Density of states for cleaved Si (111) from $L_1L_{2,3}V$ and $L_{2,3}VV$ Auger spectra

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The $L_1L_{2,3}V$ and $L_{2,3}VV$ Auger spectra obtained from vacuum-cleaved Si (111) surfaces have been debroadened and deconvoluted to obtain the occupied (surface) density of states (DOS) functions. Good agreement with theory is found for both transitions. In particular, the surface dangling bond state has been determined from Auger data for the first time. While the $L_1L_{2,3}V$ derived curve approximates closely to the DOS, the $L_{2,3}VV$ derived one shows suppression of the s^*s and s^*p peaks, and can be interpreted only in terms of a partial DOS.

INTRODUCTION

The occupied valence-band density-of-states function (DOS) for silicon is a fundamental electronic property and its accurate determination is important. One technique likely to provide this DOS information is Auger electron spectroscopy (AES), since Auger transitions of the type WVV and WXV (where W and X denote core states and V signifies a valence state) have inherent in them valence-band DOS information. Further, sufficient evidence is available indicating that AES and the DOS are related,[1-6] and in particular that in the case of silicon the $L_1L_{2,3}V$ and $L_{2,3}VV$ transitions exhibit this band character.[1,6-8]

In this report a detailed study of the structure of the peaks corresponding to the $L_1L_{2,3}V$ and $L_{2,3}VV$ transitions in the silicon AES spectrum is discussed. Using data analysis techniques which have been exhaustively tested with artificial data, the spectra obtained from vacuum-cleaved silicon surfaces were debroadened to remove instrumental broadening effects, debroadened to remove Coster-Kronig broadening in the $L_1L_{2,3}V$ case, and self-deconvoluted in the $L_{2,3}VV$ case with the object of obtaining an indication of the surface valence-band DOS. These results are compared with theoretical[9-12] results and with previously reported experimental[1,6-8,13-16] results for silicon, where the experimental AES results (with one exception) were obtained with surfaces cleaned *in vacuo* by the ion bombardment and annealing technique.

EXPERIMENTAL

The spectra used in this new measurement of the DOS were obtained using an ultrahigh-vacuum system with base pressure in the range 10^{-10} torr, and a Varian cylindrical mirror analyzer (CMA). The spectra were recorded in the $N'(E)$ mode using a 1.0-V peak-to-peak modulation of the potential of the external cylinder and a primary electron beam of 1.8-keV energy.

The n-type silicon crystals used were in the form of bars 20 mm long $\times 3\frac{1}{2} \times 3\frac{1}{2}$ mm, grooved prior to mounting and then cleaved *in vacuo* to expose a $3\frac{1}{2} \times 3$ mm (111) surface which contained a number of regions with significant tear marks. These regions were avoided when obtaining Auger spectra. The $N'(E)$ spectra obtained for the clean cleaved surface are shown in Fig. 1. There was

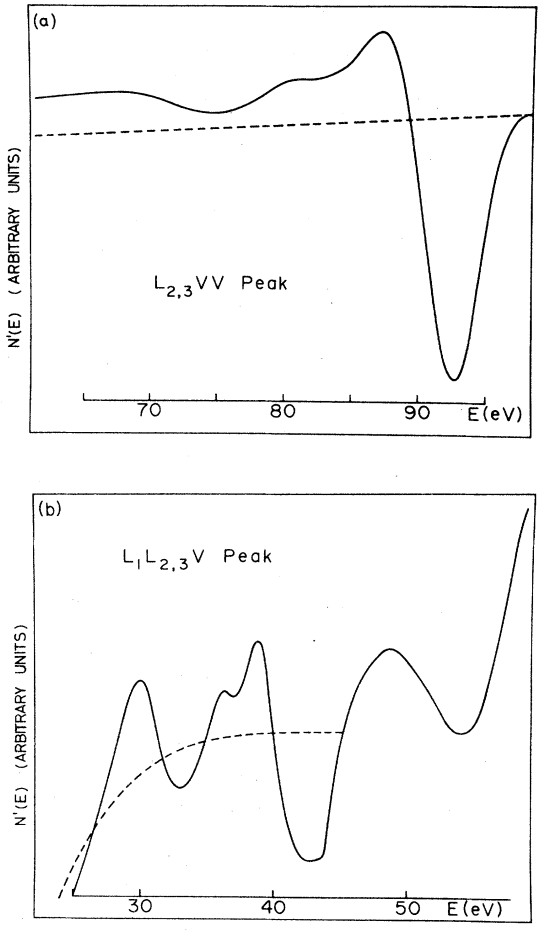

FIG. 1. Auger spectrum for a cleaved Si (111) surface: (a) $L_{2,3}VV$ peak. (b) $L_1L_{2,3}V$ peak.

