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LSV, XPS and AES investigations on composite films of 1-phenyl-5-mercaptotetrazole with Mo(W)–S–Cu cluster compounds

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Insoluble Mo(W)–S–Cu cluster compound films with a metallic lustre of various shades and colours have been applied to copper surface to provide attractive finishes. The anticorrosive characteristics of the Mo(W)–S–Cu cluster compound films with and without various passivation treatments are investigated by using accelerated chemical corrosion tests, LSV, XPS and AES determination. The results indicate that the films are liable to be oxidized gradually when exposed to air and they provide poor protective effect against Cl^- or H_2S erosion to copper. Colour loss or change as well as film degradation will occur. After PMTA passivation, not only are the colours of the films stabilized, but film degradation is also prevented. The protection effect of PMTA on the films can be attributed to the formation of a layer of dense, insoluble and transient polymeric coordination compound film via reaction of PMTA with Cu(I) in the coloured films.

1. Introduction

In previous work [1–4], surface coordination reactions of MoS_4^{2-} or WS_4^{2-} on copper were investigated. Insoluble Mo(W)–S–Cu cluster compound films with a metallic lustre of various shades and colours changing in accordance with the reaction times were applied to copper surfaces to provide attractive finishes. The bonding feature and spectral change of $Mo(W)S_4^{2-}$ on a copper surface, the mechanism of the formation of surface clusters, the potential application for surface finishing, as well as improvement and complexing of the materials, were also discussed. These films, especially the outer layer, are readily oxidized when exposed to air. This causes films to degrade and to change or lose their colours [5]. Traditionally, coloured finishes produced by sulfides on copper and its alloys are not resistant to salt dipping tests or outdoor environments. Clear lacquers, waxes, oils or other organic topcoats are required for coloured copper to withstand any humid or corrosive environment [6, 7]. However, the organic topcoating treatment will potentially cause pollution and increased production cost.

1-Phenyl-5-mercaptotetrazole(PMTA) has been shown to prevent atmospheric tarnishing and staining, as well as corrosion, under different immersion conditions of copper, due to the formation of a protective barrier of inert, insoluble and long-lasting polymeric Cu(I)-PMTA coordination compound coating on the copper surface via reaction between Cu(I) and PMTA [8, 9]. Moreover, the film is transient. The copper in the coloured films is in a monovalent state. This paper discusses the anticorrosive characteristics of Mo(W)–S–Cu cluster films before and after various passivation treatments. The protection and stabilization effect of PMTA on these films are investigated by using accelerated chemical, electrochemical corrosion tests, XPS and AES determination.

2. Experimental details

Copper specimens (2 × 2 or 1 × 1 cm^2, 0.5 mm thick) were polished mechanically with fine MgO powder, chemically degreased with acetone, etched at room temperature in 1% solution of H_2SO_4 and washed in deionized water. The washed plates were immediately immersed in 0.002 M of $(NH_4)_2MoS_4$ or $(NH_4)_2WS_4$ solution at 25 °C for different periods of time. After being removed from the $(NH_4)_2Mo_4S$ or $(NH_4)_2WS_4$ solution, the plates were rinsed with water and acetone and then dried immediately by a cold air blast. Various colours were obtained in different reaction times. For the sample passivation, the films were immersed in 0.005 M solutions of different passivation agents at 25 °C for 30 min, then rinsed with deionized water and dried by a cold air blast. Seven passive

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agents were investigated: PMTA(1-phenyl-5-mercaptotetrazole), TTA(tetrazole), BTA(benzotriazole), HBTA(hydroxybenzotriazole), MBT(2-mercaptobenzothiazole), MBI(2-mercaptobenzoimidazole), 2-AP (2-aminopyrimidine) and IBM(imidazole).

The accelerated corrosion test was performed by incubating the specimens in 10% NaCl solution at room temperature, the time for the solution to turn muddy being recorded along with the extent of corrosion.

The accelerated tarnish test was carried out at room temperature in a stoppered glass vacuum desiccator in which the concentration of H_2S was 1%. The tarnish time of the specimen was measured.

LSV tests were all conducted using an EG&G PARC M273 machine at 25 °C. A standard three-electrode electrochemical cell with a saturated calomel electrode (SCE) as reference and a platinum wire as counter electrode was used. The working electrode was a 3 mm diameter electrolytic copper plate (99.99% purity) fitted with a cylindrical acrylic resin sleeve. Before the electrochemical tests were carried out, the copper electrode was mechanically polished with sandpaper of 1200 mesh, and then treated with the same method as that by which the copper specimens were prefilmed. The supporting electrolytes were 10% NaCl solution. The LSV curves of the

Table 1. Results of accelerated corrosion and tarnish tests of Mo–S–Cu cluster compound films before and after passivation

