Conference Paper

Formation and Study of Properties of Ta and Mo Nanocluster Films

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Abstract

In this article, the results of studies of thin-film samples of nanoclusters of tantalum and molybdenum metals on the surface of silicon dioxide SiO_2/Si (001) at room temperature are presented. The chemical composition and electronic structure of the obtained nanocluster films of Ta and Mo were controlled in situ by X-ray photoelectron spectroscopy (XPS). Susceptibility to oxidation during the exposure to the atmosphere of then nanocluster films, as well as their thermal stability when heated in a vacuum to 600°C were studied ex situ by the XPS method. The size and shape of the nanoclusters composing the film were estimated ex situ by analyzing images obtained with a scanning electron microscope. The band structure before and after oxidation was studied by measuring the bandgap of the formed Ta and Mo films by the method of electron energy loss characteristic spectroscopy (REELS). Conclusions about thermoelectric properties of the formed nanocluster films of Ta and Mo were made.

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1. Introduction

Study of the properties of nanostructured materials is of current interest due to the development of nanoelectronics, in particular, micro- and nanoelectromechanical systems (MEMS and NEMS) [1]. However, one of the main constraints to wide-scale introduction of the systems is the problem of producing miniature power supplies for MEMS and NEMS [2]. One of the perspective miniature power supply units for MEMS and NEMS is radioisotope-based ones [3]. Their advantages are long, stable operation, the lack of maintenance, and the possibility of forming radioisotope sources of micron sizes. The most efficient way to convert the energy released during nuclear decay into electric one is based on thermoelectric conversion [4] and is known as Seebeck effect. However, modern semiconductor thermoelectric materials don't have sufficient efficiency for use in such systems. The efficiency of thermoelectric materials is described

by the dimensionless coefficient ZT, which is directly proportional to the electrical conductivity σ, the square to the value of the thermoelectric power S, and inversely proportional to the thermal conductivity κ [5]. Currently the maximum value of the efficiency ZT ~ 1.3 is obtained for thermoelectric material $AgSbTe_2$ [6] for the operating temperature range of radioisotope power sources 400–600K (according to [7]). The main attempts to increase the thermoelectric efficiency of the material are based on the use of semiconductor nanostructures [8]. In order to increase the efficiency of thermoelectric materials, particularly, by changing the value of the thermoelectric power, it is necessary to reduce the size of the particles making up the thermoelectric material. However, if the size of individual semiconductor nanostructures is less than 50 nm, then materials based on such structures lose electrical conductivity up to the manifestation of dielectric properties [9], and as a result they become less effective.

One of approaches to solve this problem is to use porous metal nanostructures, in particular, ensembles of nanoclusters in the form of films for this purpose [7]. Metal nanoclusters with decrease of their size are less susceptible to changes of electrical conductivity, manifesting semiconductor properties at characteristic size less than 3 nm. It is expected that the electrical conductivity of such films will be close to metallic one due to carriers tunneling between nanoclusters and percolation effects. At the same time, with the decrease of size of metallic nanoclusters, a strong increase of thermoelectric power value of nanocluster films is expected [10], since the latter depends on the density of the states at the Fermi level. Moreover, the porous structure is expected to result in a decrease of the phonon thermal conductivity due to scattering at the boundaries of nanoparticles [8]. Thus, such materials as porous films based on metal nanoclusters may be potential candidates for the role of a highly effective thermoelectric material.

In this work, thin nanocluster films of tantalum and molybdenum were formed on the surface of dielectric substrates with different sizes of nanoclusters. Analysis of the chemical composition of these films was carried out. Their susceptibility to oxidation after exposure to the atmosphere, as well as their thermal stability under heating, were studied. Evaluation of the size and shape of large-sized nanoclusters constituting the film were performed. The band structure of the films before and after oxidation was studied. Conclusions on the thermoelectric properties of the formed films were made.

