

ESCA Studies of Ag, Ag₂O and AgO

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Ag, Ag₂O, and AgO have been studied with X-ray photoelectron spectroscopy (ESCA). Attention has been paid to both photoelectrons and Auger electrons. Ag 3*d* binding energies decrease in the order Ag, Ag₂O, and AgO. The chemical shift is thus in an opposite direction here compared to all other metal-metal oxide systems reported in the literature. The chemical shift between Ag and Ag₂O is 0.4 eV and between Ag and AgO 0.7 eV. An Ag 3*d*4*d*4*d* Auger electron energy shift of 0.7 eV exists between silver in the metallic and the oxide state. In metallic Ag the 3*d*_{5/2}4*d*4*d* Auger signal is split into at least three components. The oxygen signal is the most characteristic feature of a particular compound; Ag has one O 1*s* peak at 532.2 eV, Ag₂O two peaks at 529.0 and 530.4 eV and AgO two peaks at 528.4 eV and 530.3 eV. The thermal decomposition of Ag₂O and AgO was also studied.

In X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), information is gained not only from directly excited photoelectrons but also from Auger electrons. This implies that XPS is not a very informative designation of the method, since Auger electrons are excluded. For this reason the expression ESCA is used here.

In this work metallic Ag, Ag₂O, and AgO have been studied over the temperature range 25 – 400°C. Attention has been paid to both photoelectrons and Auger electrons. The investigation has been carried out in order to get basic information that can be utilized when analyzing silver catalysts with electron spectroscopy.

EXPERIMENTAL

The experiments were performed with an AEI ES 100 electron spectrometer and the results presented here were obtained with AlK_{α1,2} radiation (1486.6 eV). The instrumental calibration has previously been described in detail,¹ according to which the binding energy of Au 4*f*_{7/2} electrons is 84.0 eV. A quadrupole mass spectrometer, AEI QMS 40, was attached to the source chamber.

Electron binding energies and Auger electron energies are given in relation to the Fermi level throughout this work.

Metallic silver studied as foil (BDH, 0.13 mm thick) whereas Ag₂O (Schuchardt, Laboratory Reagent) and AgO (BDH, Laboratory Reagent) were studied as powders fastened to a copper gauze. All three substances were studied in a temperature range from 25°C to 400°C. Information about the decomposition of the oxides was gained not only from the ESCA spectra but also from the residual gas analysis carried out by the mass spectrometer.

RESULTS AND DISCUSSION

Ag core electron spectra. The electron binding energies in metallic silver measured in this work are summarized in Table 1 together with some previously published results. Comparison with X-ray data from Bearden⁵ shows a very good consistency; the energy of Ag M_{III}M_{IV} X-rays is 229.5 eV⁵ and Table 1 gives an energy separation of 229.6 eV. Ag M_{III}M_V X-rays have an energy of 204.8 eV⁵ and exactly the same energy separation is obtained from Table 1.

Table 1. Silver electron binding energies.

Electron level	Binding energy (eV) This work	FWHM (eV) This work	Siegbahn <i>et al.</i> ²	Johansson <i>et al.</i> ³	Baer <i>et al.</i> ⁴
Ag 3s	718.4 ± 0.5	8.5	717		
Ag 3p _{1/2}	603.8 ± 0.1	3.3	602		
Ag 3p _{3/2}	572.9 ± 0.1	3.2	571	573.0	
Ag 3d _{3/2}	374.2 ± 0.1	1.15	373		
Ag 3d _{5/2}	368.1 ± 0.1	1.15	367	368.2	
Ag 4s	96.9 ± 0.2	4.9	95		
Ag 4p _{1/2}	62.7 ± 0.5		62		
Ag 4p _{3/2}	57.6 ± 0.5	12.9	56		
Ag 4d (max.)	4.8 ± 0.1	3.4	3		4.7
Ag Fermi level	0.0				

Table 2. 3d_{5/2} electron binding energies in Ag, Ag₂O, and AgO.

