Composition and Thickness of Surface Layer on Molybdenum Tips for Scanning Tunnelling Microscopy (STM) Studied by SEM/AES/(AR)XPS

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A combination of SEM, AES and angle-resolved XPS (ARXPS) has been applied to analyse the distribution of chemical compounds in the surface region of electrochemically etched molybdenum tips and to determine the contamination layer thickness. Carbon monoxide, graphite, molybdenum carbide and molybdenum oxide were found to be the main surface contaminants on molybdenum tips. Auger line profiling revealed a significant enrichment of carbon and oxygen upon the tip. The thickness of the oxygen-carbon contamination layer on the tip was estimated to be 13.5 ± 1.0 nm as measured by AES. The thickness of the contamination layer on a molybdenum sheet was found to be 8.0 ± 1.5 and 6.8 nm using AES and ARXPS respectively. Quantitative analysis of the surface concentrations of carbon, oxygen and molybdenum has been performed.

INTRODUCTION

The scanning tunnelling microscope (STM) is a useful tool for real-space imaging of near-surface electronic structure.^{1,2} The reliable formation of fine and clean tunnelling probe tips is one of the most important experimental aspects of STM operation. It is well known that a surface contamination layer can influence the tunnelling current by changing the effective resistance of the tip surface layer.^{3,4} Therefore it is of great interest to know the composition and thickness of such layers.

Unfortunately, only a few papers deal with the analysis of the surface composition of STM tips. The AES technique has been applied in the analysis of Pt/Ir⁵ and W⁶ tips. The XPS method has been employed for the determination of graphite⁷ and tungsten⁶ tip surface compositions.

The thickness of the surface contamination layers on STM tips has been determined using TEM^{4,8,9} and AES combined with Ar⁺ sputter profiling.⁶

There is a lack of surface characterization of molybdenum tips which are often utilized in STM.^{10,11}

The purpose of the present paper is to elucidate both the chemical structure and distribution of chemical compounds in the surface region of electrochemically etched STM molybdenum tips and to determine the contamination layer thickness. A combination of SEM, AES and XPS has been applied for the chemical characterization of the surface layer. The surface of the Mo STM tip contamination layer has been characterized using AES combined with Ar⁺ sputter profiling and

angle-resolved XPS (ARXPS). The combination of these methods, applied for the first time to Mo tip analysis, allowed us to make a full characterization of the Mo tip surface.

EXPERIMENTAL

Electrochemically etched molybdenum tips were fabricated by placing several millimetres of 0.7 mm cold-drawn molybdenum wire into a 1 M KOH etching solution and applying a 12 V_{eff}, 50 Hz potential to the molybdenum wire (with respect to a gold ring electrode surrounding the Mo wire and inserted into the solution). At the end of the etching procedure the potential was reduced to 6 V a.c. to obtain a sharper tip. The etching process was discontinued when the suspended wire fell off. This wire was then cleaned in distilled water and directly transported in air to the measuring system.

Two methods have been used to characterize the composition and elemental distribution in the surface region of the Mo tip, i.e. Auger line scans and multiple-point Ar⁺-ion-sputtering Auger depth profiles. The measurements have been performed with a PHI 600 SAM (scanning Auger microscope) system.

The elemental Auger line scans were recorded using the following experimental conditions: a primary beam, directed perpendicular to the axis of the wire, of energy $E_p = 15$ kV; primary beam current $I_p = 0.25$ nA; beam diameter $\varnothing \approx 30$ nm; 100 points per line; analysis time per point, $\tau = 25$ s. The resolution of the cylindrical mirror analyser, $\Delta E/E$, was set at 1.2%. Under these conditions the detection limits for carbon and oxygen are less than 2% and 0.5% (atomic concentration) respectively.¹² The line scans have been corrected for topographic effects by taking the normalized Auger

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intensity $(P - B)/B$, where P and B are the peak and background intensities respectively.¹³

The Auger spectra and Auger sputter profiles were taken using $E_p = 10$ kV; $I_p = 0.1$ μ A, $\varnothing \approx 0.4$ μ m and $\Delta E/E = 0.6\%$. The axes of the wire, electron beam and ion beam were oriented in one plane. The angles between the axis of the wire and the electron beam and ion beam were 90° and 160° respectively. The argon ion beam, with an ion energy of 3.5 kV and a current density of 0.6 μ A cm^{-2} , was produced by a differentially pumped ion gun. Calibration of the sputter rate was performed on a Ta_2O_5 layer of thickness 100 nm.