no detectable change of the spectra within one hour of cleaving.

In the analysis of Auger data the elastic peak and its associated loss peaks for a primary energy near that of the Auger peak under study must be used to remove combined analyzer broadening, potential modulation broadening, and energy-loss effects.[3,17-19] The elastic peaks corresponding to the Si $L_1L_{2,3}V$ and $L_{2,3}VV$ Auger peak energies were found to have full width at half maximum (FWHM) of 1.2 and 1.6 eV, respectively, and to be characterized by a loss structure that is insignificant[16,20] in its effect on the final shape of the Auger peaks. With an increase in sensitivity of the order of 100 times, typical characteristic silicon loss spectra[21] were obtained. The very large "loss" peaks that have been reported[7,22] previously could also be obtained, but further study indicated that these peaks were spurious and associated with the crystal holder in this case. Accordingly, only the simple elastic peaks were used for instrument debroadening.

DATA ANALYSIS

To obtain the final peak shape for each of the Auger transitions the following data reduction procedures were first employed:

(i) removal of the large secondary electron background,

(ii) integration of the $N'(E)$ data,

(iii) division by E, since the result of the integration is $E \times N(E)$,[3,23] and

(iv) debroadening to remove instrument effects.

For the $L_1L_{2,3}V$ peak an additional (core) debroadening is necessary to remove the effects of Coster-Kronig broadening[1,4,12,24] while the single debroadening for the $L_{2,3}VV$ has to be followed by an unfold (self-deconvolution) procedure. This latter procedure has a number of problems associated with it, and some previously published Si $L_{2,3}VV$ peak shapes have been debroadened only. However, to make direct comparisons between the results of other theoretical and experimental determinations involving the DOS, this unfolding procedure should be carried out.

The removal of the large secondary electron background is the most difficult problem encountered in the data reduction, and neither the multiple differentiation and integration method of Houston[25,26] nor Sickafus's[27] curve-fitting technique was found to be completely satisfactory. In the case of the $L_{2,3}VV$ peak, where the background appears to be linear with a very slight positive slope [Fig. 1(a)], the following procedure was adopted. For any isolated peak, however complicated, on a smoothly varying background (curved or linear), the algebraic sum of the areas bounded by the derivative curve above and below the base line must be zero. Thus choosing a point on the $N'(E)$ curve beyond the high-energy foot of the $L_{2,3}VV$ peak as a pivot, a straight base line was swung about this point until the areas of the $N'(E)$ curve above and below the base line were equal over an appropriate range of E. It is accepted that this base line will be affected by structure further along the energy scale, i.e., at lower energy levels, but by choosing a length of base line which minimizes the slope it is believed that a good approximation to the correct background is achieved. The same technique was also used for the $L_1L_{2,3}V$ peak, except that here a quartic curve was used for the base line [see Fig. 1(b)]. It should be noted that the position on the energy scale of the various features in the resulting DOS curve is not affected significantly by quite large adjustments of the base-line curve relative to that base line used to obtain the reported results.

