Angular dependent uv photoemission from Ag(100) and Ag(111)

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We have measured the angular dependence of photoelectrons from epitaxially grown films of Ag(100) and Ag(111) for photon energies of 16.8, 21.2, and 26.9 eV. The data are analyzed by comparing the observed structure with peak locations predicted by direct optical bulk transitions using band-structure calculations by Christensen. Good agreement is obtained in most cases, but some discrepancies are seen in the low-energy part of the spectra.

INTRODUCTION

The experimental work of Gobeli *et al.*[1] and Kane,[2] and several theoretical investigations[3,4] showed quite early the importance of studying the angular dependence for elucidating the band structure of solids from photoelectron spectra. Here we report on an angular study of uv photoemission for photon energies of 16.8, 21.2, and 26.9 eV from the (100) and (111) faces of silver.

Silver was chosen because single crystals of silver can be grown epitaxially[5,6,7] by slow evaporation onto heated substrates. The Ag(100) was prepared by evaporation onto a single crystal of potassium chloride cleaved in air.[8] For the Ag(111) a freshly cleaved mica substrate, which had been oriented using a Laue diffraction pattern, was used. Good agreement for epitaxially grown films and bulk single crystals in the angular dependent uv photoemission has been found by Nilsson and Ilver[9,10] for gold, and this suggests that crystals of Ag should behave similarly. Further, we have found that there is good agreement between our spectra and those from bulk single crystals of Roloff and Neddermeyer[11] for the (111) direction. In the (100) direction, the agreement is not as good indicating that our (100) surface is not perfect.[7] Note, however, that different angles of incidence were used and peak heights do not necessarily have to be the same.

EXPERIMENT

The experimental setup which has been described previously by Lindau and Hagström[12] and Petersson[13] is shown in Fig. 1. The base pressure of the ion pumped UHV chamber was $\simeq 5 \times 10^{-11}$ Torr. During operation of the two-staged differentially pumped resonance lamp[14] the pressure was $\simeq 2 \times 10^{-9}$ Torr. Analysis with a residual gas analyzer showed the main residual gas during the lamp operation to be He. The small, double-focusing, spherical electron energy analyzer had an energy

resolution of $\simeq 1\%$ and an angular resolution of $\pm 3°$ vertically and $\pm 1°$ horizontally. The film thicknesses were between 1000 and 2000 Å. During evaporation the pressure rose to the low 10^{-8} or high 10^{-9} Torr region.

The sample was mounted on a rotatable feedthrough which was the common axis for sample and analyzer rotation. The plane of incidence coincides with the plane of rotation of the analyzer.

The reproducibility of the data was within the error, $\pm 2°$, of positioning the analyzer. The angles of light direction θ and electron emission ϕ were measured from the sample normal. For most of the measurements the angle of incidence was kept constant at 60°, and the analyzer was rotated around the sample in 10° increments. A check was made on both sides of the sample normal to verify the symmetry of the crystal. No corrections were made for secondary electrons or for the variation of the transmission of the analyzer as a function of electron kinetic energy.

RESULTS FOR Ag(100)

In earlier work on polycrystalline silver, using 21.2 eV photons, structure was reported at −4.4, −5.1, −5.6, and −6.2 eV by Melander[15] *et al.*, and at −4.3, −4.7, −5.2, −5.6, and −6.3 eV by Eastman and Cashion.[16]

