Surface Characterization Study of the Thermal Decomposition of Ag_2O

Jason F. Weaver and Gar B. Hoflund*

Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611

Received March 8, 1994. Revised Manuscript Received June 6, 1994[⊗]

In this study the thermal decomposition of Ag_2O was examined by collecting XPS data from a pressed-powder Ag_2O sample before and after annealing at 100, 200, 300, and 490 °C. Comparative data were also collected from a polycrystalline Ag foil that had been cleaned by cycles of annealing at 500 °C and sputtering with 2-keV Ar^+ ions for an extended period. A mixture of subsurface atomic oxygen and hydroxyl groups, characterized by a broad peak in the O 1s spectrum centered at a binding energy (BE) of 531.0 eV, remains on this foil after cleaning. The compositional and chemical-state changes that occur at the Ag_2O surface during an anneal are characterized by the relative peak intensities, line-shape changes and BE shifts in the XPS spectra. The results show that the BE shift of the Ag 3d peaks obtained from Ag_2O are −0.3 eV relative to the metallic state. Several different types of contamination are present on the Ag_2O sample including a mixture of carbonate and bicarbonate species and hydrocarbon and oxygen-containing organic species. H_2O may also be present in the near-surface region of the sample. During the 100 °C anneal, a small amount of AgO and Ag metal form by disproportionation of Ag_2O. The resulting mixture yields broadened valence-band and Ag MNN features and a 0.15-eV broadening in the Ag $3d_{5/2}$ peak. Removal of about 20% of the carbon contamination also occurs during this anneal. Annealing at 200 °C causes most of the carbonate to decompose, and a small portion of the AgO decomposes to Ag_2O. Dissociation of the AgO at 300 °C produces a surface that is predominantly Ag_2O. However, a very small amount of Ag metal is present. Annealing at 490 °C for 60 min causes nearly all of the Ag_2O to decompose to Ag metal. Also, impurities including Si, S, K, and Cd contained in the bulk of the sample migrate to the surface forming a contamination overlayer. This overlayer was removed by ion sputtering, resulting in a surface that exhibits spectral features characteristic of Ag metal. The oxygen species remaining on this surface after sputtering consist of a mixture of dissolved O and OH.

Introduction

The previous study of the thermal decomposition of AgO[1] demonstrates that the presence of contaminants and multiple forms of oxygen in the near-surface region makes it difficult to understand the compositional and chemical changes that occur during reaction. As the sample is heated, numerous reactions involving both the silver oxide species and contaminants proceed at the surface at different rates depending upon the temperature. Annealing in a stepwise manner at 100, 200, 300, and 400 °C for 30 min allows the complex situation to be simplified somewhat because the various chemical changes are isolated by activation barriers to some extent. Activation barriers prevent some reactions from occurring at an appreciable rate, while other reactions may go to completion rapidly at a particular annealing temperature. Thus, comparison of the XPS spectra taken before and after a given anneal provides a means of examining the specific chemical changes that occur in the near-surface region during the anneal. Although bulk chemical reactions cannot be studied directly in this manner, the species which leave the bulk must pass through the surface region and, therefore, may contribute to the spectral features if they become trapped at the surface.

The results of the previous study[1] show that the predominant contaminant on the surface of a pressed powder AgO sample is a bicarbonate species that mostly decomposes at 100 °C. At this temperature the AgO does not decompose so the resulting spectra are characteristic of AgO. Annealing at 200 °C for 30 min results in decomposition of the AgO to Ag_2O and loss of the remaining carbonate species. The spectra obtained after this anneal exhibit Ag_2O features, but small contributions from unreacted AgO are also apparent. During the 300 °C anneal, some of the Ag_2O decomposes to Ag metal and oxygen migrates simultaneously to the near-surface region where it becomes trapped as a dissolved species when the sample is cooled. The resulting mixture of Ag_2O and Ag metal yields XPS features which contain contributions from both silver states. Nearly all of the remaining Ag_2O decomposes to silver metal during the 400 °C anneal. The most abundant form of oxygen that exists in the near-surface region after the 400 °C anneal is a dissolved, subsurface mixture of atomic oxygen and hydroxyl groups. Small amounts of remaining Ag_2O and atomically adsorbed O are also present.

The purpose of this investigation is to examine an Ag_2O surface using XPS as it is thermally decomposed in vacuum in order to observe the species formed during the decomposition and to obtain detailed XPS line-shape information from these species. XPS data were taken

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) Weaver, J. F.; Hoflund, G. B. *J. Phys. Chem.*, in press.

0897-4756/94/2806-1693$04.50/0

from an as-prepared Ag_2O powder sample, before and after annealing at 100, 200, and 300 °C for 30 min each and after annealing at 490 °C for 60 min. Similarities are observed between the data presented in this study and data taken from the AgO sample,[1] but significant differences are also found. Comparison of these data illustrates that the interaction between silver and oxygen is strongly dependent upon the history of the sample. The types and amounts of silver- and oxygen-containing species initially present on these samples dictate the chemical changes that are observed in the near-surface region during the subsequent anneals. The XPS spectra reported in this study will be useful in understanding the surface chemistry occurring in various silver–oxygen systems.