Compound	Binding energy (eV)	FWHM (eV)
Ag	368.1 ± 0.1	1.15
Ag ₂ O	367.7 ± 0.2	1.4
AgO	367.4 ± 0.2	1.8

Ag 3d_{5/2} electron binding energies and FWHM (full width half maximum) for Ag, Ag₂O, and AgO are given in Table 2. Normally the electron binding energy increases when a metal is oxidized, but here it is found that the Ag 3d electron binding energy decreases in the order Ag – Ag₂O – AgO. This has not been reported for any metal earlier. For copper⁶ no Cu 2p_{3/2} chemical shift was found between Cu and Cu₂O whereas in CuO a small shift to a higher binding energy was observed. FWHM for Cu 2p_{3/2} signals increased from 1.4

eV in Cu to 3.7 eV in CuO. A change in signal width is also found here in the silver-silver oxide system (Table 2).

AgO is considered to contain two kinds of silver atoms, and the formula Ag^IAg^{III}O₂ is often used.⁷ Ag^I is coordinated with two oxygen atoms and Ag^{III} with four oxygen atoms. The presence of chemically inequivalent silver atoms can be an explanation as to why the Ag 3*d* signals from AgO are broader than those from Ag and Ag₂O. However, chemically inequivalent atoms are not the only possible explanation for a broadened signal. Vacancy lifetimes also affect the line widths⁸ and multiplet splittings⁹ can give rise to broad signals. Nevertheless, the binding energy shifts are in an unexpected direction, but it should also be mentioned that the chemical shift is not a direct measure of the oxidation state, but is primarily determined by the Hartree potential.¹⁰

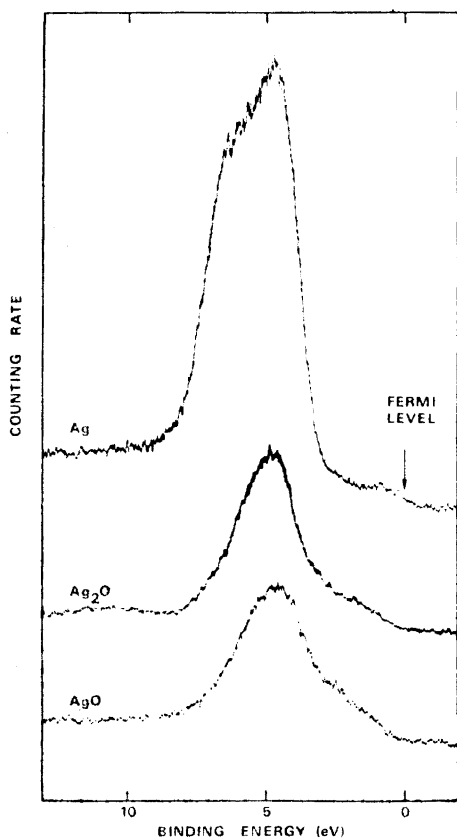


Fig. 1. Band spectra from metallic Ag, Ag₂O, AgO. Spectrum from metallic Ag recorded at 400°C. Spectra from silver oxides recorded at room temperature.

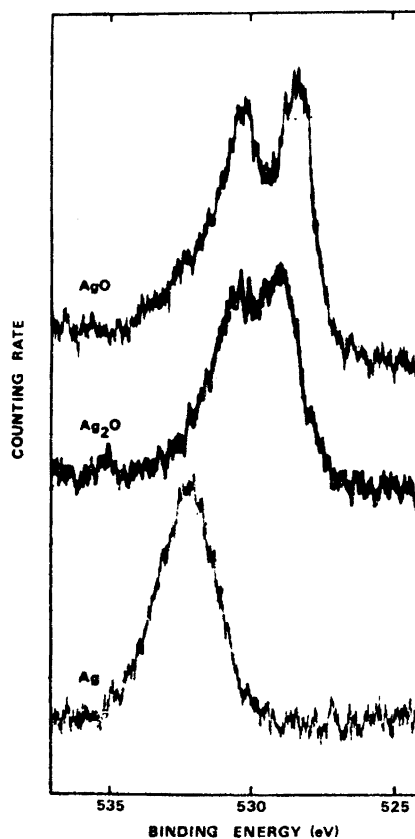


Fig. 2. Oxygen 1s spectra from metallic Ag, Ag₂O, and AgO. Spectra recorded at room temperature.