In Fig. 2, the spectra for Ag(100), $h\nu = 21.2$ eV, are shown with peaks at the locations listed in Table I. The overall shape of the $\phi = 0°$ spectrum is similar to the spectrum from a bulk single crystal,[10] but the relative intensities of the fine structure are not identical. However, there are probably slight intensity variations due to the different angles of incidence ($\theta = 60°$ and $\theta = 80°$, respectively), see, e.g., Fig. 8. However, there are two more reasons that are probably more dominant. First, if the epitaxial film is not a perfect (100) surface there may be contributions from other regions of the Brillouin zone other than from the Γ-X direction. Second, the emission angles are very
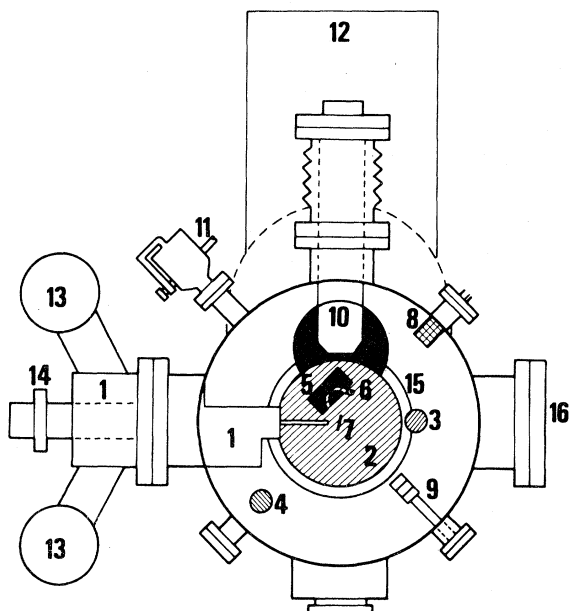

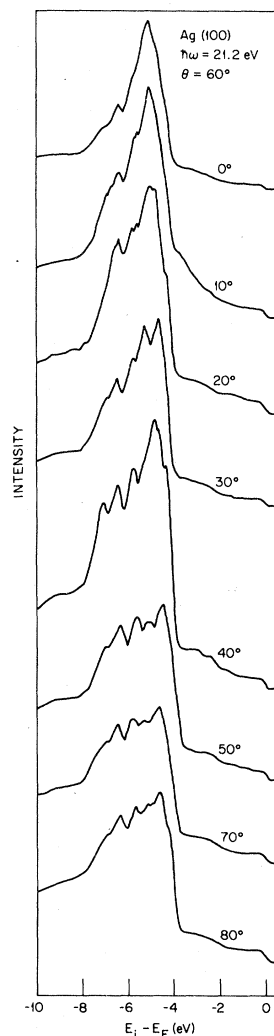FIG. 1. A schematic drawing of experimental setup. A more complete description is given in Ref. 13.

FIG. 2. Angular dependent EDC's of Ag(100) for $h\nu$ = 21.1 eV. The incident angle of the light is kept constant at 60°. All angles are measured from the surface normal and in the (001) plane.

critical near the normal and the differences in the acceptance angles of the analyzers in this case and the bulk single crystals[11] will contribute to a difference in the spectra.

Possible identification of direct transitions responsible for the structure seen in Fig. 2 was made by comparison with direct transitions occurring between bands calculated by Christensen.[17] For the $\phi = 0°$ curve, comparison could be made with the band-structure diagram for the (100) direction. Such a curve is displayed in Fig. 3. The off normal curves in Fig. 2 sample transitions occurring in the (001) plane. Using Christensen's band calculations we have mapped the behavior of the bands as they move away from the (100) axis in this plane to aid in the identification of the direct transitions responsible for the off-normal structure.

In most cases there are several possible transitions between band pairs that can account for each peak but occasionally only one interband transition matches the observed structure. In suggesting possible assignments both the peak positions and the shift of the peaks predicted by assuming direct transitions were used to assign the band pairs involved. For example, using the band diagram shown in Fig. 3, in the case of Ag(100), with $h\nu$ = 21.2 eV, the interband transition 6–10 gives a peak at −4.1 eV for $\phi = 0°$. Following this transition as $k_{\shortparallel}$ is increased, the band structure indicates that the initial state moves to a higher energy. It can be seen in Fig. 2 that as the emission is

changed from the normal to $\phi = 10°$ a broad shoulder appears at −3.8 eV. This suggests that the 6–10 transition is responsible for a portion of the high-energy shoulder for $\phi = 0°$ and also responsible for the shoulder at −3.8 eV for $\phi = 10°$. For the (100) surface there are 24 allowed direct transitions in the Γ-X direction for $h\nu$ = 21.2 eV, and peaks are predicted that match exactly with all experimental structure except those at −5.7 and −7.0 eV. For a peak at −5.7 eV the initial state would be band 3 near (0, 5, 0), where (0, 16, 0) is X, along Δ (Fig. 3). There would be a match for allowed direct transitions from bands 3–7 and 3–8 if bands 7 and 8 dropped off earlier as one moved toward X. However, for the (100) direction, the direct transition from band 3–7 does give a peak at −5.4 eV

TABLE I. Location of observed peaks for Ag(100), $\hbar\omega = 21.2$ eV.