		Accelerated test method	
Specimen	*Passive agent*	*Salt water dipping* /h[*]	*H_2S tarnish* /min[†]
Blank copper	none	3(3)	0.5(4)
Mo–S–Cu cluster compound film			
Brown	none	5(2)	0.5(4)
Brown	PMTA	80(0)	180(1)
Rose	none	5(1)	0.5(4)
Rose	PMTA	80(0)	180(1)
Blue	none	5(1)	0.5(3)
Blue	PMTA	80(0)	180(1)
Soft cyan	none	5(1)	30(2)
Soft cyan	PMTA	80(0)	180(1)
White	none	5(1)	30(2)
White	PMTA	80(0)	180(1)
White	TTA	80(2)	180(1)
White	BTA	80(2)	60(1)
White	HBTA	6(2)	40(4)
White	MBI	48(2)	40(3)
White	MBT	72(1)	40(3)
White	2-AP	6(2)	30(2)
White	IBM	6(2)	30(2)
W–S–Cu cluster compound film			
Orange	none	3(0)-5(2)-7(3)-12(4)	1(4)
Orange	PMTA	72(0)	180(0)
Orange red	none	3(0)-5(1)-7(2)-12(4)	1(4)
Orange red	PMTA	72(0)	180(0)
Rose	none	3(0)-5(1)-7(2)-12(4)	1(3)
Rose	PMTA	72(0)	180(0)
Purplish red[‡]	none	3(0)-5(1)-7(2)-12(4)	1(1)-30(2)
Purplish red[‡]	PMTA	72(0)	180(0)
Silver white	none	3(0)-5(1)-7(2)-12(4)	10(1)-30(2)
Silver white	PMTA	72(0)	180(0)
Silver white	TTA	72(1)	180(1)
Silver white	BTA	72(2)	60(1)
Silver white	HBTA	5(2)	40(4)
Silver white	MBI	48(2)	30(1)
Silver white	MBT	72(1)	40(3)
Silver white	2-AP	5(2)	30(2)
Silver white	IBM	5(2)	30(2)
Golden yellow[§]	none	3(0)-5(1)-7(2)-12(4)	10(1)-30(2)
Golden yellow[§]	PMTA	72(0)-108(2)	180(1)
Golden yellow[#]	none	3(0)-5(1)-7(2)-12(4)	10(1)-30(2)
Golden yellow[#]	PMTA	72(0)-108(1)	180(1)

[*] Parenthetical numbers mean: 0-no muddy, 1-faint muddy, 2-light muddy, 3-obvious muddy, and 4-seriously muddy

[†] Parenthetical numbers mean: 0-no tarnish, 1-faint tarnish, 2-light tarnish, 3-obvious tarnish, and 4-serious tarnish

[‡] Produced by 2 h reaction of WS_4^{2-} and copper surface

[§] Produced by 12 h reaction of WS_4^{2-} and copper surface

[#] Produced by 18 h reaction of WS_4^{2-} and copper surface prefilmed electrodes were recorded at a sweep rate of $0.05\,Vs^{-1}$.

XPS and AES measurements were made on a VG ESCALAB MK-II photoelectron spectrometer, employing an excitation source of MgK_α radiation (1253.6 eV) operated at 10 kV and 30 mA. Survey and high resolution spectra were obtained with the analyser pass energy set at 50 and 25 eV, and the voltage and current of the electron beam for AES analysis were 3 kV and 10 μA, respectively. An argon ion gun with a voltage of 4 kV, an emission current of 15 mA, and a scan area of 3 mm × 3 mm was used for depth profiling studies. The sputtering rate relative to Ta_2O_5 under the same conditions was approximately $50\,\text{Å}\,min^{-1}$. The $Au_{4f_{7/2}}$ binding energy for calibration purposes was 84.00 eV. Binding energies were corrected for charging effects by referencing to the C_{1s} line (BE = 284.6 eV), and the reproducibility of the binding energies was approximately ±0.1 eV.

3. Results and discussion

3.1. *Protecting effects of PMTA on the coloured coordination compound films*

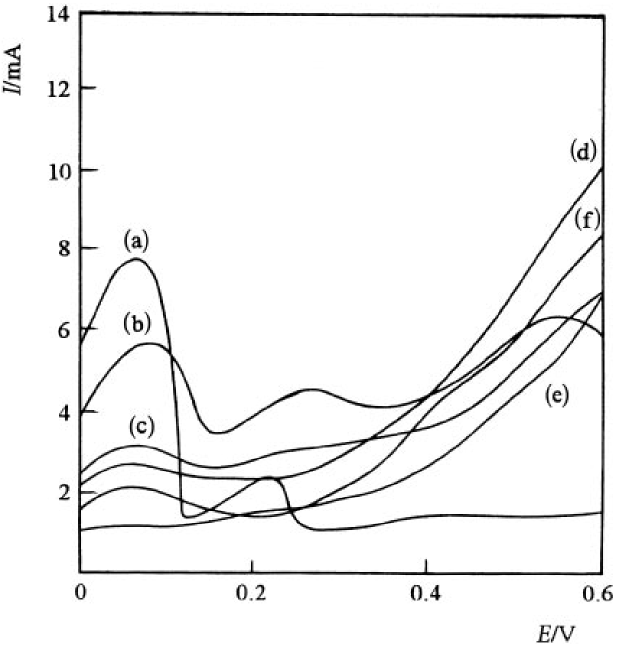

Fig. 1. LSV curves of the Mo–S–Cu cluster compound films before PMTA passivation: (a) blank copper; (b)–(f) Mo–S–Cu cluster compound films produced by 5, 20, 30, 45 and 60 min of MoS_4^{2-} treatment, respectively.