The three compounds were studied several times. Mostly no charging of the sample was found. This conclusion was drawn since the contamination carbon peak appeared at the same kinetic energy within 0.2 eV for all three compounds. The C 1s electron binding energy thus found was 284.6 ± 0.1 eV. A few times, however, the oxide samples indicated a charging of at most 0.6 eV. Both Ag 3d and C 1s electron signals were then shifted. With reference to this discussion it is concluded that the anomalous chemical shifts cannot be an effect of sample charging.

Band spectra. Distinct differences are found in the band spectra from Ag, Ag₂O, and AgO (Fig. 1). Ag₂O and AgO have a valence band structure of the same character with a maximum at 4.7 eV. The half-width in Ag₂O (2.5 eV) is smaller than in AgO (3.0 eV) and the low binding energy hump is more intense in AgO than in Ag₂O. The maximum in Ag is found at a binding energy of 4.8 eV in accordance with Baer *et al.*⁴ The Fermi level of Ag can be seen in the band spectrum at a binding energy of 0.0 eV. In Ag₂O and AgO the valence band boundary is observable at a binding energy of about 0.6 eV. Since the band gap in Ag₂O is 1.2 eV at room temperature¹¹ the Fermi level is positioned in the middle of the band gap. No band structure calculations for Ag₂O or AgO have been found in the literature with which to compare these experimental valence band structures.

Oxygen 1s electron spectra. Very characteristic differences between the three compounds are found in the oxygen 1s signals (Fig. 2). The oxygen binding energies are summarized in Table 3. In metallic silver the oxygen

Table 3. Oxygen 1s electron binding energies.

Compound	Binding energy (eV)	
Ag (25°C)	532.2 ± 0.2	
Ag (400°C)	531.4 ± 0.2	
Ag ₂ O (25°C)	530.4 ± 0.2	529.0 ± 0.2
AgO (25°C)	530.3 ± 0.2	528.4 ± 0.2

signal is due to adsorbed (or absorbed) oxygen. It is, however, possible that some other oxygen-containing molecules also contribute to the O 1s signal. When the temperature is raised to 400°C the oxygen signal decreases and changes its position from a binding energy of 532.2 eV to one of 531.4 eV. This indicates different modes of adsorbed oxygen on silver, in agreement with the general view of oxygen adsorption on silver.¹²

Oxygen found in metallic silver is quite different from oxygen present in the oxides. In both Ag₂O and AgO two distinct peaks are present. The separation in Ag₂O is 1.4 eV compared to 1.9 eV in AgO. The interpretation of these oxygen signals will be discussed in the next two sections.

Ag₂O decomposition. Ag₂O was studied at room temperature, 100, 200, 300, and 400°C. The oxygen spectra were not recorded until the sample had been kept at a particular temperature for at least 3 h. At 100°C the low-binding energy part of the oxygen signal had decreased a little, but no further

changes occurred at either 200 or 300°C. Not until 400°C was reached was an oxygen signal characteristic of metallic Ag obtained. FWHM of the Ag 3d_{5/2} signal decreased from 1.4 eV to 1.2 eV when 400°C was reached, which also indicates metallic Ag instead of Ag₂O at this temperature (Table 2).

The equilibrium oxygen partial pressure over Ag₂O is 1 atm at 190°C,¹³ but the decomposition rate is very slow at this temperature as shown by Allen,¹⁴ according to whom 5 % of the total oxygen in Ag₂O is evolved between 100 and 200°C and a further 1–2 % between 200 and 300°C. Metallic silver crystallized first above 300°C. This decomposition scheme of Ag₂O is supported by the oxygen electron spectra recorded in this work.

