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SURFACE PHOTOEMISSION IN THE 4d BAND FROM POLYCRYSTALLINE SILVER SURFACES

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Abstract

Surface induced local d-band states at the upper 4d band edge centered ∿ 4.5 eV below E_{Fermi} *have been identified for polycrystalline silver films in photoemission experiments using synchrotron radiation. A thin overcoat (10 Å) by an Al film leads to a depression of the surface induced local states, a change from s- to p-polarized excitation to an enhancement (5%), and deposition of additional silver (∿ 3 Å) at 120 K to a further enhancement (4%) of these states.*

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1. Introduction

Surface atoms experience a different local environment relative to bulk atoms which is reflected in a changed local electronic structure (potential variations, differences in bonding) near the surface compared to the bulk. In metals these changes are expected to be small, because of the short screening lengths. However, using photoemission techniques, it has recently become feasible to probe these changes in the local electronic structure near the surface for several clean metal surfaces by carefully measuring core level binding energy shifts for surface atoms (see, for example, references 1 to 4 and the references cited therein).

Surface states or resonances associated with the valence band of metals are difficult to observe experimentally, since there is no bandgap in the bulk density of states. Nevertheless, in angular resolved photoemission experiments, where $k_{\parallel}$ selected density of states (DOS) is observed, surface states have been found in s, p gaps for many nobel metals, transition metals and simple metals (see Ref. 5). Detailed calculations have indicated that these surface DOS's are generally restricted essentially to the outermost atomic layer of the samples (e.g. 6 to 9). Attempts to identify surface induced features for polycrystalline samples, thereby averaging over all angles and symmetry directions have been less successful and surface state bands or resonances have not yet been unambiguously identified (e.g. Ref. 2).

In this paper we present a direct observation of surface induced local states associated with the 4d bands of Ag on polycrystalline samples. By tuning the photon energy between 20 eV and 100 eV we were able to render the photoemission experiment extremely surface sensitive. Covering the Ag films with a thin Al overcoat leads to a depression of the surface induced features, a change from s- to p-polarized excitation leads to an enhancement, and for silver surfaces, which were prepared by depositing at 120 K a thin silver overlayer onto clean polycrystalline silver films, the surface contribution of the photoemission is further enhanced. In this way, the surface character of the local states is clearly demonstrated.

Comparing our results with recent calculations for a slab model of solid Ag by Smith et al. (8) we find a good qualitative agreement. Our results are also in accord with the general trends which can be derived from the work by Tersoff and Falicov (9) who studied the local electronic occupancy of flat and stepped (111) surfaces of Ni and Cu by LCAO calculations.

The observation of surface induced local d-band states for polycrystalline Ag films and their enhancement by cryodeposition of the silver may also yield new information concerning the origin and detailed explanation of the phenomenon of Surface Enhanced Raman Scattering (SERS) (10) from adsorbates on silver electrodes.

2. Experimental Details

Photoelectron energy distribution curves (EDC's) were measured with a commercial double-pass cylindrical mirror analyzer (CMA). Synchrotron radiation from the 5 GeV storage ring DORIS at DESY monochromatized by the FLIPPER monochromator (11) in the new synchrotron radiation laboratory in Hamburg, HASYLAB, served as a tunable light source. The count-rates were about 10^4/sec for the Ag 4d valence bands with an overall resolution (monochromator and electron energy analyzer) of 0.15 - 0.2 eV. The Ag samples were evaporated in situ onto stainless steel substrates under UHV conditions at room temperature (base pressure below 1×10^{-10}Torr, pressure during evaporation 5×10^{-10} Torr). The cryodeposited films were evaporated onto the initially prepared Ag films at 120K at a rate of 30 Å/minute. The exact microscopic structure of the films used in our experiments is not known. Thick opaque cryodeposited silver films, which are "SERS-active" (12, 13) show an extra absorption comparable to silver island films (14). This indicates a "bumpiness" of those films on a scale of 50 - 100 Å. The disorder induced Raman scattering from the accoustical phonons in these coldly evaporated silver films (13) indicates a certain concentration of bulk point defects, which are annealed near 240 K (13). We assume that a coldly evaporated silver film at 120K has more "atomic scale surface roughness" (that means a higher surface concentration of atomic scale defects of the ideal smooth surface) than a film evaporated at RT or annealed to RT (15).

