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AES and XPS study on the tarnishing of silver in alkaline sulphide solutions

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Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to follow the changes that occur on the surfaces of silver sheets when reacting with sulphide solutions of pH 12. The results obtained enabled conclusions to be drawn about the nature of the Ag_2S films. Immersion in dilute sulphide solutions ($\leqslant 3 \times 10^{-4}$ M) resulted in highly irregular films that were interrupted by shallow depressions (cavities). Inside these cavities AES analysis proved the existence of massive carbon species, the presence of which delayed healing of the cavities by the formation of Ag_2S film, thus allowing the silver metal interface to continue in contact with the solution oxygen. This explains why silver electrodes maintain the Ag/Ag_2O potential while immersed in dilute sulphide solutions. Equilibration of silver with more concentrated sulphide solutions (5×10^{-4} to 5×10^{-3} M) effected healing of the cavities through the formation of a continuous Ag_2S film. Once this continuous film is formed, the metal interface is no longer accessible to the solution oxygen. At this point the transition of potential from Ag/Ag_2O to Ag/Ag_2S occurs.

1. Introduction

In the previous work [1, 2] the tarnishing of silver electrodes in alkaline sulphide solutions was studied by both electrochemical and X-ray photoelectron spectroscopy (XPS) techniques. The reaction leading to tarnishing is reported to take place via a primary one-electron electrochemical process leading to the formation of AgSH. Two molecules of this latter compound react chemically to produce Ag_2S black film. The XPS technique proved the stoichiometry of the film formed to be that of Ag_2S. It was further reported [1] that during this stage of the reaction, Ag_2S builds up in two dimensions on a bare surface, and once a complete monolayer of Ag_2S is formed the potential of the silver electrode changes from that of the system Ag/Ag_2O to more negative values, reaching that of Ag/Ag_2S. This behaviour resulted in an S-shape relation between the measured potential and the logarithm of sulphide concentration in solution.

As far as the authors are aware, the only other published work on silver tarnishing using Auger electron spectroscopy (AES) and XPS techniques was that of Remond *et al.* [3]. They reported on the tarnishing of silver inclusions present in chalcopyrite mineral.

The present work uses AES and XPS techniques to follow the changes that occur in the surface structure and composition during the formation of Ag_2S when silver sheets are immersed in alkaline sulphide solutions of pH 12 and of different pS values, especially the range covering the transition of the potential of the silver electrode from Ag/Ag_2O to Ag/Ag_2S.

2. Experimental procedure

Spectroscopically pure silver sheets having an area of 0.6 cm × 1.2 cm were used. Conditioning of the metal surface, solution preparation and equilibration procedure are cited elsewhere [1, 2]. The tarnishing reaction was made in Na_2S solutions covering the concentration range 5×10^{-5} to 5×10^{-3} M. The pH of all solutions was adjusted to 12 by addition of 0.01 M NaOH solution. In all experiments the immersion time of silver in sulphide solutions was fixed at 3 h.

Analysis of the Ag_2S films formed was made using a Type 550 ESCA/SAM spectrometer (Physical Electronics, USA). The vacuum in the analytical chamber was better then 5×10^{-9} torr. Besides the use of the scanning electron microscope (SEM) to follow changes in surface topography of the films, different Auger techniques were applied. These involved (a) an AES survey analysis to identify the various elements present in the film, (b) scanning Auger microscopy (SAM) to plot the surface distribution of both silver and sulphur, and (c) AES depth profile analysis in the centre of a crater made by sputter-etching with a beam of argon ions. For XPS measurements, the system employed a magnesium-anode X-ray tube ($h\nu = 1253.6$ eV). The pass energy of the analyser was adjusted at 25 eV ($\Delta E = 0.15$ eV). The energy scale of the system was adjusted to match the $Au4f_{7/2}$ peak at 83.8 eV. No shift in binding energy was detected that might result from sample charging. All the spectrometer functions operated through a Digital 11/04 computer (Digital Equipment Corporation, Maynard, Massachusetts) using the V006 B program (Physical Electronics, USA).