Since a distinct change occurred in the temperature interval 300–400°C, the decomposition was closely examined in this region. The result is shown in Fig. 3. At 300°C, as mentioned above, the O 1s spectrum is very similar to that

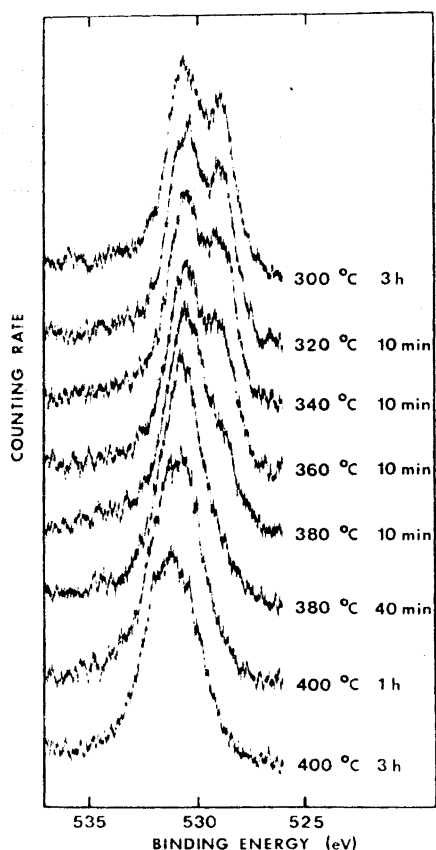


Fig. 3. Oxygen 1s spectra from Ag₂O during thermal decomposition. The figure indicates how long time the sample was kept at a particular temperature before the spectrum was recorded.

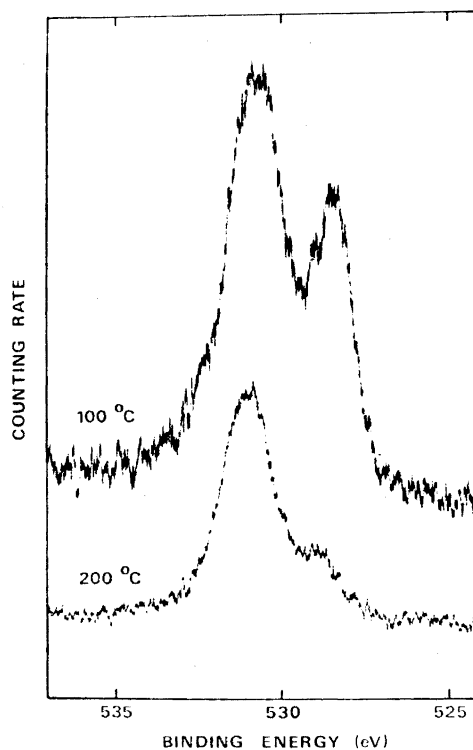


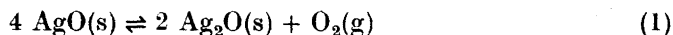
Fig. 4. Oxygen 1s spectra from AgO during thermal decomposition.

at 25°C shown in Fig. 2. The only difference is that the low-binding energy part of the signal has become somewhat smaller. Upon raising the temperature the low-binding energy peak continually decreases, and above 360°C a more rapid change is observed. After 40 min at 380°C only one oxygen peak is present. This single signal is narrow, but as the temperature is raised to 400°C a broader signal appears, simultaneously with a slight shift of the signal to a higher binding energy. The last spectrum gives an O 1s binding energy of 531.3 eV, which agrees with the O 1s binding energy observed on metallic silver foil at 400°C (Table 3).

These results indicate that the low-binding energy O 1s peak is due to lattice oxygen, since this peak decreases simultaneously with the oxide decomposition. The high-binding energy oxygen is interpreted as due to adsorbed oxygen. The binding energy of this oxygen peak changes continuously from oxygen adsorbed on Ag₂O to oxygen adsorbed on metallic Ag. The same interpretation of O 1s doublets from metal-oxygen systems have been given for, *e.g.*, Ni,^{15,16} Cu,^{6,15,17} and Zn.¹⁸

The decomposition rate was also followed by the mass spectrometer. By comparing the oxygen partial pressures at 300°C and at 380°C and relating these partial pressures with decomposition rates, an activation energy of 55 kcal/mol was calculated, in good agreement with the value given by Allen.¹⁴

AgO decomposition. AgO is much less stable than Ag₂O. It readily decomposes according to the reaction,



Allen¹⁹ studied this reaction over the temperature region 83–134°C and found an activation energy of 30 kcal/mol.