The geometry used in our experiments essentially corresponds to an average over photoemission angles. The axis of the CMA is perpendicular to the incoming photon beam and tilted by 45° against the plane of the electric vector of the radiation. The samples are illuminated under 60° (measured from the surface normal) by s-polarized or p-polarized light (16). With respect to the surface normal of the sample, polar angles between 28° and 90° are accepted. The collection geometry remains unchanged for excitation with s- or p-polarized light.

3. Results and Discussion

In Fig. 1, the valence-band spectra of Ag are shown measured at three different photon energies. The EDC at $h\nu$ = 40 eV obtained at room temperature is compared to a spectrum obtained from a sample prepared and measured at 120 K. Data for all spectra have been accumulated under otherwise identical conditions. We note in passing that the angle integrated photoelectron spectrum at 40 eV closely resembles previous results obtained with $\mathrm{He}^{\mathrm{II}}$ (40.8 eV) excitation (17) and that the gross features of the angle integrated photoelectron spectra are well understood (18).

The 40 eV spectrum shows a strong peak at the upper 4d band edge at initial energy E_i = -4.2 eV which is difficult to explain. Atomic cross-section effects, as discussed by Wehner et al. (19) for the Ag 4d bands, can be ruled out as origin for the extra peak at $h\nu$ = 40 eV. The 4d cross-section shows a smooth $h\nu$ -dependence in this energy range with a broad maximum at $h\nu$ = 60 eV (19, 20). We argue that a significant part of the maximum at E_i = -4.2 eV for $h\nu$ = 40 eV is due to surface emission from the uppermost atomic layer. Several observations support this assignment:

(i) The escape depth Λ for Ag has only been determined for a few kinetic energies ($\Lambda^{7\ \mathrm{eV}}$ = 36 Å, $\Lambda^{75\ \mathrm{eV}}$ = 4 Å, $\Lambda^{350\ \mathrm{eV}}$ = 8 Å) (21). Nevertheless, it seems clear that it has its minimum below 100 eV kinetic energy with only a few Å and hence the experiment is extremely surface sensitive.

(ii) Recent self-consistent local-orbital calculations by Smith et al. (8) for Ag(100) predict a large density of surface states near the top of the 4d bands for silver. According to their calculations, the surface states contribute 22% to the charge density in the surface plane. We note that at hν = 40 eV the onset of the 4d emission is extremely sharp (HWHM = 0.15 eV) and comparable to the width of the Fermi edge (Figs. 1 and 2).

(iii) A thin overcoat by an Al film leads to a predominant attenuation of the surface induced local states at the top of the d-bands (Fig. 2), whereas the deeper lying parts of the d-bands remain essentially unchanged. Thus, the spectrum for hν = 40 eV with the Al overlayer becomes very similar to the XPS result (17) which is more representative for the bulk.

(iv) Finally, the photoemission spectra from thin (ca. 3 Å) silver films deposited at LNT onto the polycrystalline Ag samples corroborate our identification of surface induced local d-band states at the upper 4d band edge. The results in the 4d range carefully measured with good statistics are displayed in Fig. 3 (panel I) on an expanded scale. The EDC for the cryodeposited Ag-film in s-polarisation (curve c) shows a 4% increase in emission intensity in a narrow range at the top of the d-band. The emission excited with p-polarized light shows a further 5% increase for the cryodeposited Ag-film (curve b). Note that the enhancement for p-polarized geometry occurs now in a broader range of roughly 1.5 eV width. After several hours of annealing at room temperature, the cryodeposited films resemble the d-band structure of Ag prepared at room temperature. No enhanced emission in the s, p-band range extending from E_F down to - 4 eV was observed within our experimental accuracy for the same samples.

Similar observations have been made for hν = 20, 30 and 50 eV. The enhancement for cryodeposited films at the upper d-band edge has also been observed by us with unpolarized He^{I} radiation in a different apparatus. We restrict, however, the following discussion to the 40 eV spectra, since they show the most prominent effects.