Table 1 summarizes the data of salt water dipping and H_2S accelerated tarnish tests for the Mo(W)–S–Cu cluster compound films before and after passivation, and the results indicate that Mo(W)–S–Cu cluster films provide poor protection against Cl^- or H_2S attack on the copper substrate. Loss and change of colour and film degradation were observed upon exposure to aggressive media. If the films are passivated by PMTA, their protection abilities will be greatly enhanced and the colours stabilized. Like Cu [8, 9], PMTA is superior to TTA, BTA, MBT, MBI, 2-AP, IBM and HBTA both in protecting these coloured surface coordination compound films and in enhancing the resistance of copper substrate against aggressive attack [10, 11].

The LSV curves of the Mo–S–Cu cluster compound films before PMTA passivation are given in Fig. 1(a)–(f). The newly polished copper is susceptible to attack by aggressive media. Once the anodic potential exceeds zero, corrosion occurs. Such was also the case of the Mo–S–Cu cluster compound films generated from the interface reaction between MoS_4^{2-} and the copper, thus the copper substrate underneath was easily corroded. However, the corrosion currents of the copper electrodes covered by Mo–S–Cu cluster films were lower than those of the uncoated blank copper. This indicates that the cluster films do provide some protection. It is reported in previous work [1, 2] that longer reaction times generate thicker films. Fig. 1 clearly shows that the corrosion current decreases while the reaction time for film formation increases, which suggests that the thicker the Mo–S–Cu cluster films, the more protective they are.

W–S–Cu cluster films yield similar results. (See Fig. 2(a)–(f).) Obviously, W–S–Cu cluster films are more effective for copper protection than Mo–S–Cu films. The onset of film failure is slower and the corrosion currents are lower. However, these W–S–Cu films are also not sufficiently protective to completely prevent electrochemical corrosion. No matter how thick the W–S–Cu cluster films, the corrosion currents occur even when anodic voltages are close to zero, but they do not increase immediately with voltage. For the electrode treated with 5 min of WS_4^{2-} immersion, the corrosion current maintained at 0.56–0.67 mA, and degradation of the cluster film did not take place, when the anodic voltage ranged between 0 and 0.1 V. A low level of corrosion of copper substrate was observed. The W–S–Cu film began to show obvious failure against corrosion beyond approximately 0.1 V, and the corrosion current increased rapidly thereafter. As a result of 30 min of WS_4^{2-} dipping, the W–S–Cu cluster film provided better protection. The corrosion current was 0.25–0.76 mA between 0 and 0.23 V, implying that the film was stable and no evident electrochemical corrosion occurred. However, the current increased rapidly after the threshold limit anodic voltage of 0.23 V; this indicates that the total degradation of the W–S–Cu film, as well as serious corrosion, occurs. The LSV curves for the electrode covered by W–S–Cu cluster films generating from 50, 120 min of interface reaction can be interpreted similarly. The trend is that a longer reaction time used for treating a copper electrode with WS_4^{2-} will result a thicker film, a wider voltage region for constant corrosion current, and a lower corrosion current level. Particular attention should be paid to the electrodes which had reacted with WS_4^{2-} for 480 and 1080 min. The corrosion current was by far lower than that in any case