2. Materials and Methods

Silicon dioxide substrate SiO_2/Si (001) with a size of 10 mm x 10 mm was chosen for the samples, since a heat and electrical insulating material is required for the effective operation of the thermoelectric material. Tantalum and molybdenum were chosen, since these materials have different signs of thermoelectric power value, they are high-melting and well-evaporated with the magnetron sputtering method.

Thin films were formed using a magnetron deposition source NanoGen 50 (Mantis Deposition, UK) in the preparation chamber of ultrahigh vacuum system Multiprobe MXPS RM VT AFM-25 (Omicron NanoTechnology GmbH, Germany). In the preparation chamber, the pressure was p $\approx 10^{-3}$ Torr during deposition process. The working parameters of the cluster source were: buffer gases fluxes: Ar from 15 to 30 sccm, He – 0–50 sccm; magnetron power – 20–90 W; aggregation zone – 2–10 cm. In the process of nucleation in this source, nanoclusters acquire a single charge, which allowed the size filtration with a dispersion of 2% in the quadrupole mass spectrometer MesoQ (Mantis Deposition, UK). Positive voltage of 800 V was applied to the substrate for better adhesion and formation of porous films consisting of individual nanoclusters. When applying voltage above this value, a continuous homogeneous film was formed due to the 'hard' deposition of nanoclusters. Otherwise, when the voltage on the substrate is less than 800 V, the film does not form due to the poor adhesion of the nanoclusters of these metals to the surface of the silicon dioxide. The chemical composition of the surface was controlled in situ (at a level of 0.1%) by XPS (the source of radiation MgKα, 1253.6 eV). The thickness and morphology of Ta and Mo films consisting of large clusters was studied ex situ by scanning electron microscopy using a microscopes JSM 7001F (JEOL, Japan) and HELIOS 660 (FEI, USA). Samples were then again analyzed in the XPS spectrometer Theta Probe (Thermo Fisher Scientific Inc.; the source of radiation MgK_{α}) after exposure to the atmosphere in order to study their susceptibility to oxidation and thermal stability when heating in vacuum ($5{\cdot}10^{-9}$) up to 600°C. The band structure of nanocluster films before and after exposure to the atmosphere was studied using REELS method realized in the UHV analysis chamber Multiprobe MXPS RM VT AFM-25 (initial energy of electrons was 500 eV).

3. Results and Discussion

As a result of the work, two series of samples with monodisperse tantalum films consisting of nanoclusters of various sizes in the range from 1.3 to 5.8 nm, and molybdenum films with sizes of nanoclusters from 1.4 to 7.5 nm were formed.

