

FUNCTIONAL TUNGSTEN-BASED THIN FILMS AND THEIR CHARACTERIZATION

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Abstract

Anodizing is a technique by which thin oxide layers can be formed on a surface. Thin oxide layers have been found to be useful in a variety of applications, including emitters of electrons. Tungsten is still a common choice for cold field emitters in commercial microscopy applications. Its suitable quality can be further improved by thin film deposition. Not only the emission characteristic can be improved, but also the emitter operating time can be extended. Tungsten oxide is known for its excellent resistance to corrosion and chemical attack due to its stable crystal structure and strong chemical bonds between tungsten and oxygen atoms. Many techniques with different advantages and disadvantages have been used for this purpose. Anodization was chosen for this work because of the controllable uniform coverage of the material and its easy availability without the need for expensive complex equipment. The anodizing process involves applying an electrical potential to tungsten while it is immersed in an electrolyte solution. This creates a thin layer of tungsten oxide on the surface of the metal. The thickness and properties of the resulting oxide layer can be controlled by adjusting the anodization conditions, such as the electrolyte solution, voltage, and the duration of the process. In this work, H₃PO₄ was used as the electrolyte to test whether these tungsten oxide layers would be useful for electron emitters, for use in electron guns and other devices that require high-quality electron emitters. The properties were evaluated using appropriate techniques. In general, anodization of tungsten to form thin layers of tungsten oxide layers is a promising technique for producing high quality electron emitters.

Keywords: Cold-field emission, thin layer deposition, tungsten oxide, resonance enhanced tunneling, anodization

1. INTRODUCTION

Field electron emission was first mentioned by Lilienfeld, who found that field-induced electron emission is an independent phenomenon (not a side-effect of gas in vacuum) [1]. Commonly, Tungsten/Zirconium Oxide (W/ZrO) cathodes operating in Schottky mode are used as the primary electron emission sources. The main reason for this is the longer lifetime and lower vacuum mode of operation compared to cold-field emitters. However, in recent years, the emergence of new allotropes of various refractory metals, metalloids, semiconductors, carbon allotropes and various nanorods and nanoparticles has led to their investigation as functional components of cold field emitters [2-4]. Modification of conventional tungsten emitter by a nanolayer can prevent removal of tungsten atoms by high-energy ions and can passivate the surface. During field emission, the nanolayer can serve as filter for tunnelling electrons or create resonance enhanced tunnelling, which increases the probability of electron emission. [4] If a small energy spread can be achieved, this will be particularly advantageous for applications such as transmission electron microscopy (TEM), scanning transmission electron microscope (STEM), because the ability to operate at low accelerating voltages results

in a sharp, high-contrast image without major radiation damage. As a result, exceptionally clear and high contrast images can be obtained without causing substantial radiation damage to the observed specimen [4]. It is necessary to select right thickness and material, so layers are stable and functional. Also, the roughness of the surface of a cold electron emitter is an important factor that can affect the efficiency of electron emission from the emitter. Edges, points, and irregularities on the surface can create localized high electric fields [5]. In some cases, a rough surface may be advantageous. However, in our case, we have a non-conductive layer with a high work function, and we want to test quantum phenomena such as tunneling through the layer.

2. METHODS

Anodization is one of the methods capable of creating thin layers with desired properties. In the case of tungsten, thin layers of tungsten oxide can be grown on the surface. The anodization process involves applying an electrical potential to tungsten while it is immersed in an electrolyte solution. To find the best experimental conditions for the formation of a layer that will enhance the properties of the emitting cathode, we have run a series of tests and measured a difference in the roughness and chemical composition of grown layers, including the differentiation between tungsten dioxide WO_2 and tungsten trioxide WO_3 [6]. Although from measurement of WO_2 nanotubes itself had better turn-on field and threshold field, we want make use of the dielectric properties of WO_3 to form a non-conducting barrier on top of the tungsten. Therefore, the intention is to obtain layers with a composition rich in WO_3 oxide. Similarly, the roughness of the grown layers must be as low as possible. The thickness and properties of the resulting oxide layer can be controlled by adjusting the anodization conditions, such as the electrolyte solution concentration, voltage, and duration of the process.

