Effect Of Al₂O₃ Barrier On The Field Emission Properties Of Tungsten Single-Tip Field Emitters

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Abstract—This research aims to obtain a more in-depth understanding of the field emission properties of tungsten single-tip field emitters (STFEs) coated with a several tens of nanometer thin barrier of Al₂O₃. The introduction of an additional barrier into the metal-vacuum interface system of the emitter can be beneficial to improve its performance. The tungsten emitters were prepared using a two-step electrochemical drop-off etching technique. Thin oxide barrier coatings were prepared by using low-temperature atomic layer deposition (ALD), a chemical vapor deposition technique. Field emission was studied in an internally developed field emission microscope (FEM) working in UHV vacuum (< 1·10⁻⁷ Pa), and the experimental field emission data were analyzed by the so-called Murphy-Good plots. The value of the local work function of the grown oxide layer were investigated using Ultra-violet photoelectron spectroscopy (UPS).

Keywords—Cold field emission, single-tip field emitters, tungsten tip, aluminum oxide, dielectric coatings, Murphy-Good plot

1. INTRODUCTION

Motivation

The cold-field emitters which can be macroscopically described as a single-tip (STFEs) play the main role in the experiments presented in this report. STFEs can be prepared by electrochemical etching of refractory metals, which is generally a fast, few-step process not requiring costly equipment compared to the fabrication of large area field emitters (LAFEs), which is based on several time and resource consuming steps (often >10) including electron beam/UV/laser lithography. In this report, a polycrystalline tungsten wire was chosen as the main material for the fabrication of STFEs.

In electron physics, the fabrication of field emitters with enhanced emission characteristics is much sought upon. By introducing a dielectric layer into metal-vacuum interface, a new metal-dielectric-vacuum system is formed. The dielectric layer introduces new surface electron states into the electronic structure of the emitter. Altogether with the work function of the dielectric, energy gap, impurities [1], all these parameters affect the efficiency, spatial and temporal resolution of the emitted electrons.

Field Emission Theory

In the case of cold field electron emission (CFE), most electrons tunnel from electron states below Fermi level. Tunneling is assumed through the Schottky-Nordheim (SN) barrier. The basis of the emission analysis is built upon Murphy-Good field electron emission theory. The so-called extended Murphy-Good equation (EMG) is employed [2,3]:

\[ I(V) = \{ A^{SN}(\theta, \eta) V_R \} \exp\left( \frac{\theta}{\eta} V \right) \]  

where \( A^{SN} \) is the formal emission area assuming SN barrier tunneling, \( V_R \) is a (constant) reference measured voltage [2] needed to pull the top of the SN barrier down to Fermi level [3], \( \theta(\phi) \) and \( \eta(\phi) \) are scaling parameters, the parameter \( \kappa(\eta) \) is calculated: \( \kappa = 2 - \eta/6 \) [2].

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Applying the natural logarithm to (1):

$$\ln\left\{ I / V^K \right\} = \ln\left\{ A^{SN} (\theta \exp \eta V_R - k) V^K \right\} - \eta V_R / V$$

the equation becomes linear, $\ln\left\{ I / V^K \right\} = (1 / V^K) \left\{ \frac{1}{V} \right\}$, this form is called theoretical Murphy-Good plot.

2. METHODOLOGY

Electrochemical Etching

The base tungsten emitter was prepared by two-step electrochemical etching of a polycrystalline tungsten wire (GoodFellow, 99.9+%, diameter 0.3 mm), in a 3M aqueous solution of NaOH. A precise electrochemical etching station developed at ISI Brno [4] was used. The tungsten wire connected as the anode is submerged in the electrolyte, the tungsten wire is encircled by a Pt ring also submerged in electrolyte, which acts as the cathode. Due to a precise stepper motor and a programmable breaker circuit of the etching station, sharp tungsten tips with a tip radius of 100 nm and less can be obtained. To ensure that the tip surface is cleaned off hydroxide and oxide residues, the etched tips are chemically cleaned in 38% hydrofluoric acid (HF) for 20 minutes.