3. Results and discussion

SEM pictures were taken to show the surface topography of the Ag_2S films formed when silver sheets

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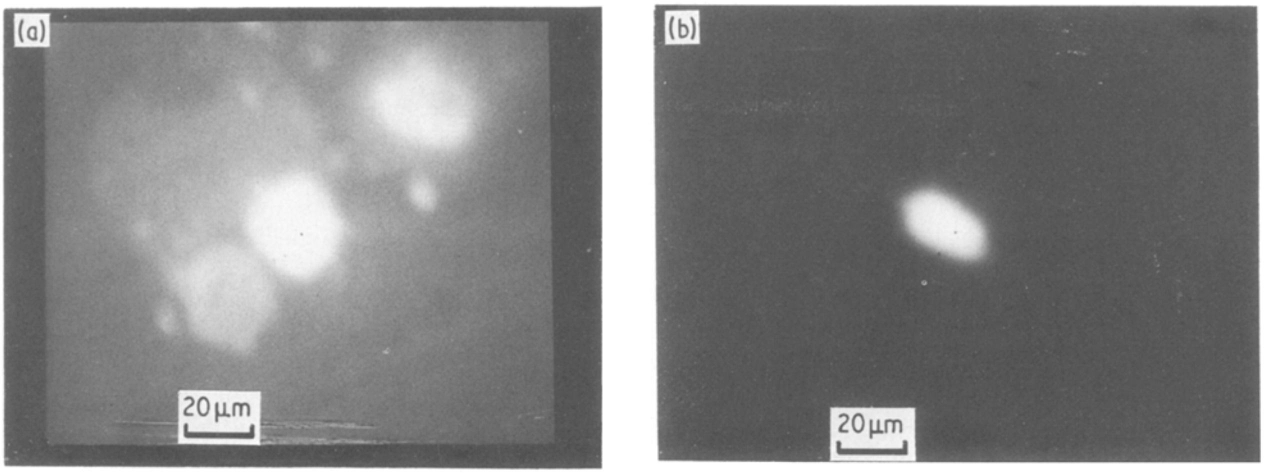


Figure 1 SEM photographs of silver surfaces after immersion in (a) 10^{-4} and (b) 5×10^{-4} M Na_2S solutions.

were immersed in Na_2S solutions of concentration 5×10^{-5}, 10^{-4}, 3×10^{-4}, 5×10^{-4}, 10^{-3} and 5×10^{-3} M. Because of the similarity of many of the photographs, only representative shots are shown in Figs 1a and b. These correspond to films formed in 10^{-4} and 5×10^{-4} M Na_2S, respectively. These two selected concentrations represent two points on the E–logC_S plot [1]. The point at lower concentration corresponds to the potential of the silver electrode while still governed by the Ag/Ag_2O system. The higher concentration represents a point on the plot after the transition of the potential to that of Ag/Ag_2S. From the pictures one general conclusion could be drawn. Films formed in dilute sulphide solutions ($\leqslant 3 \times 10^{-4}$ M) are characterized by large numbers of cavities, while those formed at higher concentrations ($\geqslant 5 \times 10^{-4}$ M) show a lower density of such depressions. Although the surface of silver was conditioned before immersion in sulphide solutions with the finest grades of metallographic papers to a mirror-like appearance, yet the surface still retained cavities.

It was possible to raster the electron beam as a microprobe (SAM) on the Ag_2S surface to trace the distribution of both silver and sulphur. In all cases the rastered area, which measured 160 μm × 130 μm, was selected to cover places where cavities existed. The

