PHYSICAL REVIEW B VOLUME 15, NUMBER 12 15 JUNE 1977

The $M_{4,5}VV$ Auger spectra of silver surfaces: An analysis based on the self-convolution of measured photoelectron spectra

James M. Burkstrand and Gary G. Tibbetts
Research Laboratories, General Motors Corporation, Warren, Michigan 48090

(Received 27 September 1976)

Our measured $M_{4,5}VV$ Auger spectra of silver and oxidized silver can be accurately described as the self-convolution of the valence-band densities of states, as approximated by measured ultraviolet photoemission spectra. While a single final-state relaxation energy shift adequately accounts for many-electron effects, inclusion of different relaxation energies for each of the three possible configurations of holes in the t_{2g} or e_g-like final states of clean silver improves the agreement.

In 1953, Lander[1] suggested that the valence-band density of states could be derived from Auger-electron-energy distributions. Since then much progress has been made in deconvoluting densities of states of *sp*-band metals.[2] Although ion-neutralization spectroscopy has been successfully used by Hagstrum[3] to derive densities of states for *d*-band metals, attempts to obtain this information using electron-stimulated Auger-electron spectroscopy have been generally fruitless. Auger studies of Zn and Cu,[4] and Ni and Cu,[5] have recently utilized quasiatomic rather than bandlike descriptions of the final states, implying a strongly localized interaction between the two final-state holes.

The Ag $M_{4,5}VV$ Auger spectrum has been investigated by Powell[6] and by Bassett *et al.*[7] Powell self-convoluted a measured low-resolution valence-band x-ray photoemission spectrum and noted that the calculated linewidth was much broader than the experimental one. He concluded that a quasiatomic explanation of this spectrum was necessary. Bassett *et al.* noted, as did Powell, that too large an energy shift was required for any possible free-electron-like description to adequately describe this Auger spectrum, so they tried to construct a spectrum of possible quasiatomic final states from optical data. The large number of Ag III ($4d^8 5s$) states available for manipulation made this possible, but the agreement was not convincing.

Our results indicate that the silver $M_{4,5}VV$ spectrum can indeed be simply related to the density of initial states if a simple many-electron correction is included. Using our measured He II ultraviolet-photoemission spectra (UPS) as an approximation to the density of initial states, we can explain the major features of the measured Auger spectra, including the full width at half-maximum (FWHM), without involving multiplet structure.

We have described our apparatus and procedures in a previous publication.[8] As in Ref. 8, all of the data presented here were taken with the crystal surface at right angles to the symmetry axis of the cylindrical mirror analyzer. This means that only the electrons ejected in a conical sector with a half-angle of 42.3° are collected. The silver (111) single crystal was cleaned using argon ion sputtering and annealed at over 550 °C. Figure 1 shows $M_{4,5}VV$ Auger-electron spectra for clean and oxidized Ag (111) surfaces made at 0.3-eV resolution. The clean Ag results agree well with previous measurements.[6,7] The binding energies of the M_4 and M_5 silver core levels were found to be 374.5 and 368.5 eV, respectively, with x-ray photoemission spectroscopy (1253.6-eV photon energy). These binding energies did not change when the silver was oxidized. All energies are specified with respect to the Fermi energy.

The energy E of an M_5VV Auger electron may be obtained from

$$E = E_{M_5} - \zeta_1 - \zeta_2 - (F - R), \tag{1}$$

where E_{M_5} is the binding energy of the M_5 core hole, and ζ_1 and ζ_2 are the binding energies of the electrons participating in the Auger process.[9] In a first approximation, many-electron effects are taken into account in Eq. (1) by subtracting a term equal to the difference between the excess Coulomb energy F required to create a two-hole final state and a relaxation energy term R, caused by screening of the hole states. In this approximation these effects merely cause an energy displacement of the Auger spectrum.

If one makes the assumption that the probability of each electron in the valence band making an "up" or "down" Auger transition is identical, the Auger transition probability depends only on the density of states $U(\zeta)$. With the energies ζ_1 and ζ_2 referenced to an average energy ζ so that $\zeta_1 = \zeta + \Delta$, $\zeta_2 = \zeta - \Delta$, the probability of Auger ejection is proportional to $U(\zeta + \Delta)U(\zeta - \Delta)$. The total energy distribution is obtained from

$$N(2\zeta) = N[E_{M_5} - E - (F - R)] = \int_{\text{valence band}} U(\zeta + \Delta)U(\zeta - \Delta)\, d\Delta, \tag{2}$$

