved surface SB structure by photoemission spectroscopy using synchrotron radiation. We also applied Auger electron spectroscopy to probe for Al overlayer formation and for Al/Si chemical bonding states. In this report we concentrate primarily on a discussion of the electronic structure of this interface just after completion of SB formation. The discussion is based upon the present photoemission and Auger electron results.

II. Experimentals

Clean Si(111) surfaces were prepared by cleaving blocks of high purity (~ 130Ωcm) P doped n-type Si single crystals. These surfaces were exposed to an Al molecular beam source. Base pressure of the system was below 2×10^{-10} Torr and pressure during Al evaporation was below 5×10^{-10} Torr. Measurements of photoelectron EDC and Auger electron yield (AYS) spectra were made using synchrotron radiation of storage ring DORIS and the Flipper monochromator at DESY. The AES spectra were taken in the 2nd derivative mode using an electron beam as the excitation source.

III. Results and Discussion

The Si $L_{2,3}$ VV Auger structure, which does not greatly change its line shape, was used as a measure of the Al coverage of the surface. This line intensity v.s. Al exposure curve (I-X curve) indicates that layer growth takes place until about 1.5 monolayer coverage has been reached. When the coverage θ exceeds ~ 1.5, the

I-X curve deviates from the predicted layer growth curve. This deviation may be taken as a result of three dimensional nucleation and growth. The Al plasmon satellites appear in the Al KLL Auger lines in the surfaces with this Al coverage region. This fact also suggests the existence of three dimensional Al nuclei on the surfaces.

The SB formation process can be briefly summerized as follows: The surface work function decrease of about 0.5 eV, which we monitor by low energy cut off of the EDC, is completed before 0.4 monolayer coverage is reached. However, the increase in band bending, which we deduce from the Si 2p core binding energy shift due to Al coverage, continues until the monolayer coverage is reached. The saturation value of the band bending is estimated to be ~ 0.2 eV. Thus SB formation is completed at the monolayer coverage in this system. The spectroscopically determined SB height is 0.8 eV, which is slightly larger than the reported values of 0.5 ~ 0.77 eV [7].

Evolution of the valence band structure during SB formation is evident in the EDC and AES. The clean surface EDC shows an intrinsic surface state structure below the Fermi level. The Al coverage replaces this structure with an extrinsic surface state structure whose shape gradually changes in the course of SB formation. Comparison of EDC with AES enables us to assume that this extrinsic state originates from Al 3p orbitals. Indeed, the Al $L_{2,3}VV$ AES is much more sensitive to the evolution of the chemical bonding states than is EDC. At monolayer coverage, the Al $L_{2,3}VV$ Auger structure shows a sudden line shape change, i.e., the appearance of a shoulder-and-dip structure at its high energy edge. The EDC also shows a steeper rise in the middle of which Fermi level is situated. In the region of $1 \gtrsim \theta \gtrsim 2$, the line shapes of both AES and EDC are almost unchanged.

The EDC, and Al and Si $L_{2,3}VV$ AYS of the $\theta \simeq 1.5$ surface are shown in Fig. (1a). The energies for EDC and AYS are taken as $h\nu - E_k$, and $h\nu - E_c$, respectively. Here, E_k is electron kinetic energy, and E_c is the involved core level binding energy. The Al and Si $L_{2,3}VV$ AYS reflect the empty state densities localized in the Al and Si layers at the interface since the yield of these $L_{2,3}VV$ transitions is essentially determined by optical transition of the Al and Si $L_{2,3}$ levels to empty states. The 2nd derivative Al and Si AES's are shown in Fig. (1b) in the energy scale of $(E_k - E_c)/2$ to compare them with the EDC and the AYS. These Al and Si $L_{2,3}VV$ AES's are related to Al and Si 3p partial state densities [8].

On the basis of the above discussion, the results shown in Fig. (1a) and (1b) are interpreted as; The filled state

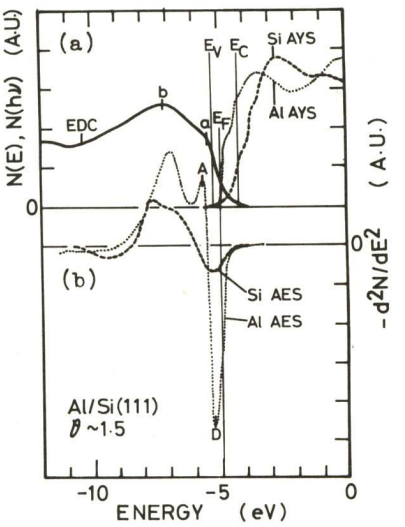

Fig. 1

(a) EDC, and Al and Si $L_{2,3}VV$ AYS's for the $\theta \simeq 1.5$ surface

(b) Al and Si $L_{2,3}VV$ 2nd derivative AES's for the $\theta \simeq 1.5$ surface

maximum and empty state minimum in the Al layer contact each other just at the Fermi level position. In other words, the Al introduced surface states form two dimensional metallic or semimetallic bands in the Si bandgap region. The shoulder-and-dip structure denoted by A in Fig. (1b) which coincides within experimental error with the Fermi level is then attributed to the Fermi edge in the Al 3p-like filled states. The Al 3p-like charge estimated from the Al $L_{2,3}VV$ AES intensity is almost the same as that in bulk Al, i.e., the charge transfer in this interface is small. Meanwhile, the Si layers at the interface continues semiconducting with a bandgap of 1 eV. No Fermi edge-like structure is seen in the Si 3p-like filled states. Small tailing of the Si state density into the bandgap region may exist.