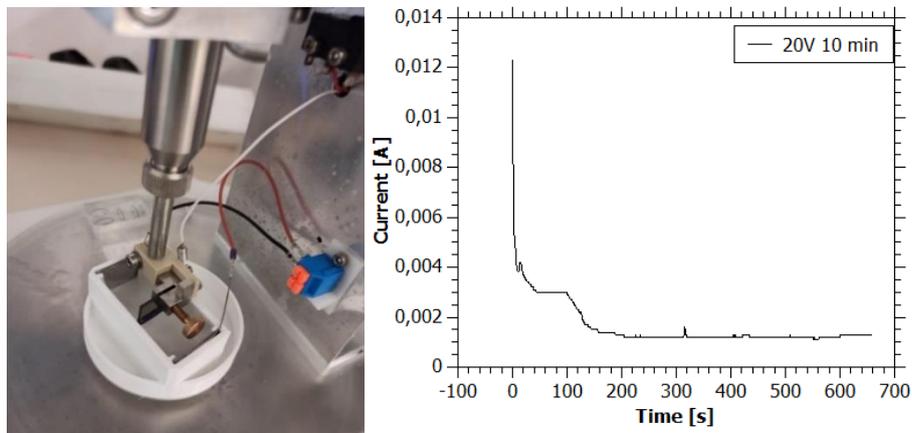


Figure 1 Device for anodization in left; time-current graph at fixed voltage of 20 V graph showing the decrease in current due to the formation of non-conductive layer in right.

2.1 Anodization Procedure

A cleaned tungsten sample was immersed into 0.33 M H_3PO_4 . The length of time that the anodization took, and the voltage used were varied. The process was carried out in low relative humidity, <40 % at room temperature. Depending on the thickness of the layer, the coloration on the tungsten changed, therefore, we could have a preliminary idea of how thick we could expect the oxide to be after we determine the thickness of the individual colors. After the anodization, sample were left to dry for at least 1 h before proceeding to testing. For the anodization setup consisted of a direct current adjustable voltage source (KEYSIGHT E3643A), capable of reaching voltages up to 60 V, and a benchtop multimeter (KEYSIGHT 34410A).

The data was recorded and processed by a MATLAB script on a PC. During the measurement, the change in resistance was monitored as the current increased. Polycrystalline tungsten planar samples had dimensions of 10 x 10 mm x 1 mm and purity of 99.95 % served as the anode. When suitable conditions would be determined, the anodization of the tips can be subsequently carried out.

3. RESULTS

3.1 Tungsten Reference Sample

Polycrystalline tungsten planar samples of 10 x 10 mm without grown layer were tested on scanning electron microscope (SEM), electron backscatter diffraction (EBSD) and energy-dispersive X-ray spectroscopy (EDS). The **Figure 2** shows that the tungsten substrate has larger crystalline regions in the form of several micrometers, which are oriented in a specific direction, as well as smaller areas where the grain direction changes slightly. Furthermore, these variations are partially visible in the SEM image itself, as different orientations have distinct electron reflectivity properties, resulting in some areas appearing darker or brighter.

