Pure, smooth and dense W films obtained by an anodic arc plasma

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Tungsten films have a number of important applications. The techniques to produce quality films are very few and most of them use gases as precursors or as buffer. The Thermoionic Vacuum Arc (TVA) plasma is an original technique capable of producing pure, dense and very smooth Tungsten films of thicknesses from nanometers to tens of micrometers with no buffer gas or gas precursors. This paper presents characterisation of Tungsten films obtained by TVA in terms of composition and topography using XRF, XPS and AFM. The films studied are pure and contain a very thin surface oxide of WO_3. The influence of water vapors inherently present on the chamber walls to the film surface composition is also presented.

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1. Introduction

Tungsten has attractive properties for very high temperature applications owing to its high melting point – the highest of all metals, good thermal conductivity, lowest vapor pressure and low erosion rate on ion bombardment. This is the material of choice for facing tokamak plasma [1]. Tungsten is also used for X-ray masks and mirrors, in electronic industry and space.

Bulk tungsten cannot be machined and welded with ease. In order to widen its applicability, plasma coatings technologies were developed. Chemical Vapour Deposition (CVD), air plasma spray technology and evaporation are common processes in industry for tungsten deposition.

The properties of W films obtained by using different techniques are inherently different. For example, the microstructure of tungsten coatings varies with the technology used for its fabrication, this influencing thermal conductivity [2]. W films deposited by techniques involving gases as buffer or as precursor, contain either gas inclusions or oxidated phases [3].

We obtained W films using an original plasma source in vacuum, based on a hot cathode anodic arc PVD technique, also called Themoionic Vacuum Arc (TVA). In TVA, the energies of the ions forming the film can be easily controlled and can have values of hundreds eV, as reported elsewere [4]. This technique does not require the use of a buffer gas and the precursor is in the solid state. Gas inclusion is thus avoided.

In this work, W films obtained by TVA are characterised in terms of composition and topography using XPS, XRF and AFM.

2. Experimental setup

Tungsten films were deposited onto Si and also W substrates using the Thermoionic Vacuum Arc plasma (TVA). The substrates were cleaned 15 minutes in acetone and 15 minutes in isopropilic alchool using an ultrasonic bath then dried using a flow of nitrogen gas.

The plasma source

The deposition of tungsten was carried out in a stainless steel vacuum chamber vacuumed at a base pressure of 8×10^{-7} torr, using a TVA plasma source. The TVA ensamble briefly consists of an electron source (the cathode) and the target (the anode). The basic principle is heating the target with energetic electrons until a steady evaporation is obtained, followed by ignition of a high voltage arc in these vapors. Further details can be found in [5-8].

This plasma source can be used to deposit conductive materials. For materials with low melting temperature (less than 2000 °C), the target material is placed in a crucible and during film deposition full melting is obtained. For the deposition of higher melting point materials, like Tungsten, the anode can be made into a rod and the plasma is obtained by layer by layer evaporation. Tungsten rods are usually made by sintering and cannot be machined easily into small mushroom-shaped anodes needed in TVA. A specially designed anode, made of tungsten wire is presented in Fig. 1.

Fig. 1. Experimental setup of the TVA source with the Tungsten anode.

Several films were obtained using arc currents and voltages of 1.4 – 2.6 A and 1.5 – 2.3 kV, respectively. In-situ film growth was monitored using an Inficon XTC deposition controller based on a quartz oscillator. Measurement of film thickness was undertaken after deposition also, using a computer controlled Mitutoyo profilometer. Thin and also thick films of thicknesses ranging from 50 nm to 17.8 microns were obtained with TVA. The substrate temperature during deposition was room temperature and increased gradually with plasma conditions up to 275°C. No additional cooling or heating system was used during deposition, apart from the constant water cooling of the chamber walls.

Film analysis

X-ray Fluorescence (XRF)

The XRF measurements were performed using a portable spectrometer X-MET 3000TX+, from Oxford Instruments. The excitation source of this instrument is a miniaturised X-ray tube, equipped with a Rhodium anode, powered at a maximum current of 6 μA and maximum voltage of 40 kV. The measurement spot size is about 30 mm^2. The detection system is a PIN silicon diode detector, with Peltier cooling. The resolution of the detector is 270 eV for the K_α line of Mn (5.89 keV). The X-MET XRF analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage.