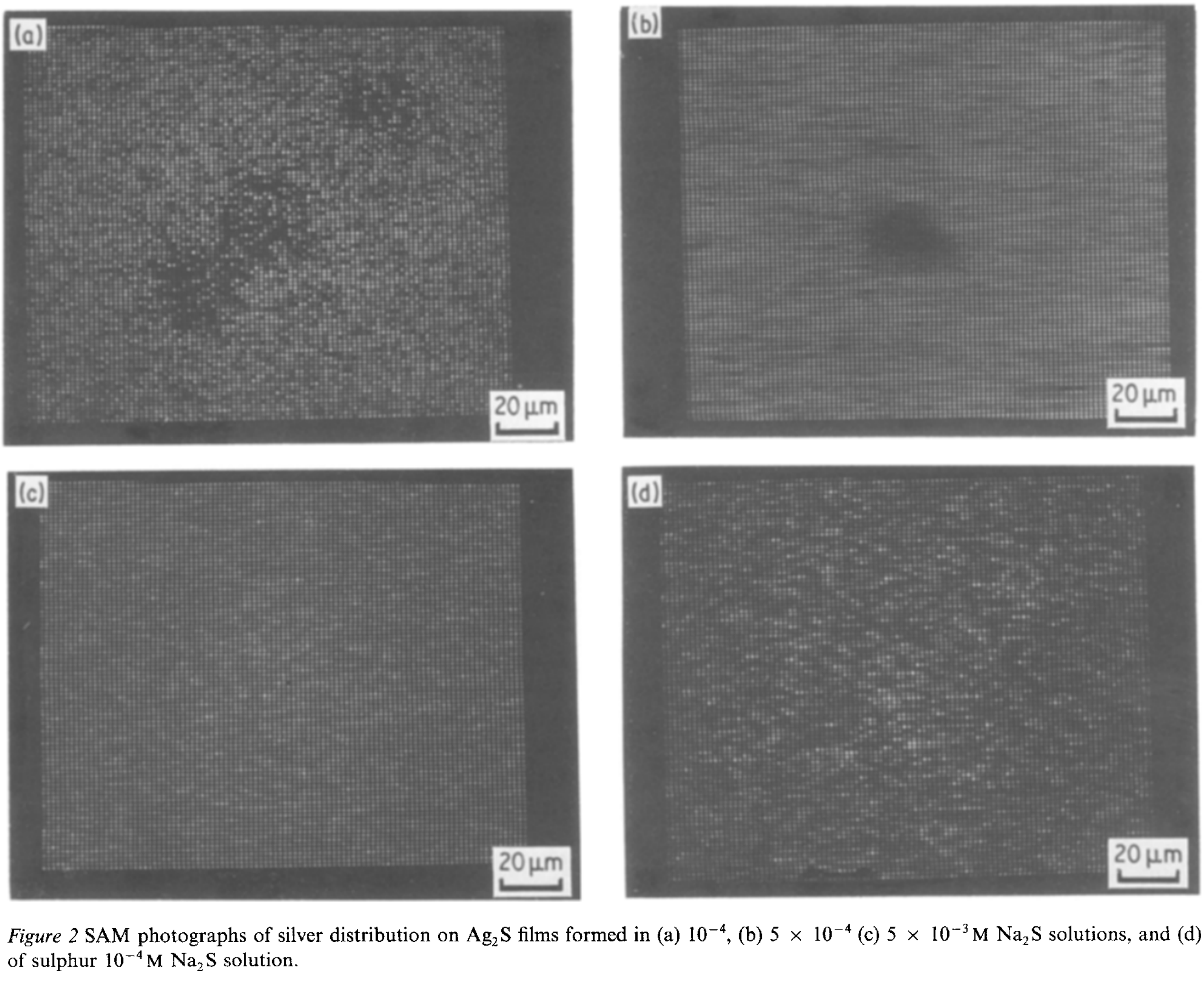


Figure 2 SAM photographs of silver distribution on Ag_2S films formed in (a) 10^{-4}, (b) 5×10^{-4} (c) 5×10^{-3} M Na_2S solutions, and (d) of sulphur 10^{-4} M Na_2S solution.

photographs of Figs 2a, b and c represent Auger maps for the silver distribution in films formed in sulphide solutions of 10^{-4}, 5×10^{-4} and 5×10^{-3} M, respectively. A representative map of the sulphur distribution is shown in Fig. 2d and corresponds to 10^{-4} M Na_2S.