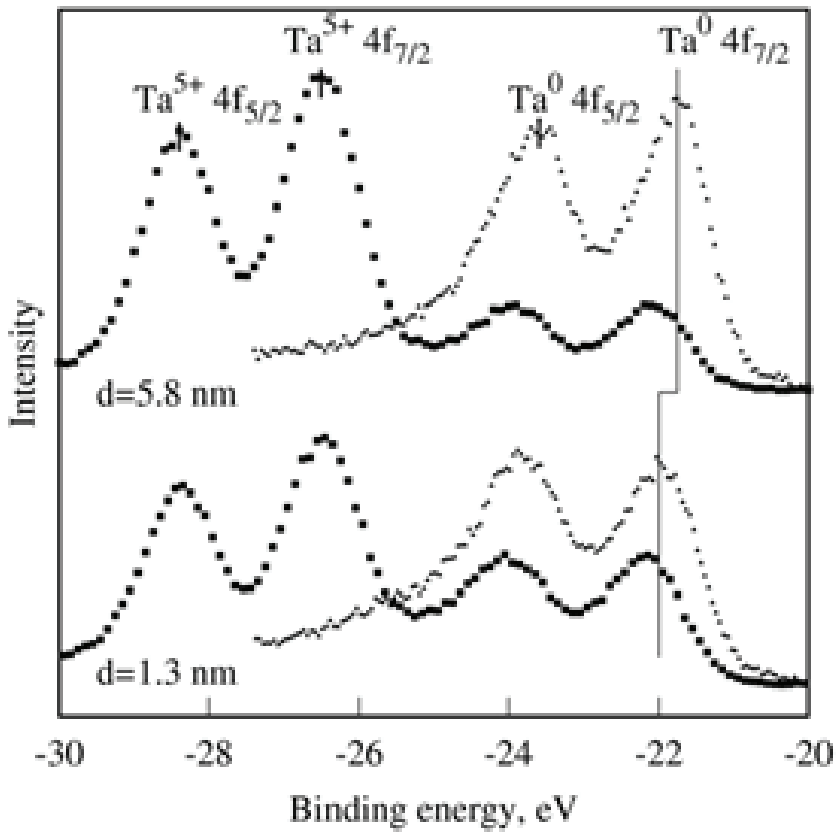

Figure 1: Typical X-ray spectra of the core levels of Ta films consisted of nanoclusters of 1.3 nm (bottom spectra) and 5.8 nm (upper spectra) in diameter obtained in situ (▲) and ex situ (■) with the XPS method.

Typical X-ray spectra of the core levels of monodisperse films consisted of Ta nanoclusters of sizes 1.3 nm and 5.8 nm in diameter, as well as Mo nanoclusters sizes of 1.4 nm and 7.5 nm in diameter before and after exposure to the atmosphere are shown in Figures 1 and 2. The analysis of the in situ X-ray spectra showed that all samples immediately after the deposition process are of a metallic state (Ta or Mo) with low oxygen and carbon content (< 10%). According to the absence of peaks in the in situ spectra (Figures 1 and 2) corresponding to the oxide states, it can be concluded that oxygen is adsorbed into the near-surface layers of the films without forming a chemical bond with the atoms of the nanoclusters.

It is shown that with the decrease of characteristic sizes of the nanoclusters composing the films, the binding energy of the core levels (Ta*4f* and Mo*3d*) shifts toward

