Study of surface topography and emission properties of thin Mo and Zr films

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Abstract. Thin films of Mo and Zr were deposited on Si wafers by the magnetron sputtering process with controlled parameters. Correlation between their field-emission properties and surface morphology was investigated. The study results were found to be in good agreement with previous data acquired for carbon nanocluster films, which witnesses that morphology can have greater effect on field emission capability of thin films than their chemical composition and work function.

1. Introduction
Currently, there is an increasing interest in “cold” electron sources used in vacuum microelectronics devices [1-9]. Cold field emitters have possible advantages before the traditional thermionic cathodes, such as higher energy efficiency and zero turn-on time. Presently, field cathodes based on carbon nanotubes [10, 11] and silicon tips [11-13] have the widest application areas. Though, the cold cathodes utilizing the capability of high-aspect morphological features for local electric field concentration have some inherent drawbacks. In such structures the destructing factors (Joule heating, ion bombardment, ponderomotive forces, etc.) are also highly concentrated, which often results in emission instability and non-uniformity and limits cathode lifetime [14, 15]. Consequently, the field cathodes not utilizing the principle of field concentration on sharp surface protrusions can have substantial benefits for various practical applications.

Previous studies performed in our laboratory [16-18] have showed that thin carbon films with island morphology and smooth vacuum boundary can be capable of cold electron emission in electric field with macroscopic magnitudes starting from a few V/µm (or even less). The mechanism of this phenomenon has not been reliably established. Though, an emission model had been suggested [19], associating the observed emission capability with the presence of isolated nanoclusters of graphitic carbon on the surface of the cathode. Later studies [20] have demonstrated that thin nanocluster films of Mo on Si wafers can also produce electron emission current in electric field with comparable macroscopic magnitudes (~V/µm). The present work continued the study of field-emission properties of thin films of different metals deposited on crystalline silicon substrates.

2. Film Samples: Fabrication and Morphology
Samples of thin films of two metals – Mo and Zr – were fabricated by the magnetron sputtering technique with the use of a Mantis Deposition facility equipped with a 4-inch magnetron. Residual gas pressure was of the order of $10^{-3}$ mbar. Effective film thickness was determined with a calibrated quartz crystal microbalance gauge. To exclude the substrate-related effects, all samples were fabricated
on identical substrates representing ~1 cm²-area plates of a KDB-10 silicon wafer with specific surface resistivity 10 Ohm·cm, p-type conductivity and naturally oxidated surface with (100) orientation. Film material, deposition rate and the maintained substrate temperature were varied. Deposition parameters for the studied samples are listed in table 1.

Table 1. Parameters of the studied samples.

| №  | Film | Effective thickness, nm | Deposition rate, Å/s | Substrate temperature, °C | Wafer |
|----|------|------------------------|----------------------|---------------------------|-------|
| 1  | Mo   | 6                      | 0.13                 | 100                       | KDB-10|
| 2  | Mo   | 6                      | 1                    | 100                       | KDB-10|
| 3  | Mo   | 6                      | 1                    | 150                       | KDB-10|
| 4  | Zr   | 6                      | 0.5                  | 100                       | KDB-10|

Surface topography of the samples was studied with scanning electron microscope (SEM) Lira (manufactured by Tescan Co). The SEM images are presented in figure 1. They demonstrate that morphology of the fabricated films was affected by both the deposition rate and the maintained temperature of the substrate.

Figure 1. SEM images of the fabricated samples of thin metal films.
The SEM image of the Mo film sample №1 deposited at 100°C and low deposition rate 0.13 Å/s shows that the film is composed by islands (clusters) with average lateral size ~20 nm. Their surface density is ca. 500 µm⁻². The Mo film sample №2 (see in figure 1) fabricated at the same temperature but at higher deposition rate comprises islands with larger mean size (30-40 nm) and, correspondingly, lower surface density (300 µm⁻²). Increase of the substrate temperature maintained during the deposition process to 150 °C (Mo sample №3) gave more irregular film structure and average size of the islands 15-20 nm; their density is ca. 700 µm⁻². The film of another metal, zirconium, designated as sample №4, also comprises nanoclusters. Their mean lateral size is ~30 nm and density ~400 µm⁻².