ϕ				$|E_i - E_F|$ (eV)			
0°		4.3 [a]	4.7 [a]	5.1	5.7 [a]	6.4	7.0 [a]
10°	3.8 [a]	4.3 [a]		5.1	5.6 [a], 5.7 [a]	6.4	6.9
20°		4.3 [a]	4.8	5.1	5, 6 [a], 5.7 [a]	6.4	7.0 [a]
30°		4.5		5.1	5.6	6.3	6.8 [a]
40°		4.3	4.8, 4.9	5.3 [a]	5.7		7.0
50°	3.9 [a]		4.6	5.2	5.7	6.4	6.7, 7.0
70°		4.3 [a]	4.6	5.2	5.7	6.4	7.1 [a]
80°		4.2 [a]	4.7	5.1		6.3	6.9

[a] Shoulder.

and, following the bands as the emission angle is moved toward the (110) direction, the transitions 3–7, 3–8, and 3–9 match very well with the structure seen at –5.7 and –5.6 eV for the various emission angles. Also, for $\phi = 0°$ the transitions 1–9 and 2–9 give peaks at –6.8 and –6.7 eV, respectively. At the larger emission angles there
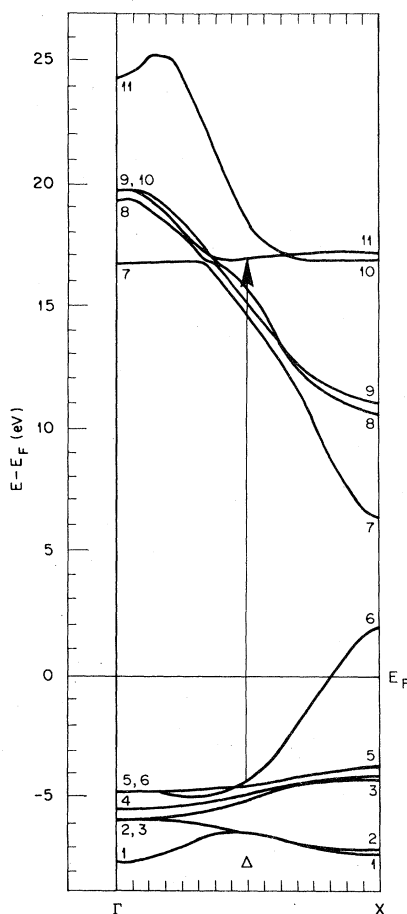

FIG. 3. Band diagrams for $\phi = 0°$. The band diagram for the (100) direction was taken from a figure in Ref. 18.

would have to be a slight lowering of bands 1, 2, and 9 at points farthest from Γ to account for the peak 7 eV below the Fermi edge by direct transitions. In the case of the structure at –6.4 and –6.3 eV the direct transitions (1 and 2) to (7 and 8) seem to be the main contributors initially, but as ϕ is increased, the interband transitions 1–(7 and 8) give the best match. In Table II a summary of the band pairs that match with the observed structures is given.

As the emission angle ϕ is increased there is a continuous change in the shape of the energy distribution curves (EDC), with only small shifts in the peak locations. On the high-energy side of the EDC around –4.3 eV the match with direct transitions varied from good to fair for the different angles. The major problem was at the low-energy side of the d band at –7.0 eV. In most cases where there was disagreement, a slight lowering of the upper bands seemed to be needed.

RESULTS FOR Ag(111)

For Ag(111) we show in Fig. 4 energy dependent spectra, $h\nu = 16.8$, 21.2, and 26.9 eV, for elec-

TABLE II. Summary of band pairs that match the observed structure seen in the EDC's of Ag(100) for a photon energy of 2.12 eV.