In contrast to the silver maps, sulphur shows an even distribution on the film surfaces even in places where cavities exist, and the intensity of sulphur detection depends linearly on the concentration of the equilibrating Na_2S solution. The detection of sulphur and not silver in cavities (Figs 2d and 2a, respectively) can be explained on the basis that sulphur exists in two compounds: one on the regular surface as Ag_2S (outside cavities) resulting from the reaction of silver metal with the equilibrating Na_2S solution, and the other in the cavities as Na_2S which might have escaped washing after the equilibration process.

The maps of silver distribution, on the other hand (Figs 2a and b), clearly indicate that for Ag_2S films formed in 10^{-4} and 5×10^{-4} M Na_2S, silver is not detected in the cavities. Several reasons might lie behind this finding. These could be the non-formation of Ag_2S in the cavities, or the large depth of the cavities making the inside film out of the detection limit of the electron beam, and/or the presence of foreign impurities screening any silver species present. Differentiation between these cases will be discussed later. On the other hand, silver was evenly detected inside and outside cavities for films formed in higher sulphide concentration of $\geqslant 5 \times 10^{-3}$ M (Fig. 2c). In these cases, the sulphide concentration in solution is believed to be high enough to effect the building up of a relatively thick Ag_2S film lining the cavity inside. This film, although detected by SAM, is still outside the detection limit of SEM, and the cavities are still recorded.

It was possible through the versatility of the spectrometer to direct the electron beam to specific points of the film surface as small as 5 μm, in order to identify the constituent elements. This AES survey analysis was performed both inside and outside cavities. The spectra shown in Figs 3a, b and c are representative of this type of analysis for films formed in Na_2S solutions of 5×10^{-5} to 10^{-4}), 5×10^{-4} and 10^{-3} M, respectively. Several facts could be drawn out depending on the concentration of the equilibrating sulphide solution and on the location of analysis (either inside or outside cavities):

(a) The sulphur signal, in general, is very small for films formed in dilute sulphide solutions ($\leqslant 5 \times 10^{-4}$ M) and has the same intensity both inside and outside cavities. This equality in signal does not mean that sulphur existed as Ag_2S at both locations of the surface. As stated before, sulphur outside cavities is mainly due to Ag_2S formation while that inside cavities is due to part of the equilibrating Na_2S that escaped washing and resisted removal, and it accidentally happened that both came out equal. Increasing the sulphide concentration in the equilibrating solutions to $\geqslant 10^{-3}$ M resulted in well-developed sulphur signals both inside and outside cavities, as indicated by the spectra of Fig. 3c. In this figure it is clear that the sulphur signal is due to Ag_2S formation as indicated from its intensity after correction for the atomic sensitivity factor [4, 5] relative to that of silver.