In Fig. 3 we also display difference curves to enhance the visibility of the surface induced emission (curve II and IV). The intensities have been adjusted at the high binding energy part of the d-bands. These fits resulted in equal intensities in the s-band region at the same time. In order to avoid structure being introduced to the difference spectra by improper energy scale alignment, we have adjusted the curves at the top of the d-band in their energy scales. Here, shifts up to 30 meV have been applied. This is in the order of the accuracy of the measurements. Adjustment of the curves in their energy scales at the bottom of the d-bands resulted in larger intensity differences in the upper d-band range, but we prefer to display here only the more conservative results. In any case, the subsequent discussion is not depending on any of these changes, since the shape of the difference curves remains essentially unchanged. The sharp onset of the d-bands at around - 4 eV is limited by the experimental resolution. We have measured curve a and c with better overall resolution (ΔE = 0.15 eV) in order to determine precisely the onset of the difference curve IV. Again, the sharp onset of the difference curve is resolution limited.

In discussing the difference curves in Fig. 3 in more detail, we first observe a remarkable similarity of curve II (p-polarized minus s-polarized) to the surface state DOS for Ag(100) as calculated by Smith et al. (8) (histogram curve III). This difference curve is qualitatively the same, whether obtained at room temperature or at 120 K, though the difference is somewhat larger at 120K. The comparison with the calculated results for an Ag(100) surface is made in absence of any other slab calculation, although we assume largely a (111) orientation for polycrystalline films.

We can safely assume that the observed polarization effect is not due to $\underline{k}$-dispersion, since we are working with polycrystalline films and in a geometry which corresponds to an average over photoemission angles. Recent studies of surface photoemission (22), both experimental and theoretical, have shown that excitation with p-polarized light enhances the surface photoemission. Without going into a detailed discussion of this point, we can argue that the difference curve II shows a strong contribution of the uppermost layer of the Ag film to the photoemission for a binding energy range from - 4.0 to ca. - 5.5 eV. Moreover, this observation is corroborated by (i) the close similarity in width and energy position of this emission with those parts of the 4d-bands which are preferentially attenuated by the Al overlayer (Fig.2), and the preferential attenuation of photoemission at the upper 4d band edge observed in photoemission adsorbate studies on silver (e.g. Ref. 23) and (ii) by the close similarity with a calculated surface state DOS (curve III, Fig. 3). We expect this extra emission with p-polarized light to be present also on an ideally smooth single crystal surface, since it is associated with extended two-dimensional states in the surface layer.

The difference spectrum (curve IV) between a sample prepared and measured at RT minus the 120K-case shows a pronounced sharp (0.4 eV, FWHM) peak at the upper d-band edge. We associate this extra emission with defect sites at the surface (e.g. adatoms at steps, socalled "fuzzy steps"), the number of which is increased by the preparation at 120K. This interpretation is supported by the following observations: (i) the extra-emission disappears upon annealing, (ii) the difference curve IV resembles closely the photoemission spectrum from silver atoms (24, panel V). Further support of our interpretation comes from the general conclusions which can be drawn from the local density of states calculations by Tersoff and Falicov (9) for flat and stepped transition metal surfaces. In the latter investigation it was found that while there is a net deficit of electrons at the surface, the number of d-like electrons increases and further that the resulting local atomic configurations are shifted to the upper edge of the d-band for those atoms, which are positioned at edges and steps.

The annealing of the extra photoemission closely resembles the observed irreversible annealing of the "SERS-activity" (13) which has been attributed to "SERS active sites of atomic scale roughness" (25). What concerns the hypothetical nonclassical SERS mechanism beyond the classical local field enhancement (14), this present work does not indicate new electronic excitations at the clean surface in the range between 2 and 3 eV due to a different electronic structure of the surface. The present work shows changes in the electronic ground state only at energies 4 eV below the Fermi level. Provided that Koopman's theorem holds, this involves changes of the optical properties only in the spectral range above 4 eV.

However, in this context one should mention the recent observations of Schmeisser et al. (26). They report strong charge transfer excitations at 2 - 4 eV for CO, O_2, C_2H_4 and C_5H_5N adsorbed on a silver film evaporated at 20 K. These excitations are nearly absent for a silver film evaporated at RT and cooled to 20 K. This indicates that the charge transfer excitations may only exist for adsorbates at surface defect sites.