For debroadening, that is deconvolution with the elastic peak to remove apparatus and interaction broadening effects, an iterative self-consistent–type computer program was used, based on a method described by Taylor.[28] This program has been extensively tested with artificial data and found to give reliable results. In this testing, both simple broadening peaks similar to the elastic peak actually obtained with the spectrometer and broadening peaks with a far-from-insignificant satellite peak were used. For the "original" data, spectra with three or four sharp peaks were postulated and then the original data were convoluted with the broadening peak to obtain the "experimental" data. As criteria of the efficacy of the deconvolution routine, (i) the deconvoluted experimental data was compared by superposition with the original data and (ii) the reconvolution (i.e., the convolution of the deconvoluted experimental data with the broadening peak) was compared with the experimental data. An example of a comparison of the deconvoluted experimental data with the original data is illustrated in Fig. 2(d). Figure 2 also shows the postulated original and broadening data [Figs. 2(a) and 2(b)] and the experimental (i.e., convoluted) data [Fig. 2(c)]. Obviously while this test by superposition indicates satisfactory debroadening of artificial data, it cannot be used with actual experimental results where the original data is still being sought.

In the case of the second criterion, when the reconvolution of the deconvoluted data was compared with the experimental data, it was found that the reconvoluted data points differed on the average from the experimental data points by less than 0.1% of the height of the largest peak. This

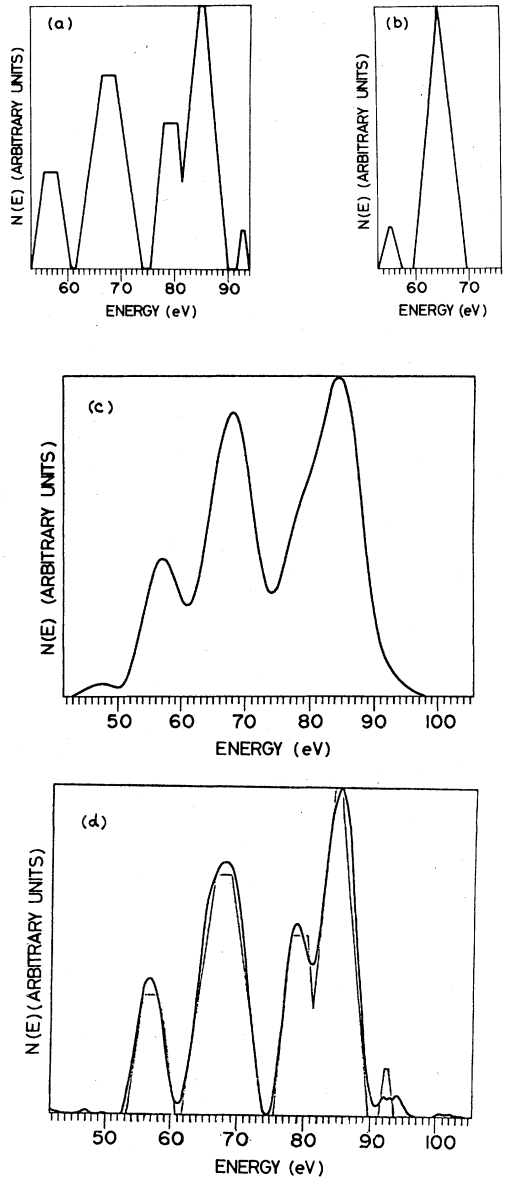

FIG. 2. Typical artificial data curves: vertical scale arbitrary. (a) Postulated "original" data; (b) postulated broadening peak with satellite; (c) convolution of curves in (a) and (b); (d) data recovered by deconvolution from (c), superimposed on original data [curve (a)].

degree of agreement using the artificial data has subsequently been found also to be the case when dealing with real experimental data. Experimental noise was not included in these trials because (a) the actual experimental data did not contain significant noise and (b) the integration process itself considerably reduces any noise that may be present. Noise introduced in the iterative debroadening process is minimized by a filter subprogram. It is intended to describe the data analysis techniques employed in a separate paper.

The $L_{2,3}VV$ data were then unfolded (deconvoluted with itself) using essentially the routine previously described by Hagstrum and Becker.[29] The only difference was in the criterion used to indicate satisfactory completion of the unfolding. In the method used, the unfolding calculations were continued out to a ξ value of 30 eV. If the choice of origin[29] was not correct, low-amplitude, low-frequency oscillations occurred, masked occasionally by large-amplitude, high-frequency noise. This high-frequency noise could always be eliminated by smoothing, which would reveal the underlying low-frequency oscillations; and these were then eliminated by shifting the origin.[29] When all periodic structure had been thus removed, a satisfactory unfold was obtained. The validity of this unfold (U) was subsequently independently confirmed in two ways: first by comparing it with the derivative (F') of the experimental data,[29,30] and secondly by convoluting it with itself. Additionally this Hagstrum and Becker procedure was tested with artificial data and very satisfactory results were obtained.