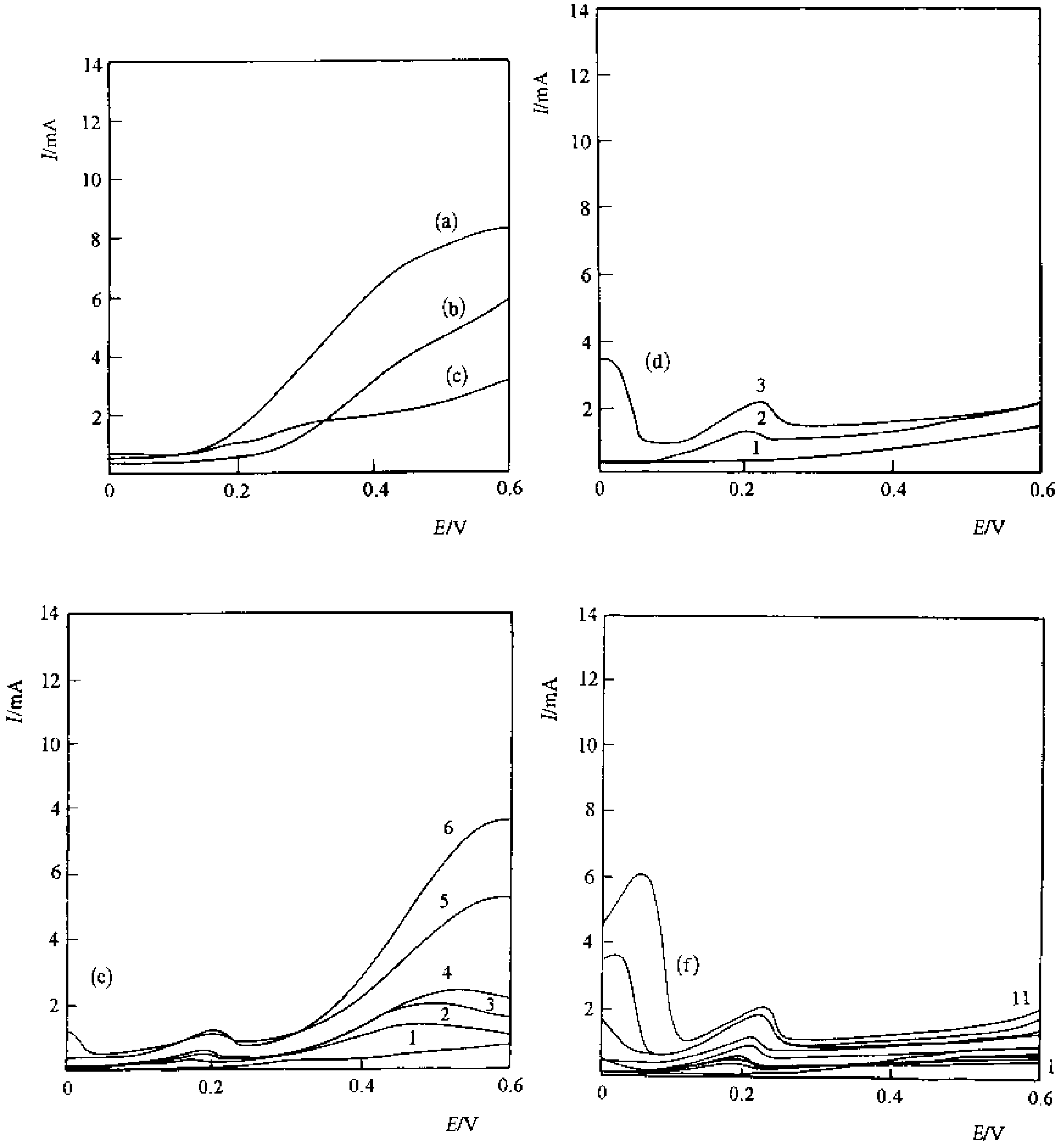

Fig. 2. LSV curves of the electrodes covered by W–S–Cu cluster compound films after (a) 5, (b) 30, (c) 50, (d) 120, (e) 480 and (f) 1080 min of interface reaction with WS_4^{2-}.

discussed previously and was almost constant in the whole experimental anodic voltage range. This is due to the thickness of the W–S–Cu cluster compound film formed from 480 min or 1080 min of interface reaction. The film could not be completely destroyed by only one cycle of LSV scan. The aggressive species had to pass through a much thicker barrier to attack the metal substrate. With the LSV scanned one after another, the corrosion current increased gradually until a LSV curve analogous to that of the blank copper appeared. For the electrodes prefilmed with 120, 480 and 1080 min of WS_4^{2-} treatment, 3, 6 and 11 cycles of LSV scans should be carried out respectively to damage the cluster films on copper surface.

The representative LSV curves for the PMTA passivated Mo(W)–S–Cu cluster compound films are illustrated in Fig. 3. Obviously, these colour films, along with the copper substrate underneath, are effectively stabilized or protected.

3.2. *XPS and AES investigation of PMTA/Mo(W)–S–Cu cluster films*

In order to verify the interaction of PMTA with Mo(W)–S–Cu cluster compound films, XPS and AES determination combined with Ar^+ sputtering depth profile analysis were conducted. Figure 4 shows the representative survey XPS spectrum of the Mo–S–Cu