X-Ray Photoelectron Spectroscopy (XPS)

The XPS analyses for this work were carried out in a spectrometer using Mg anode with E = 1253,6 eV radiation, an anode voltage U of 12 kV and a current of 20 mA. A base pressure better than 5×10^{-9} torr was maintained in all experiments.

The samples to be analysed were analysed after exposure to the ambient air for several weeks.

The spectra were processed using XI SDP software. Curve synthesis of the W window (30 - 40 eV) was used for qualiative and quantitative quantification. Deconvolution using Gaussian fit parameters was undertaken.

The W XPS window contains the 4f and 5p peaks of metallic W and WO_3 oxide. Table 1 presents the binding energies of all peaks in the W window.

Table 1. Binding energies of the peaks used for deconvolution in the W window.

	4f7/2 Met.W	4f5/2 Met.W	5p3/2 Met.W	4f 7/2 WO_3	4f 5/2 WO_3
B.E.[eV]	31.23	33.37	36.7	35.4	37.5
FWHM[eV]	0.97	1.21	1.4	1.34	1.35

The calculation of oxide layer thickness using XPS data was undertaken from a model described by Briggs and Seah [6] and it is briefly presented in the following.

The model is based on the assumption that both the oxide overlayer and the substrate are amorphous.

The XPS signal coming from the substrate $S_{substrate,}$ here tungsten, can be written as:

$$S_{substrate} = S_{substrate}^{\infty} \exp(-d/\lambda \cos\theta) \tag{3}$$

The signal coming from a component of the oxide layer S_{oxide} is given by

$$S_{oxide} = S_{oxide}^{\infty} [1 - \exp(-d/\lambda \cos\theta)] \tag{4}$$

When more than a single oxidation state is formed in the overlayer and there is more than one component in the layer beneath the oxide, the thickness of the oxide layer d can be calculated as

$$d = \lambda \cos\theta \ln(S_{oxide} C_{substrate} / S_{substrate} C_{oxide} + 1) \tag{5}$$

where λ is the mean free path of photoelectrons through either substrate or oxide overlayer (considered equal [9]). C_{oxide} and $C_{substrate}$ are the concentrations of a component from the layer (the overlayer and the substrate, respectively) and can be easily calculated from the XPS data, using the values for signal and concentration of one of the oxides present in the oxide overlayer [10].

In this work, a value of 13.4 Å was used for the mean free path of electrons of 1450 eV kinetic energy traveling through the oxide layer (taken from [9]).

Only WO_3 was formed in our samples and therefore C_{oxide} is 1.

The analysis of surface compounds using different photoelectron emission angles (e.g. take-off angles) probes different sampling depths and is called angle resolved XPS

(ARXPS). This technique is non-destructive but its maximum sampling depth is only a few tens of nm at best. Another drawback of the technique is the fact that the signal from deeper layers contains information from the outermost layers also. Nevertheless, ARXPS is usefull for studying compositional distribution of surface oxide.

In order to probe greater specific depths, it is necessary to remove some of the sample surface and expose the underling layers for analysis. The most popular method is in-situ inert gas ion etching. A major limitation of this technique is the destructive nature of the ion-beam which can lead to erroneous conclusions. When the surface is sputtered, reduction of surface oxides and damage of layers usually occur. In this work, the technique was used to study film composition beneath the surface oxide and observe if any oxide formed during W deposition. Argon ions accelerated at 4kV and a 8 μA current for 5 minutes were used in this investigation.

AFM

The tungsten film topography was performed using an atomic force microscope, M*ultiMode NanoScope IIID Controller* (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA) model. Images were obtained by applying the Tapping Mode with phosphorus (n) doped Si cantilever. The TappingMode operates by scanning a tip attached to the end of an oscillating cantilever across the sample surface. Tip (RTESP – Veeco Instruments GmbH) was used at driving frequency around 290 kHz. Height and phase images of sample regions were acquired simultaneously with resolutions of 256×256 pixels and a scan rate of 1.0 kHz. All measurements were carried out at room temperature. The acquisition and the offline analysis were performed using the NanoScope software version 531r1.