REFERENCES

+ Work supported in part by Bundesministerium für Forschung und Technologie BMFT from Funds for Research with Synchrotron Radiation

1. JOHANSSON B. and MARTENSSON N., Phys. Rev. B21, 4427 (1980).
2. CITRIN P.H., WERTHEIM G.K. and BAER Y., Phys. Rev. Lett. 41, 1425 (1978).
3. DUC T.M., GUILLOT C., LASSAILLY Y., LECANTE J., JUGUET Y. and VADRINE J.C., Phys. Rev. Lett. 43, 789 (1979).
4. Van der VEEN F.J., HIMPSEL F.J. and EASTMAN D.E., Phys. Rev. Lett. 44, 189 (1980).
5. See e.g. GARTLAND P.O. and SLAGSVOLD B.J., Phys. Rev. B12, 4047 (1975); HEIMANN P., HERMANSON J., MIOSGA H. and NEDDERMEYER H., Phys. Rev. B20, 3059 (1979); HIMPSEL F.J. and EASTMAN D.E., Phys. Rev. Lett. 41, 507 (1978); HANSSON G.V. and FLODSTRÖM, S.A., Phys. Rev. B18, 1562 (1978), HIMPSEL F.J., EASTMAN D.E. and KOCH E.E., Phys. Rev. B24, 1687 (1981).
6. See e.g. GAY J.G., SMITH J.R., ARLINGHAUS F.J. and CAPEHART T.W., Phys. Rev. B23, 1559 (1981) and references therein.
7. WANG D.-S., FREEMAN A.J., KRAKAUER H. and POSTERNAK M., Phys. Rev. B23, 1685 (1981).
8. SMITH J.R., ARLINGHAUS F.J. and GAY J.G., Phys. Rev. B22, 4757 (1980).
9. TERSOFF J. and FALICOV L.M., Phys. Rev. B24, 754 (1981).
10. CHANG R.K. and FURTAK T.E., eds., *Surface Enhanced Raman Scattering,* Pergamon Press, London (1981).
11. EBERHARDT W., KALKOFFEN G. and KUNZ C., Nucl. Instr. Methods 152, 81 (1978) and BARTH J. and GERKEN F., unpublished.
12. WOOD T.H. and KLEIN M.V., Solid State Commun. 35, 263 (1980).
13. POCKRAND I. and OTTO A., Solid State Commun. 38, 1159 (1981).
14. OTTO A. in: *Light Scattering in Solids,* CARDONA M. and GÜNTHERODT G., eds., Springer-Verlag, Heidelberg, Vol. II, in preparation and references therein.
15. OTTO A., submitted to Phys. Rev. B.
16. KALKOFFEN G., Thesis University of Hamburg, 1978.
17. HÜFNER S., WERTHEIM G.K., SMITH N.V. and TRAUM M.M., Solid State Commun. 11, 323 (1972); BATTYE F.L., GOLDMANN A., KASPER L. and HÜFNER S., Z. Physik B27, 209 (1977).
18. e.g. CHRISTENSEN N.E., phys. stat. sol. (b) 54, 551 (1972) and CHRISTENSEN N.E., J. Phys. F Metal Phys. 8, L51 (1978).
19. WEHNER P.S., STÖHR J., APAI G., McFEELY F.R., WILLIAMS R.S., SHIRLEY D.A., Phys. Rev. B14, 2411 (1976).
20. The changes of the 4d partial cross-section in the upper and lower part of the 4d bands will be discussed elsewhere.
21. PALMBERG P.W. and RHODIN T.N., J. Appl. Phys. 39, 2427 (1968); KANTER, H., Phys. Rev. B1, 522 (1970); SEAH M.P., Surface Science 32, 703 (1972).
22. LEVINSON H.J., PLUMMER E.W. and FEIBELMAN P.J., Phys. Rev. Lett. 43, 952 (1979).
23. See e.g. TIBBETTS G.G. and BURKSTRAND J.M., Phys. Rev. B16, 1536 (1977); KELEMEN S.R. and KALDOR A., Chem. Phys. Lett. 73, 205 (1980).
24. KRAUSE M.O., J. Chem. Phys. 72, 6474 (1980); DYKE J.M., FAYAD N.K., MORRIS A. and TRICKLE I.R., J.Phys. B: Atom. Molec. Phys. 12, 2985 (1979).
25. OTTO A., POCKRAND I., BILLMANN J. and PETTENKOFER C. in Ref. 10.
26. SCHMEISSER D., DEMUTH J.E. and AVOURIS, Ph., preprint: Metal-Molecule Charge Transfer Excitations on Silver Films.