The XPS and ARXPS experiments were carried out in a Kratos 800 system controlled by a PDP 11 micro-computer. The spectrometer was calibrated by measuring the Ag $3d_{5/2}$ peak and the x-ray-induced Ag MNN Auger peak on a clean, sputtered silver sample using an Mg anode¹⁴ and its linearity was checked. The analysed area was about 0.2 mm^2 by using a diaphragm and comprised both the tip and the surrounding areas. The spectra were taken and quantitatively evaluated using DS 800 software.¹⁵ In all simulations the asymmetrical Gaussian-Lorentzian mixed functions were used for the molybdenum peaks and 100% Gaussians for the oxide and carbide peaks. Such curve synthesis of Mo x-ray photoelectron spectra has been reported by Kojima and Kurahashi¹⁶ to be sufficiently flexible to represent an XPS peak.

RESULTS AND DISCUSSION

AES measurements

Figure 1 shows an SEM image of a molybdenum tip on which analysis has been done.

The Auger spectrum of the STM molybdenum tip in the surface region is presented in Fig. 2. It reveals

Figure 2. Auger spectrum of molybdenum STM tip surface before Ar^+ sputtering.

oxygen and carbon in addition to molybdenum. The Auger line scans in Fig. 3 display the topographically corrected carbon and oxygen Auger intensities along the tip in the SEM image (Fig. 1, indicated by arrows).

It can be seen that the oxygen and carbon concentrations are not homogeneous in the measuring area (0 – 2 μ m). A significant enrichment (relative atomic concentration) of both elements is detected at the top of the Mo tip. This could be due to carbon and oxide formation as a result of the high local temperature generated during the formation of the tip at the end of the electrochemical etching procedure.

In order to get a better insight to the distribution and thickness of carbon and oxygen contamination, multiple-point Ar^+ -ion-sputtering Auger depth profiles have been measured on both the Mo tip and a large-area Mo sheet of the same material after the same electrochemical etching and cleaning procedure. The results

Figure 1. Scanning electron micrograph of electrochemically etched molybdenum STM tip analysed by AES.

Figure 3. Auger elemental line scans recorded between the two arrows in the SEM image of Fig. 1. The Auger signal is given in arbitrary units.

are presented in Fig. 4. The peak-to-peak heights of the Mo MNN, C KLL and O KLL Auger peaks, divided by the standard sensitivity factors,¹⁷ have been plotted in atomic concentration mode as a function of sputter time.

It can be seen that the time required for sputtering of oxygen and carbon from the tip [Fig. 4(a)] is significantly longer than that recorded on the Mo sheet [Fig. 4(b)].

The calculation of the thickness must be done very carefully. For a rough calculation a linear relation between sputtering time and removed layer may be

Figure 4. Auger sputter depth profiles (a) molybdenum STM tip and (b) Mo sheet. Sputter rate 0.8 nm min^{-1} .

assumed. In our system the sputter rate was found to be 0.8 nm min^{-1} by calibration performed on a Ta_2O_5 layer. On the basis of the fact that the surface-binding energy for tantalum and molybdenum¹⁸ as well as the sputter yield¹⁹ and depth resolution for Ar profiling of Ta and Mo²⁰ are similar, we can use the above value of the sputter rate to estimate the molybdenum oxide-carbon layer thickness. The influence of the ion- and electron-induced effects accompanying AES depth profile measurements²¹ seems to be comparable for thin Ta and Mo layers and has been neglected.

The thickness of the molybdenum oxide-carbon layer on the Mo tip and Mo sheet was estimated to be 13.5 ± 1.0 and $8.0 \pm 1.5 \text{ nm}$ respectively. The latter value has been verified by comparison with the results of the ARXPS measurements.

Analysis of the Ar^+ -ion-sputtering Auger depth profiles afforded the possibility of comparing the character of carbon and molybdenum compounds in the bulk and in the surface region of the Mo tip. Figure 5 shows the C KLL and Mo MNN Auger lines before and after 16 nm depth sputtering of the Mo tip.