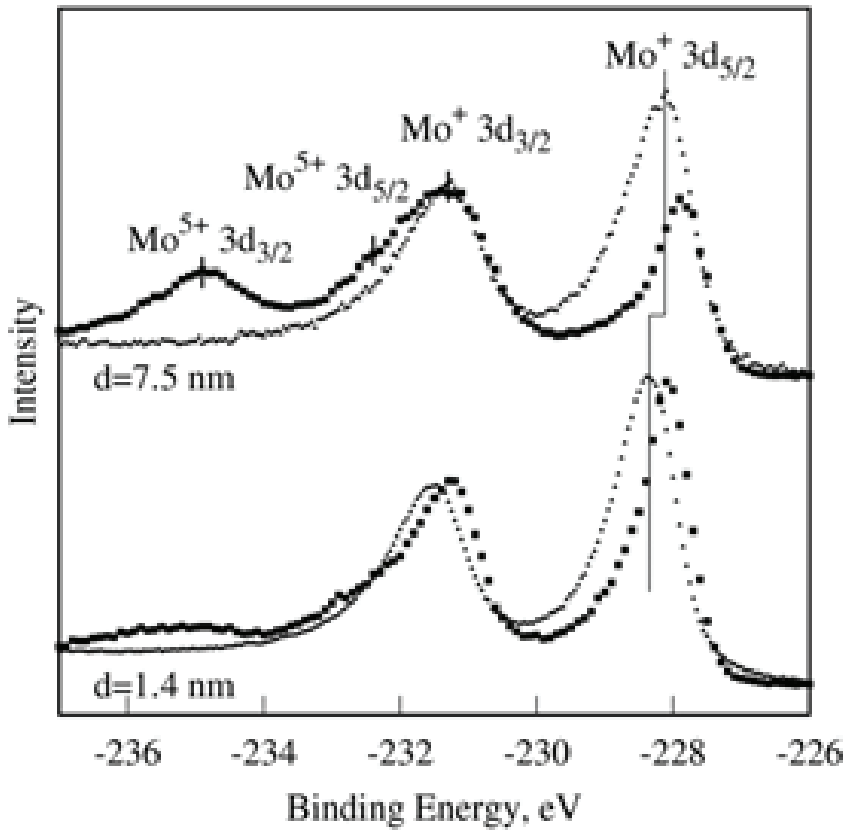

Figure 2: Typical X-ray spectra of the core levels of Mo films consisted of nanoclusters of 1.4 nm (bottom spectra) and 7.5 nm (upper spectra) in diameter obtained in situ (▲) and ex situ (■) with the XPS method.

larger values (see Figures 1 and 2), which may be related to the size effect [11]. Indeed, let us consider an electron located on the core level of an atom in a nanocluster. The energy of the initial state of the electron (before the photoionization process) in absolute value coincides with the orbital energy of an electron on a given atomic shell. Photoionization leads to the formation of an uncompensated positive charge (hole) in the atom acting as a potential of disturbance on the electrons remaining in the solid. As a result of the relaxation of the electronic subsystem (screening of the core hole), the relaxation energy is released. Since the time of intraatomic relaxation is comparable with the time of the photoelectron leaving the atom, the released energy is acquired by the photoelectron, leading to an increase of its kinetic energy and, consequently, to a decrease of a binding energy measured by the XPS. The weakening of the shielding of the core hole by the remaining electrons occurs due to the narrowing of the valence band with respect to the bulk metal in the nanocluster with a decrease of its size. This leads to the fact that the absolute screening decreases, and its difference with the bulk screening increases, thus the energy of the core level recorded with XPS method shifts toward higher values.

An analysis of the ex situ spectra of tantalum and molybdenum showed that exposure of the samples to the atmosphere leads to strong oxidation of the films (see Figures 1 and 2). In the X-ray spectra for nanocluster tantalum and molybdenum films, there are peaks corresponding to two phases: oxide Ta_2O_5 (or Mo_2O_5) and metallic Ta (or Mo), which is confirmed by stoichiometric analysis. At the same time, analogously to the samples not exposed to oxidation, the positions of Ta4f (and Mo3d) peaks corresponding to the metallic phase also exhibit a dimensional shift of the binding energy for all samples of nanocluster films (see Figures 1 and 2). Also, the analysis of the X-ray spectra of oxidized samples of nanocluster films showed the presence of typical oxide and metal phases of the valence band spectra of all samples of Ta and Mo. This may indicate the preservation of the conductive properties of nanocluster films of these metals, regardless of the size of nanoclusters. In addition, from the spectra (Figures 1 and 2), it can be seen that films consisted of larger nanoclusters are more susceptible to oxidation than films made from nanoclusters of smaller size. Thus, this may indicate a lower catalytic activity of Ta and Mo films consisted of nanoclusters of size less than 2 nm and it may be important for their further use.

Typical SEM images of tantalum and molybdenum nanocluster films deposited onto SiO_2/Si (001) are shown in Figure 3 (the view from above). Figures 3(a) and 3(b) clearly show that the formed films on the surface consist of separate nanoclusters and are continuous. It should be noted that the size of nanoclusters, estimated from the SEM images obtained, exceeds the size specified in the process of filtration in a quadrupole mass spectrometer. This may be a result of coagulation of nanoclusters and requires further study.