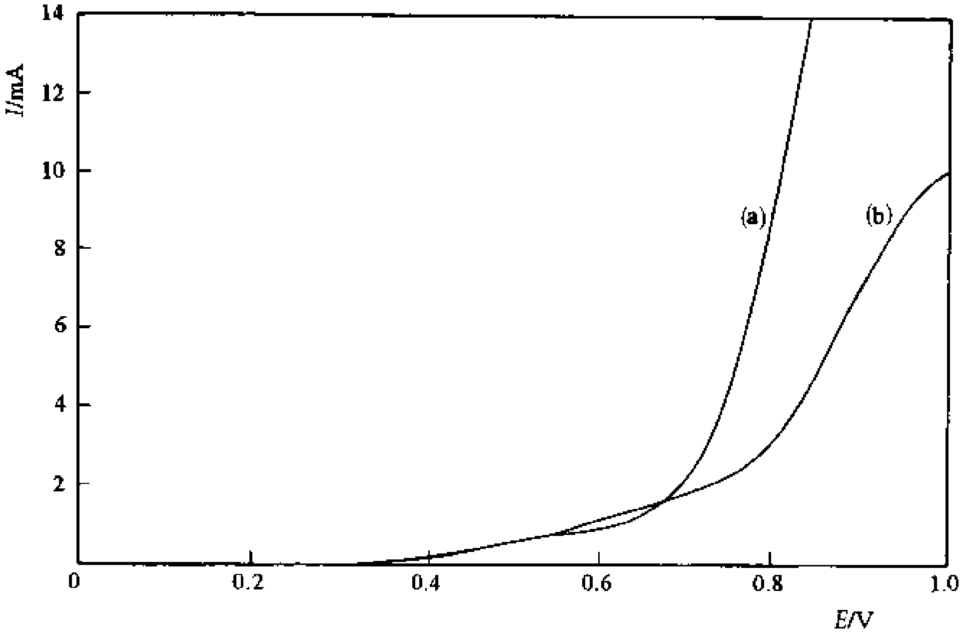

Fig. 3. Representative LSV curves for the PMTA passivated (a) Mo–S–Cu and (b) W–S–Cu cluster compound films.

cluster compound film treated with PMTA. Cu_{2p}, Cu_{LM}, Cu_{3s}, Cu_{3p}, O_{1s}, N_{1s}, C_{1s} and S_{2p} peaks were observed, while no peak corresponding to Mo was found. The peaks of N_{1s}, C_{1s} and S_{2p} belong to PMTA molecule, and this suggests that the Mo–S–Cu cluster compound film might be covered by a layer of PMTA film. Further evidence in favour of this comes from the AES spectra before and after Ar^+ sputtering (see Fig. 5). Only S, C, N, O and Cu peaks, being consistent with the survey XPS results, were observed for the PMTA passivated Mo–S–Cu films unsputtered. After 5 min of sputtering, the S and N peaks were almost constant, the C peak was even stronger than ever before while the O peak was still weak, and no Mo peak was detected. This suggests that a thick and complete Cu–PMTA film had formed. The relatively weak O peak supports the assertion that the Cu–PMTA film might establish on the basis of Mo–S–Cu cluster compound film instead of Cu_2O layer. However, after 30 min of sputtering, the spectrum changed greatly. The C and S peaks vanished, all this indicating that the Cu–PMTA film had been removed. The Cu peak was almost constant, while the S peak became much stronger and

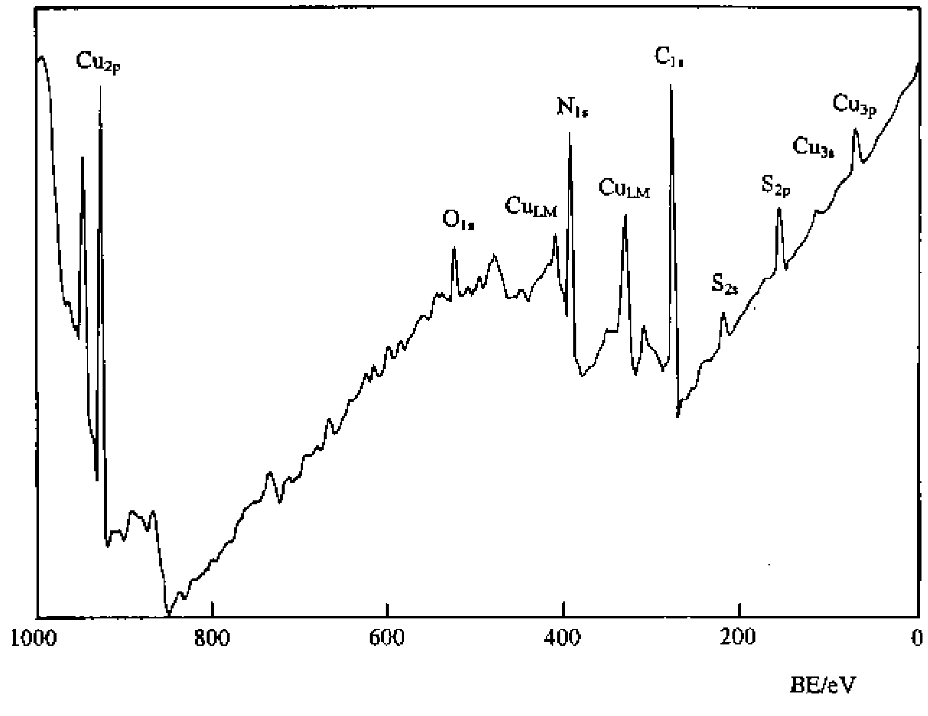

Fig. 4. Representative full XPS spectrum of the PMTA treated Mo–S–Cu cluster compound film.