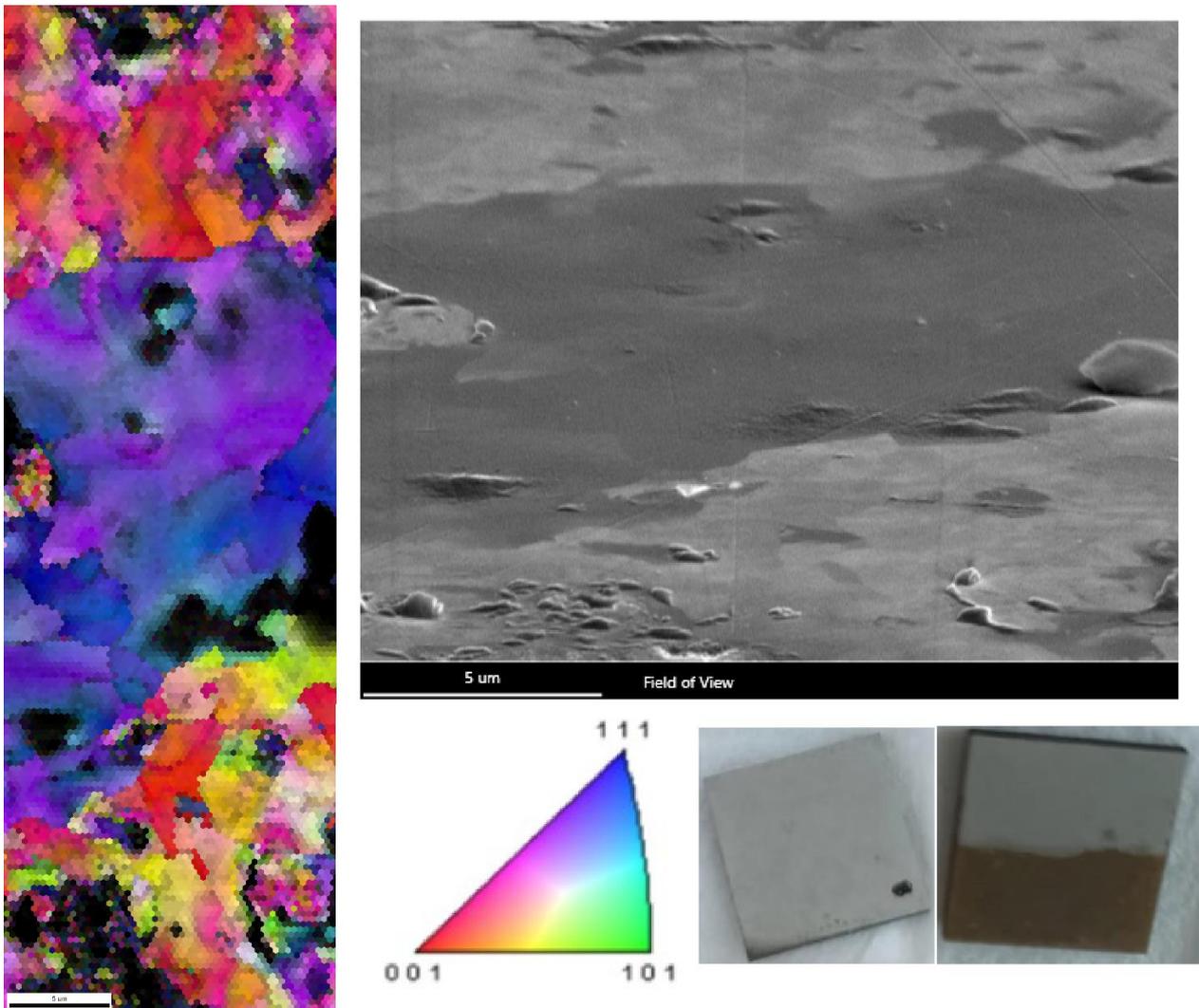


Figure 2 Tungsten reference sample, EBSD, where crystalline structure is visible (left), crystal structure shown on the SEM with different colorization (right). From EBSD, blue is 111 orientations, red is 001 and green 101. Black area was indistinguishable. On bottom is shown reference untreated tungsten sample and sample anodized at 12.5 V.

3.2. Anodized Samples

It would be better to have a controllable, less rough surface to observe how the layer changes the properties of the bare emitter, without having to deal with random localized high fields. We used an atomic force microscope (AFM) for determining roughness, and the example results are shown in **Figure 3**. On the left, it shows the AFM image in the middle of the surface, while on the right it shows the interface. The latter was

created at 35 V and shows gradual jumps at approximately 200 nm intervals. However, it was difficult to identify the interface from other samples because the acid surface was moving slightly. Therefore, it was challenging to determine their thickness. To determine the layer thickness in the future, we will probably use polymethyl methacrylate (PMMA) to partially cover samples and after anodization dissolved it in dichloromethane.