Experimental peak locations $\|E_i - E_F\|$ (eV)	Direct band transitions
3.8	6–10
3.9	6–9
4.3	6–9, 5–9
4.5 and 4.6	5–9
4.7 ± 0.1	5–7, 5–8, 4–9, 6–7, and 6–8
5.1 and 5.2	4–7, 4–8, 4–9, and 3–9
5.6 and 5.7	3–7, 3–8, and 3–9
6.3 and 6.4	1–(7 and 8)
	2–(7 and 8)
6.9 and 7.0	1–9 and 2–9
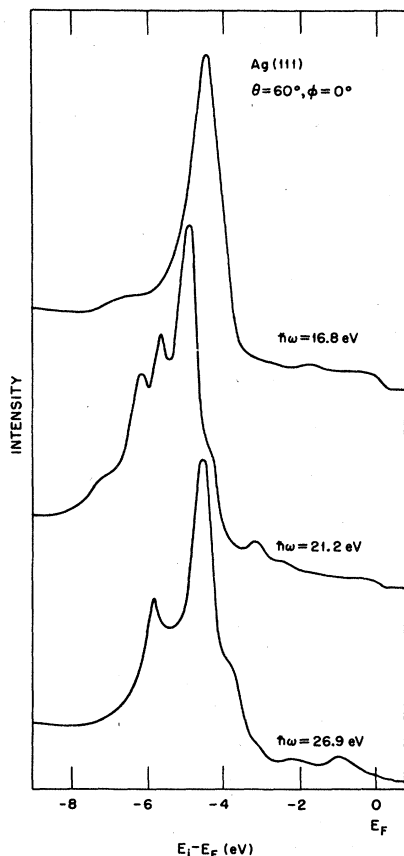
FIG. 4. EDC's of Ag(111) with emission on the (111) di- rection for different photon energies.
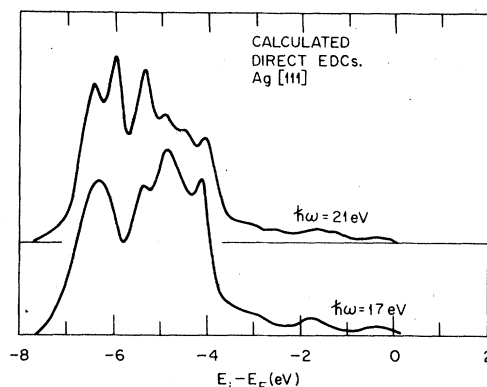

FIG. 5. Calculated EDC's of Ag(111) for $h\nu = 17.0$ and $h\nu = 21.0$ eV (from Ref. 17).

shapes but peak positions are still in good agree- ment, except for the calculated peaks around -5.3 and -6.4 eV which need to be shifted by about 0.3 and 0.6 eV, respectively.
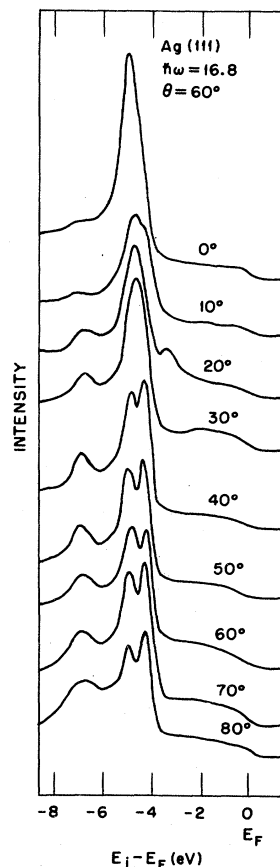

FIG. 6. Angular dependent EDC's of Ag(111) for $h\nu$ $= 16.8$ eV. The incident angle of the light is kept con- stant at 60°. All angles are measured from the surface normal and in the $(\bar{1}\bar{1}2)$ plane.

trons emitted normally from the surface. For $h\nu$ $= 16.8$ eV, the main peak is seen at -4.8 eV with small shoulders on the high- and low-energy sides and small peaks around -6.9 and -1.9 eV. These structures match the allowed direct transitions for 16.8 eV very well. The main peak corresponds to the momentum-conserving transition from band 5 to 7. Christensen[17] has calculated the EDC for the (111) direction at 17.0 eV assuming direct transi- tions (Fig. 5). The shape of the experimental and theoretical curves shows bad agreement, but a close inspection reveals that peak locations are very much the same. However, the low-energy peak in the calculated EDC needs to be shifted to a lower energy by about 0.6 eV.