The C KLL spectrum peaks at 273, 254 and 241 eV suggest the graphitic nature of carbon in the surface region of the Mo tip as reported by Haas *et al.*²² The shift of the C KLL Auger peak at 273 eV to lower energies after sputtering and the shape of the Auger lines [Fig. 5(a)] seem to be indicative of the carbide character of carbon in the bulk.²² Similar features in the carbon Auger spectrum have been observed on an electrochemically etched tungsten STM tip.⁶

Figure 5. AES lines in the differentiated mode for (a) C KLL and (b) Mo MNN of the molybdenum tip before (lines 1) and after (lines 2) 16 nm Ar^+ sputtering.

The broad Mo MNN Auger peak was recorded before sputtering [Fig. 5(b)]. This shape of spectrum has been reported for oxidized molybdenum and was interpreted to be due to the presence of two valence states of Mo giving overlapping spectra separated in energy by about 4 eV.²² The observed 4 eV shift in energy of the lower-kinetic-energy maximum of the Mo MNN spectrum due to sputtering [Fig. 5(b)] appears to confirm the existence of an oxidized molybdenum state on the Mo tip.

XPS measurements

Figure 6 shows the XPS spectra of Mo 3d, C 1s and O 1s of the STM molybdenum tip. Two Gaussians and one Lorentzian–Gaussian doublets were used in the deconvolution of the Mo 3d spectrum, whereas pure Gaussians were applied in the simulation of the C 1s and O 1s peaks. The thinner lines represent the deconvoluted peaks. The sum of these lines is given as the thicker solid line.

The binding energy (BE) of the Mo 3d_{5/2} signal (228.0 eV) was found to be close to that reported by other authors (Table 1). Quantitative evaluation and deconvolution of the Mo 3d spectrum revealed additional peaks at BE = 229.8 and 228.3 eV [Fig. 6(a)]. On the basis of the results of the fitting procedure and comparing these results with the binding energies reported earlier for some molybdenum compounds (Table 1), we

can confirm the coexistence of Mo, MoO₂ and Mo₂C in the surface region of molybdenum tips.

The C 1s spectrum presented in Fig. 6(b) discloses the existence of four XPS peaks at 283.2, 284.9, 286.2 and 287.7 eV which can be attributed to molybdenum carbide,^{24,39,40} graphite,⁴¹ hydrocarbon carbon⁴² and molecular adsorbed CO.⁴³ The interpretation can also be based on three different states of CO adsorption (β at 282.7 eV, α at 288 eV and 'virgin' at 284.6 eV) on polycrystalline Mo.⁴³ Nevertheless, application of the 'virgin' state formed at 77 K⁴³ seems to be rather doubtful in our case.

Similar analysis of the O 1s spectrum [Fig. 6(c)] reveals the existence of XPS peaks at 530.9 and 532.5 eV which can be attributed to MoO₂ or MoO₃ (Table 1) and chemisorbed O₂ and CO⁴³ respectively.

The results of quantitative evaluation of C, O and Mo concentrations are presented in Table 2. Relatively high concentrations of carbon were found by XPS and AES on both tips and sheets. Nevertheless, the resulting concentrations of C determined by XPS are lower than those established by AES. This discrepancy can be explained by the difference in the mean free path for inelastic scattering of emitted electrons.¹⁴ In XPS the escape energy ($h\nu - BE$) for Mo 3d is about 1027 eV whereas the emission energy of the Mo MNN Auger peak is about 186 eV. Therefore in this case the XPS method seems to be slightly less surface-sensitive than AES. The results of ARXPS measurements performed at 60°, which revealed a significant enrichment of carbon in the surface region of the Mo sheet (Table 2), appear to confirm the above suggestion.

The concentrations (atomic per cent) of Mo, C and O in the different compositions obtained from XPS measurements on the Mo sheet are given in Table 3. This enables us to cross-check the mass balance for MoO₂ and Mo₂C. The results for MoO₂ are in good agreement and those for Mo₂C in reasonable agreement.