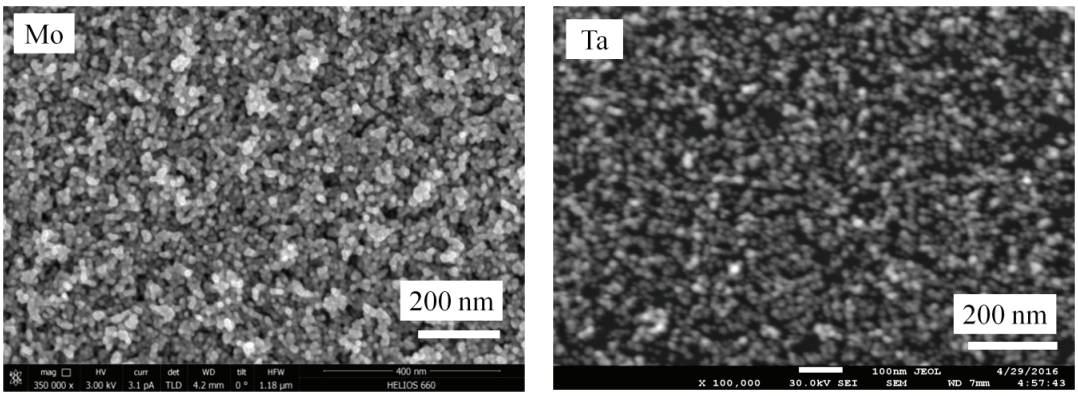

Figure 3: Typical SEM-images of films consisted of nanoclusters of Mo (left side) and Ta (right side) (top view).

The cleavage of the substrate SiO_2/Si (001) with nanocluster films was made to estimate the thickness and internal structure of the films deposited. Typical SEM image of the cleavage, which is made for a sample with Ta nanocluster film on the SiO_2/Si

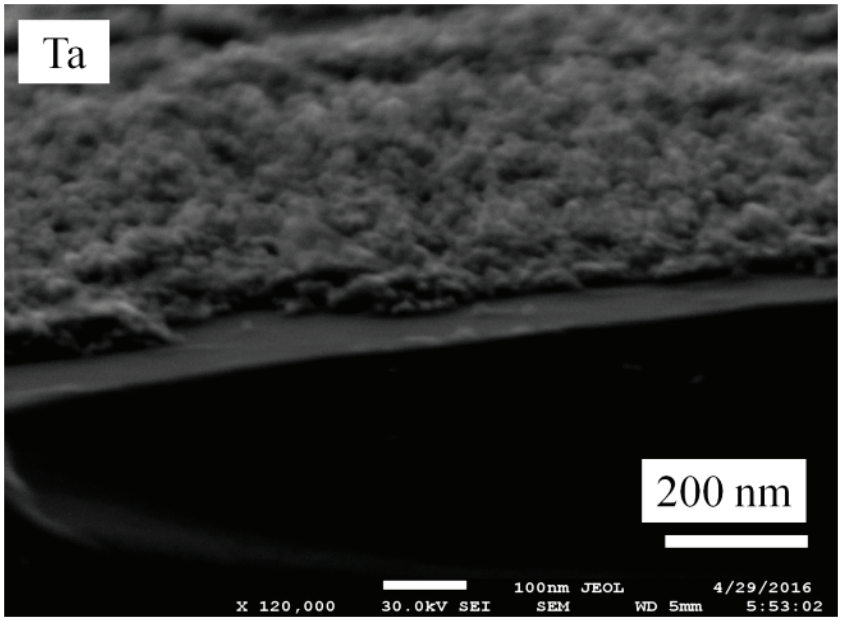

Figure 4: SEM-image of substrate SiO_2/Si (001) with nanocluster films of Ta (side view).