Experimental Section

The silver oxide used in this study was a high-purity powder (99.9% Ag_2O) obtained from the AESAR company. The sample was prepared by pressing the powder into a pellet in an Al cup. This as-prepared sample was then attached to a stainless steel sample holder and inserted into the ultrahigh vacuum system ($P < 1 \times 10^{-10}$ Torr). The sample heating procedure, experimental apparatus and method of XPS data collection have been described previously.[1] Survey spectra were collected at an analyzer pass energy of 50 eV and high-resolution spectra were collected at a pass energy of 25 eV using a nonmonochromatized Mg Kα X-ray source. Auger electron spectroscopy (AES) was performed in this study by operating the double-pass cylindrical mirror analyzer (CMA) in the nonretarding mode and using a primary beam energy of 3 keV. The conventional experimental geometry[2] was used to collect the AES data. Phase-sensitive detection was used with a 0.5 V_{pp}, 10 kHz sine wave applied to the outer cylinder of the CMA. Ion-scattering spectroscopy (ISS) data were collected using the CMA in the nonretarding mode, pulse counting detection,[3] a scattering angle of 144° and 1 keV He^+. The beam exposure was minimized in both AES and ISS to reduce sample alteration. Sputtering was achieved using 2 keV ions generated with a 1:1 mixture of helium and argon at 1×10^{-5} Torr. Cryogenic/titanium sublimation pumping was used during sputtering and ISS data collection to remove contaminants from the sputter gas.

Results and Discussion

As-Prepared. An XPS survey spectrum obtained from the as-prepared Ag_2O sample is shown in Figure 1. The peaks apparent in this spectrum include the Ag core-level and Auger peaks, the O 1s and Auger peaks, the C 1s peak, and the valence-band peak. Both the O 1s and C 1s peaks contain shoulders that are distinguishable in this spectrum indicating that multiple chemical states of carbon and oxygen are present on this surface. Information regarding the specific nature of these carbon and oxygen species can be gained by examining the high-resolution XPS spectra shown in Figures 2–6.

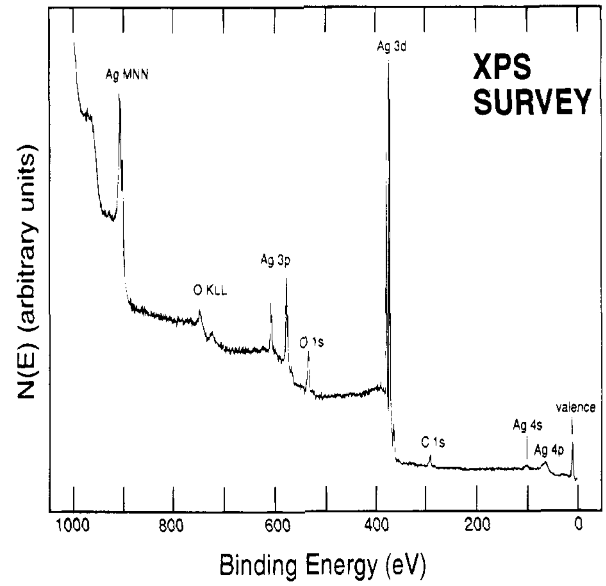

Figure 1. XPS survey spectrum obtained from the as-prepared Ag_2O sample.

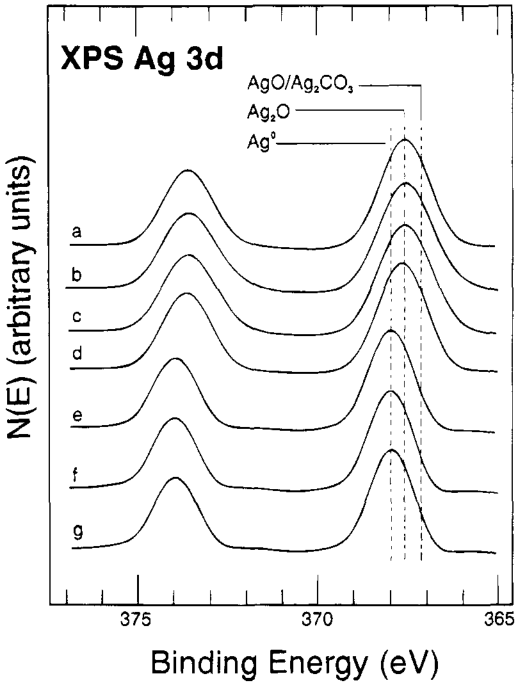

Figure 2. High-resolution XPS Ag 3d peaks obtained (a) from the as-prepared Ag_2O sample, (b) after annealing at 100 °C, (c) after annealing at 200 °C, (d) after annealing at 300 °C, (e) after annealing at 490 °C, (f) after sputtering, and (g) from the polycrystalline Ag foil after cleaning.

The Ag 3d peaks obtained from the as-prepared Ag_2O sample are presented in Figure 2a. The BE of the $3d_{5/2}$ peak is 367.7 eV referenced to the Fermi level, and it has a fwhm of 1.50 eV. These values are in good agreement with those reported by Schon[4] (BE = 367.7, fwhm = 1.6 eV), Hammond et al.[5] (BE = 367.5 eV, fwhm = 1.1 eV), Gaarenstroom and Winograd[6] (BE = 367.8 eV), and Tjeng et al.[7] (BE = 367.6 eV, fwhm = 1.5 eV). Comparison of these peaks with the 3d peaks obtained from metallic Ag (Figure 2g) reveals some major differences. The BE shift of the Ag 3d peak between Ag metal (BE = 368.0 eV) and Ag_2O (BE = 367.7 eV) is negative. This is opposite to that expected

---

[2] Hoflund, G. B.; Asbury, D. A.; Corallo, C. F.; Corallo, G. R. *J. Vac. Sci. Technol. A* **1988**, *6*, 70.

[3] Gilbert, R. E.; Cox, D. F.; Hoflund, G. B. *Rev. Sci. Instrum.* **1982**, *53*, 1281.