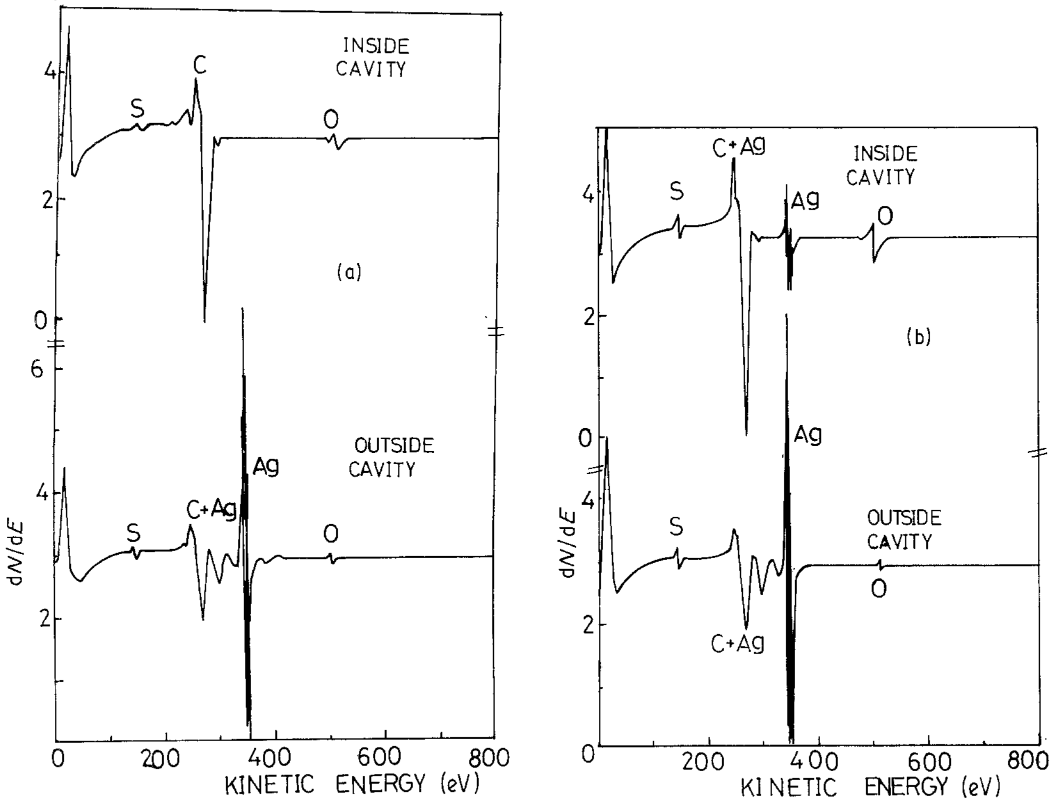
(b) The silver signals of Figs 3a and b, which correspond to dilute sulphide solution films ($\leqslant 5 \times 10^{-4}$ M), show interesting features. In contrast to the very weak sulphide signals in the same films, silver shows enhanced signals outside cavities. These exaggerated silver peaks are due to the very thin nature of the Ag_2S films formed, which allow the electron beam to detect silver both from the Ag_2S film and from the metallic interface. Ag_2S films formed in more concentrated sulphide solutions ($\geqslant 10^{-3}$ M) build up and become thick enough such that the recorded silver peaks correspond to their normal intensities relative to sulphur in Ag_2S. Inside cavities the silver signals show a quite different behaviour. Silver started to be deteted only as a small peak in films formed in 5×10^{-4} M sulphide solutions (Fig. 3b). The silver peak acquired its normal intensity relative to sulphur in Ag_2S – similar to the analysis outside cavities – only for films obtained from sulphide solutions of higher concentration ($\geqslant 10^{-3}$ M).

It is of interest to note that the non-detection of silver in the cavities of dilute-solution films (Fig. 3a) is associated with the recording in the spectra of an intense carbon peak. This last peak has gradually decreased, and completely disappeared, for AES analysis in cavities the surface films of which were formed in 5×10^{-4} and 5×10^{-3} M sulphide, respectively. The parallelism of recording an intense carbon peak and the non-detection of silver in cavities corresponding to dilute-solution films ($\leqslant 10^{-4}$ M) indicates that some sort of massive carbon species exists, the presence of which either prevents the formation of a continuous Ag_2S film bridging the cavity or hides it and prevents detection. As will be presented later in the profile analysis, the non-formation of Ag_2S in cavities is the cause of its non-detection.

The continuity of the Ag_2S film across cavities started only when the concentration of the equilibrating sulphide solution was increased ($\geqslant 5 \times 10^{-4}$ M, Fig. 3b). A further increase in sulphide concentration results in well-developed Ag_2S films inside cavities that prevented, to a certain extent, the carbon from being detected (Fig. 3c).

At this point it is worth drawing attention to the fact that the carbon *KLL* peak traced in this study exists in the range 257 to 287 eV [4] which coincides with one of the minor silver peaks located at 266 eV. This latter is unavoidably recorded whenever silver is present during carbon analysis, so that the carbon signal in the Auger spectrum is usually enhanced by an amount equal to the height of this minor silver peak.

(c) In the spectra of Fig. 3, the oxygen peaks are always larger for inside-cavity AES analysis than for outside. Because the oxygen concentration in cavities has a direct relation to the mechanism of the electrochemical behaviour of the silver electrode during the tarnishing reaction, it looks more reasonable to consider the oxygen signal in the following discussion dealing with depth profile analysis.



