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Surface and Bulk Contributions to Ultraviolet Photoemission Spectra of Silicon

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Photoemission measurements have been made on clean silicon surfaces having (111) 7×7, (111) 2×1, and (100) 2×1 low-energy electron diffraction patterns. An approximate separation of the data into surface and bulk components yields a bulk distribution which is in better agreement with the theoretical density of states than previous results. The surface distribution for the (111) 7×7 surface contains five distinct features.

Recently there has been a great deal of interest in the use of ultraviolet photoelectron spectroscopy (UPS) to obtain bulk valence-band density-of-states curves of several semiconductors.[1] Similar results[2] have also been obtained by x-ray photoelectron spectroscopy. We present UPS results for silicon which indicate that, in addition to bulk features, the experimental data contain significant contributions due to surface states over the entire ∼12-eV width of the valence band. An approximate separation of the raw data into bulk and surface contributions results in a significantly improved bulk "density of states" as well as the identification by *photoemission* of additional surface states due to lattice relaxation of the (111) surface as predicted by the calculations of Appelbaum and Hamann.[3]

Previous UPS studies of silicon have been restricted to cleaved (111) surfaces and have identified both dangling-bond surface states and bulk band-structure features.[1,4,5] The use of higher photon energies, $\hbar\omega > 12$ eV, has the advantage of exposing the entire valence band but the complication that the escape depth[4] of photoelectrons is near its minimum (5–10 Å), resulting in both surface and bulk contributions. This weights the surface more heavily than lower photon energies corresponding to longer escape depths. In this paper we present UPS results for annealed (111) and (100) silicon surfaces as well as for cleaved

(111) surfaces at a photon energy $\hbar\omega = 21.2$ eV. Similar measurements have also been performed at $\hbar\omega = 16.8$, 26.9, and 40.8 eV; however, these data will be presented in a subsequent paper.

The silicon surfaces were prepared by standard argon ion bombardment and annealing (1100 K) techniques[6] or by cleaving in a stainless steel chamber with a base pressure of $\sim 3\times10^{-11}$ Torr and were monitored by low-energy electron diffraction (LEED), Auger-electron spectroscopy, electron energy loss spectroscopy[6] (ELS), as well as by UPS.[7] LEED indicated well developed 7×7 patterns for the (111) annealed surfaces, 2 ×1 patterns (with two domains) for the (100) annealed surfaces, and 2×1 patterns (frequently with a single domain) for the cleaved surfaces. Bulk dopings were less than 5×10^{17} cm^{-3} in order to minimize band-bending effects ($l_D > 500$ Å) over the escape length of photoelectrons. Surface impurity effects were minimized by the high pumping speed (~2500 l/sec) of a 77-K titanium sublimation pump, and the maximum impurity transitions as measured by Auger-electron spectroscopy were 1000 times smaller than the 92-eV *LVV* transition of silicon. It is estimated that this corresponds to approximately 0.01 monolayer or less on the surface. Oxygen is particularly important to eliminate since more detailed studies[8] have shown that the UPS total yield at one monolayer of adsorbed oxygen is approximately 5 times that of clean silicon at $\hbar\omega = 21.2$ eV.

The experimental UPS data at $\hbar\omega = 21.2$ eV are shown in Fig. 1 for clean silicon with the following LEED patterns: (a) (111) 7×7, (b) (111) 2×1, and (c) (100) 2×1. The electron analyzer was operated in a retard mode at a constant resolution of 0.25 eV with the analyzer transmission decreasing with increasing electron energy. The residual gas as measured by a quadrupole mass spectrometer was more than 90% helium, and active gases such as CO, CH_3, and CO_2 were usually below the limit of detectability. For these conditions approximately 4 h were required to produce a measurable change in the data although each curve in Fig. 1 required only 10 min. The data were stored in a PDP-8/L minicomputer used for signal averaging and data reduction. An estimated contribution[1,4] due to secondary photoelectrons is shown as a shaded area in each of the curves. The zero of energy is taken at the valence band edge, E_v, using values of ionization energy from previous work.[9] The Fermi energy E_F was determined by substituting a metallic emitter, such as tantalum or molybdenum, for the silicon sample. The work functions derived from these measurements were 4.7, 4.8, and 4.9 ± 0.1 eV consistent with previously reported values[9] obtained by other methods. Our results on cleaved silicon are in good agreement with the data of Eastman and Grobman[1,4] and the data of Wagner and Spicer[5] even though different energy-analyzer geometries ere used. As seen in Fig. 1, the details of the UPS results are different for each of the three surfaces studied. One possibility is that these differences are due to angular effects of emission from bulk energy bands. However, this can be ruled out as the main effect because of the large solid angle of the energy analyzer and since it would predict essentially the same results for both (111) surfaces. A more likely explanation is that the electronic band structure