The origin shift required in this particular unfolding was 0.3 eV. The resultant self-deconvoluted $L_{2,3}VV$ peak is illustrated in Fig. 3(b). In the case of the $L_1L_{2,3}V$ peak, the next step after the debroadening to remove instrument effects is a second debroadening using the same procedure as for the first debroadening to remove the effects of Coster-Kronig broadening.[1,4,12,24] For this purpose a 1.6-eV Lorentzian peak was used and the result is shown in Fig. 3(a).

DISCUSSION

The two curves of Fig. 3 are substantially different, as predicted by recent theoretical cal-

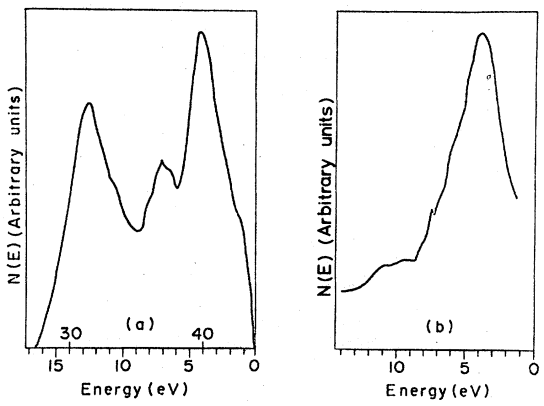

FIG. 3. (a) Silicon DOS from $L_1L_{2,3}V$ peak; (b) silicon PDOS from $L_{2,3}VV$ peak.

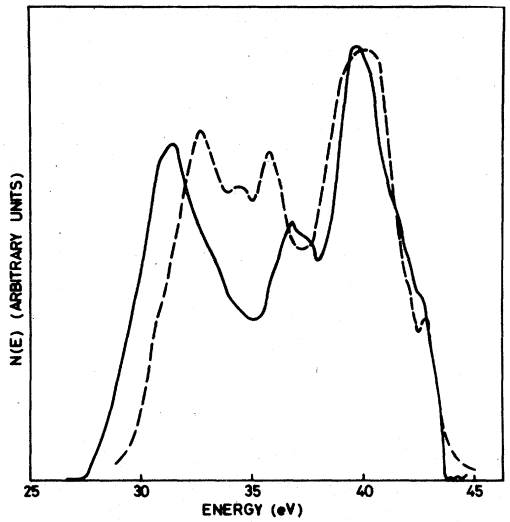

FIG. 4. Comparison of experimental data for the Si (111) $L_1L_{2,3}V$ line (solid curve) and the theoretical curve (dotted curve) of Feibelman and McGuire (Ref. 12). The energy scale corresponds to the experimental data, and the theoretical curve has been shifted to obtain agreement between them at the main peak position.

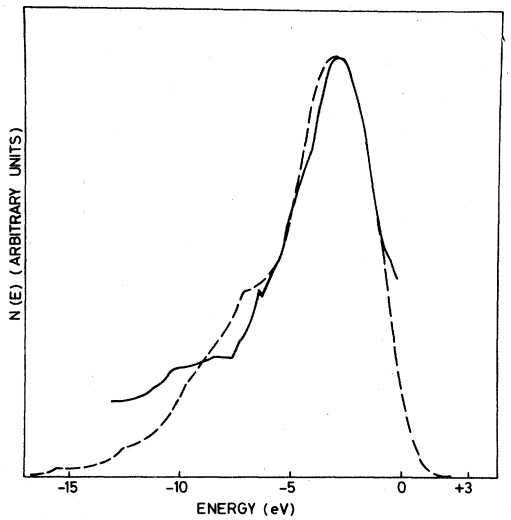

FIG. 5. Comparison of deconvoluted experimental data for the Si (111) $L_{2,3}VV$ transition and the theoretical p^*p curve of Jennison (Ref. 32). The energy scale is that for the theoretical data, and the experimental curve has been superimposed on the theoretical curve so that the main peaks coincide.

culations. The curve in Fig. 3(a), derived from the $L_1L_{2,3}V$ Auger spectrum, would seem to approximate quite closely to the theoretical surface DOS curve, while that in Fig. 3(b), derived from the $L_{2,3}VV$ spectrum, can only be a partial DOS (PDOS) curve.