[4] Schon, G. *Acta Chem. Scand.* **1973**, *27*, 2623.

[5] Hammond, J. S.; Gaarenstroom, S. W.; Winograd, N. *Anal. Chem.* **1975**, *47*, 2193.

[6] Gaarenstroom, S. W.; Winograd, N. *J. Chem. Phys.* **1977**, *67*, 15.

[7] Tjeng, L. H.; Meinders, M. B. J.; van Elp, J.; Ghijsen, J.; Sawatzky, G. A.; Johnson, R. L. *Phys. Rev. B* **1990**, *41*, 3190.

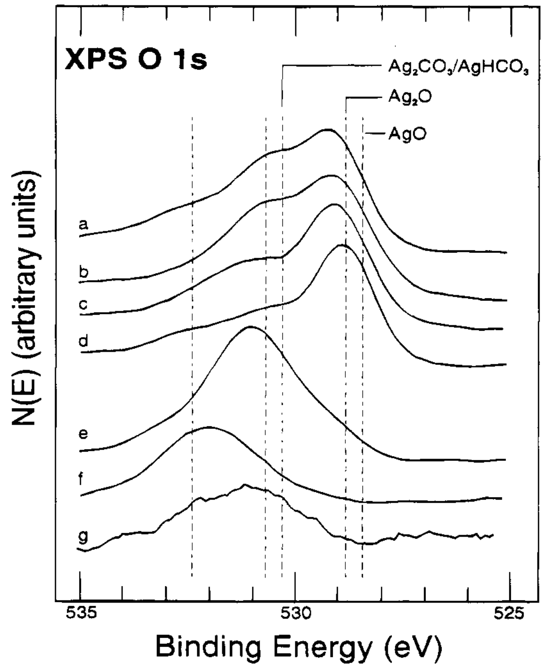

Figure 3. High-resolution XPS O 1s peaks obtained (a) from the as-prepared Ag_2O sample, (b) after annealing at 100 °C, (c) after annealing at 200 °C, (d) after annealing at 300 °C, (e) after annealing at 490 °C, (f) after sputtering, and (g) from the polycrystalline Ag foil after cleaning.

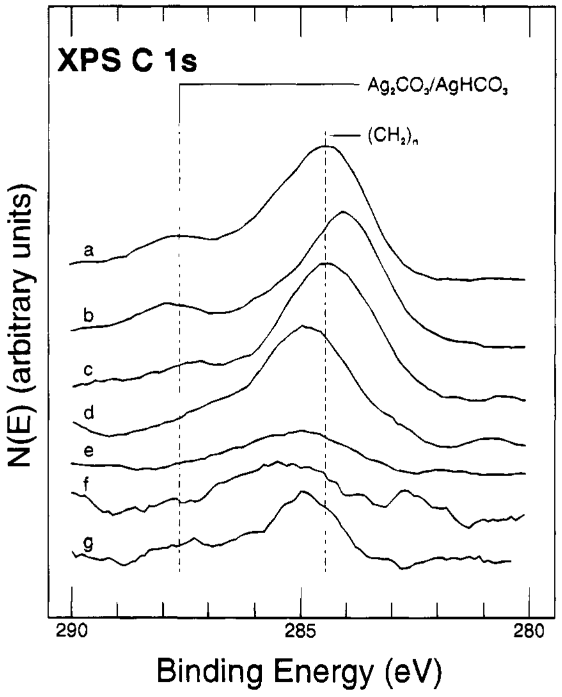

Figure 4. High-resolution XPS C 1s peaks obtained (a) from the as-prepared Ag_2O sample, (b) after annealing at 100 °C, (c) after annealing at 200 °C, (d) after annealing at 300 °C, (e) after annealing at 490 °C, (f) after sputtering, and (g) from the polycrystalline Ag foil after cleaning.

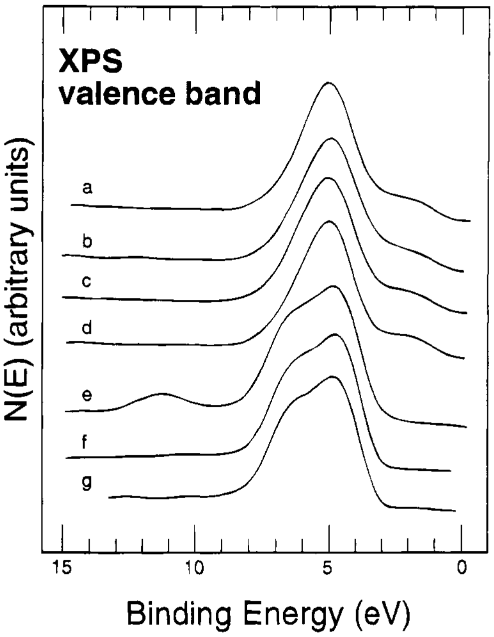

Figure 5. High-resolution XPS valence-band peaks obtained (a) from the as-prepared Ag_2O sample, (b) after annealing at 100 °C, (c) after annealing at 200 °C, (d) after annealing at 300 °C, (e) after annealing at 490 °C, (f) after sputtering, and (g) from the polycrystalline Ag foil after cleaning.