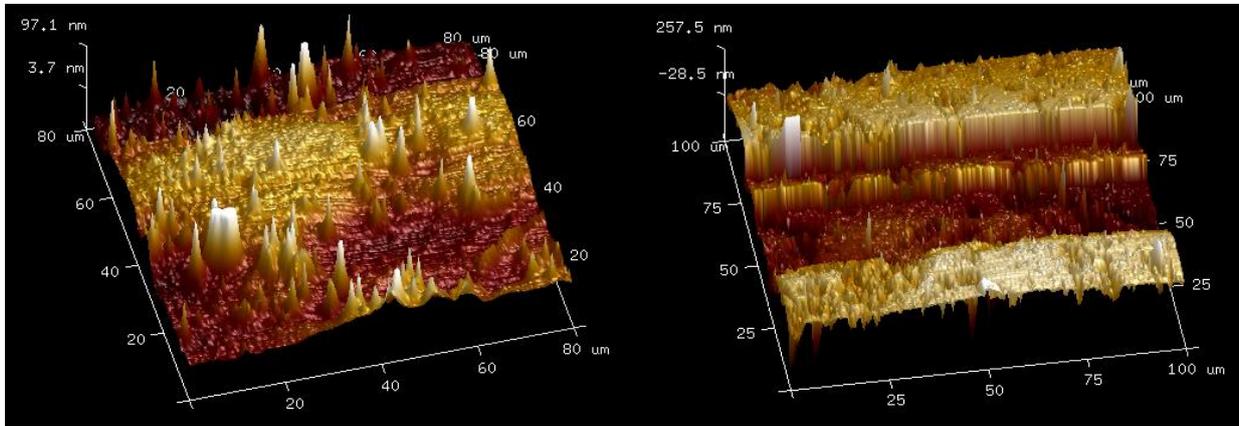


Figure 3 AFM measurements: on left, anodization for 10 min at 5 V. on right, anodization for 10 min at 35 V at edge between layer of oxide and bare tungsten.