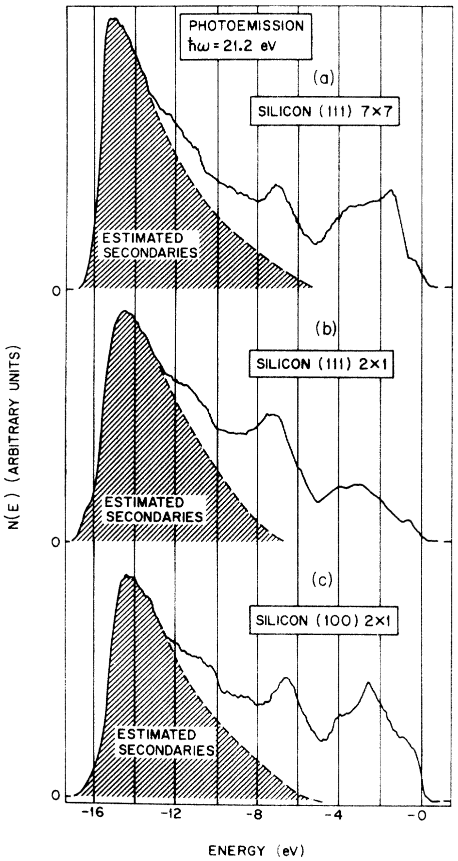

FIG. 1. Photoemission spectra at $\hbar\omega = 21.2$ eV for clean silicon surfaces with the following LEED patterns: (a) (111) 7×7, (b) (111) 2×1, and (c) (100) 2×1. The energy zero was taken at the bulk valence band maximum using ionization energies of 4.9, 5.1, and 5.2 eV for curves in (a), (b), and (c) respectively (see Ref. 9). The shaded areas show the estimated contribution of secondary electrons to the data.

is spatially dependent[10] near the surface (over a distance of 1–3 atom layers) and that one measures a mixture of surface and bulk bands due to the short escape depth (4–8 atom layers) of photoelectrons at this photon energy.

The surface effects evident from Fig. 1 extend over the entire ~ 12.5-eV width of the valence band. Thus it is not possible to separate surface and bulk contributions by adsorption studies as used in previous UPS measurements[4,5] of the dangling-bond surface states near the top of the valence band. Adsorbate states overlap low-lying silicon surface states and an alternative method of separating surface and bulk effects must be used. The bulk contribution is assumed to be an average of the experimental distributions available, since the surface electronic states are expected to appear at different energies for different LEED structures while bulk states are at the same energies.

The bulk "optical density of states" obtained by averaging the data in Fig. 1 is remarkably similar to the bulk density of states calculated by Kane[11] as shown in Fig. 2. Also shown in Fig. 2 is an x-ray emission curve due to Wiech[12] obtained by averaging the x-ray emission data for both L and K shells. The UPS results show, in general, considerably more of the predicted details than do the x-ray results as a result of higher resolution. This does *not* imply that k conservation and direct transitions are no longer important at $\hbar\omega = 21.2$ eV but that considerable averaging over final states has been performed in arriving at the results in Fig. 2. In this sense our consideration of additional surfaces is an extension of the "optical density of states" for cleaved surfaces discussed by Grobman and Eastman.[1]