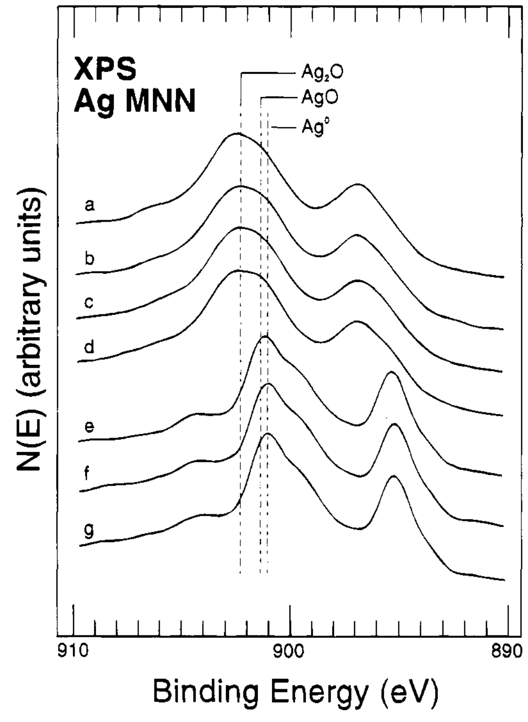

Figure 6. High-resolution XPS Ag MNN peaks obtained (a) from the as-prepared Ag_2O sample, (b) after annealing at 100 °C, (c) after annealing at 200 °C, (d) after annealing at 300 °C, (e) after annealing at 490 °C, (f) after sputtering, and (g) from the polycrystalline Ag foil after cleaning.

according to simple electronegativity arguments. As discussed previously,[1] this shift is determined by factors other than electronegativity differences such as lattice potential, work function changes and extraatomic relaxation energy. The influence of extraatomic relaxation energy on core-level BE shifts is discussed in detail by Gaarenstroom and Winograd[6] for various cadmium and silver compounds. Another difference between the Ag 3d spectra obtained from Ag_2O and Ag metal is that the peaks from Ag_2O are broader with a fwhm of 1.50 eV compared to 1.15 eV for Ag metal but not as broad as those obtained from AgO (fwhm = 1.75 eV).[1] The broad Ag 3d line shape may be due to the electronic potential in Ag_2O, unresolved contributions from different Ag chemical states as a result of interactions with contamination at the sample surface or the presence of a mixture of Ag_2O and AgO or an intermediate oxide or a defect-laden oxide resulting in multiple states that contribute to the Ag 3d spectrum. This point is discussed further below.

Curve-resolution techniques can be useful for analysis of XPS data particularly when the chemical species present, their line shapes, and their peak positions are known. Even though this is not the case in this present study, a numerical curve resolution of the spectral lines into the various contributions has been carried out using procedures described by Briggs and Seah.[8] The detailed results of the analysis are not given, but the discussion below is consistent with this analysis.

The O 1s spectrum obtained from the as-prepared Ag_2O sample is shown in Figure 3a. As expected, it reveals the presence of multiple states of oxygen. The peak due to O in Ag_2O is present at a BE of 528.8 eV.[1] This value is somewhat lower than the O 1s BEs of Ag_2O reported by Schon[4] (BE = 529.2 eV) and Hammond et al.[5] (BE = 529.0 eV). The presence of C contamination moves the apparent BE of the Ag_2O O 1s peak to higher BEs as seen in Figure 3a–d. A large shoulder almost as intense as the Ag_2O feature is present between 530.0 and 531.5 eV due to C-containing contamination. Several species probably contribute to this feature. A peak at 530.2 eV was previously assigned to a carbonate species that forms on the sample surface during air exposure.[1] This BE is in good agreement with the O 1s BE reported by many authors for Ag_2CO_3.[5,9–13] Another feature at 531.3 eV probably results from the presence of other oxygen-containing carbon contamination. A small peak at 532.4 eV also appears in Figure 3a which probably arises from the presence of adsorbed water, but an oxygen-containing carbon compound may also contribute in this region as discussed below.

The C 1s spectrum taken from the as-prepared Ag_2O sample is shown in Figure 4a. Two distinct BE regions containing peaks are observed in this spectrum. The first is centered around 284.5 eV. The predominant asymmetric peak is due to a mixture of adsorbed hydrocarbons and oxygen-containing carbon compounds. The latter is responsible for the discernible shoulder at a BE of 285.3 eV. The higher BE peak lies in the vicinity of surface Ag carbonate.[5,9–13] It has a low intensity and is slightly asymmetrical. Previously,[1] a peak was reported at a BE of 287.3 eV which differs from literature values of the C 1s BE from Ag_2CO_3 (288.0 eV). On the basis of this BE discrepancy and the fact that decomposition occurs at 100 °C, which is about 100 °C below that of Ag carbonate decomposition, this peak was assigned as due to a bicarbonate species. Thus, the broad feature centered at 287.6 eV in Figure 4a is believed to originate from a mixture of $AgHCO_3$ and Ag_2CO_3.

The valence-band spectrum obtained from the as-prepared Ag_2O sample is shown in Figure 5a. It exhibits a broad peak with a maximum at a BE of 5.1 eV and a fwhm of 2.3 eV. These values are consistent with previously reported literature values.[4,6,7] The small peak at about 2.0 eV originates from valence orbitals of O 2p character.[14] The differences in the valence-band spectra between Ag_2O and metallic Ag can be observed by comparing Figure 5a and 5g. The maximum in the density of states (DOS) occurs at a BE of 4.8 eV for the metal, and the feature has a fwhm of 3.3 eV. This spectrum exhibits a shoulder on the high BE side of the maximum that is not present in the valence-band spectrum obtained from Ag_2O. This shoulder has been attributed to photoelectrons from Ag 5s-type orbitals[14] that would not exist in any Ag cation in its ground state. Furthermore, the low-BE shoulder at 2.0 eV is not present in Figure 5g.

