

Size dependence of the Anderson singularity index and Seebeck coefficient of thin monodisperse nanocluster metal films

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ABSTRACT

The paper presents the results of the study of thin monodisperse Co and Ta nanocluster films deposited by magnetron sputtering method onto highly oriented pyrolytic graphite (HOPG) and silicon dioxide surfaces by means of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) methods. The evolution of X-ray photoelectron spectra asymmetry of the core levels Co2p, Ta4f as the dependence on typical sizes of nanoclusters are studied. It is found experimentally that the Anderson singularity index α (i.e. asymmetry parameter) increases with decreasing of nanocluster's size. The correlation between α and Seebeck coefficient is discussed for pure bulk metals. It is shown that Seebeck coefficient of Co nanocluster films consisted of 1.2 nm sized nanoclusters can reach 120 $\mu\text{V}/\text{K}$. The applicability of the nanocluster films obtained for the development of highly efficient thermoelectric materials is discussed.

1. Introduction

Study of properties of nanostructured materials is of great interest particularly due to the recent development of nanoelectronics and micro- and nano-electromechanical systems [1–3]. Thin films consisted of metal nanoclusters of one size are of such materials. Such films appears to be perspective materials for the development of highly efficient catalysts [4], semiconductor devices [5], and the new generation of thermoelectric materials [6]. It is caused by the fact that one expects significant increasing of thermoelectric power value of such films with decreasing of nanoclusters sizes due to quantum effects [7,8]. At the same time electrical conductivity of such films is provided by the tunnelling of electrons among nanoclusters and percolation effects and phonon thermal conductivity is decreased due to porosity of such films (phonons scatter at clusters boundaries) [9]. Being proportional to electrical conductivity, square Seebeck coefficient and inverse proportional to thermal conductivity, thermoelectric figure of merit of such material may significantly differ from the one of bulk material [10]. That may be a basis for the development of the new generation thermoelectric materials. Therefore the study of electron properties evolution of thin nanocluster films with decreasing size of nanoclusters is very interesting for the development of a highly effective thermoelectric materials. The most interesting thing is the size dependent changes of density of electron states (DOS) of such nanostructured

materials near Fermi level. The reason is that one of the factors contributing to thermoelectric figure of merit of the material is the Seebeck coefficient that is dependent exactly on the change of DOS at Fermi level [8].

One of the methods allowing one to study electronic properties of nanostructured materials is a x-ray X-ray photoelectron spectroscopy (XPS). This method is sensitive not only to chemical surroundings of atom but also to the DOS of the material [11]. Particularly, the effect of the core level asymmetry in XPS spectra characterized by the Anderson singularity index α [12] is connected to the DOS of the material at Fermi level [13]. Thus the study of XPS spectra of nanostructured materials allows one to find qualitative changes of DOS behaviour at the Fermi level of the desired material and make conclusions on the potential thermoelectric properties of the studied material.

In this paper we present the results of XPS and SEM studies of thin monodisperse Co and Ta nanocluster films deposited with magnetron sputtering method onto highly oriented pyrolytic graphite (HOPG) and silicon dioxide surfaces. The evolution of x-ray X-ray photoelectron spectra asymmetry of the core lines Co2p and Ta4f as the dependence on typical sizes of nanoclusters in films are studied. It is found experimentally that the Anderson singularity index α increases with decreasing of nanocluster's size. The correlation between α and Seebeck coefficient is discussed for pure bulk metals. It is shown that Seebeck

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coefficient of Co nanocluster films consisted of 1.2 nm sized nanoclusters can reach 120 $\mu\text{V}/\text{K}$. The applicability of the nanocluster films obtained for the development of highly efficient thermoelectric materials is discussed.

2. Experimental techniques

Formation of thin film samples composed of metal nanoclusters onto the surface of silicon oxide $\text{SiO}_2/\text{Si}(001)$ (1 μm in thickness) for Ta and onto HOPG for Co was conducted by cluster deposition in the gas phase using the nanocluster source Nanogen-50 with the quadrupole mass spectrometer MesoQ (Mantis Deposition Ltd., UK) integrated in the preparation chamber of UHV surface analysis system Multiprobe MXPS VT AFM-25 (Omicron NanoTechnology GmbH, Germany). The formation of nanoclusters in the source was a result of magnetron sputtering of a target in an inert gases streams (Ar at the range 15–45 15–45 sccm, He at the range 5–80 5–80 sccm) at sufficiently low pressure $p \approx 1 \times 10^{-3}$ Torr. Cooling of atoms of sputtered target resulted in the formation of a metallic phase nucleation, and subsequent growth of nucleation centres during the passage of atoms through the aggregation area. The size analysis and separation of negatively charged clusters were carried out in real time using the quadrupole mass spectrometer MesoQ placed at the outlet of the aggregation zone. The size (diameter d) range of formed nanoparticles depends on the length of the aggregation area, and may vary from 1 to 8 nm. If the mass-spectrometer is adjusted to the filtering mode, the nanoclusters beam emitted from the source will have a very narrow size distribution with a variance of about $\pm 2\%$. That possibility allowed formation of monodisperse nanocluster films consisted of desired sizes of nanoclusters formed from the target material.

During the deposition process the substrate was biased up to $U = +800$ V, in order to increase nanocluster adhesion at the substrate surface and provide a “soft” regime of deposition (< 1 eV per atom) [14] with the formation of a film consisted of individual non-deformed nanoclusters without coagulation. As the result the samples of monodisperse Co and Ta nanocluster films with nanocluster sizes in the range of $d = 1$ to 8 nm were obtained.