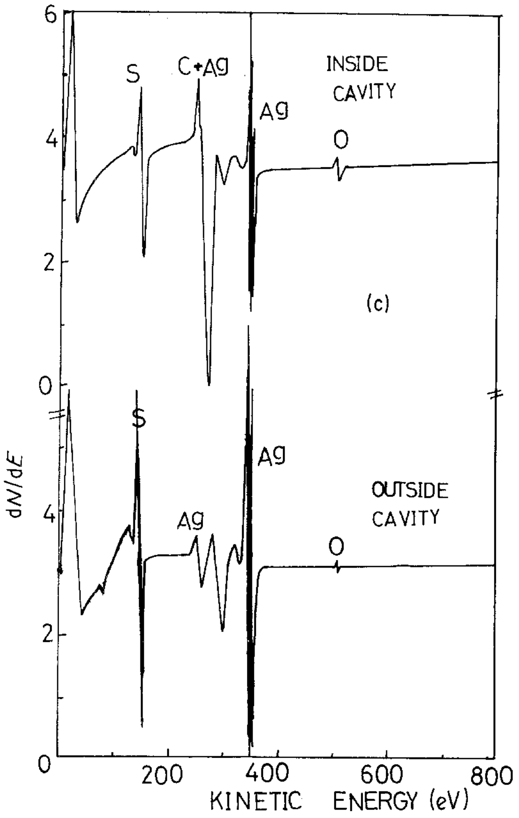


Figure 3 AES survey analysis of Ag_2S films formed in (a) 10^{-4}, (b) 5×10^{-4} and (c) 10^{-3} M Na_2S solutions.

When AES analysis is made in the centre of a crater made by argon ion sputtering, a depth profile analysis results. This type of analysis usually throws light on the constituents of the film throughout its thickness. Depth profile analyses were made on Ag_2S films formed during equilibration in Na_2S solutions of 5×10^{-5}, 10^{-4}, 5×10^{-4}, 10^{-3} and 5×10^{-3} M. For each film two depth profile analyses were performed, one inside a cavity and the other outside. It is to be noted that these profiles were made in the same locations where the previous survey AES analyses were registered. Because the profiles obtained follow a certain trend, only representative examples are included in Figs 4a, b and c which display the main features of that trend. Fig. 4c is the depth profile analysis made outside a cavity for an Ag_2S film formed in 5×10^{-4} M Na_2S solution. Here the interface is reached within one minute, indicating the very thin nature of the film formed. The carbon signal also decays very quickly, indicating that this surface carbon is mainly from adsorbed atmospheric hydrocarbons. Oxygen and sulphur signals show constant levels through the profile and represent minor quantities. It is worth repeating here that the carbon signal cannot decay to a zero level at the interface because of the interference with one of the silver signals. Exactly similar profiles were obtained for films made in more dilute sulphide solutions ($\leqslant 5 \times 10^{-4}$ M). The profiles of more concentrated sulphide solutions ($\geqslant 10^{-3}$ M) show a similar trend, except that the interface was reached at longer time periods. In such cases the sulphur profile is the mirror image of that of silver.

Figs 4a and b correspond to profile analyses inside cavities for Ag_2S films made in 10^{-4} and 5×10^{-4} M Na_2S solutions, respectively. Both profiles show the following features. The interface in both profiles is reached within 22 to 24 min, which reflects the relatively thick nature of the films. As is clear from both profiles, the main bulk that was sputter-etched is not Ag_2S but a massive carbon-containing material. The silver and sulphur signals in Fig. 4a indicate that equilibrating silver in 10^{-4} M Na_2S did not build up any Ag_2S in cavities, while in Fig. 4b these signals indicate that the equilibration of silver in 5×10^{-4} M Na_2S built up a very thin film of Ag_2S that could be sputter-etched within a few seconds.