It is reasonable to expect that the Ag MNN Auger peaks would exhibit larger energy shifts and shape changes than the XPS Ag 3d peaks with varying chemical state because a single Auger transition involves three electrons and many-body effects. The Ag MNN spectrum obtained from the as-prepared Ag_2O sample is shown in Figure 6a. The maximum appears at a BE of 902.6 eV (kinetic energy (KE) = 351.0 eV). Comparing these peaks with the Ag metal peaks shown in Figure 6g reveals a BE shift of 1.5 eV in the opposite direction of the XPS Ag 3d shifts. With respect to the Ag metal Auger peaks, the Ag_2O Auger peaks are fairly featureless and broad and exhibit less splitting between peaks. Also, the shoulder that occurs on the low-BE side of the large metallic peak resulting from spin–orbit coupling[4] is not resolved in the spectrum obtained from the as-prepared Ag_2O sample. The peak-shape difference and the BE shift between the Auger spectra obtained from the as-prepared Ag_2O sample and Ag metal are quite significant. Contrary to statements made by Rehren et al.,[9] this demonstrates that meaningful chemical-state information concerning the O/Ag system is contained in the AES Ag MNN spectra.

100 °C Anneal. The Ag $3d_{5/2}$ peak shown in Figure 2b does not shift in BE from its original value after annealing at 100 °C, but its fwhm is increased from 1.50 to 1.65 eV. In the previous study[1] a loss of carbonate species after annealing the AgO sample at 100 °C results in a decreased fwhm of the Ag 3d peaks compared with the 3d spectrum taken from the as-prepared AgO. The decreased peak width is attributed to reducing the amount of different Ag chemical states that contribute to the Ag 3d line shape. Kaushik[15] also observed a broadened Ag 3d peak in the XPS spectrum taken from an AgO/Ag_2CO_3 mixture relative to that obtained from AgO. However, this is not the case for the Ag_2O sample because the amount of carbonate present decreases by about 20% during the 100 °C anneal. The broadening appears to be due to spectral contributions by Ag metal and AgO at 368.0 and 367.3 eV, respectively. These subtle changes are difficult to detect in Figure 2, but they are clear when the enlarged features are overlaid. An explanation for these observations is that some of the Ag_2O undergoes a disproportionation reaction in which AgO and Ag metal form during the 100 °C anneal. On the basis of the contributions of Ag_2O, AgO, and Ag metal to the Ag 3d peak, only a few percent of the Ag_2O decomposes.

---

(8) Briggs, D.; Seah, M. P. *Practical Surface Analysis*; John Wiley & Sons: Chichester, 1983.

(9) Rehren, C.; Muhler, M.; Bao, X.; Schlogl, R.; Ertl, G. *Z. Phys. Chem., Bd.* **1991**, *174*, 11.

(10) Boronin, A. I.; Bukhtiyarov, V. I.; Vishnevskii, A. L.; Boreskov, G. K.; Savchenko, V. I. *Surf. Sci.* **1988**, *201*, 195.

(11) Campbell, C. T.; Paffett, M. T. *Surf. Sci.* **1984**, *143*, 517.

(12) Bigelow, R. W. *Appl. Surf. Sci.* **1988**, *32*, 122.

(13) Barteau, M. A.; Madix, R. J. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *31*, 101.

(14) Romand, M.; Roubin, M.; Deloume, J. P. *J. Electron Spectrosc. Relat. Phenom.* **1978**, *13*, 229.

(15) Kaushik, V. K. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *56*, 273.

The O 1s spectrum shown in Figure 3b exhibits attenuation of the broad carbonate peak centered at 530.2 eV relative to the peak due to Ag_2O at 528.8 eV. The peak at a BE of 532.4 eV due to adsorbed H_2O or some oxygen-containing contamination is reduced compared with the O 1s spectrum obtained from the as-prepared sample, but the peak at a BE of 531.3 eV is not noticeably different. This is consistent with changes in the C 1s spectra described below. The shoulder at a BE of 528.5 eV that appears on the low-BE side of the predominant O 1s peak in Figure 3b is more pronounced than in Figure 3a, indicating that more AgO is present in the near-surface region of the sample after annealing at 100 °C. This is consistent with the suggestion of disproportionation of some of the Ag_2O.

In addition to the 20% reduction of the C 1s peak area (Figure 4b) during the 100 °C anneal, the position of the maximum of the low-BE portion is reduced from 284.5 to 284.1 eV. The most prominent change in the C 1s spectrum is the loss of intensity of the shoulders on the high-BE side of the large C 1s peak. The intensities of the peaks centered at BEs of 284.5 and 285.3 eV are significantly diminished. This spectral change in conjunction with the reduction of the O 1s peak at a BE of 532.4 eV in the O 1s spectrum suggests that the same oxygen-containing carbon compound may be responsible for both spectral features. The C 1s peak at 287.3 eV is now smaller in comparison to the peak at 287.9 eV indicating that more $AgHCO_3$ decomposes than Ag_2CO_3 at 100 °C.

The shift of the C 1s peak maximum illustrates an important point. Using the C 1s BE of adventitious carbon as a BE reference in XPS spectra can lead to inaccurate results. In nearly all cases the chemical forms of carbon present in the near-surface region of a sample under study are not well-characterized, and the C 1s peak is usually broad with a complex shape. The species present depend upon the nature of the sample surface and its exposure to various carbon-containing compounds. Furthermore, using this method of correcting BEs after various sample treatments yields inconsistent results if the types and amounts of carbon species on the sample change during the treatment as observed in this study.