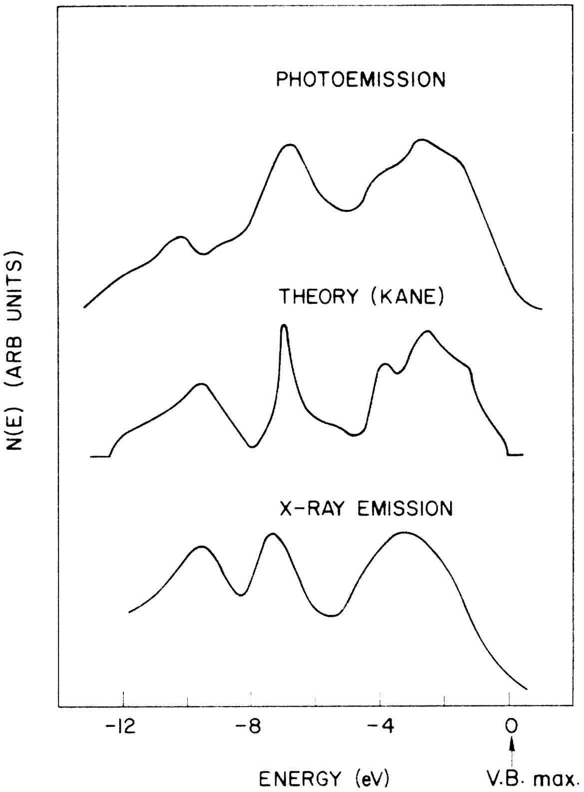

FIG. 2. Approximate bulk silicon density of states from analysis of photoemission data (see text) compared with Kane's theoretical results and with an x-ray emission "optical density of states" from Ref. 12.

The surface distributions can now be found by using the bulk distribution if the relative weight α of bulk to surface contributions is known. A more detailed discussion of the results for all three surfaces will be presented in another paper.[13] However, the results on the (111) 7×7 surface are shown in Fig. 3 with numerical values given in Table I for relative weight $\alpha = 3$. The statistical noise is approximately 3 times smaller than the peak A_1 at 0.1 eV and has been smoothed in Fig. 3. The peak positions were independent of the detailed choice of α within the uncertainty given in Table I. Of the five peaks shown, three (A_1, A_2, and A_3) are identified as surface states corresponding to the initial states of ELS transitions previously observed.[6] The other two peaks (B_1 and B_2) are identified as surface resonances because they overlap strong structure in the bulk density of states (see Fig. 2). These states could

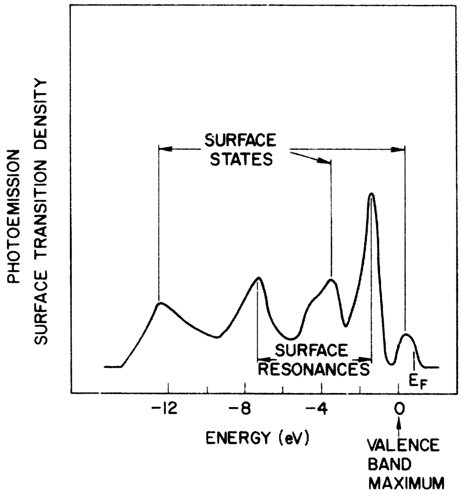

FIG. 3. Approximate surface density of states from analysis of photoemission data (see text) for the Si(111) 7×7 surface structure.

TABLE I. Surface characteristic features[a] in the photoemission transition density for the Si(111) 7 × 7 structure.

Surface state	Surface resonance[b]	Experiment (eV)	Theory (eV)
A_1	...	$+0.1 \pm 0.2$	0.0 to $+0.9$
A_2	...	-3.6 ± 0.2	-2.0 to -3.6
A_3	...	-12.3 ± 0.6	-10.7 to -12.9
...	B_1	-1.5 ± 0.2	...
...	B_2	-7.5 ± 0.4	-7 to -9[c]

[a] Energies measured relative to E_v, the valence band maximum.

[b] These could also be bound surface states in some parts of the surface Brillouin zone.

[c] Ref. 14.

also be true surface states in one part of the surface Brillouin zone and surface resonances in another part.[14] The feature B_1 has been previously identified as a surface state by Hagstrum and Becker[10] using ion neutralization spectroscopy. They also observe the surface state A_1 and the feature B_2 although there are some uncertainties in the energy scale origin for the (111) 7×7 surface.[15]

The detailed UPS results for the cleaved (111) 2×1 surfaces give a dangling-bond surface state A_1 at -0.5 eV[4,5] and back-bond surface state A_3 at -11.7 eV. The surface resonance B_2 is much more intense on the cleaved surface than on the annealed (111) 7×7. A more complete discussion of results for cleaved (111) 2×1, annealed (111) 7×7, and annealed (100) 2×1 surfaces as well as a comparison with the ELS results[6] will be presented in a later publication.[13]

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