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Calculation of the component composition of the surface layers of titanium carbide sputtered with light ions

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On the basis of the previously tested model of sputtering binary layered inhomogeneous targets with light ions, a method for calculating the component composition of the surface layers of titanium carbide under stationary (stoichiometric) sputtering with light ions is proposed. The results of calculations of the component composition of the altered surface layer of titanium carbide are given in comparison with experimental data and the results of computer simulation. The proposed method for calculating the component composition based on the model of sputtering binary layered inhomogeneous targets made it possible to estimate the thickness of the changed surface layer. The proposed calculation method allows developing a technology for creating titanium carbide surfaces with a given ratio of components.

Keywords: modified surface, layered-heterogeneous surfaces, titanium carbide, partial sputtering coefficient, stationary (stoichiometric) sputtering.

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Introduction

The vast majority of structural materials used in installations, the elements of which are subjected to ion irradiation, are multicomponent compounds. Many of these materials are metal carbides, in particular titanium carbide. Long-term irradiation of the surface of titanium carbide (as well as the carbide of any metal) with an ion flux leads to a change in the composition of the surface of this compound. The reason for the change in the surface composition of the material during ion bombardment of the target can be ion sputtering, ion-induced diffusion, radiation-induced segregation, and other phenomena. In this paper, we solve the problem of changing the surface composition of titanium carbide as a result of long-term ion sputtering. Note that this problem was repeatedly studied earlier [1–15] both theoretically and experimentally. However, in all theoretical studies the process of stationary (stoichiometric) sputtering of homogeneous two-component materials was considered, which does not correspond to the actual situation. The application of the model of sputtering of a layered-heterogeneous two-component target by light ions [16,17] makes it possible to describe the phenomenon more reliably, as well as to estimate the thickness of the modified layer. When using this sputtering model, the modified layer is considered as a homogeneous two-component material with a component composition different from that of the main target. Comparing the values of the partial sputtering coefficients of the components at different layer thicknesses, one can make an unambiguous conclusion about the thickness of the modified layer in the case of stationary sputtering of titanium carbide.

1. Model and estimate of the modified layer thickness

To describe the sputtering process of titanium carbide by light ions with modified surface layer, the previously tested model [17,18] is used, according to which the sputtering of the target is the result of the action of two mechanisms, and the sputtering of each component of the layer is described as a sequence of processes initiated by ascending and descending ion fluxes regardless.

Each mechanism was reviewed as the sequence of processes leading to the sputtering of i-th component of the upper layer of the target. The graphic representation of the sequence of processes is shown in Fig. 1.

Upward sputtering of ions [16,17] (left side of the Figure): ions passage through layer of titanium carbide x thick; reflection of the ion stream from the underlying layers of the target; knocking out by the reflected ion from the two-component layer of heterogeneity of the primary recoil atom with an effective charge Z_{eff}; emission of knocked out atoms

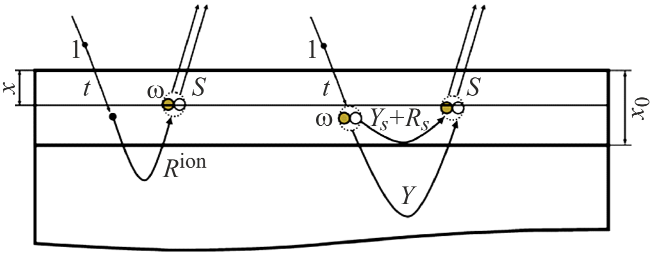

Figure 1. The sequence of processes leading to the sputtering of the target with modified layer on the surface.

of the binary layer of heterogeneity moving from depth x to the surface.

Downward sputtering of ions [16,17] (right side of the Figure): ions passage through the layer of titanium carbide with thickness of x; knocking out from the two-component layer of heterogeneity of primary recoil atoms with effective charge Z_{eff} in the direction deep into the target; reflection of the knocked out atoms of the binary layer of heterogeneity from the underlying layers of the target or sputtering of the underlying atoms of the target; emission of knocked out atoms (primary and secondary) moving from depth x to the surface.

The model is described in more detail in the papers [16,17], in which, after a series of mathematical transformations and the use of various approximations, a formula was obtained that makes it possible to calculate the partial sputtering coefficients of i-th component of the material of the upper binary layer of target heterogeneity by light ions Y_i.