The predominant feature in the valence-band spectrum shown in Figure 5b is also broader with a fwhm of 2.55 eV. The valence-band peak shifts to a BE of 4.9 eV which is close to the previously reported value of 4.8 eV for AgO.[1] The broader shape and increased shoulder on the low-BE side of the predominant peak are more similar to AgO features. The Ag MNN peaks shown in Figure 6b also exhibit characteristics that are more similar to those obtained from AgO in that the peaks are shifted to a higher KE (351.3 eV), become broader and exhibit less splitting. The region near a BE of 901.2 eV is enhanced due to the formation of both AgO and Ag metal. These facts are consistent with the observed broadening of the Ag 3d line shape discussed above.

200 °C Anneal. The Ag $3d_{5/2}$ peak taken after annealing at 200 °C is shown in Figure 2c. It does not reveal a BE shift, but its fwhm of 1.60 eV is 0.05 eV smaller than the fwhm of the peak obtained before this anneal. This decrease is due partially to the loss of carbonates. An overlay of enlarged spectra indicates that a small amount of AgO decomposes during this anneal and that the amount of Ag metal present is slightly increased. The loss of some AgO also contributes to the decrease in the fwhm. Nevertheless, the fwhm of the Ag $3d_{5/2}$ peak is still larger by 0.1 eV than the FWHM of the $3d_{5/2}$ peak obtained from the as-prepared Ag_2O. The valence-band feature (Figure 5c) shifts to a BE of 5.1 eV, and the low-BE shoulder is only slightly reduced relative to the spectrum obtained prior to annealing at 200 °C (Figure 4b). Both the valence-band and Ag MNN spectra (Figure 6c) exhibit a slight narrowing, and the splitting of the Ag MNN peaks is somewhat greater. These spectral changes are subtle but illustrate the influence of Ag carbonates and AgO on the peak shapes. In the previous study most of the AgO was found to decompose to Ag_2O during the 200 °C anneal. This observation suggests that differences in structure and/or contamination stabilize the small amount of AgO present on the sample used in this study.

The corresponding O 1s spectrum is shown in Figure 3c. An overlay of enlarged spectra b and c indicate that the broadening due to O in AgO is decreased. Decomposition of surface carbonates occurs during the 200 °C anneal causing attenuation of the peak centered at a BE of 530.2 eV. The total carbon content is reduced to less than 50% of the initial amount, and the carbonate features centered at 287.6 eV in Figure 4c are negligible. In the O 1s spectra obtained from the as-prepared sample and after the 100 °C anneal, the carbonate O 1s peak at 530.2 eV contributes to the intensity of the feature centered at a BE of 530.7 eV. Thus, the loss of intensity in the peak at 530.7 eV is mostly due to the disappearance of the O 1s peak at 530.2 eV. Furthermore, the predominant peak is shifted more toward the O 1s BE for Ag_2O as the C contamination O 1s features are reduced in size.

An increase in the intensity of the O 1s peak at 532.4 eV in Figure 3c probably relates to changes occurring in the C 1s spectrum. The low BE C 1s peak obtained after the 200 °C anneal shown in Figure 4c now has a maximum at a BE of 284.5 eV and exhibits shoulders on the high-BE side with a distinguishable peak at a BE of 285.3 eV. This feature is similar to the peak at a BE of 284.5 eV in the C 1s spectrum obtained from the as-prepared Ag_2O sample (Figure 4a). In both spectra the BE of the maximum of the first C 1s peak is the same and the shoulders present on the high BE side of this peak reveal a peak at 285.3 eV. The O 1s peak at a BE of 532.4 eV is apparent only when the first C 1s peak contains these features. Thus, it is likely that the spectral feature in the O 1s spectrum at a BE of 532.4 eV and the features at 284.5 and 285.3 eV in the C 1s spectrum are both due to the same oxygen-containing carbon compound present in the near-surface region of the sample. After exposing a cleaned Ag foil at 200 °C to 5 Pa of O_2 for 90 min, Boronin et al.[10] observed two peaks in both the O 1s (BEs = 530.8 and 533.0 eV) and C 1s (BEs = 284.4 and 287.5 eV) spectra. They attribute these peaks to oxygen-containing compounds that form when surface carbon reacts with oxygen. Similar reactions may occur during this 200 °C anneal. Another less likely explanation is that subsurface H_2O migrates to the near-surface region at 200 °C and contributes to the 532.4 eV peak.

300 °C Anneal. The Ag 3d, valence-band, and Ag MNN spectra obtained after the 300 °C anneal are more characteristic of a single Ag state than are the spectra obtained after annealing at 100 and 200 °C. The Ag $3d_{5/2}$ peak in Figure 2d has a BE of 367.7 eV with a decreased fwhm of 1.50 eV, and the broadening due to AgO is no longer apparent, indicating that the remaining AgO decomposes during the 300 °C anneal to form Ag_2O. The reduction in the amount of C-containing species discussed below is also partially responsible for the reduction in the fwhm of the Ag $3d_{5/2}$ peak. Metallic Ag does not form during the 300 °C anneal. Therefore, the spectra obtained after the 300 °C anneal are characteristic of spectra which would be obtained from pure Ag_2O. The O 1s spectrum shown in Figure 3d exhibits significantly reduced contaminant signals and a predominant feature at a BE of 528.8 eV which is characteristic of the O 1s signal from pure Ag_2O.