The chemical composition and electronic structure of nanocluster films deposited on $\text{SiO}_2/\text{Si}(001)$ surface were controlled in situ by X-ray photoelectron spectroscopy (XPS). To this purpose, immediately after the deposition the sample was moved in the analysis chamber of the UHV ($p \approx 1 \times 10^{-10}$ Torr) system by means of the rod. In order to excite photoelectrons the $\text{MgK}_{\alpha 1,2}$ ($h\nu = 1253.6$ eV) emission line was used. The binding energy measuring error is defined by the measurement precision of the spectrum line maximum and depends on the energy analyzer and electron detector errors, the energy scale calibration and the reliability of the line fitting. Electrons kinetic energy is measured with Omicron EIS Sphera 2000 spectrometer with an energy step of 0.05 eV, that provides measurement error ± 0.05 eV. Calibration of the binding energy scale was made using metallic gold $\text{Au}4f_{7/2}$ spectral line position with binding energy 84.00 eV. According to the XPS data, the nanocluster films remained in metal (non oxidized) state with insignificant carbon impurities ($< 2\%$) during XPS analysis. That allowed studying the change of electron properties of the films caused by structural features (i.e. by typical size of nanoclusters of which the film is made) but not chemical compounds formation.

The analysis of XPS lines shape was performed according to the well known procedure [15], by approximation of the experimental data with theoretical curve:

$$I(E) = I_0 \int_{-\infty}^{\infty} I_{DS}(E')G(E - E')dE' \quad (1)$$

The Eq. (1) is a convolution of asymmetric Doniach-Sunjc function [16]:

$$I_{DS} = \frac{\cos\left[\frac{\pi\alpha}{2} + (1 - \alpha)\arctan\left(\frac{E}{\gamma}\right)\right]}{(E^2 + \gamma^2)^{\frac{1-\alpha}{2}}} \quad (2)$$

with a Gaussian function $G(E)$:

$$G = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right) \quad (3)$$

Here $E = E_b - E_b^0$ is the binding energy E_b , measured from the peak maximum position E_b^0 , γ is the intrinsic line width, α is the Anderson singularity index, $\sigma^2 = \frac{W^2}{2\sqrt{2\ln 2}}$, W is the instrumental broadening. The function (2) is a result of Lorentzian function convoluted with the asymmetric power function $1/E^{1-\alpha}$. Lorentzian function describes the broadening of the spectral line due to the limited core-hole lifetime ($\tau \approx \hbar/\gamma$). Asymmetric power function $1/E^{1-\alpha}$ is corresponded to the $e-h$ pairs excitation spectra at valence electrons shielding of the suddenly formed core hole (formed upon the photoexcitation). Gaussian function describes the instrumental broadening W . Fitting of the experimental XPS spectra is a task of finding the optimal solution in many-dimensional space defined by the following set of parameters: $\bar{x} = (\alpha, W, \gamma, \text{core peak positions } E_b^0, \text{ their intensities } I_0, \text{ parameters of linear background})$. The use of the linear background for this task is defined by the necessity of saving the information about XPS spectra asymmetry. Generally used Shirley [17] and Tougaard [18] backgrounds are unsuitable for this task because they distort the initial spectra. In this paper a programme based on the simulated annealing algorithm is used to fit the experimental XPS spectra. This algorithm is widely used for the global minimum finding in space of many variables [19]. Calibration of the fitting algorithm was made using the experimental $\text{Au}4f$ XPS spectra of bulk gold. The fitting parameters of the $\text{Au}4f_{7/2}$ line obtained are: $\alpha = 0.03 \pm 0.01, \gamma = 0.25 \pm 0.02, W = 1.1 \pm 0.1$ eV. These values corresponds correspond to the known experimental data [20] within the measurement error.

In order to evaluate the cluster size in our work we rely on mass-spectra obtained from MesoQ mass-spectrometer. Previously reported comparisons between the mass spectrometry (using the same equipment: Nanogen-50 nanocluster source and MesoQ mass-spectrometer) and atomic force microscopy or transmission electron microscopy measurements of nanoclusters show a close correlation of cluster size distributions [21–24]. Fig. 1 represents experimental mass-spectra for different Ta nanocluster samples (corresponding to different average sizes). Though the size resolution of MesoQ working in filtering mode is only $\pm 2\%$ according to data sheet, in case of our impossibility to prove it in situ by scanning tunneling or atomic force microscopy, we estimate the maximum size error as FWHM of mass-spectra of the corresponding samples.

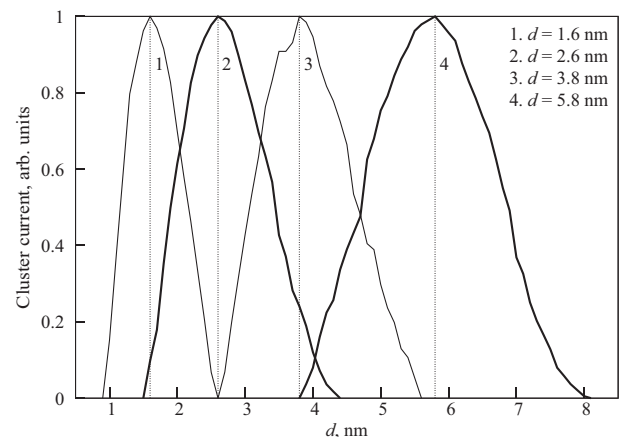


Fig. 1. Experimental mass-spectra for different Ta nanocluster samples (corresponding to different average sizes).

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