In the stationary mode of sputtering, based on the balance condition for the number of atoms, using the Patterson and Schearn ratio [11], the ratio of the number of sputtered atoms of the components (equal to the ratio of the partial sputtering coefficients of the components of the modified layer) shall be proportional to the ratio of the concentrations of the components (titanium and carbon) of main target material:

$$\frac{Y_{\mathrm{Ti}}(E_0, \theta_0, x_0)}{Y_{\mathrm{C}}(E_0, \theta_0, x_0)} = \frac{c^b_{\mathrm{Ti}}}{c^b_{\mathrm{C}}}.$$

Taking into account that the partial sputtering coefficients depend both on the concentration of components in the modified layer c^s_i, and on the concentration in the base material c^b_i, the resulting ratio is a non-linear equation with respect to the concentration of components c^s_i in the modified layer. This equation with respect to the component concentration in the modified layer was solved numerically by dividing the segment in halves with an accuracy of 0.0001.

Note that the partial sputtering coefficients significantly depend on the surface bond energy of the components, which, in turn, change with change in the concentration on the surface. The surface bond energy of atoms of i-th component in the compound U_i is calculated by the formula

$$U_i = \frac{U_{0i} + \Sigma^2_{j=1, j\neq i} c^s_j U_{0j}}{1 + \Sigma^2_{j=1, j\neq i} c^s_j},$$

where U_{0i} — bond energy of atoms of i-th component in single-component material.

An additional independent parameter in this equation is the thickness of the modified layer x_0, its determination is a separate task. In many papers [1–6] the thickness of the modified layer was estimated in the range from 0.1 to 10 nm. It is obvious, and this is confirmed by the results of computer simulation [7,19], that the sputtered atoms fly out mainly from the two upper layers, however, due to the redistribution of atoms (not considering the accompanying phenomena), the component composition shall change in the thicker layer. Using the obtained formula for the partial sputtering coefficients of the components under the condition of a stationary (stoichiometric) sputtering mode at different thicknesses of the modified layer, it is possible to analyze the obtained dependences and to make conclude relating the modified layer thickness.

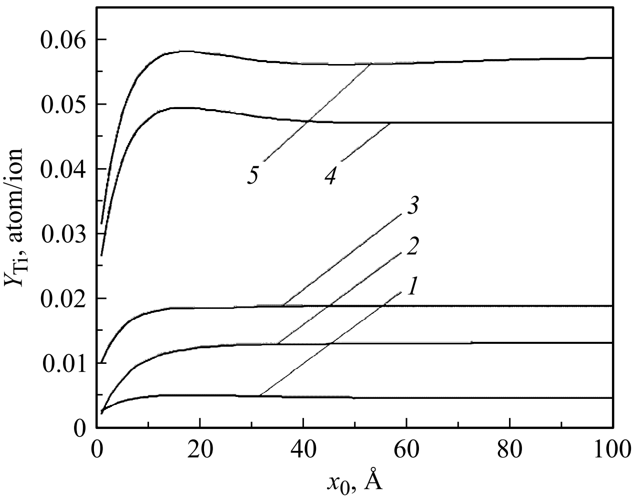

Figure 2. The results of calculations of partial coefficients of Ti sputtering from a modified layer of titanium carbide by hydrogen ions with energies $E_0 = 500\,\mathrm{eV}$ (*1*), 1 keV (*2*), helium with energies $E_0 = 100\,\mathrm{eV}$ (*3*), 500 eV (*4*), 1 keV (*5*) depending on the thickness of the modified layer.

Fig. 2 shows the calculated dependences of the titanium partial sputtering coefficient in the case of stationary sputtering of titanium carbide by hydrogen ions with energies of 500 eV and 1 keV (normal incidence) and by helium ions with energies of 100 eV, 500 eV and 1 keV (normal incidence) depending on the thickness of the modified layer. It can be seen from the graphs that depending on the type of ion and its energy at thicknesses of the modified layer more than 15−40 Å the partial sputtering coefficients of titanium (or carbon — they are the same in this case) reach the maximum (stationary) value and practically do not change anymore (within the calculation error In this case, the concentration of components in the modified layer did not change (within the calculation error), despite the increase in sputtering coefficients with thickness increasing of the modified layer. Based on the Hamilton principle, we can conclude that the thickness of the modified layer shall correspond to the value at which the sputtering coefficient reaches a stationary value. In accordance with the presented results of calculations, depending on the type of ion and its energy the thickness of the modified layer shall be within 15−40 Å.