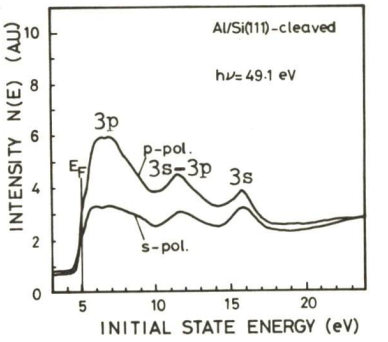

Fig. 2

Valence band EDC of the $\theta \simeq 2$ surface with s- and p-polarization configuration

Figure (2) shows EDC's of the $\theta \simeq 2$ surface taken with s- and p-polarization configurations. The 3p-like band peak intensity is about twice that for p-polarization than that for s-polarization, while 3s and 3s-3p band intensities are seen to be almost equal in these two EDC's. This suggests that filled 3p-like states near the Fermi level are mainly $3p_z$-like.

Silicon 2p core emission lines of the $\theta \simeq 1.5$ surface taken with various photon energies are shown in Fig. (3). The peak shifts to the lower energy side and the line becomes broader with increasing photon energy. When the photon energy increases, emitted electron kinetic energy also increases, resulting in a decrease in probing depth. The peak shift, therefore, is to be interpreted as originating from spatial variation of the Si 2p core binding energy. Because the electric field due to space charge is too small to account for the peak shift in such low carrier concentration samples used in the present measurements, the local field at the interface may be the only possible explanation. The peak shift can take place if one or two Si layers at the interface have somewhat lower 2p core binding energy than that of bulk Si, and this binding energy difference is accidentally comparable to the line width. Broadening of the surface Si 2p core emission line seen in Fig. (3) also suggests the existence of a local field at the interface because it could possibly cause the Si 2p

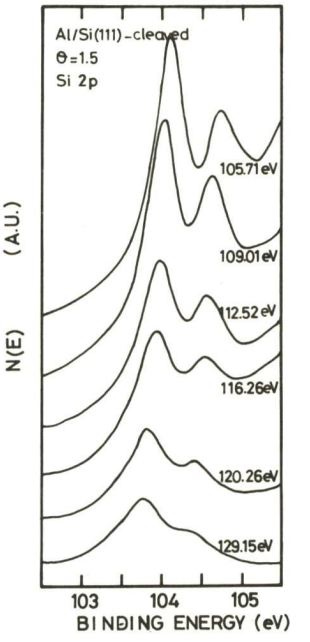

Fig. 3

Si 2p core spectra of the $\theta \simeq 1.5$ surface taken at various photon energy

core to broaden.

Figure (4) shows evolution of Al 2p core emission lines with increasing X. The lowest X spectrum has peaks at ~ 0.15 eV higher binding energy side comparing with higher X spectra. And line broadening is seen in the low X spectra. Providing these peak shift and line broadening come from the local field effect discussed above, the indiscernible peak shift and line narrowing seen in Fig. (4) in the spectra with $X \geq 1.6$ ($\theta \geq 1.5$) reasonably understood as an indication of the Al layer metalization. This interpretation is quite consistent with the appearance of Fermi edge in the Al $3p_z$ derived states when monolayer coverage is reached.

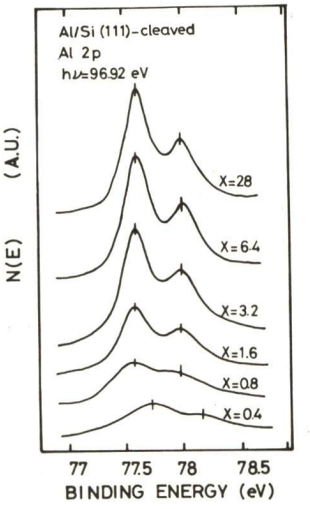

Fig. 4
Al 2p core spectra evolution during Al overlayer formation

IV. Summary

The present results are summarized as follows: Monolayer of Al on Si(111)-cleaved surface introduces an Al $3p_z$-like "metallic" band in the Si bandgap region and the Fermi level is stabilized in this band. This Al $3p_z$-like band is related to the Al-Si covalent bonds which are formed by Si dangling bond orbitals and Al $3p_z$ orbitals. A local field at the interface is assumed to come from charge redistribution at the interface due to this covalent bond formation. The work function decrease is 0.5 eV, and SB height is 0.8 eV. All these are consistent with Zhang and Schlüter's on-top covalent geometry model in the pseudopotential calculations of Al monolayer on a Si(111) surface[6].

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