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Applications Note

X-ray Photoelectron Spectroscopy Study of a Copper-Based Biocidal Film

MO513(A)

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Overview

X-ray photoelectron spectroscopy (XPS) is ideally suited to the study of copper-based biocidal films. This application note provides an insight into the use of XPS in understanding the surface chemistry, elemental composition, and mechanisms of copper-based biocidal films. By employing XPS, it is possible to gain valuable insights into the oxidation states of copper, the presence of contaminants, and the chemical bonding at the film surface. This knowledge contributes to the optimization of film design and performance, ultimately leading to enhanced antimicrobial properties and improved hygiene.

Introduction

The persistence of pathogenic bacteria and viruses on surfaces act as sources of infection on contact. This is a particular problem in healthcare environments with the existence of antibiotic-resistant bacteria. Thin coatings combining anti-microbial copper oxides and photocatalytic titania on metal and glass have been deposited by an open environment chemical vapour deposition (CVD) process, which mimics an industrial online process. The deposition is sequential with copper oxide deposited before the titania.

X-ray photoelectron spectroscopy and sputter depth profiling were used to characterise the lateral and depth distribution of the copper within the thin film. Group array analysis allows the homogeneity of the CVD film to be probed over the entire sample, allowing specific areas of interest to be identified and further analysed.

Experimental

The combined copper oxide-titania thin film on glass substrate sample was mounted on the sample bar with no further preparation. As the thin film was not in electrical contact with the sample holder the low energy, electron only charge neutraliser was used during data acquisition.

All measurements were performed using the AXIS photoelectron spectrometer. A large area (700 x 300um) survey spectrum was acquired at highest sensitivity using 160 eV pass energy. Photoelectrons were excited using monochromatic Al Kα X-rays (1486.6 eV).

The elemental depth distribution was determined by destructive sputter depth profiling. Monoatomic 5 keV Ar^+ ions were rastered over a 2x2 mm crater, with spectra

collected from a 110 μm diameter analysis area at the centre of the etch crater.

Results and Discussion

The survey spectrum from the as-received sample is shown in figure 1 and showed clear evidence of Cu on the surface confirming that it had diffused through the subsequent titania layer due to the high deposition temperature (500 °C). Also observed in the survey spectrum are the Ti core levels, indicating that the Cu layer is either continuous and thinner than the 10 nm sampling depth of XPS or non-continuous with island-like growth. Carbon and oxygen are also measured and are assumed to be associated with atmospheric contamination. It is assumed that the oxygen will also be associated with the photocatalytic titania layer as well as oxidation of the copper.

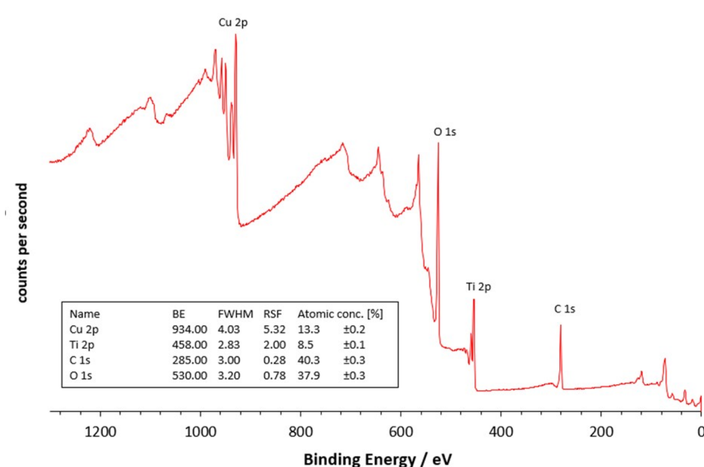

Figure 1. large area survey spectrum, including relative atomic concentration, from as-received sample.

To further investigate the Cu distribution, a group array acquisition was performed. Here, a 9 x 13 array of discrete analysis positions was defined with spectra acquired from a 300x700 μm analysis area at each position. Total acquisition time was 4½ hours. Automated quantification of each spectrum

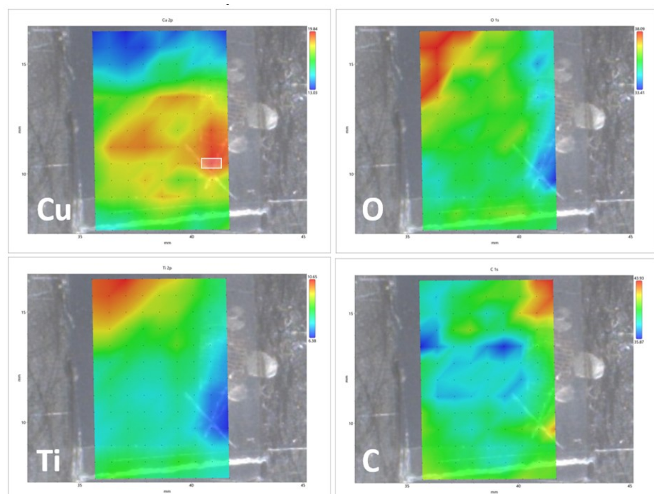

Figure 2: Elemental distribution displayed as a 'thermal map' overlaid on the optical microscope image of the sample.

and subsequent graphical display, figure 2, demonstrates that the copper distribution across the entire sample is *not* uniform. Higher relative elemental concentrations are shown in 'hotter' colours, highlighting that the oxygen is predominantly associated with the titanium.

To determine the chemical state of the copper a high energy resolution narrow region scan was performed at position M96 where the graphical display indicates highest Cu concentration. The analysis area is represented by the white outlined area in the Cu array analysis in figure 2.