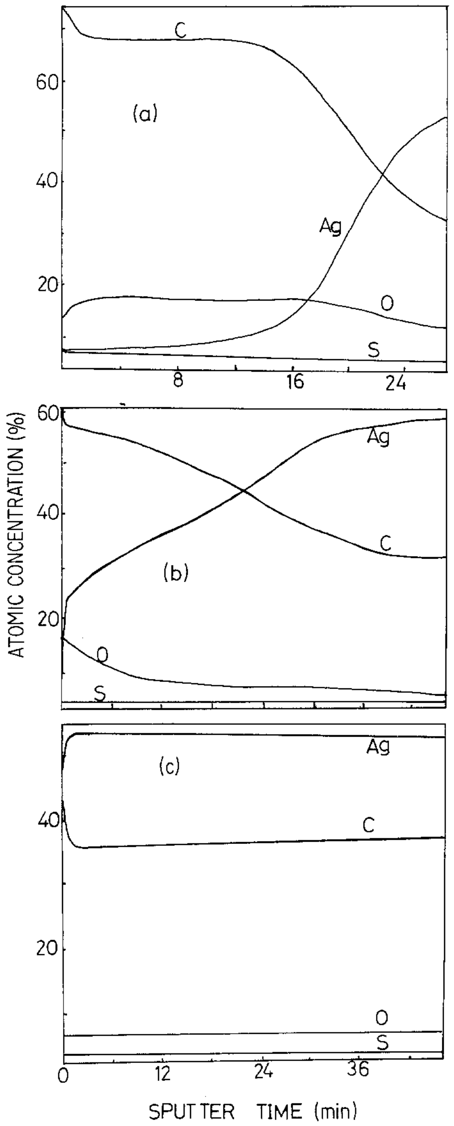


Figure 4 AES depth profile analysis of Ag_2S film formed in (a) 10^{-4} and (b, c) 5×10^{-4}M Na_2S solutions: (a, b) inside cavity, (c) outside cavity.

An important feature in both Figs 4a and b is the oxygen profile in the cavities. In Fig. 4a, corresponding to immersion in 10^{-4}M Na_2S, the oxygen signal indicates its presence in cavities in about 18% relative atomic concentration, and lasts along the profile depth until the interface is reached. On the other hand, the oxygen signal of Fig. 4b, corresponding to immersion in 5×10^{-4}M Na_2S, rapidly decays. The change in oxygen signal in both profiles explains why the previously reported electrochemical change of potential of the silver electrode from Ag/Ag_2O to Ag/Ag_2S occurred only when the ambient sulphide concentration was $\geqslant 5 \times 10^{-4}$M. At a lower concentration, as in Fig. 4a, it seems that although the silver surface is already covered by an Ag_2S film, yet oxygen still finds a route to the metal interface through the cavities to maintain the Ag/Ag_2O potential. On the other hand, the rapid decay of the oxygen signal before reaching the metal interface in Fig. 4b can be explained on the basis that in the presence of 5×10^{-4}M Na_2S, these concentrations seem to be enough both to salt-out oxygen from the cavities and to build up Ag_2S to form a continuous film covering all of the metal surface inside and outside cavities. Under these conditions the continuity of the film interrupts the oxygen supply to cavities and thereafter to the metal interface.

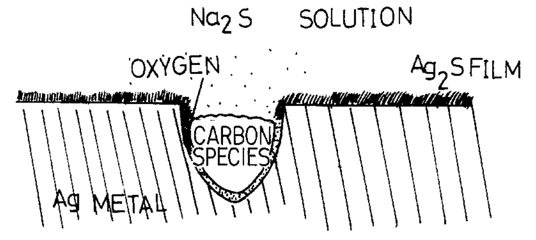


Figure 5 Proposed schematic diagram for a cavity.