3. Results and discussion

We have previously demonstrated that the energy of Tungsten ions arriving at the substrate is very high (of many hundreds eV) and can be controlled via the arc voltage. We present here further investigations on the composition and topography of the films obtained by TVA.

A high purity of the W films is demonstrated by XRF, as can be observed in Fig. 2, where only the peaks belonging to W are present. The peak of Fe in the spectrum is an artefact and appears in all samples, regardless of their nature or composition [11]. XPS analysis have also confirmed the purity of our W films. This is due to the fact that no buffer gas and no gas precursors are used for the deposition of W films by TVA. Instead, high vacuum of 8×10^{-7} torr is used. As the TVA plasma is localised and does not fill the chamber, no impurification from any of the components in the chamber takes place.

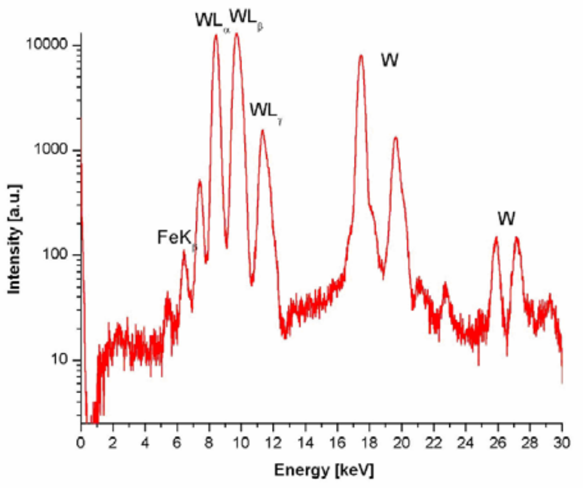


Fig. 2. XRF spectrum of a typical tungsten film obtained by the anodic arc plasma

In Fig. 3, the Tungsten XPS window of a typical film is presented. The only oxide found was WO_3.

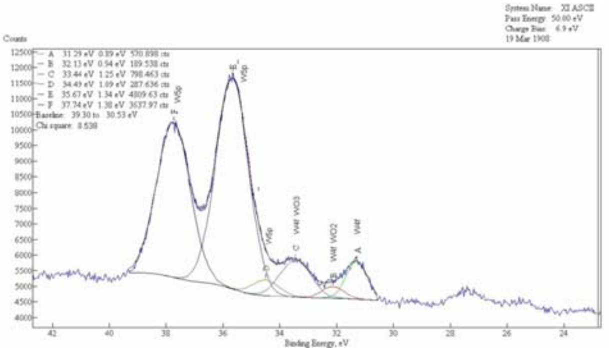


Fig. 3. The Tungsten XPS window of a typical film obtained by the anodic arc plasma.

XPS analysis on a set of W films obtained using identical plasma conditions but different thicknesses revealed a deposition parameter that is very important for the final film surface. The temperature of the chamber walls directly affects the amount of water vapors present during deposition. These vapors provide the oxygen that affects the as deposited layer to form the oxide. Higher film thicknesses means longer deposition time which further increases the temperature of the chamber walls, liberating water vapors.

This phenomenon was put in evidence by studying the oxide thickness. The calculated value of the oxide thickness formed on the surface of our tungsten films increased with Tungsten film thickness, which corresponds to a longer deposition time and to a higher temperature of the chamber walls. The XPS spectra of these Tungsten films are shown in Fig. 4. By sputter-depth profile analysis using Argon ions, the superficial oxide was removed revealing a pure metallic film, also shown in this figure.

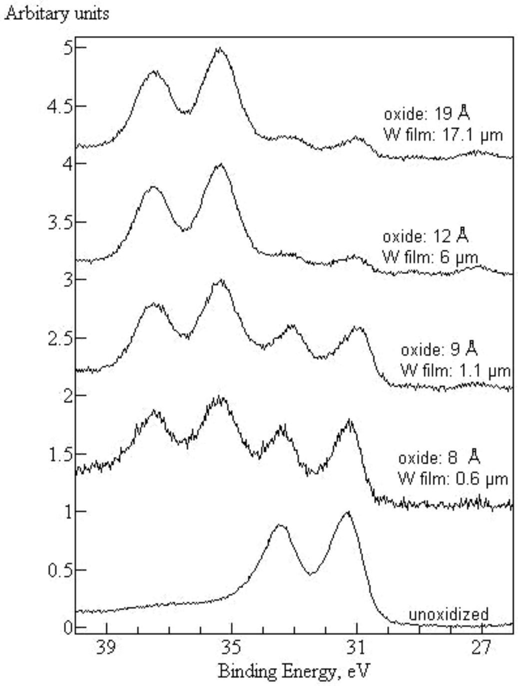


Fig. 4. XPS spectra of tungsten films of different thicknesses and their corresponding oxide layer thickness.