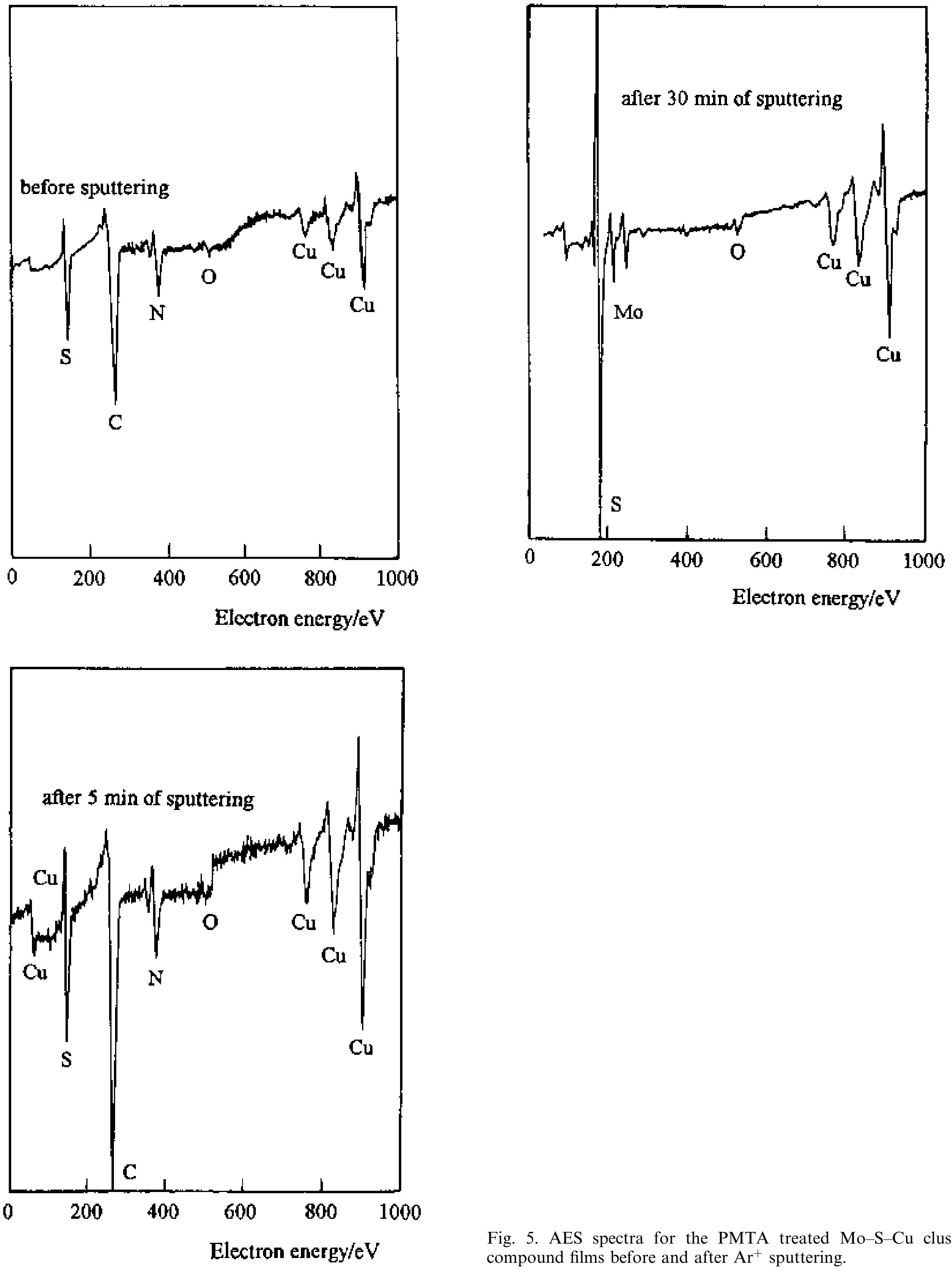

Fig. 5. AES spectra for the PMTA treated Mo–S–Cu cluster compound films before and after Ar^+ sputtering.

two Mo peaks emerged, indicating that the sputter had reached the Mo–S–Cu film. Based on the AES results, it can be concluded that the PMTA passivated Mo–S–Cu cluster compound film is a composite film, containing two layers. The outer layer is a Cu–PMTA coordination compound film, while the inner layer is a Mo–S–Cu cluster compound film.