Complex changes occur with regard to the types and amounts of carbon present on the sample after the 300 °C anneal. Only about 30% of the initial amount of carbon remains on the surface, and the maximum of the C 1s peak (Figure 4d) is shifted to a BE of 284.9 eV. The intensity of the peak at 284.5 eV is decreased relative to the other C 1s peaks, and a feature centered at about 285.3 eV is now present, as is a broad shoulder lying on its high-BE side. This indicates that chemical changes in the carbon contamination are occurring during the 300 °C anneal and/or that certain carbon-containing compounds desorb. Both processes would alter the C 1s peak shape. Examination of the O 1s and C 1s spectra illustrates that the changes in relative peak intensities are complicated and cannot be used to assign O 1s and C 1s BEs to a particular oxygen-containing carbon compound.

The valence-band feature shown in Figure 5d is not shifted in energy but is narrower with a fwhm of 2.4 eV, and the low-BE shoulder is slightly less intense. These valence-band features are similar to those obtained from the as-prepared Ag_2O sample and the Ag_2O which forms after an AgO sample decomposes to Ag_2O at 200 °C.[1] Both of these surfaces consist mostly of this single oxide state. The Ag MNN peaks (Figure 6d) are not shifted in energy but exhibit a broadening on the high-KE side which is probably due to the presence of a small amount of metallic Ag. The splitting of the peaks is not changed noticeably, but the peak widths are slightly reduced. A detailed analysis of the Ag_2O Ag Auger peak shape has been presented by Tjeng et al.[7]

490 °C Anneal. The spectra taken from the sample after annealing at 490 °C for 60 min are shown in Figures 2e through 6e. The spectral features are now quite similar to those obtained from metallic Ag, but some differences still remain. The fact that Ag_2O is stable in vacuum up to 490 °C is unexpected based on a thermodynamic equilibrium calculation which predicts that Ag_2O should decompose at room temperature while pumping the vacuum system down. Tjeng et al.[7] also found that Ag_2O is stable in ultrahigh vacuum. This indicates that the decomposition of Ag_2O is activated. The Ag $3d_{5/2}$ peak shown in Figure 2e occurs at a BE of 368.0 eV with a fwhm of 1.35 eV. This peak has the same BE as Ag metal but is broader by 0.2 eV. Although the valence-band spectrum shown in Figure 5e closely resembles that obtained from metallic Ag (Figure 5g), some subtle differences can be discerned. The high-BE shoulder at about 6.4 eV in Figure 5e is broader and more pronounced than the corresponding feature in Figure 5g even though the maxima of the predominant peaks occur at a BE of 4.8 eV for both. The peak centered at a BE of 11.5 eV in Figure 5e is due to a cadmium impurity that migrated to the surface during the anneal. The low-BE peak at 2 eV is barely discernible which is consistent with the assertion that most of the Ag oxide decomposed during the 490 °C anneal. The corresponding Ag MNN peaks (Figure 6e) are also very similar to those obtained from Ag metal (Figure 6g). The KEs of the Ag MNN peaks in Figure 6e are about 0.2 eV less than those in Figure 6g, and the peaks are broader with less splitting between the peaks compared to the Ag metal Auger peaks. These facts indicate that some Ag oxide is still present after the 490 °C anneal or that contamination affects the Auger spectrum. The C 1s spectrum shown in Figure 4e consists mostly of noise indicating that nearly all of the carbon is removed during the 490 °C anneal. The O 1s spectrum taken after the 490 °C anneal exhibits a large peak centered at a BE of 531.0 eV, which is asymmetric on both sides. A shoulder is distinguishable at a BE of 528.8 eV corresponding to the O 1s BE of Ag_2O.

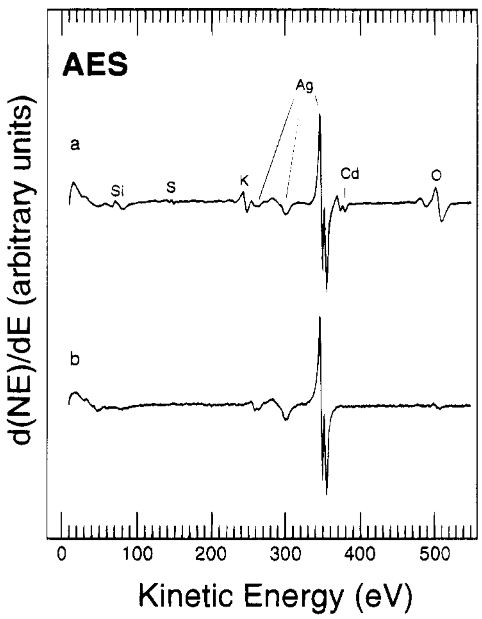

Figure 7. AES spectra obtained (a) from the Ag_2O sample after annealing at 490 °C for 60 min, and (b) after sputtering.

The remaining O 1s peaks are due to the presence of several bulk impurities that migrate to the sample surface during this anneal. These impurities react with oxygen to form a multicomponent mixture of oxides at the sample surface. An AES spectrum taken from the sample after the 490 °C anneal is presented in Figure 7a. The peaks apparent in this spectrum are due to Ag, Cd, Si, S, O, and K. These contaminants most likely are present in an oxide form and include CdO (O 1s BE = 529.2 eV), CdO_2 (BE = 530.5 eV), $Cd(OH)_2$ (BE = 531.8 eV), SO_4^{2-} (BE = 531.8 eV), KOH (BE = 531.5 eV), and SiO_2 (BE = 532.8 eV). An ISS spectrum taken from the sample surface is shown in Figure 8a. It exhibits a large Ag peak in addition to smaller peaks at lower KEs. The next largest peak in this spectrum