In Fig. 2 the O 1s electron spectrum from AgO at room temperature is shown. Fig. 4 shows O 1s spectra at 100 and 200°C. Already at 100°C the low-binding energy peak, which again is interpreted as due to lattice oxygen, has decreased but is still characteristic of AgO. At 200°C the lattice oxygen signal is very small and has changed its position to that of Ag₂O.

According to reaction (1), Ag₂O is present after the decomposition, which means that the position of the lattice oxygen peak at 200°C is correct. However, when comparing this spectrum with that from Ag₂O at 300°C in Fig. 3, the lattice oxygen signal is obviously much smaller in decomposed AgO than in heated Ag₂O. The spectrum of Ag₂O at 200°C was almost identical to that at 300°C. The surface composition of decomposed AgO is thus not identical to that of Ag₂O. The oxygen evolved upon AgO decomposition might give a very oxygen-rich surface layer, and this oxygen is not lattice oxygen but adsorbed or absorbed oxygen.

Both position and half-width of the Ag 3d_{5/2} signal at 200°C indicated Ag₂O and not metallic Ag. The narrow signal (1.2 eV) of metallic Ag was not found until 400°C. This excludes the possibility of metallic Ag in the surface region at 200°C, which also could have been an explanation for the low lattice oxygen signal.

Ag Auger electron spectra. In electron spectroscopy, Auger electrons are analyzed as well as directly excited photoelectrons. Fig. 5 shows Auger signals from metallic silver at 400°C. The intense doublet is due to 3d4d4d (M_{IV,V}N_{IV,V}

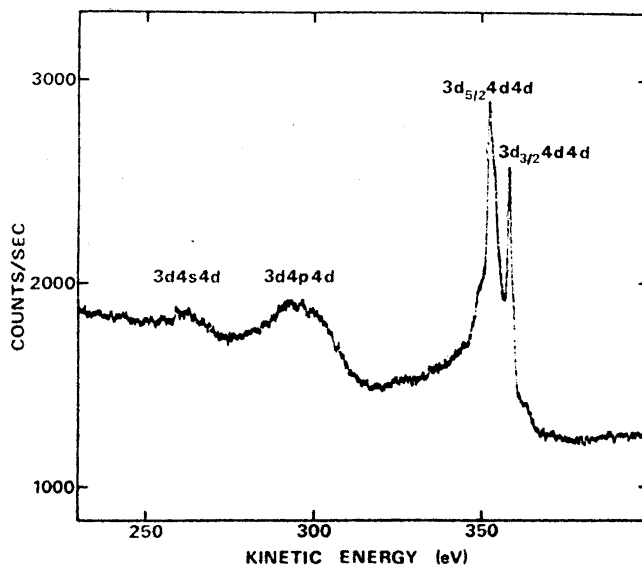


Fig. 5. Auger electron spectrum from metallic Ag. Spectrum recorded at 400°C.