The AES depth profile curves of a Cu–PMTA/Mo–S–Cu cluster composite film are given in Fig. 6. Two constant composition regions appear around 0.5–6.5 (Cu–PMTA) and 16.5–33.0 (Mo–S–Cu) min. The average contents of each elements in these two layers are: Cu 35.4, N 10.1, O 2.4, Mo 1.7, C 41.6, S 8.7 (Cu–PMTA layer); Cu 36.9, N 3.3, O 2.6, Mo 12.4, C 2.5, S 42.3 (Mo–S–Cu layer). Calibrated by Ta_2O_5, the thicknesses of the two layers were estimated to be 300 and 825 Å, respectively.

High resolution XPS determination was carried out to investigate the oxidation state of each element in the composite film. High resolution Cu_{2p} and

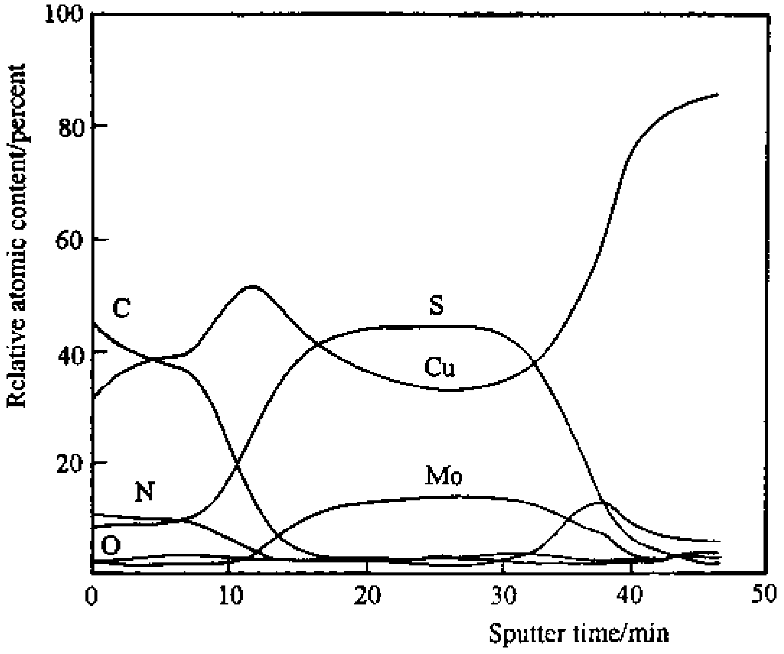

Fig. 6. AES depth profile curves of a PMTA passivated Mo–S–Cu cluster compound film.

CuL$_3$VV line XPS spectra of samples before and after Ar$^+$ sputtering were recorded (see Figs 7 and 8). Whether the film was sputtered or not and irrespective of the length of sputter time, the Cu$_{2p_{3/2}}$ binding energies were 932.3, 932.9 and 932.5 eV, and the peak values of CuL$_3$VV lines were 337.5, 336.7 and 336.0 eV, all being in agreement with those of Cu$^+$ [12–16]. No Cu^{2+} was observed.

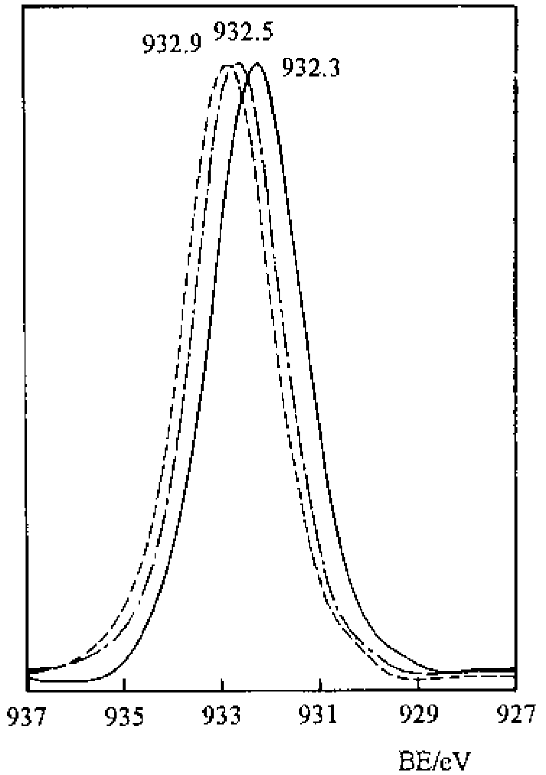

Fig. 7. High resolution XPS spectra of Cu$_{2p}$ before and after Ar$^+$ sputtering. Key: (———) before sputtering; (- - - - -) after 5 min of sputtering; (-—) after 30 min of sputtering.

High resolution S$_{2p}$ XPS spectra of the PMTA treated Mo–S–Cu film before and after sputtering are shown in Fig. 9. The peak at 163.2 eV of the unsputtered sample might be caused by contamination. The peaks at 162.5 and 161.8 eV of the sample after 5 and 30 min of sputtering, belong to the S^{2-} of Cu–PMTA and Mo–S–Cu cluster compound film, respectively. No sulfur in higher oxidation state was detected.

XPS and AES investigations of other PMTA treated Mo–S–Cu cluster compound films, as well as W–S–Cu cluster films, give similar results.