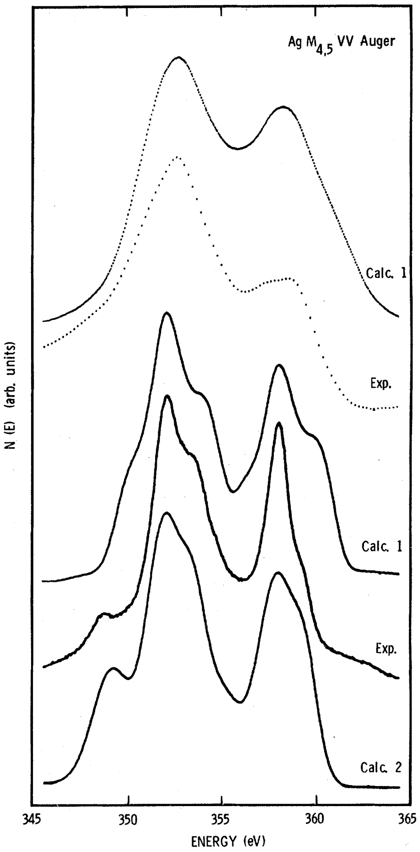

FIG. 1. Experimental and calculated silver $M_{4,5}VV$ Auger spectra for clean (full line) and oxidized (dashed line) silver (111). The inelastic background has been subtracted from the clean silver spectrum using the method of Martin (Ref. 10).

and the line shape depends only on U.

As an approximation to $U(\xi)$, the initial density of states, we use measured He II ultraviolet photoemission spectra. Figure 2 shows the UPS (40.8-eV photon energy) spectra for clean and oxygen-covered Ag(111). These spectra were taken with an energy resolution of less than 0.3 eV. To account for inelastically scattered electrons in our measured spectrum, we subtract a background correction calculated with the method of Martin.[10] This correction is shown as a dotted line in Fig. 2. The resulting profile is a good approximation to the initial density of states, as is seen by comparing our photoemission results to theoretical calculations of the silver density of states.[11-13]

A similar calculation is made for transitions involving the M_4 core level and the total $M_{4,5}VV$ spectrum is computed by summing the individual spectra. We have empirically determined $(F-R)$ by aligning one of the peaks in the measured Auger spectrum with one of the peaks in the calculated

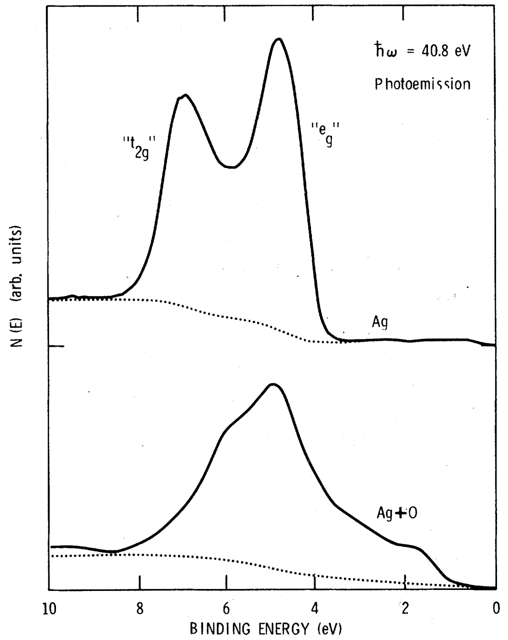

FIG. 2. He II photoemission measurements (solid curves) from clean and oxidized silver (111). The binding energies are referenced to zero at the Fermi energy. The dotted curves are the calculated inelastic backgrounds, as described in the text.

lineshape. The results are shown as calculation 1 in Fig. 1 where we have used $F-R=+5.0$ eV for clean silver and $F-R=+6.1$ eV for oxygen covered silver.

The calculation for the clean silver spectrum reproduces the number of peaks, the relative intensities, the peak position, and the peak widths. For instance, the experimental shoulders at about 353 and 359 eV are present in the clean silver calculation and the experimental shoulder at about 348.5 eV is matched by a shoulder at ~349.3 eV. The corresponding M_5VV shoulder at ~356 eV agrees in position to within 0.8 eV. The remaining four peaks agree to within 0.25 eV. Note also that the peak widths are also about 2.0 eV for both the calculated and measured spectrum. Furthermore the experimental $M_{4,5}VV$ spectrum for oxidized Ag(111) is in good agreement with the calculated line shape for oxidized Ag. Thus, in both cases we have computed the line shapes with the assumptions of constant transition matrix elements and constant energy correction $F-R$.

For free silver atoms, $F-R\approx 14$ eV.[7] Solid-state effects, including the added mobility of the two holes in the final state and the added screening by the valence band will considerably reduce this value in metallic silver. Kowalczyk *et al.*[14] calculated an $F-R$ value of 5.8 eV for this transition in silver metal, in satisfactory agreement with our experimental value of 5.0 eV. Significantly, $F-R$ for oxidized silver is somewhat higher at 6.1 eV.