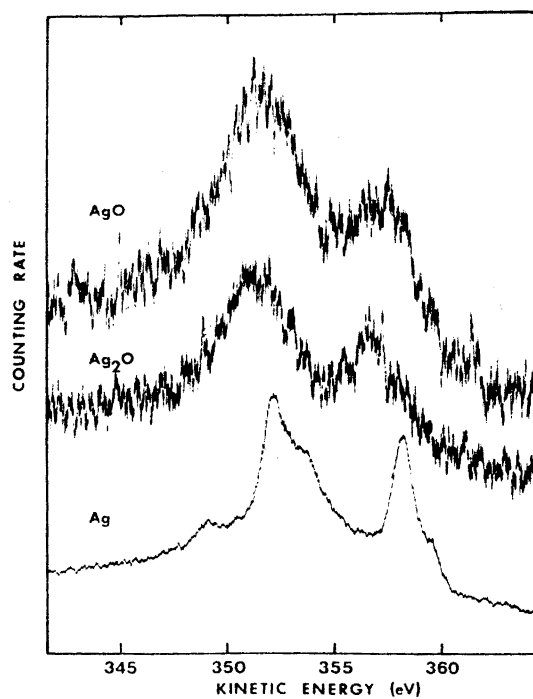


Fig. 6. Ag 3d_{4d}4d electron spectra from metallic Ag, Ag₂O, and AgO. Spectrum from metallic Ag recorded at 400°C. Spectra from silver oxides recorded at 25°C.

$N_{IV,V}$) Auger electrons and is shown in greater detail in Fig. 6. This designation means that a $3d$ vacancy is filled by a $4d$ electron with simultaneous ejection of another $4d$ electron. The two main peaks are separated by 6.1 eV, which is exactly the same difference as between Ag $3d_{5/2}$ and Ag $3d_{3/2}$ electron binding energies (Table 1). The $3d_{5/2}4d4d$ Auger signal is split into at least three components, and a similar splitting is indicated for the $3d_{3/2}4d4d$ signal.

The splittings are due to spin-orbit couplings which give rise to different final states in the Auger process.^{20,21} High resolution MNN spectra from gases have been studied extensively by, *e.g.*, Werme *et al.*²² High resolution Auger spectra from solids are not very often presented. The fine structure of the Ag $3d4d4d$ Auger electron signal was, however, partially resolved by Aksela²³ and Pattinson and Harris.²⁴ Their results are included in Table 4. According to the interpretation by Siegbahn *et al.*²⁰ the main peaks are due to 1D_2 terms.

No change in the silver Auger spectra during the temperature rise, when the adsorbed mode of oxygen changes, was observed. This supports the study by Bradshaw *et al.*²⁷ on silver, where attempts to observe chemical shifts of the silver Auger peaks were unsuccessful.

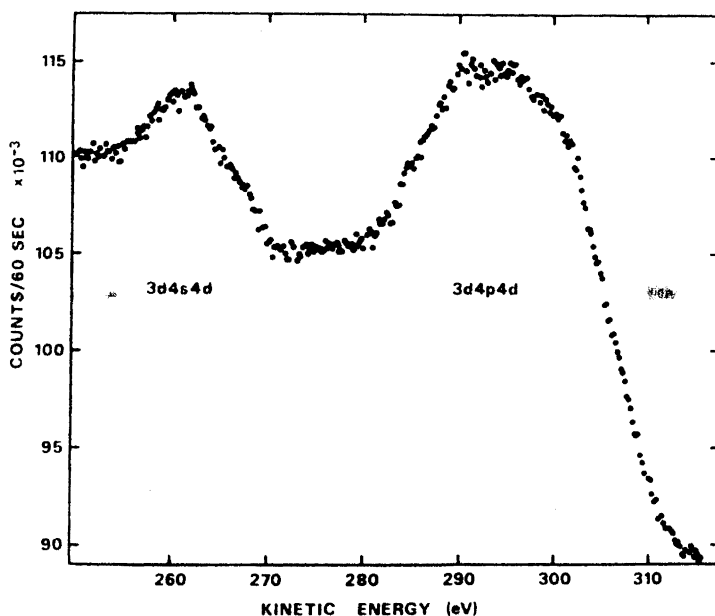


Fig. 7. $3d4s4d$ and $3d4p4d$ Auger electron signals from metallic Ag. Spectrum recorded at 400°C.

In Fig. 7 Ag $3d4s4d$ and Ag $3d4p4d$ Auger signals are shown in greater detail. The spectrum was not continuously recorded as in the previous spectra. Each point represents the number of counts during 60 sec. In the $3d4s4d$ signal a doublet is indicated by the hump about 6 eV from the main peak, which is in

accordance with a splitting due to the difference in binding energy between Ag $3d_{3/2}$ and $3d_{5/2}$ electrons. The $3d4p4d$ signal is very broad, which agrees with the broad $4p$ photoelectron signal (Table 1). No definite fine structure is resolved in this signal.