Figure 4 shows a comparison of these $L_1L_{2,3}V$ data [for a (2×1) surface structure] with those calculated by Feibelman and McGuire[12] for an unreconstructed Si (111) surface broadened by a Lorentzian of 0.8-eV width.

There is a striking measure of agreement between the two curves, particularly in the number of peaks and their relative heights. Noteworthy is the definite indication of the presence of the dangling bond peak in the experimental data ~3 eV from the main peak and on the high-energy side of it. This peak has previously been found in photo-

TABLE I. Comparison of DOS measurements for Si (111). Location of principal features in eV, measured (where not tabulated by authors) from the valence-band maximum in the published curves.

Authors	Method	Main peak	Other peaks	
Feibelman and McGuire (Ref. 12)	Theory } surface	−3.9	−8.4	−11.5
Pandey and Phillips (Ref. 11)	Theory } surface	−3.9	−8.4	−10.6
This work ($L_1L_{2,3}V$)	AES } cleaved	−4.1	−6.7	−12.4
Arnott and Haneman (Ref. 16)	AES } cleaved	−4.3		−12.3
Houston, Moore, and Lagally (Ref. 12)	AES	−4.1		
Amelio (Ref. 7)	AES } ion bombarded and annealed	−2.1	−6.8	−9.1
Ferrer, Baró, and Salmerón (Ref. 8)	AES } ion bombarded and annealed	−2.8	−6.3	−10.2
Tagle *et al.* (Ref. 6)	AES } ion bombarded and annealed	−2.1	−6.9	−10.6
Rowe and Ibach (Ref. 15)	UPS	−2.8	−6.8	−10.1
Grobman and Eastman (Ref. 14)	UPS	−2.9	−6.4	−10.2
Weich (Ref. 13)	SAXS[a]	−2.5	−6.4	−8.8
Pandey and Phillips (Ref. 11)	Theory (bulk)	−2.3	−7.0	−10.0
Kane (Ref. 9)	Theory (bulk)	−2.6	−7.1	−9.7
Stukel and Euwema (Ref. 10)	Theory (bulk)	−2.7	−6.6	−9.4

[a] Small-angle x-ray scattering.

emission[15] and predicted by theory but this is the first confirmation of the presence of such a peak using Auger spectroscopy. Further, the experimental curve shows an indication of the existence of a backbonding peak ~6.5 eV from, and on the low-energy side of the main peak. Finally, there is a marked discrepancy in the overall widths and in the widths of the high-energy peak exhibited by the two curves. The overall width of the experimental curve presented here agrees extremely well with that obtained previously by Houston *et al.* and illustrated in Fig. 5 of Ref. 12. Reasons for this ~1-eV difference in width as compared with theoretical results are still unresolved. Also, both the experimental curves shown in Fig. 3 indicate a much narrower high-energy peak than has been obtained theoretically and this is possibly the reason for the middle experimental peak in Fig. 4 falling on the dip in the theoretical curve as noted previously.[12]

A more general comparison of the position (in eV) of the three main peaks in the $L_1L_{2,3}V$-derived data with previously published theoretical and experimental DOS data is given in Table I. This table shows two important results. First, there is a striking correlation between the theoretical DOS predictions for the first-atom layer of a relaxed unreconstructed Si (111) surface calculated by Pandey and Phillips[11] and Feibelman and McGuire,[12] and the results presented here for clean cleaved crystals. There is good agreement also with the Arnott and Haneman[16] and Houston, Moore, and Lagally (see Ref. 12) data. These results are consistent with the substantially surface nature of AES measurements.[4]

Second, while the ultraviolet-photon-spectroscopy (UPS) data predictably agree with the DOS calculated for bulk,[9-11] the AES data[6-8] for ion-bombarded and annealed surfaces [(7×7) structure] also agree with this bulk data rather than with that for the cleaved surface [(2×1) structure]. The question as to whether this difference is significant in terms of the surface structural changes, including surface state effects, or is due to the possibility that the annealed surface is not clean compared to that of a freshly cleaved surface, has yet to be resolved.