According to the results obtained from SAM, AES survey analyses inside and outside cavities, and the corresponding depth profile analyses for silver, sulphur, carbon and oxygen, it can be concluded that some defective points of the silver surface are characterized by shallow depressions. In these depressions some sort of massive carbon species is deposited which prevents the formation of Ag_2S in the depressions when silver is immersed in dilute ($\leqslant 3 \times 10^{-4}$M) Na_2S solutions. At the same time these sulphide concentrations seem to be not enough to exclude the pre-immersion oxide film from the metal surface in the cavities. These cavities represent a route by which the solution oxygen keeps in contact with the metal oxide interface, to maintain the potential of the system at Ag/Ag_2O while silver is immersed in such dilute sulphide solutions. It is worth mentioning that the area of the cavities appears to represent a small fraction of the much larger area available to Ag_2S. If one considers the surface roughness effect inside cavities, the surface area available to Ag_2O would be much larger than the geometric area. This enhanced area explains the electrochemical behaviour of the silver electrode in dilute sulphide solutions. A proposed schematic diagram showing the composition of one such cavity is seen in Fig. 5.

It is worth throwing some more light on the identity of the type of carbon that was detected in the cavities. In contrast with the carbon detected on the regular surface, which could readily be removed (Fig. 4c), the depth profile analysis of carbon in cavities (Figs 4a and b), which represents 60 to 80% atomic concentration, resisted removal by argon ion sputter-etching. This difference in the rates of sputter-etching of carbon inside and outside cavities may be due to differences in film thickness and/or the type of carbon present. Both reasons are expected to be operative. Information about differences in film thickness can be gained from the differently shaded areas present in Figs 1a and 2a. The existence of different types of carbon species in the film may be proved beyond doubt from the XPS spectra of carbon in the range 280 to 290 eV for films formed in dilute sulphide solutions (10^{-4}M). A composite peak was recorded that could be resolved into two sub-peaks. The first, at 284.6 eV, represents about 80% of the area and corresponds to carbon in the adsorbed atmospheric hydrocarbons [4]; the second, corresponding to the minor area, is located at 287 eV. As the total number of cavities on the surface of any of the samples is limited, and consequently their inside geometric areas are expected to represent only a small fraction of the surface area subjected to XPS analysis, it is quite acceptable to assign the smaller sub-peak occurring at higher binding energy to carbon present in the cavities. The identity of this type of carbon could not be precisely determined due to a lack of standard data on carbon in various inorganic compounds. Although one of the forms that carbon can form in alkaline media is Ag_2CO_3 [4, 5], yet it is not confirmed by the present analytical method.

The presence of this carbon material in the cavities was suspected to originate from small particles of the abrasive material used in metal surface preparation. However, this was ruled out because a peak for silicon associated with carbon in the SiC abrasive papers would have been recorded in the AES analysis of Fig. 3. In previous work a silicon peak was recorded associated with carbon in SiC of the abrasive material used to prepare the surface of a steel sample [6]. Further confirmation of this conclusion was gained from the depth profile anlysis inside and outside cavities of a silver surface that was cleaned by abrasion, washed with distilled water and dried without any further treatment. Two identical profiles resulted, showing a complete absence of such carbon material in the cavities. In another experiment, the profiles were repeated on the same silver surface but after being immersed in 0.01 M NaOH for 3 h. The resulting profiles, as well as the AES survey analysis, both showed the existence of a carbon material in the cavities. This finding proved beyond doubt that the carbon detected in surface cavities has originated during immersion of silver sheets in the alkaline solutions. As NaOH and Na_2S solutions used in this study were made from analytical-grade stocks and prepared according to standard procedures, they are not expected to be a source of any carbon impurity. Similarly, the silver metal used is spectroscopically pure and cannot be suspected. The only source that is left to explain the detection of carbon in cavities is the reaction of atmospheric CO_2 with the alkaline sulphide solutions at some specific points of the metal surface that are characterized as depressions. These latter appear to help the aggregation of such carbon material in the cavities. This case is different from that of O'Neill and Westwater [7] who detected excess carbon on silver plates used for dropwise condensation of steam, and could not find in their case any source of carbon except the stainless steel and copper of the condensers.

Although the presence of carbon material in depressions does not play a role in the chemistry of tarnishing, yet it interferes physically as a barrier by preventing the lining of the cavity walls in dilute sulphide solutions with Ag_2S. Under these conditions, the metal interface in the cavity maintains its oxide film and the silver electrode consequently measures the potential of the Ag/Ag_2O system [1] although it is immersed in dilute sulphide solution.

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