Figure Captions

Fig. 1 Angle integrated photoelectron energy distribution curves excited with s-polarized light for polycrystalline silver samples for photon energies 30 eV, 40 eV and 50 eV (full curves). The films were prepared and measured at room temperature. The dashed curve for hν = 40 eV shows the enhanced emission at the upper 4d band edge for a sample prepared and measured at liquid nitrogen temperature.

Fig. 2 Photoelectron energy distribution curves at hν = 40 eV excited with s-polarized light for polycrystalline silver (full curve) in the 4d band range and for the sample with an Al cover layer of 10 Å thickness (dashed curve). Note the preferential intensity decrease at the upper d-band edge corresponding to a quenching of surface resonances.

Fig. 3 Photoelectron energy distribution curves with ΔE = 0.2 eV overall resolution at hν = 40 eV (I); difference curves (II, IV), theoretical surface density of states for Ag (100) by Smith et al. (8) (curve III) and He^{II} photoelectron spectrum for gas phase Ag by Krause (24) (curve V). In the upper panel (I) curve (a) represents the RT-s-polarized case, curve (b) the 120K-p-polarized case and curve (c) the 120K-s-polarized case. The calculated surface state DOS (curve III) has been shifted by 875 meV to larger initial energies in order to obtain an optimal fit with the experimental difference spectrum (curve II).