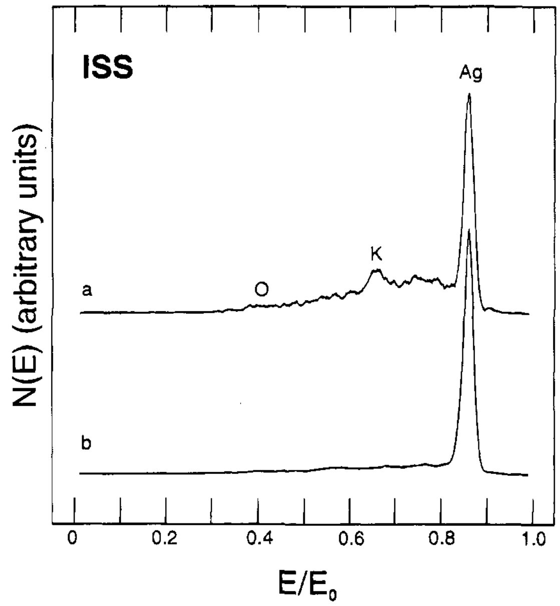

Figure 8. ISS spectra obtained (a) from the Ag_2O sample after annealing at 490 °C for 60 min, and (b) after sputtering.

is due to surface K, and other peaks result from trace amounts of Cu, Si, S, Mn, Cu, and O that reside on the outermost surface layer.

Removal of Surface Impurities. An AES spectrum taken after sputtering the sample is shown in Figure 7b, and the corresponding ISS spectrum is shown in Figure 8b. Both of these spectra indicate that sputtering removes the surface impurities. Thus, XPS data obtained after sputtering (Figures 2f through 6f) represent spectra from an impurity-free surface of decomposed Ag_2O. These spectra are similar to those taken prior to sputtering, but some differences can be seen. The Ag $3d_{5/2}$ peak shown in Figure 2f is quite similar to that in Figure 2e. Both peaks have a BE of 368.0 eV, but sputter removal of the contamination reduces the fwhm by 0.1 eV. The valence-band feature obtained after sputtering (Figure 5f) has a decreased fwhm of 3.2 eV compared to a fwhm of 3.3 eV taken before sputtering (Figure 5e), and the feature at a BE of 11.5 eV due to the impurity is gone. The BE of this peak is not shifted after sputtering, but the high-BE shoulder is narrower and more similar to the valence-band feature obtained from Ag metal (Figure 5g). The Ag MNN peaks (Figure 6f) have the same KEs as those obtained from Ag metal (Figure 6g) but are slightly broader. The C 1s spectrum shown in Figure 4f consists mostly of noise. The O 1s spectrum taken after sputtering and shown in Figure 3f is quite different than the O 1s spectrum taken prior to sputtering (Figure 3e). It exhibits a broad peak centered at about 532.0 eV that is similar in shape to the O 1s spectrum obtained from metallic Ag (Figure 3g). Shoulders are discernible at BEs near 531.0 and 532.4 eV corresponding to dissolved, subsurface oxygen and OH or H_2O, respectively. A portion of the peak at 532.4 eV may be due to some oxygen associated with small amounts of remaining carbon. Rehren et al.[9] report that the O 1s peak of dissolved oxygen in Ag metal shifts to a higher BE when the amount of dissolved, subsurface OH is increased relative to the amount of dissolved O. Thus, the positive BE shift observed between the peaks in Figure 3f and 3g is probably due to a greater amount of OH in the dissolved, subsurface oxygen mixture contained in the decomposed Ag_2O compared with the amount of OH in the dissolved oxygen mixture in the Ag foil.

Conclusions

A pressed Ag_2O powder has been investigated using XPS as it was decomposed in a stepwise manner by annealing in UHV for 30 min at 100, 200, and 300 °C and for 60 min at 490 °C. XPS data were taken from the as-prepared sample, from the Ag_2O sample after each anneal, from the sample after sputtering the contamination layer off and from a polycrystalline Ag foil for comparison purposes. The decomposition is very complex because many chemical species, reactions, and processes are involved.

There are inherent advantages in the approach used in this study. Collecting spectra from the same sample at various stages of decomposition allows for comparison of the spectra in a straightforward manner. The different chemical and physical processes involved in the decomposition are isolated to some extent because they proceed at different rates at the various anneal temperatures. This allows for a better understanding of each individual step. Furthermore, it is generally quite difficult to produce fairly pure forms of materials such as AgO and Ag_2O from which reliable reference spectra can be obtained. This has been accomplished in this study.

Multiple chemical states of oxygen are present on the as-prepared Ag_2O surface including lattice oxide, carbonates, absorbed water and various oxygen-containing carbon compounds. Annealing at 100 °C results in the loss of some of the carbonates, H_2O and/or some of the carbonaceous contaminants and increases the amount of AgO by a small amount at the surface through a disproportionation reaction. Annealing at 200 °C slightly reduces the amount of AgO present and results in loss of the surface carbonates. Annealing at 300 °C causes the remaining AgO to decompose resulting in the presence of mostly Ag_2O and a small amount of Ag metal. Annealing at 490 °C results in nearly complete decomposition of the Ag_2O to Ag metal and the migration of bulk impurities such as cadmium, potassium, sulfur and silicon to the surface forming a contaminant overlayer. This overlayer was removed by sputtering with 2 keV Ar^+ for 60 min. The resulting surface is metallic Ag that contains a mixture of dissolved, subsurface OH and O. The spectral features are quite similar to those obtained from the Ag metal foil.

Acknowledgment. Financial support for this research was received from the National Science Foundation through Grant CTS-9122575. The authors appreciate the assistance of Professor Marjorie A. Langell with regard to spectral analysis.