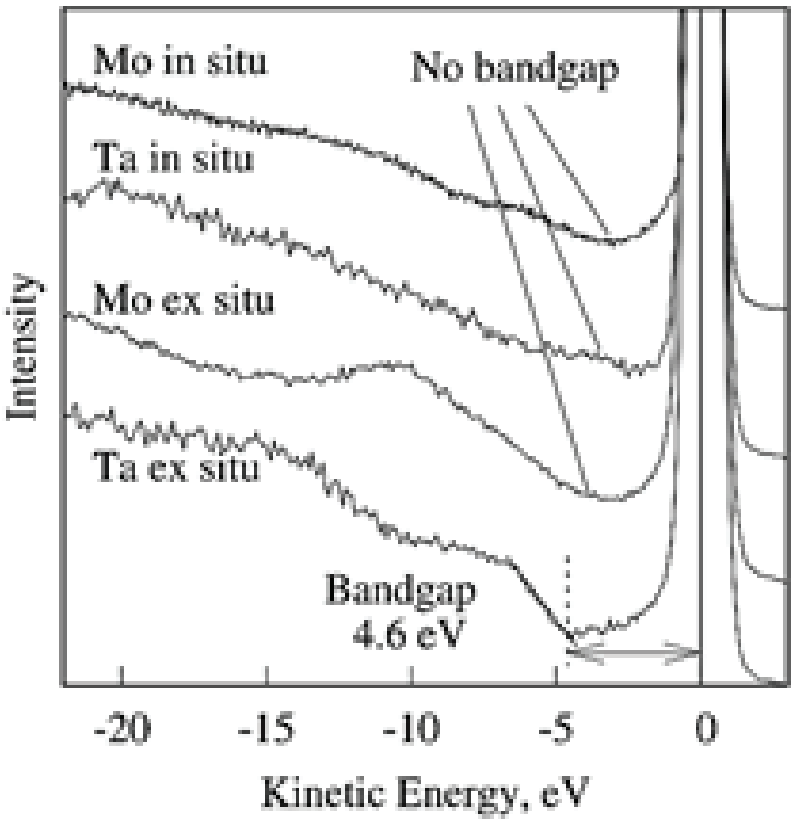

Figure 5: Spectra of characteristic electron energy loss obtained in situ and ex situ for Ta and Mo nanocluster films.

(001) surface, is shown in Figure 4. From the analysis of the image (see Figure 4), we can conclude that the thickness of the nanocluster film is of the order of 10 nm. In

addition, it is seen that the shape and size of the clusters contacting the substrate and lying on the surface coincide.

The analysis of the band structure was carried out with the REELS method by measuring the width of bandgap of the formed Ta and Mo nanocluster films. Figure 5 shows the spectra of the characteristic losses of the electron energy obtained ex situ and in situ. It was found that the samples of Ta nanocluster films after exposure to the atmosphere have a bandgap about 4.6 eV. An XPS analysis with angular resolution was additionally carried out to determine the depth of oxidation of the resulting films. It was concluded that the formed nanocluster films of Ta after exposure to the atmosphere show only surface oxidation, remaining metallic in the depth (more than 2–3 nm from the surface). It is possible that Mo nanocluster film samples are conductive, because it is difficult to conclude that there is bandgap from the loss spectra for Mo. Since while using these films as thermoelectric materials, their heating will occur, the thermal stability of the obtained samples was studied by heating in a vacuum to 600°C, followed by an analysis of changes in chemical composition by the XPS method. Differences in the spectra obtained before and after heating were not found. Thus, due to the absence of shifts in the binding energy of the core levels, it can be concluded that the size of the nanoparticles don't change after heating, and the resulting nanocluster films do not lose their porous structure due to heating. This fact is important for solving the problem of creating a highly effective thermoelectric material.

Thus, the nanocluster films obtained have a clear porous structure, consist of individual nanoclusters, are conductive and resistant to heating up to 600°C. The following work will be devoted to the study of thermoelectric properties of the nanocluster films obtained.

4. Conclusion

Thus, deposition parameters of high-melting metals Ta and Mo nanocluster films deposition with a clear porous structure on the surface of the SiO_2/Si (001) dielectric substrate by magnetron sputtering were determined. The analysis of the chemical state of the nanocluster films obtained was made. Their susceptibility to oxidation after exposure to the atmosphere, as well as their thermal stability under heating were studied. Evaluation of the size and shape of large-sized nanoclusters constituting the film were performed. The band structure of the films before and after oxidation was studied.

Funding

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