Atomic Layer Deposition

ALD is a high-vacuum deposition technique, in which the growth of layers is based on sequential, self-limiting surface reactions of two vapour phase precursors. ALD offers exceptional conformality, which allows the growth of a uniformly thin layer on very complex or sharp structures [5]. The nature of layer formation allows for sub-angstrom control of thickness [5] due to atom-by-atom sequential reactions of the two precursors. Thin Al$_2$O$_3$ coatings were prepared at the CEITEC Nano facility in the Ultratech-Cambridge Nanotech Fiji 200 ALD tool. The precursors used were trimethylaluminum (TMA) and water vapor, the process temperature was set at 150 °C, and the number of cycles was set at 150. Each ALD cycle consisted of steps: 1) injection of TMA, duration 0.06 s, 2) purge, duration 20 s, 3) injection of H$_2$O, duration 0.06 s, 4) purge, duration 20 s. The process described here results in a 15 nm thin layer of Al$_2$O$_3$.

Field Emission Microscopy Measurement

Measurements of the emitter with and without the Al$_2$O$_3$ coating layer were all performed in the in-house developed FEM. The schematic diagram can be seen in Fig. 1. The emitters were tested in triode configuration: the emitters themselves were mounted as a cathode, a steel cylinder with the hole of 1 mm of diameter was acting as an extractor electrode, an Al-coated YAG scintillator acting as collector electrode. The emission current was measured between the Al-coating of the scintillator and the ground wire using a RBD 9103 Pico ammeter. The distance between the tip of the cathode and the scintillator was set at 40 mm. Up to +50 V bias was applied to the scintillator from the external battery supply to improve the collection of primary electrons and to suppress the generation of the secondary electrons.

![Figure 1: Diagram of the FEM in triode configuration; Al-coated Ce:YAG acts as the collector electrode.](image-url)
3. RESULTS AND DISCUSSION

To protect the emitter from exploding during the measurement, the I-V characteristics shown in Figure 3 were captured in this manner: After the first ignition, the extraction voltage had been increased, so the Pico ammeter would collect a current of no more than 10 µA. This seemingly arbitrary value depends on the electron collection efficiency of the conductive Al layer sputtered on top of the scintillator, the applied bias voltage and the condition of Al layer. Based on our calculations and previous experiments, the current value of 10 µA is regarded as “safe” for the emitters with the tip radius around 100 nm. The actual measurement of current and voltage started around the “safe” value and then the extraction voltage was lowered to the point there were no emission. Additionally, the coated emitter shows a very strong switch-on effect, i.e., the first emission does not begin at the lowest measurable current, but at a value often several orders of magnitude higher [6], in all subsequent runs the emitter behaves normally without the switch-on effect.

For the Murphy-Good plot analysis, the work function of the polycrystalline W tungsten emitter is 4.5 eV. Work function of Al₂O₃, which was acquired experimentally by ultraviolet photoelectron spectroscopy, see Figure 2.

![Figure 2: Determination of the local work function of Al₂O₃ thin layer. He I line 21.22 eV. Reproduced from [7].](image)

Murphy-Good plots based on the collected data are shown in Figure 3. Both emitters showed nontrivial behavior, passing the orthodoxy test when the extraction voltage was set low and failing the test when the extraction voltage was set high. This is common in tungsten emitters; at high extraction voltage, slight macroscopic changes in the electrostatic field at the emitter can occur and morphology of the emitter may irreversibly change. The emission images of the Al₂O₃ coated emitters were resembled those of the multi spot emission patterns of composite emitters [6].

![Figure 3: Murphy-Good plots of experimental I-V characteristics of measured emitter(s). Reproduced from [7].](image)
4. SUMMARY

The research shows the possibility of fabrication of ultrathin Al₂O₃ coated tungsten emitters. Coated emitter exhibits a strong switch-on effect. Orthodox behavior can be observed when it is operated in low extraction voltage. Applying dielectric barrier coating to the emitter plays an important role in the changes of its electron emission and it is reflected in the extracted formal emission parameters. Based on experiments in similar ultra-high vacuum and extraction voltage conditions, the effect of chemical or surface geometry alterations of the emitter tip is estimated to be lower than the effect of applying Al₂O₃ coating. The atomic layer deposition technique enables fine tuning of layer thickness and high layer uniformity, features very useful for fabricating advanced field emitters with thin barrier layers. Some morphology changes were observed during the FEM measurements, which may indicate modifications of the emitter. Due to the complex nature of the interfaces in metal-dielectric-vacuum emitters, deeper understanding through simulations is anticipated soon.

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