Electron microscopy of the effect of heat treatment on the structure of metal containing nanocomposites with silicon-carbon matrix

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Abstract. The influence of heat treatment in vacuum and in oxygen on the composition and distribution of tantalum containing nanocomposites in silicon-carbon matrix has been investigated. It is shown that the influence of heat treatment determines the interaction of oxygen with the atoms in the amorphous matrix as well as with nanocrystals of tantalum carbide. We propose a qualitative model of the processes occurring in these interactions.

1. Introduction
Amorphous silicon-carbon films (SCF) and amorphous films of metal nanocomposites within silicon-carbon matrix (MCN) are a class of modern materials with an extremely wide range of functional properties and potential applications [1]. The unique properties of the amorphous matrix, the ability to choose the composition and concentration of nanocrystals allow us to change, for example, the electrical conductivity by 18 orders of magnitude.

2. Materials and methods
Silicon-carbon films were prepared by plasma decomposition of a silicon-containing organic matter, polyphenylmethylsiloxane (PPMS)-(CH₃)₃SiO(CH₂C₃H₆SiO)₃Si(CH₃)₃ [2]. To obtain tantalum-based nanocomposites tantalum magnetron sputtering was conducted simultaneously with the growth of the SCF by plasma decomposition of PPMS.

The influence of thermal treatments in vacuum and oxygen atmosphere on the composition and distribution of the nano-sized material was investigated in films about 400 nm thick with an average 70 wt. % of tantalum deposited on a single crystal silicon substrate. Heat treatment of the films in vacuum or in an oxygen atmosphere was carried out at a temperature of 395 °C for 400 min [3]. The samples for transmission electron microscopy (TEM) were prepared by focused ion beam (FIB) with an FEI Helios NanoLab 600. Studies of membranes were made from films as-grown or heat-treated under the above modes, using a Titan 80-300 TEM/STEM (FEI, USA) with energy dispersive X-ray spectroscopy (EDXS).
3. Experimental

3.1 Scanning electron microscopy (SEM) of focused ion beam thinned membrane

The FIB made cross-section (Fig.1) of MCN films gave possibility to study the Ta distribution in the volume of the films and the influence of the anneal temperature.

![Figure 1. FIB made cross-sectional TEM sample (SEM image)](image1)

Transmission electron microscopy (TEM) (Fig.2) shows that the introduction of tantalum leads to the formation of nanocrystals 2 to 6 nm in size over the entire depth of the film, where the lattice parameter, d, corresponds to that of TaC.

![Figure 2. HR-TEM image of TaC nanoparticles (NP) in Si-C amorphous matrix (AM). Inset: FFT from NP and AM.](image2)
3.3 Scanning transmission electron microscopy (STEM)
Heat treatment in vacuum has practically no effect on the structure and composition of the films. Another situation is observed after film treatment in oxygen. An area that has a darker contrast in annular dark-field Z-contrast micrographs and does NOT contain any nanocrystals is formed near the free surface of the film. Moreover, the concentration of tantalum in this area is reduced substantially (Fig.3).

Figure 3. Annular dark-field STEM image of tantalum depletion in the cross-section of the sample after heat treatment in oxygen and plots of distribution of the concentration of oxygen (a), carbon (b) and tantalum (c) in the near surface state of the film after heat treatment in vacuum (dotted line) and in oxygen atmosphere (solid line)

4. Conclusions
Results of the study of the chemical composition and the thickness changes of the near-surface region of a tantalum implanted silicon carbide amorphous film after heat treatment in vacuum and oxygen are shown in Fig.3.

One can see from Fig.3a that the oxygen concentration in the surface region significantly increases as a result of heat treatment in oxygen atmosphere. In contrast, the carbon concentration (Fig.3b) in the surface region is decreased by about half. The change in the concentration of tantalum is more complex (Fig.3c): it is reduced (by about 20 wt. %) in the surface region, and there is a slight increase of Ta in the depth of the layer.

Based on the data a model of the processes occurring during the heat treatment in oxygen MNCs may be proposed. The effect of heat treatment on the structure of tantalum silicon-carbon nanocomposites consists of three stages (Fig. 4):
Figure 4. Influence of the heat treatment on oxygen on the MCSCN structure.

1st The interaction of oxygen with carbon atoms at the film surface forms volatile compounds of CO, CO\(_2\) and volatilization of these carbon compounds from the surface region of the structural network.

2nd The interaction of oxygen with carbon and volatilization of formed compounds cannot explain the observed increase in the oxygen concentration in the surface layer. That is why the reaction of oxygen with SiO\(_x\) forming SiO\(_2\) and reaction of oxygen with tantalum forming tantalum oxide may be expected. Moreover, since at the surface region there are no nanocrystals it is necessary to assume that the nascent tantalum oxide particles are amorphous. The latter assumption seems very reasonable since it is known that Ta\(_2\)O\(_5\) films may persist in the amorphous state at temperatures up to 700 °C.

3rd The remaining tantalum carbide nanocrystals are displaced by the growth boundary of silicon oxide.

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