Finally, as discussed previously,[3,4,12,31,32] the peak heights associated with the $L_{2,3}VV$-derived experimental DOS peaks bear little relationship to the theoretical DOS values shown in Fig. 4. In this case the peak at 4 eV associated with the p^*p final state[12] is still the dominant peak of the structure, but those peaks representing the s^*p (ca. 8 eV) and the s^*s (ca. 12 eV) final states are very weak relative to the p^*p peak. This would seem to confirm that the $L_{2,3}VV$ Auger peaks are mainly associated with the p^*p state, that is, they represent only a partial DOS (PDOS), being the fold of the DOS for the p-like electron distribution. This is further confirmed by the excellent agreement between the experimental PDOS obtained here from the $L_{2,3}VV$ transition and the theoretical results of Jennison,[31,32] as shown in Fig. 5 where this experimental PDOS is superimposed on the theoretical p^*p curve.

[1]J. E. Houston, G. Moore, and M. G. Lagally, Solid State Commun. 21, 879 (1977).
[2]P. J. Feibelman and E. J. McGuire, Phys. Rev. B 15, 3575 (1977).
[3]M. A. Smith and L. L. Levenson, Phys. Rev. B 16, 2973 (1977).
[4]P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. B 16, 5499 (1977).
[5]P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. B 17, 1799 (1978).
[6]J. A. Tagle, V. M. Sáez, J. M. Rojo, and M. Salmerón, Surf. Sci. 77, 77 (1978).
[7]G. F. Amelio, Surf. Sci. 22, 301 (1970).
[8]S. Ferrer, A. M. Baró, and M. Salmerón, Solid State Commun. 16, 651 (1975).
[9]E. O. Kane, Phys. Rev. 146, 558 (1966).
[10]D. J. Stukel and R. N. Euwema, Phys. Rev. B 1, 1635 (1970).
[11]K. C. Pandey and J. C. Phillips, Phys. Rev. B 13, 750 (1976).
[12]P. J. Feibelman and E. J. McGuire, Phys. Rev. B 17, 690 (1978).
[13]G. Wiech, in *Soft X-Ray Band Spectra*, edited by D. J. Fabian (Academic, New York, 1968), pp. 59–70.
[14]W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 29, 1508 (1972).
[15]J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974).
[16]D. R. Arnott and D. Haneman, Surf. Sci. 45, 128 (1974).
[17]W. M. Mularie and W. T. Peria, Surf. Sci. 26, 125 (1971).
[18]J. E. Houston, Surf. Sci. 38, 283 (1973).
[19]J. E. Houston, J. Vac. Sci. Technol. 12, 255 (1975).
[20]M. F. Chung and L. H. Jenkins, Surf. Sci. 26, 649 (1971).
[21]J. E. Rowe, H. Ibach, and H. Froitzheim, Surf. Sci. 48, 44 (1975).
[22]W. M. Mularie and T. W. Rusch, Surf. Sci. 19, 469 (1970).
[23]R. Weibmann, W. Schnellhammer, R. Koschatzky, and K. Müller, Appl. Phys. 14, 283 (1977).
[24]G. D. Davis and M. G. Lagally, J. Vac. Sci. Technol. 15, 1311 (1978).
[25]J. E. Houston, Appl. Phys. Lett. 24, 42 (1974).
[26]J. E. Houston, Rev. Sci. Instrum. 45, 897 (1974).
[27]E. N. Sickafus, Rev. Sci. Instrum. 42, 933 (1971).

[28]K. Taylor, Astrophys. Space Science 26, 327 (1974).
[29]H. D. Hagstrum and G. E. Becker, Phys. Rev. B 4, 4187 (1971).
[30]H. D. Hagstrum and G. E. Becker, Phys. Rev. B 8, 1580 (1973).
[31]D. R. Jennison, Phys. Rev. Lett. 40, 807 (1978).
[32]D. R. Jennison, Phys. Rev. B 18, 6865 (1978).