For $h\nu = 21.2$ eV the main peaks are at -5.0, -5.6, and -6.2 with shoulders at -4.3 and -7.0 eV. Small peaks are also seen at -2.5 and -3.2 eV. The peak at -3.2 eV is at least partially due to the 23.1 eV HeI resonance line.[13] Again the struc- ture locations are predicted by assuming direct transitions. Comparison of this EDC with that cal- culated by Christensen[17] for $h\nu = 21.0$ eV, Fig. 5, again shows bad agreement with regard to the

Next, continuing to the spectra for $h\nu = 26.9$ eV in Fig. 4, the main peaks are at -4.8 and -6.0 eV with a pronounced shoulder at -4.0 eV and smaller structure at -1.1, -2.4, -3.3, and -6.8 eV. The peak at -1.1 eV is due to the 30.5 eV NeII resonance line.[18] There is another resonance line at 27.7 eV that will add to the shoulder at -4.0 eV, but the contribution should be small and on the order of the peak at -1.1 eV.[18] The experimental peaks were compared with the location of the peaks predicted by assuming direct transitions. There should be peaks around -4.2 eV and at -7.2 eV. Although the peaks at -4.8 and -6.0 eV are not predicted by assuming direct transitions they do match with bands 5 and 6 and bands 2 and 3 near point $(2,2,2)$, where $(8,8,8)$ is L in K space. For the final states, band 10 would have to be raised or band 11 lowered to account for observed structure. It is possible that the peaks are due to nondirect transitions. However, an angular study[19] of Ag(111) for $h\nu = 26.9$ eV shows a strong dependence on the emission angle, which indicates that direct transitions are playing the major role.

In Figs. 6 and 7 the spectra at various angles for the (111) face of Ag are shown. As the analyzer was rotated around the sample, the direction of the emitted electrons was always in the $(\bar{1}\bar{1}2)$ plane defined by the [111] and [$\bar{1}$10] directions. Figure 6 shows for $h\nu = 16.8$ eV that as ϕ is increased the main peak broadens and then, at $\phi = 40°$, splits into two peaks with energies of -4.2 and -4.7 eV. At $\phi = 20°$, a peak emerges at -3.4 eV and as the emission angle is increased to $22.5°$, $25°$, and $30°$, the peak shifts to -2.9, -2.4, and -2.0 eV, respectively. The peak is very broad at $\phi = 30°$ and has disappeared completely at $\phi = 40°$. There is also a broad peak with varying relative intensity located at around -6.8 eV. From the band calculations a check was made on the position of the direct transitions for $h\nu = 16.8$ eV. In most cases these direct transitions account very well for the structure seen in the EDC's. The shoulder at -4.2 eV which becomes a peak at larger emission angles is due to transition $6-7$. The peak around -4.7 eV in the spectra, which is due mostly to transition $5-7$ at $\phi = 0°$, appears to have increasing contributions from transitions $4-7$, $4-8$, and $5-8$ as ϕ is increased. As is the case of Ag(100) the low-energy peak around -7.0 eV does not match well with the direct transitions. The peak location predicted by the transition $1-7$, with additional contribution from the transition $1-8$ at some angles, always needs to be shifted to lower energies. The small high-energy peaks seen at $\phi = 0°$ and at angles between 20 and $30°$ (Fig. 6), seem to follow the changes in bands 6 and 8 for the different emission angles.

In Fig. 7 the angular dependent spectra for Ag

FIG. 7. Angular dependent EDC's of Ag(111) for $h\nu = 21.2$ eV. The incident angle of the light is kept constant at 60°. All angles are measured from the surface normal and in the $(\bar{1}\bar{1}2)$ plane.

(111), $h\nu = 21.2$ eV, are shown, with the peak positions given in Table III. No close study was made of the contributions seen in the s-p region for $h\nu = 21.2$ eV, but several peaks did appear for various

TABLE III. Location of experimental structure for Ag(111), $\hbar\omega = 21.2$ eV.