3. Low-Field Emission

Emission characteristics of the fabricated metal film samples were measured with the use of the experimental device previously described in [5]. Emission current was collected from the area of ca. 0.3 cm² when the electric voltage with magnitude up to 5 kV was applied between the sample and a flat-top anode separated by ~0.6 mm distance. Emission tests were performed in technical vacuum with residual gas pressure of the order of 10⁻⁶ Torr.

Samples №1 and №4 produced measurable emission current in the as-fabricated state, while the two other samples required preliminary activation. The activation procedure consisted in the gradual heating of the sample to ~450 °C with simultaneous application of a small extracting voltage. The next stage implied heating to 600 °C for 15 minutes with the electric field turned off. After sample cooling to 450 °C, the extracting field was re-applied, and the temperature was slowly reduced to ambient. After such treatment, the two remaining samples yielded emission current.

The acquired room-temperature emission characteristics for the studied film samples are presented in figure 2; the insets show them in the Fowler-Nordheim (FN) coordinates. Their shapes confirm field-emission nature of the extracted current. For all samples, the threshold field values (corresponding to the appearance of measurable nA-scale emission current) were as low as 3.2-4.3 V/µm.

Numeric parameters of emission characteristics are listed in table 2. The two last columns give the values of effective workfunction calculated from emission characteristics plotted in FN coordinates. These calculations require the knowledge of the field enhancement factor β. Its values were approximately calculated for each sample from its surface topography exhibited in figure 1. These values were used to determine the effective workfunctions listed in the last column in table 2. They are in good agreement with each other. Column 5 of the table gives workfunction values calculated for the maximum β-factors which could be expected for the films of the observed morphology – we gave it the rough estimate of β = 10. Even for this case, the effective workfunction did not exceed 0.35 eV. This value is much lower for the known values for both deposited metals in the bulk form (4-5 eV). And it cannot be accepted as the “true” workfunction value – otherwise, thermionic emission at room temperature would be observed.

Thus, the acquired experimental data give a new confirmation for the previously made suggestion [8] that the low-field cold emission from thin nanocluster films deposited on Si wafers follows a physical mechanism different from the direct one-step tunneling electron transfer into vacuum, assumed in the FN model.

Table 2. Characteristic values for emission from the studied samples.

| №  | Film | Threshold voltage, V | Maximum extracted current, µA | Effective workfunction, eV (for β=10) | Eff. workfunction, eV (for β calculated from figure 1) |
|----|------|----------------------|-------------------------------|-------------------------------------|-----------------------------------------------|
| 1  | Mo   | 1930                 | 4.16                          | 0.35                                | 0.19                                          |
| 2  | Mo   | 2500                 | 23.7                          | 0.27                                | 0.13                                          |
| 3  | Mo   | 2200                 | 1.53                          | 0.23                                | 0.18                                          |
| 4  | Zr   | 2600                 | 7.2                           | 0.25                                | 0.15                                          |
4. Summary
Emission experiments were performed with thin films of two metals (Mo and Zr) deposited on p-type Si wafers. The films had effective thickness of a few nm and were comprised of smoothly-shaped nanoclusters with lateral sizes 15-40 nm. All tested samples showed the capability of low-field electron emission at room temperature starting from the macroscopic field magnitudes 3.2-4.3 V/µm. The new data are in perfect agreement with the results of previous experiments [16-18] performed with graphitic carbon nanocluster films of similar morphology. In combination, these experimental results witness that the morphology of nanocluster films deposited on crystalline Si has much stronger effect on their emission capability than chemical composition of the film – provided that the clusters are conductive. This observation may be helpful for definition of the emission mechanism realized for such cluster films, which is definitely different from the classical Fowler-Nordheim emission model.

Further investigations of low-field electron emission from nanocluster films will include experiments with other metals, such as Ni, W and Cr.

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