Centers of cold electron emission from molybdenum thin films

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Abstract. Thin-film semiconductor devices and functional metal-oxide-semiconductor structures have drawn attention as being applicable for on-chip electronics. Similar structures, however, were also reported to be promising as efficient sources of electrons. This paper presents the results of scanning electron microscopy analysis of molybdenum thin films capable of low-macroscopic-field electron emission. Supposedly, the images show the centres of cold-field emission at different stages of their life cycles from activation to destruction. It is assumed that initially continuous Mo films experience dewetting under heating and ion bombardment, which is caused by the emission current flow. The results contribute to understanding the mechanism of low-field emission from thin metal films, which seems to be different from those previously proposed for thin carbon coatings.

1. Introduction
One of the attractive applications of nanostructured materials is their use in cold cathodes for vacuum electronic and microelectronic devices. At present, metallic spikes or carbon nanotubes are most often used in this capacity. However, cold cathodes that do not use elements with high aspect ratio look promising, especially in terms of durability under harsh operating conditions and current stability [1-5].

To obtain emission currents uniformly distributed over a large area, cathodes based on vertical metal-oxide-semiconductor (MOS) structures were proposed [6, 7]. The underlying idea is that applying an electric field of the appropriate polarity between the metal and semiconductor layers leads to the injection of electrons from the semiconductor into the metal through the separating thin dielectric layer. If the thickness of the metal film does not significantly exceed the electron mean free path in this metal, some of the electrons pass through the metallic layer and are emitted into vacuum. It was noted that the fraction of emitted electrons was maximal if the metal layer was highly defective or discontinuous [8], but still it did not exceed 0.1-1%, which means rather poor efficiency of vertical MOS cathodes. As a way of enhancing it, the realization of quite similar structures in horizontal geometry has been proposed. In this case, the electron conductive current flows in a plane parallel to the plane of the electrodes, and at least some of the unavoidable events of elastic electron scattering in metal play a beneficial role in the emission process by changing the direction of motion of electrons towards the vacuum boundary. The efficiency of such cathodes is usually assessed by the ratio of the conductive (in-plane) current value and the emission current value and reaches approximately 1/3 for some prototypes [5].

Another type of structures which has been investigated as potentially useful for the fabrication of planar cold cathodes is thin metallic or carbon islet films deposited onto dielectric substrates [9,10]. The emission of electrons from such structures was observed during the flow of in-plane current which was realized in the form of tunnelling transport of electrons through the vacuum gaps between the islets, which resembles the case of the aforementioned “horizontal tunnelling diode” emitter. An assumption was made that electrons were emitted from high-energy “hot” states, as the peculiarities of the...
mechanism of energy transfer between electronic and ionic systems in nanoscale objects may provide conditions for overheating of electrons as a result of current flow [11-13]. It is noteworthy that this hypothesis is supported by the fact that realizing energy input by other means (specifically, exposing the films to IR radiation) also led to the appearance of an emission current [14]. Another relevant embodiment of planar cold cathodes includes carbon nanoslet films on silicon substrates. Such films were reported to produce a measurable emission current at room temperature when exposed to a relatively weak macroscopic electric field (down to 1 V/μm and less) and, unlike the previously mentioned ones, without any other external stimulation [15,16]. The proposed model describing this phenomenon also utilizes the concept of hot electrons characterized by prolonged lifetimes due to specific features of the electronic structure of nanosized graphite-like carbon. Recent experimental results reveal that not only thin carbon films, but also metallic (primarily Mo and Zr) ones demonstrate such a capability of low-macroscopic-field electron emission. It is currently a pending question whether the mechanism of electron emission from these two types of coatings is the same.

The aim of this work is to present the results of microscopic investigation of surfaces of molybdenum thin films capable of low-field electron emission and to describe the structural changes occurring as a result of emission current flow.

2. Experimental

2.1. Samples preparation
Molybdenum thin films were deposited onto flat substrates of doped monocrystalline Si by means of vacuum magnetron sputtering of a pure Mo target. The deposition was performed in a HEX apparatus (by Mantis Deposition) at a residual gases pressure of ~1⋅10⁻⁶ mbar. The substrates pre-cleaned in an ultrasonic bath with acetone were mounted onto a rotating Ta holder table and additionally thermally cleaned by heating up to ca. 150°C in vacuum of ~10⁻⁵ mbar. During the deposition, the temperature of the substrates was maintained at 100°C. The deposition rate and effective thickness of the coatings were monitored and controlled by means of the quartz crystal microbalance (QCM) method.