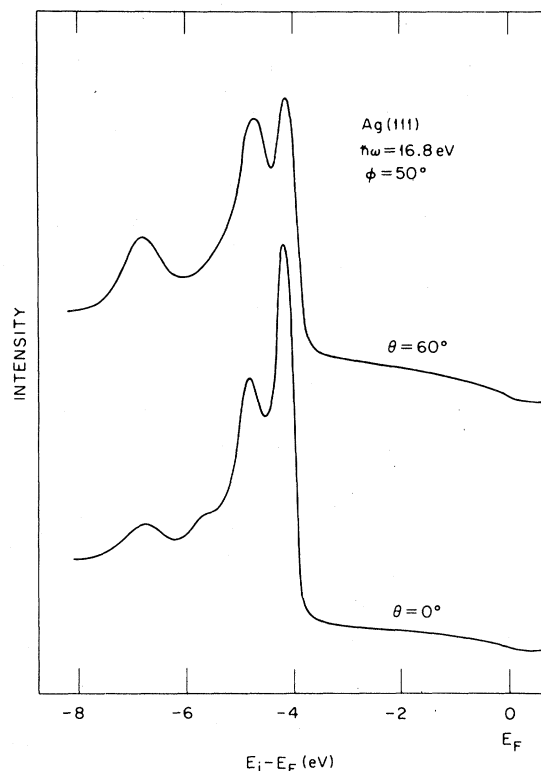| ϕ		$|E_i - E_F|$ (eV)				
0°	4.3 [a]		5.0	5.6	6.2	7.0 [a]
10°	4.3 [a]		4.9, 5.1		6.0	7.0 [a]
20°	4.2 [a]	4.6		5.4	6.2	6.9
30°	4.2		5.2	5.5	6.2	7.0
40°	4.2		5.0	5.7	6.1	6.7
50°		4.6	5.0	5.7	6.3	6.9
60°	4.3		5.2	5.5	6.3	6.8 [a]
70°	4.3		5.3	5.7	6.4	6.9 [a]
80°	4.3		5.2	5.5	6.3	6.8 [a]

[a] Shoulder.

FIG. 8. EDC's of Ag(111) for $h\nu = 16.8$ eV with the light at normal incidence and at 60° from the normal. The emission angle is 50°.

emission angles. A small peak was seen at −3.2 eV and a shoulder at −2.5 eV for $\phi = 0°$ and $\phi = 10°$. As mentioned earlier the peak at −3.2 eV is at least partially due to the 23.1 eV HeI resonance line.

Although the study was not extensive, several checks were made on the effect of varying the light incidence angle in the case of Ag(111). No change was seen in the positions of the peaks, but there was a modulation of the peak intensities. This was also observed in earlier work on gold.[10] An example is given in Fig. 8 for Ag(111), $h\nu = 16.8$ eV. Here the emission angle is 50° and the incident angle θ of the light relative to the surface normal is 0° and 60°. There was also an increase in the relative intensity of the leading peak for $h\nu = 21.2$ eV. For glancing incidence $\theta = 85°$ an angular de-

pendent series was taken for $h\nu = 21.2$ eV, and the relative intensities were found to be approximately the same as when $\theta = 60°$.

CONCLUSIONS

In this preliminary angular dependent study of Ag, most of the structure seen in EDC's could be accounted for by assuming direct transitions. However, there will have to be some adjustment of the bands to account for the low-energy peaks and, in a few cases, the high-energy peaks close to the Fermi edge. It was seen that in order to give an accurate description of the EDC's both the photon direction and emission angles must be specified. For the energy dependent spectra of Ag(111), there was a good match with the allowed direct transitions for $h\nu = 26.9$ eV. The structures of the spectra seem to be well represented by using a model of direct transitions. The remaining discrepancies seem to be due to the uncertainty of the location of the higher unoccupied bands.[17]

We have not attempted to study the surface states of the (111) face of Ag. These states are located[20,21] in the L gap but have low cross sections at the photon energies used in this investigation.

Although several evaporations and checks of the data were made, there is always the question of the quality of the silver films. A more complete study should be made of the angular dependent photoemission using cleaved and polished single crystals. Some work using oriented single crystals of silver has already been completed[21] recently.

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