The $3d4d4d$ Auger signals from metallic Ag are very narrow, as seen in Fig. 6. The width of the $4d$ band is 3.4 eV which means that the Auger signals are narrower than a level doubly involved in the transition giving rise to the Auger electrons. This is a behaviour previously observed and discussed for Cu,¹ Zn,¹⁸ and Ga.¹⁸

In Table 4 calculated Auger electron energies are also included. The energies were calculated by the equation:

$$E_{vxy(z)} = E_{v(z)} - E_{x(z)} - E_{y(z+1)}$$

where $E_{vxy(z)}$ is the Auger electron energy in element z when a v vacancy is filled by an x electron under ejection of an y electron, $E_{v(z)}$ and $E_{x(z)}$ are binding energies of electrons v and x in element z and $E_{y(z+1)}$ is the binding energy of electron y in element $z+1$. Compared to Ag the element $z+1$ is Cd. The Cd $4d$ electron binding energy in metallic Cd is measured to 11.1 eV in this work. The Ag electron binding energies in Table 1 are used for the calculation, with an Ag $4p$ binding energy of 59.6 eV. The agreement between calculated and experimental Auger energies is very good as is shown in Table 4. The consistency between different investigations is also good.

Table 4. Silver Auger electron energies (eV).

Assignment	This work		Palmberg and Rhodin ²⁵	Aksela ²³	Pattinson and Harris ²⁴	Wagner ²⁵ (Ag ₂ O)
	Measured	Calculated				
$3d_{5/2}4s4d$	261.0 ± 0.5	260.1				
$3d_{3/2}4s4d$	267.0 ± 0.5	266.2	268			
$3d_{5/2}4p4d$		297				
$3d_{3/2}4p4d$	296 ± 1	303	308			
$3d_{5/2}4d4d$	349.1 ± 0.2					
	352.2 ± 0.2	352.2	362	353.4	352.5	351
	353.7 ± 0.2			354.6	354	
$3d_{3/2}4d4d$	358.2 ± 0.2	358.3		359.3	358.5	356
	359.5 ± 0.2					

In Fig. 6 Ag $3d4d4d$ Auger spectra from Ag₂O and AgO are also shown. These signals are broader than from metallic Ag and no fine structure is resolved. An Auger electron energy shift between metallic Ag and the silver oxides is also found, as can be deduced from Table 5. The shift of 0.7 eV is smaller than the Auger shift found between Cu and Cu₂O (1.3 eV),⁶ Zn and ZnO (4.3 eV),¹⁸ and Ga and Ga₂O₃ (5.7 eV),¹⁸ but this shift of 0.7 eV is in an opposite direction compared to the binding energy shifts discussed earlier in this paper.

Table 5. Ag 3d4d4d Auger electron energies in Ag, Ag₂O, and AgO.

Assignment	Auger electron energy (eV)		
	Ag	Ag ₂ O	AgO
3d _{5/2} 4d4d	352.2 ± 0.2	351.4 ± 0.3	351.7 ± 0.3
3d _{3/2} 4d4d	358.2 ± 0.2	356.8 ± 0.3	357.4 ± 0.3

CONCLUSIONS

The 3d electron binding energy decreases in the order Ag, Ag₂O, and AgO although the formal oxidation number increases. This has not been observed for any metal – oxygen system earlier. The Ag 3d4d4d Auger electron energies are 0.7 eV lower in the oxide state than in the metal state. Thus electron binding energies and Auger electron energies are shifted in opposite directions, which shows that the relation between Auger shifts and binding energy shifts is complex.

Different binding energies for adsorbed oxygen on silver are found, but ultrahigh vacuum conditions are necessary to make definite adsorption studies with ESCA. Oxygen signals from Ag₂O and AgO are interpreted as due to lattice oxygen and adsorbed oxygen. When the temperature is increased the lattice oxygen disappears due to decomposition, but the adsorbed mode changes its position only slightly.

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