The appearance of water vapors in the process chamber immediately after plasma ignition was also found when another high evaporation point material was used: Carbon. This effect was undoubtedly put in evidence by Mass spectrometry analysis [12].

ARXPS analysis on our tungsten films revealed an oxidized surface suggested by the increase of the oxide signal with decreasing the sampling depth, as observed in Fig. 5.

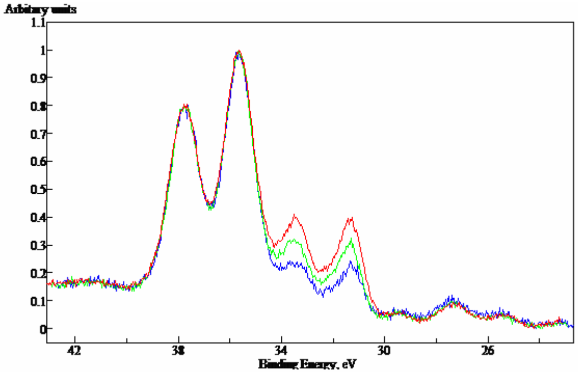
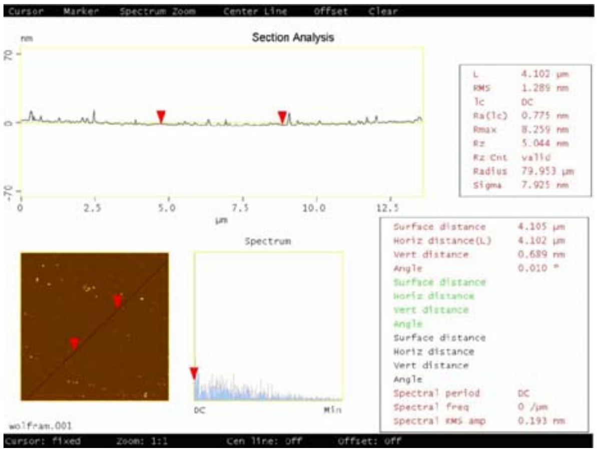


Fig. 5. ARXPS analysis of a typical W film deposited by TVA

The total disappearance of the oxide overlayer obtained by argon ion sputtering in the XPS chamber shows that Tungsten films deposited by TVA are highly dense and do not allow oxidation of W atoms immediately below the first surface layer. This characteristic can be explained by the fact that, apart from Tungsten vapours, highly energetic tungsten ions are involved in the TVA deposition process. In this work, the ion energies of W were varried between 120 and 650 eV.

Fig. 6 presents the surface topography of a typical TVA tungsten coating. It can be observed that the coating is very smooth.



L	4.102 μm
RMS	1.289 nm
lc	DC
Ra(lc)	0.775 nm
Rmax	8.259 nm
Rz	5.044 nm
Rz Cnt	valid
Radius	79.953 μm
Sigma	7.925 nm

Surface distance	4.105 μm
Horiz distance(L)	4.102 μm
Vert distance	0.689 nm
Angle	0.010 °
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	DC
Spectral freq	0 /μm
Spectral RMS amp	0.193 nm

Fig. 6. 2D view of a typical W film topography, 10μm x 10μm. The roughness along the shown line is also given.

4. Conclusions

Tungsten films of thickness from nanometers to microns were deposited in vacuum using an original plasma source. The main feature of this technique is the high energy of the ions forming the film without using substate biasing. This results in the formation of dense films. As no buffer gas is used, no gas atoms or molecules are included into the forming film. Moreover, the gentle evaporation of the anode material provides fine vapors for the ignition of the TVA plasma, this resulting in the synthesis of very smooth films.

The TVA plasma is a valuable technique for the deposition of pure, dense and smooth films. We have strong reasons to believe that TVA is a promissing deposition tool for industrial applications.

Acknowledgements

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