ARXPS measurements

The non-destructive ARXPS method is used often to study the thickness of the outermost top layer of solid materials.⁴⁴ We have applied 'absolute' ARXPS measurements described recently by Aarnink *et al.*⁴⁴ In this method the same XPS peak is measured at various photoelectron take-off angles and its intensity is normalized to the normal take-off angle.

For the intensity of the XPS peak of molybdenum measured at different electron take-off angles (α) and normalized to its intensity at normal take-off angle ($\alpha = 0$) we may write⁴⁴

$$N(\alpha) = \frac{I_{\text{Mo 3d}}(\alpha)}{I_{\text{Mo 3d}}(0)} = G(\alpha) \exp \left[\frac{d}{\lambda_{\text{Mo 3d, surf}}} \left(1 - \frac{1}{\cos \alpha} \right) \right] \quad (1)$$

where d is the uniform thickness of the surface layer and $\lambda_{\text{Mo 3d, surf}}$ represents the inelastic mean free path of the photoelectrons in this layer.

The function $G(\alpha)$, which depends on the geometry of the experimental set-up, sample and sample holder, has been measured directly on a clean, sputtered silver

Figure 6. (a) Mo 3d, (b) C 1s and (c) O 1s XPS spectra of molybdenum STM tip. Deconvoluted peaks are described in the graphs.

Figure 7. (a) Mo 3d XPS peaks of Mo sheet at photoelectron take-off angles of 0° and 60°. (b) Simulation of Mo 3d XP spectrum at 0° take-off angle.

70°. In Fig. 7(a) two XPS spectra of the Mo 3d peak measured on the sheet are shown, taken at electron take-off angles α of 0° and 60°. The deconvoluted spectrum of Mo 3d at 0° take-off angle is presented in Fig. 7(b). The thinner lines 'b' and 'c' represent the Mo 3d doublets of Mo₂C and MoO₂, while line 'a' describes the pure Mo 3d doublet of molybdenum. The sum of these Mo lines is given as the thicker solid line.

The thickness calculation has been performed with the Mo 3d low-BE component (the line with the highest intensity), normalized to the intensity at normal take-off angle and divided by the measured function $G(\alpha)$.

The result of the application of Eqn (1) for the surface layer thickness determination is presented in Fig. 8. In the co-ordinate system

$$\ln \frac{N(\alpha)}{G(\alpha)} \text{ vs. } \left(1 - \frac{1}{\cos \alpha}\right)$$

a straight line with correlation factor 0.998 was obtained. The calculated value of $d/\lambda_{\text{Mo 3d, surf}}$ was 2.20. Taking a value of $\lambda_{\text{Mo 3d, surf}}$ from the literature,^{45,46} we can estimate the thickness d to be 6.8 nm, which is in good agreement with the AES experimental result obtained on the sheet of molybdenum (8.0 ± 1.5 nm).

Figure 8. Examination of Eqn (1) for the thickness of the contamination layer on molybdenum determined using ARXPS measurements. The points represent experimental results while the straight line is the result of the fit.

CONCLUSIONS

The following conclusions can be drawn.

- (1) A combination of XPS, AES, Auger line profiling and multiple-point Ar⁺-ion-sputtering Auger depth profiles appears to be very useful for qualitative and quantitative analysis of the surface contamination of molybdenum STM tips. This is helpful for a preliminary selection of good-performance tips.
- (2) Graphite, molybdenum carbide, carbon monoxide and hydrocarbons were found as the main carbon contaminants on the molybdenum tip surface.
- (3) Chemisorbed oxygen, carbon monoxide and molybdenum oxide were revealed as oxygen contaminants on the Mo tip surface.
- (4) Higher concentrations of carbon and oxygen were detected on top of the Mo tip.
- (5) The thickness of the contamination layer on the Mo tip was estimated to be 13.5 ± 1.0 nm using Ar⁺-ion-sputtering Auger depth profile measurements. The contamination layer on the Mo tip was found to be much thicker than that reported on a W tip (1 ± 3 nm).^{6,47}
- (6) The thickness of the oxide-carbon layer on an Mo sheet was evaluated to be 8.0 ± 1.5 and 6.8 nm using AES and absolute ARXPS measurements respectively.

Acknowledgement

The authors would like to thank Mr B. Otten for preparing the SEM images.

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