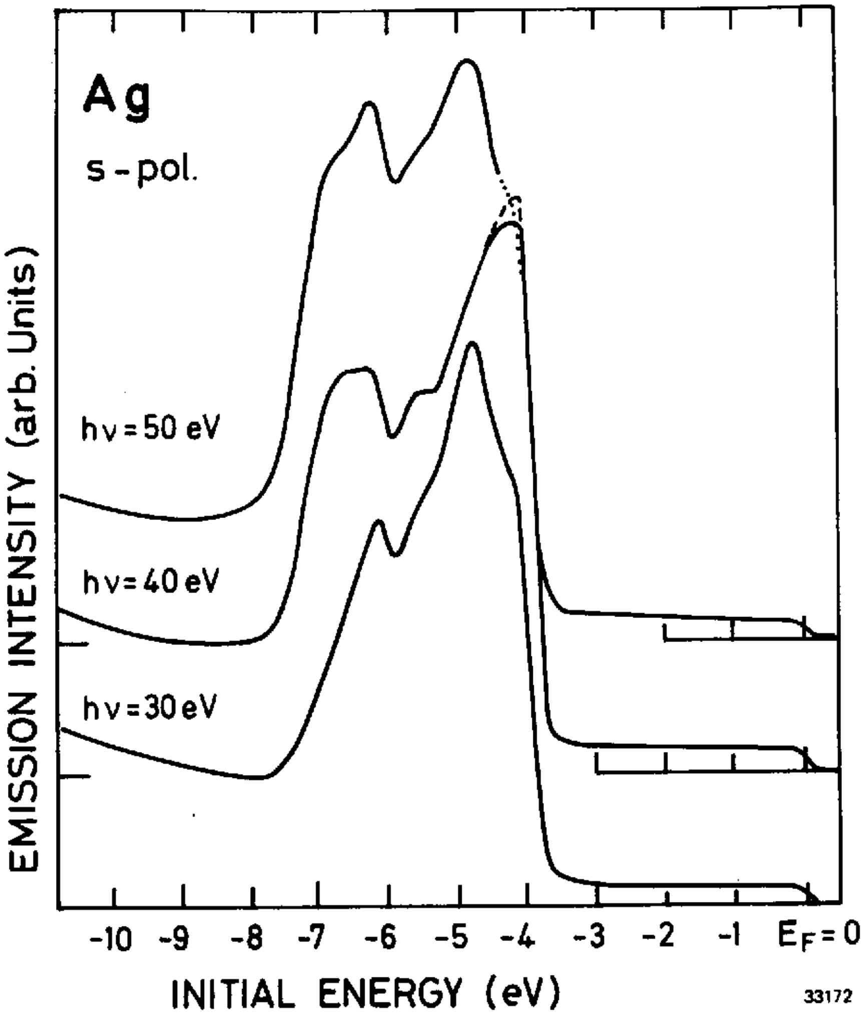

Fig. 1

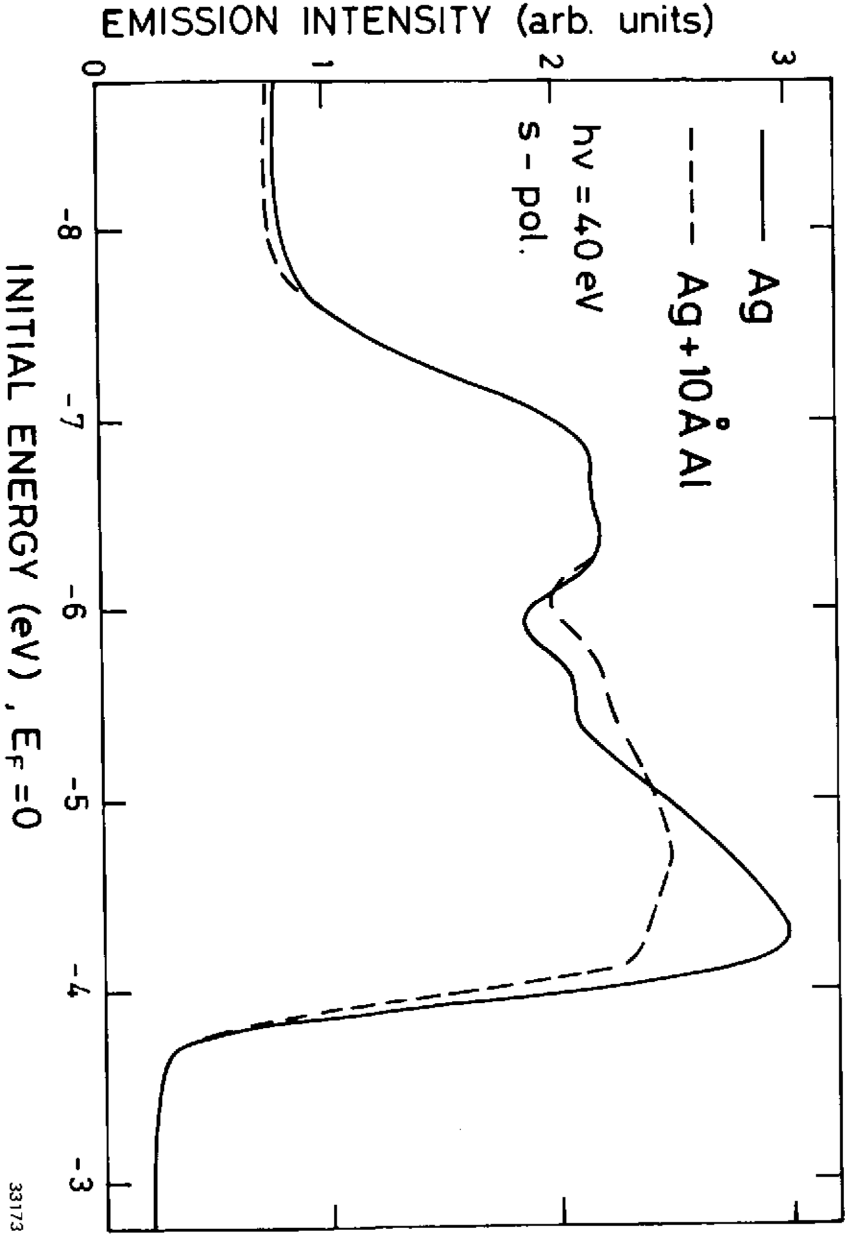
EMISSION INTENSITY (arb. units)
0
1
2
3
— Ag
- - - Ag+10Å Al
hν =40 eV
s - pol.
-8
-7
-6
-5
-4
-3
INITIAL ENERGY (eV) , E_F =0
33173