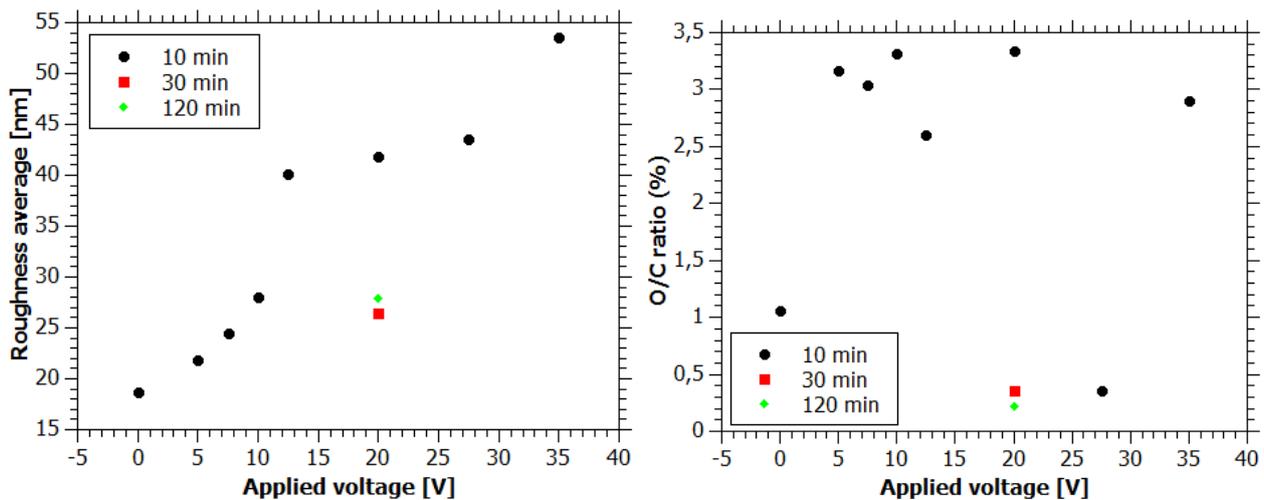


Figure 4 On left the plot of measured average roughness from samples anodized at different voltages. On right, the degree of oxidation depends on the applied voltage during anodization, calculated from XPS analysis. The concentration is 0.3 M H₃PO₄ for all samples.

Roughness average represents the arithmetic average of the deviations of the surface profile from its mean line over a defined measurement area. Can be calculated from:

$$Ra = \frac{1}{A} \int_0^L |y(x) - y_{mean}| dx \tag{1}$$

where:

A is the assessment length (nm),

L is the sampling length (nm),

y(x) is the height of the surface profile at a given position (nm)

x, and y_{mean} is the arithmetic mean of the surface profile heights over the assessment length (nm).

A graph in **Figure 4** was created from various surface scans based on the anodization voltage values. Electrolyte concentration was 0.3 M H₃PO₄ and 10 to 120 min was anodization time. There was a jump between 10 and 12.5 V and another between 27.5 and 35 V, where the otherwise relatively linear dependence does not hold. It seems that at lower currents as at 12.5 V or lower voltage, the layer grown is smoother. However, roughness is not the only criterion and therefore we will have to find a suitable compromise, considering the thickness and chemical composition of the layer. To determine the chemical composition, we performed energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Although EDS showed possible contamination and oxide content, XPS allowed us to determine whether the layer was predominantly WO₃ or WO₂, based on the binding energy of its tungsten 4f core-level electrons. WO₃ has higher peaks (around 35.6 eV) and less flattened peaks, while WO₂ shows significant traces of the tungsten peaks [7].

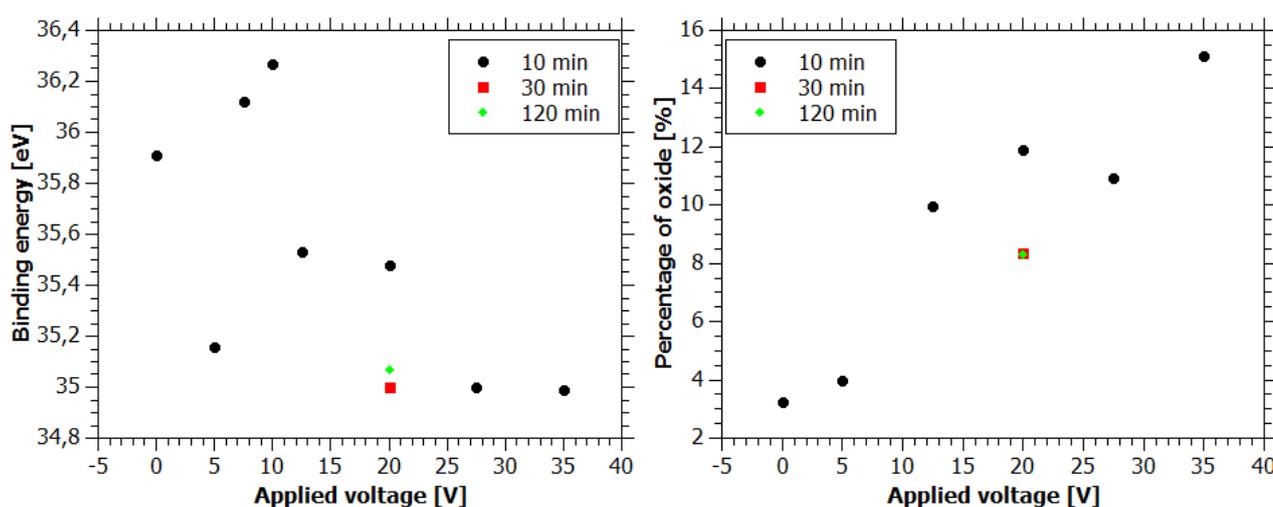


Figure 5 Position of WO₃ 4f 2/2 in spectra of binding energies on the left. The oxygen content obtained from EDS analysis at 10 kV on the right. The concentration is 0.3 M H₃PO₄ for all samples.