2.2. Field emission tests
Field emission (FE) tests were performed in vacuum at a residual gas pressure of the order of 10⁻⁹ mbar. The electric field was produced in a planar gap of adjustable width (0.2…1.0 mm) between the sample and the flat end of a 6 mm-diam. cylindrical anode when a positive potential of 0…4.5 kV was applied to the anode with respect to the grounded sample serving as the cathode. The cathode unit was equipped with a filament heater allowing in situ heating of the tested samples up to 600°C.

2.3. Scanning electronic microscopy
A TESCAN Lyra3 scanning electronic microscope (SEM) was used for investigation of the sample topography. Surface morphology was determined using an In-beam SE detector. The distance from the pole piece of the objective lens to the sample was 5 mm, which made it possible to obtain the most complete secondary-electron signal. The values of the accelerating voltage and beam current were chosen so as to obtain the maximum resolution for a given type of microscope. The microscope was also equipped with a detector for energy-dispersive X-ray spectroscopy (EDS), with help of which the elemental analysis of the investigated structures was carried out.
3. Results and discussion

An overview image of the film surface modified by extraction of the emission current is presented in Figure 1. The large crater-like features are assumed to be ruptures of the film, which occurred during the FE test. They have various shapes, mostly round-like, and sometimes they seem to merge with each other. At the same time, some smaller structural elements can be seen in between: an image of a part of the considered region at a higher magnification is given in figure 2(a).

![Figure 1](image1.png)

**Figure 1.** Typical view of a ‘destroyed’ region of the Mo film surface after the field emission test.

![Figure 2](image2.png)

**Figure 2.** (a) SEM image of a part of the ‘destroyed’ region and (b) EDS elemental analysis profile of the island circled in part (a).
Our study included the elemental analysis of islet-like objects located at central regions of some of the ruptures, a typical result of which is presented in figure 2(b). Molybdenum is the element that dominates the spectra of such objects, but a considerable amount of oxygen can also be detected. As the shapes of Mo and O lines seem to correlate, we may assume that the considered islets consist of oxidized molybdenum, especially since Mo thin films are reported to be oxidized rather quickly even at room temperature [17]. On the other hand, oxygen from the underlying SiO₅ layer or possible organic contaminants can also contribute to the signal and affect the results of elemental analysis. As seen from figure 3, the boundaries of round-like features surrounding the islets also consist of Mo, which supports the assumption that these features appear as a result of disruption of the film. The absence in the EDS profile of a maximum corresponding to the central islet (which is seen quite clearly in the SEM image) can be explained by insufficient spatial resolution of the EDS method for detecting such small (less than approximately 40 nm in diameter) structures.

![Figure 3. EDS elemental analysis result of the depicted structure along the line shown in yellow in the left part of the figure](image)

We suggest the following mechanism of surface modification during the electron emission process: initial emission centers (ECs) can be localized at crystalline inclusions in a continuous amorphous Mo film. Heating an EC by the emission current in combination with ion bombardment of the EC itself and its vicinity are able to initiate thin film dewetting [18] and, thus, lead to the appearance of the observed
ruptures. After the rupture has appeared, favorable conditions for electron emission are formed at its boundaries, which results in the spatial propagation of the rupture and its eventual merging with others, and the central islet is sooner or later completely destroyed. We assume that, in fact, the features observed in the SEM images of Mo thin films after emission tests are ECs at different stages of their temporal evolution with small islets surrounded by a continuous film that are not yet activated centers. Apart from dewetting, the structure of thin films can be affected by ion bombardment via altering the phase composition of the films, as reported, for example, in case of diamond-like carbon coatings [19]. Thus, the specific mechanism of the observed structural conversion of Mo thin films on silicon substrates is still to be determined.

4. Conclusion
A microscopic investigation of the surface structure modifications of molybdenum thin films caused by the extraction of the emission current leads to an assumption that dewetting of metallic thin films (or a transition of another type resulting in structural changes) occurs during the emission process, thus leading to the conversion of an initially continuous coating into a discrete one. Such a case is impossible for thin carbon films on silicon substrates, which have to be initially discrete in order to be capable of low-macroscopic-field electron emission. This fact suggests that the mechanisms of low-field electron emission from thin carbon and metallic coatings differ, and the investigation of the latter looks challenging. Further experiments can be focused on a detailed study of the films topography by means of, for example, the method of impedance spectroscopy. The results may contribute to finding ways of enhancing the stability of the electron emission current from thin metallic film planar emitters.

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