This calculation and determination of $F-R$ assumes that this energy term is independent of the configuration of the two-hole final state. However, the crystal field in silver splits the d orbitals into energy regions having predominantly e_g-like or t_{2g}-like symmetry[11-13]; these regions are labeled in Fig. 2. Depending on the energies of the two final-state holes, three different many-electron corrections must be used in the above calculation for clean silver: $(F-R)_{e_ge_g}$, $(F-R)_{t_{2g}t_{2g}}$, and $(F-R)_{t_{2g}e_g}$. These factors are applied by fitting two Gaussians to the measured elastic uv photoemission spectrum (with an accuracy of 0.2% rms maximum deviation) and calculating each term in Eq. (2) with its appropriate energy correction.

Calculation 2 in Fig. 2 shows the results for $(F-R)_{t_{2g}t_{2g}}=5.8$ eV, $(F-R)_{e_ge_g}=5.3$ eV, and $(F-R)_{t_{2g}e_g}=5.0$ eV. All six peaks present in the experimental and calculated spectra agree to within 0.1 eV, with relative intensities and peak widths also in good agreement. The experimental half-widths are difficult to determine accurately because of the overlapping structure. For the two major peaks at 352.1 and 358.1 eV, we estimate that the FWHM is between 1.6 and 2.0 eV. For the corresponding calculated peaks, we find the FWHM is equal to 2.0 eV in good agreement with experiment. A more accurate calculation of the relative intensities of the peaks and shoulders must await accurate calculations of Auger matrix elements.

It should be noted that a simple change in the energy spacing of the two peaks in the UPS spectrum would not lead to improved agreement in the peak positions or widths. An increase in the UPS peak spacing only increases the energy separation between the two Auger satellite peaks associated with either of the two core holes. This will improve the agreement between one satellite and experiment, but worsen the agreement for the other. A decrease in the UPS peak spacing has the opposite effect.

The many-electron fit thus gives three slightly different values of $F-R$, with the values of hole-hole repulsion for both holes having the same symmetry being greater than if they have different symmetries. This is in accord with one's physical intuition of hole-hole repulsion.

In conclusion, we have accurately calculated the $M_{4,5}VV$ Auger line shape for both clean and oxygen covered Ag(111). This was accomplished by assuming (i) the He II UPS spectrum is a reasonable measure of the Ag initial density of states in the valence band, (ii) the transition matrix elements are constant, and (iii) to first order, the many-electron correction to the one-electron approximation is an energy shift of the calculated energy distributions. As a further refinement, we have introduced an energy correction which is a function of the final state of the system. This is justified since the crystal-field splitting allows us to separate the electrons participating in the Auger process into two predominant symmetries: t_{2g}-like and e_g-like. Our results show that if the two holes in the final state have the same symmetry, then there is a larger interaction energy than in the case with holes of different symmetry.

ACKNOWLEDGMENTS

We gratefully acknowledge Professor Gabor Somorjai for providing the Ag(111) crystal and F. J. Arlinghaus, J. G. Gay, J. R. Smith, and J. C. Tracy for helpful discussions. The skillful technical aid of D. W. Gorkiewicz and R. B. Hall is gratefully acknowledged.

---

[1] J. J. Lander, Phys. Rev. 91, 1382 (1953).

[2] For Si, see G. F. Amelio, Surf. Sci. 22, 301 (1970); and, most recently, P. J. Feibelman, E. J. McGuire and K. C. Pandey, Phys. Rev. Lett. 36, 1154 (1976); for Be, see R. G. Musket and R. J. Fortner, *ibid.* 26, 80 (1971); for Mg_2Sn, see J. Tejeda, N. J. Shevchik, D. W. Langer, and M. Cardona, *ibid.* 30, 370 (1973); for Al, see J. E. Houston, J. Vac. Sci. Technol. 12, 255 (1975).

[3] H. D. Hagstrum, Phys. Rev. 50, 495 (1966).

[4] L. Yin, I. Adler, T. Tsang, H. M. Chen, and B. Crasemann, Phys. Lett. A 46, 113 (1973).

[5] A. M. Baro, M. Salmerón, and J. M. Rojo, J. Phys. F 5, 826 (1975).

[6] C. J. Powell, Phys. Rev. Lett. 30, 1179 (1973).

[7] P. J. Bassett, T. E. Gallon, J. A. D. Matthew, and M. Prutton, Surf. Sci. 35, 63 (1973).

[8] J. M. Burkstrand, G. G. Kleiman, G. G. Tibbetts, and J. C. Tracy, J. Vac. Sci. Technol. 13, 291 (1975).

[9] C. S. Fadley and D. A. Shirley, J. Res. Nat. Bur. Stand. A 74, 543 (1970).

[10] A. D. Martin, J. Phys. D 8, 2074 (1973).

[11] N. E. Christensen, Phys. Status Solidi G 54, 551 (1972).

[12] E. C. Snow, Phys. Rev. 172, 708 (1968).

[13] C. Y. Fong, J. P. Walter, and M. L. Cohen (unpublished).

[14] S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 381 (1974).