Table 1 Table of XPS measurements results for anodized tungsten samples. The elemental composition is provided for the entire spectrum as well as for the specific peak regions of tungsten 4f. The concentration is 0.3 M H₃PO₄ for all samples. Time of anodization were 10 min, if not stated otherwise.

	ref	5 (V)	7.5 (V)	10 (V)	12.5 (V)	20 (V) 10 (min)	20 (V) 30 (min)	20 (V) 120 (min)	27.5 (V)	35 (V)
O1s	44.92	57.49	57.24	58.09	56.16	57.79	23.90	16.38	23.9	56.57
C1s	42.53	18.19	18.86	17.50	21.6	17.33	67.10	75.88	67.1	19.46
N1s	3.41	0.66	0.40	0.57	1.22	0.94	2.79	4.50	2.79	0.36
W4d	8.56	1.67	0.82	0.96	2.06	1.72	1.50	3.43	1.50	1.54
P2p		21.98	22.68	22.88	18.97	22.21	4.71	1.30	4.71	22.07
W 4f 7/2	27.31									
W 4f 5/2	21.62									
WO ₃ 4f 2/2	30.82	59.98	51.34	52.17	54.22	60.32	63.35	61.18	63.41	51.75
WO ₃ 4f 5/2	20.26	39.88	46.22	45.32	42.56	36.92	34.85	37.35	34.65	44.62
WO ₃ loos		3.14	2.44	2.51	3.22	2.76	1.80	1.47	1.94	3.62

The dependence on the positions and the overall percentage of the components are given in **Figures 4** and **5**. The chemical composition of anodized samples is given in **Table 1** and **Table 2** for XPS and EDS respectively. Growth of layers rich in WO_3 is anticipated. It has been shown that with increasing anodization time (30 min, 120 min), the change in composition and roughness does not significantly vary any further. Analysis of the W region in the XPS spectrum of the reference sample reveals the formation of a native tungsten oxide layer. The highest percentage of WO_3 is found in samples anodized at voltages of 12.5 V and 20 V. At the same time, the roughness of the anodized layers should remain low. Therefore, further measurements were taken in the range of 5 to 12.5 V, which showed a shift in binding energy to higher values and a relatively high O/C ratio. The anodization procedure at voltages from 5V to 12.5 V is the most viable for application to electron emitters.

Table 2 Table of results of EDS measurements for anodized tungsten samples. Elemental composition was calculated from EDS spectrum obtained at primary beam energy of 10 kV. The concentration is 0.3 M H_3PO_4 for all samples. Time of anodization were 10 min, if not stated otherwise.

	ref	5 (V)	12.5 (V)	20 (V) 10 (min)	20 (V) 30 (min)	20 (V) 120 (min)	27.5 (V)	35 (V)
W	95.70	96.02	88.29	86.98	89.19	89.77	86.28	83.31
O	3.23	3.98	9.95	11.89	8.37	8.31	10.94	15.12
P			1.76	1.14				1.39
Others	1.07				2.44	1.92	2.77	0.18

4. CONCLUSION

The aim was to find anodization parameters to achieve suitable physical and chemical properties of the oxide layer that could be used to improve the characteristics of cold field emitters. Various analytical techniques, including X-ray, AFM and microscopy, were used to gain insight into these relationships and provide surface sensitive information. From the analysis we found which parameters give relatively low rough surfaces and seem to have a higher percentage of WO_3 , compared to WO_2 . That is with voltage around 10 V for 10 min anodization in 0.3 M H_3PO_4 .

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