Figure 3 shows the Cu 2p core-level spectrum. Chemical state analysis of copper species by XPS is difficult due to the complexity of the Cu 2p spectrum. Cu(II) species have a significant shake-up structure, whilst Cu metal and Cu(I) species have overlapping binding energies. To simplify the analysis of the copper chemical state a simple 3-peak model was used, shown in figure 3, with the primary core-level photoemission peak (green) at 933.1 eV and two well-documented shake-up satellite components (yellow). For this study the Cu $2p_{3/2}$ peak shape is interpreted qualitatively to conclude that the copper is present as Cu(II). This is supported by comparison to a reference spectrum and calculation of the Cu $2p_{3/2}$ – Cu $L_3M_{4,5}M_{4,5}$ Wagner (chemical state) plot [1]. It is noteworthy that despite the array analysis being acquired prior to the narrow region Cu 2p scan, reduction of Cu(II) had not been

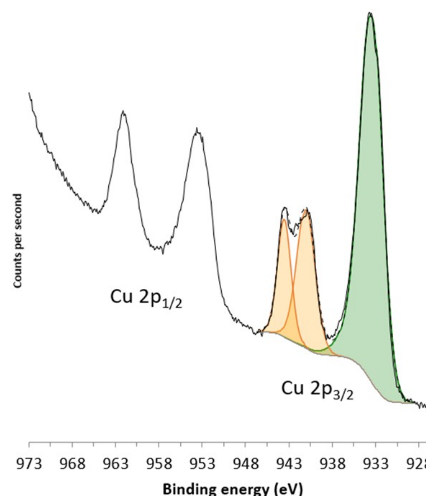

Figure 3: Cu 2p high resolution spectrum acquired from array position M96

induced by X-ray flux or electron charge neutralisation.

Position M96, corresponding to highest Cu concentration, was chosen to acquire a sputter depth profile to determine the depth distribution of the copper.

Survey spectra were acquired after each etch cycle, shown in figure 4 (overpage). An elemental depth profile was generated from this data, shown in figure 5. Of specific interest is the copper concentration through the surface coating. The initial as-prepared copper concentration at the surface is 35 rel. at. %. This drops to *ca.* 5 at. % through the titania thin film and

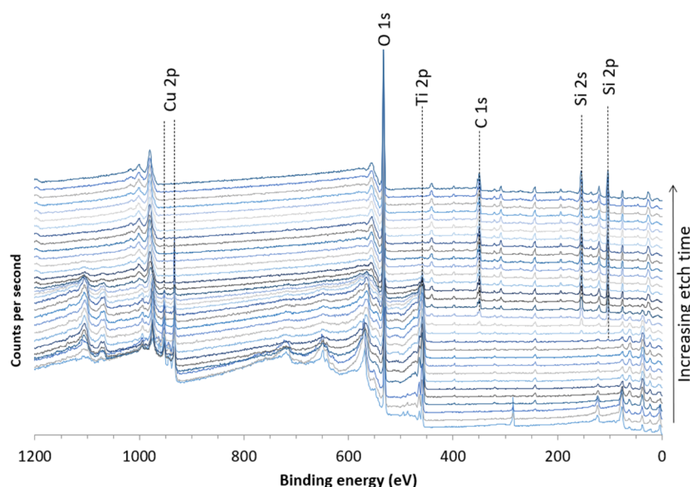

Figure 4: survey spectra acquired from a 110um diameter analysis area centred in a 2 x 2 mm etch crater created using 5 keV Ar^+ ions.

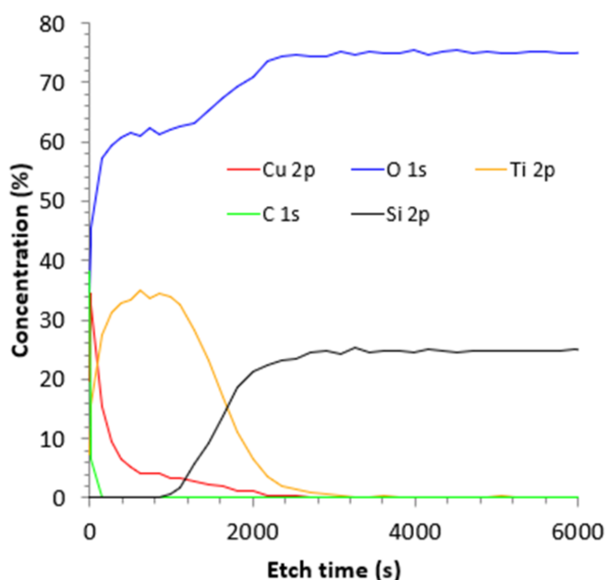

Figure 5: Elemental concentration depth profile generated from survey spectra shown in figure 4.

decreases until the interface between the titania and silicon dioxide of the substrate. There is no evidence that Cu has diffused through the SiO_2 layer. As the titania layer was deposited after the copper oxide, the depth profiling confirms the migration of copper ions through the titania.

By way of comment, it is noted that position M96 also shows trace contamination of tin, the Sn 3d doublet being observed at 485 eV binding energy. The tin is removed after the first two etch cycles. Origin of tin for this sample is unexplained, as it is not present in any of the precursors used for the Cu or titania CVD coating process. One suggestion is that it may be due to contamination from glass cutting tools. Carbon surface contamination is removed after the first etch cycle.

Conclusions

The lateral and depth distribution of copper within a CVD grown copper-titania composite thin film has been determined using XPS array analysis and sputter depth profiling. Copper was observed over the entire surface, although the distribution across the surface was shown to vary.

Copper at the surface was shown to be present as Cu(II), assumed to be CuO. The depth distribution shows that, as expected, the copper concentration is highest at the as-received surface with lower concentration through the titania film. No copper is observed in the silica substrate.

Acknowledgements

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References

[1] M.C. Biesinger, Surf. Interface Anal. 49 (2017) 1325-1334.

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