4. Conclusions

The Mo(W)–S–Cu cluster compound films are liable to be oxidized gradually when exposed to air. They provide limited protective effect against Cl$^-$ or H$_2$S erosion to copper substrate. Film colour loss or change and film degradation occur upon contacting the aggressive media. PMTA passivation not only stabilizes the colours of these films, but also prevents the film from degradation and the copper substrate from corrosion. The protection effect of PMTA on these films can be attributed to the formation of a layer of dense, insoluble and transient polymeric coordination compound films via reaction of PMTA with Cu(I) of the coloured films.

Acknowledgements

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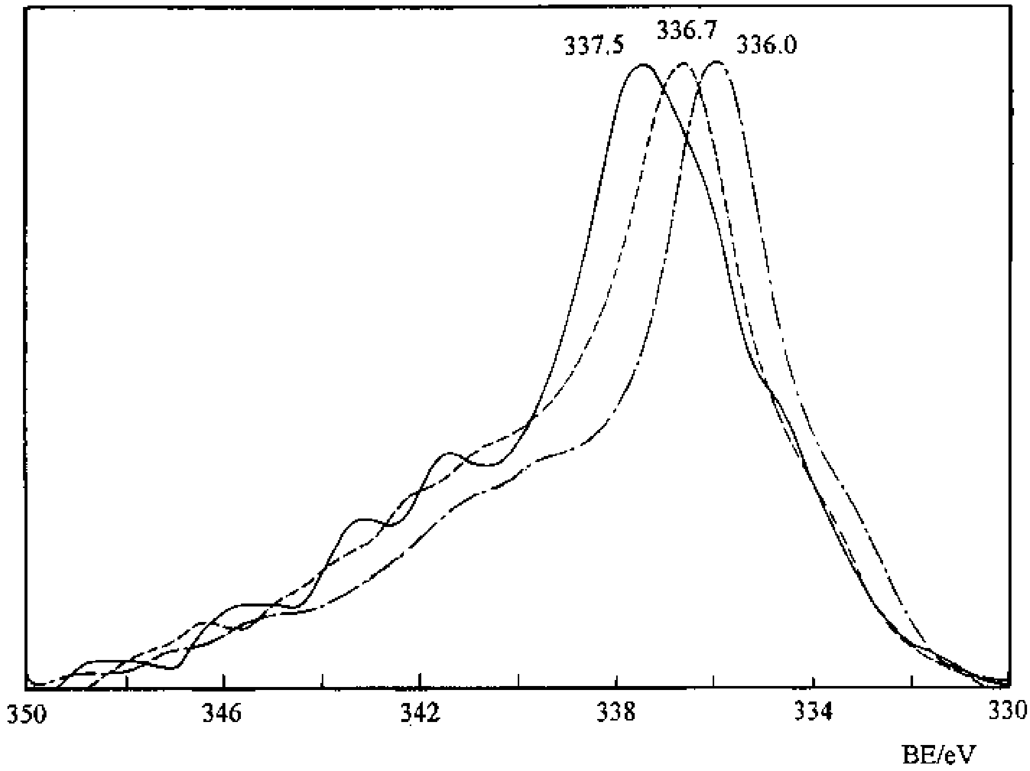

Fig. 8. High resolution CuL$_3$VV line XPS spectra before and after Ar$^+$ sputtering. Key: (———) before sputtering; (- - - - -) after 5 min of sputtering; (-·-·-) after 30 min of sputtering.

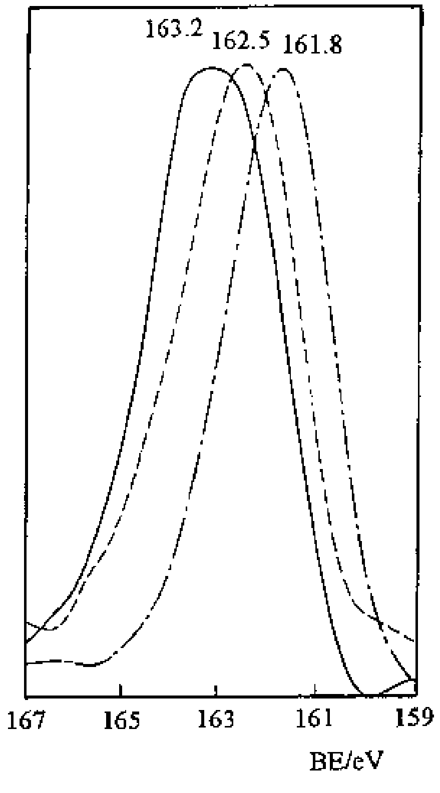

Fig. 9. High resolution S$_{2p}$ XPS spectra for the PMTA treated Mo–S–Cu film before and after sputtering. Key: (——) before sputtering; (- - - - -) after 5 min of sputtering; (-·-) after 30 min of sputtering.

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