Fig. 2

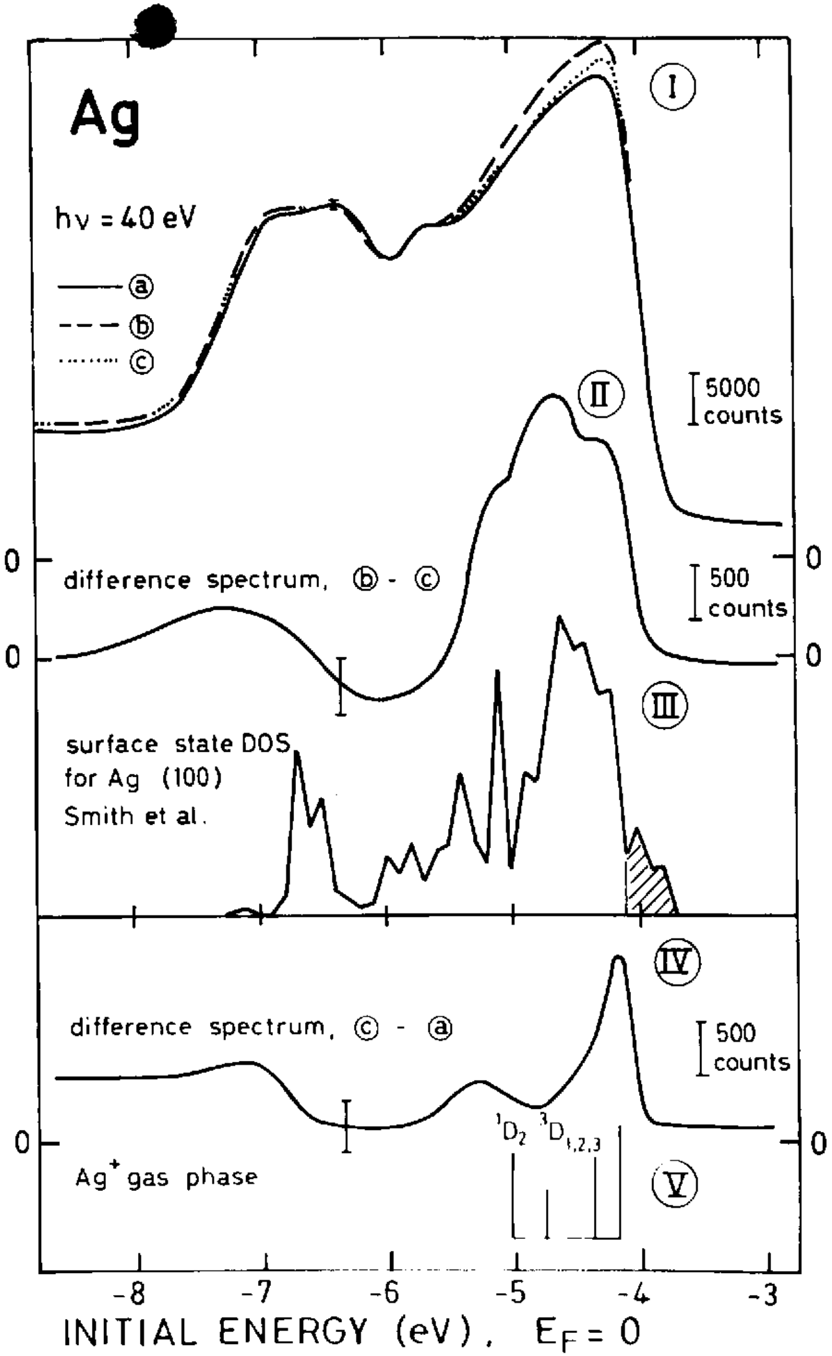
Ag
hν = 40 eV
ⓐ
ⓑ
ⓒ
Ⓘ
5000 counts
Ⅱ
0
difference spectrum, ⓑ - ⓒ
500 counts
0
0
0
Ⅲ
surface state DOS
for Ag (100)
Smith et al.
Ⅳ
difference spectrum, ⓒ - ⓐ
500 counts
0
0
$^1D_2$ $^3D_{1,2,3}$
Ag^+ gas phase
Ⅴ
-8
-7
-6
-5
-4
-3
INITIAL ENERGY (eV), E_F = 0
33304

Fig. 3