Considering that, as a result of sputtering, the distribution of atoms in the upper layers is heterogeneous, the sputtered atoms are emitted from the first two monolayers, and the thickness of the modified layer can reach several tens of angstroms, only the average concentration of components in the modified layer can be determined. This value was calculated as a weighted average between the concentration in the first two layers (determined according to the Patterson and Shearn ratio) and the concentration in the rest of the volume of the modified layer.

2. Calculation results

Fig. 3 shows the results of calculating the average relative concentration of titanium as a function of the energy of H and He ions (normal incidence) in the stationary mode of titanium carbide sputtering in comparison with experimental data [12]. A rather good agreement is observed between the calculated values and the experimental results depending on the ion energy. With an energy increase of the bombarding ions, the concentration of titanium tends to the value which the base material has. At a certain ion energy, stoichiometric (without changing the surface layer composition) sputtering of the titanium carbide target can be observed.

The observed differences (less than 20%) between the experimental data and the results of calculations in the values of the relative concentration of titanium are probably due to the fact that in the experiment the redistribution of the concentration of components was influenced by ion-induced diffusion, radiation-induced segregation, and other processes. Besides, although paper [12] does not indicate the measurement error, it was probably not less than 10%, and the thickness of the layer under study is much larger than 10 Å.

Fig. 4 shows the results of study of stationary sputtering of titanium carbide by helium ions as a function of the ion energy during target bombardment at angle of 30°. The results of the relative concentration calculation of titanium in the modified layer are compared with computer simulation data [7]. In this case, the results agree much better, since the calculations are based on models that are close in meaning.

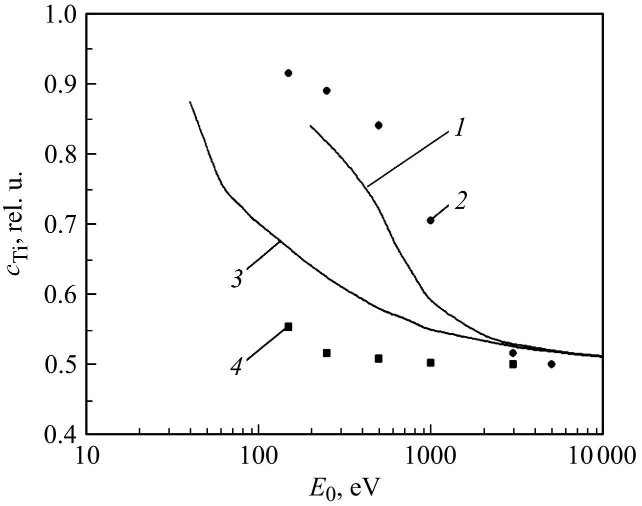

Figure 3. The results of calculations of the relative concentration of titanium in the modified layer of titanium carbide during stationary sputtering of TiC by H (*1, 2*) and He (*3, 4*) ions (solid lines — calculation, symbols — experimental data) depending on the ion energy (normal incidence).

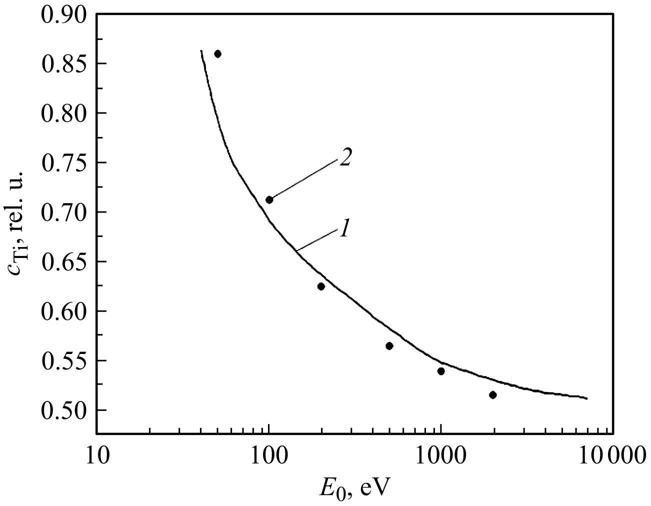

Figure 4. The results of calculations of the relative concentration of titanium in the modified layer of titanium carbide during stationary sputtering of TiC by He ions (*1* — calculation, *2* — computer simulation data) depending on the ion energy (incidence at angle 30°).

Conclusion

The presented results of calculations in comparison with experimental data and computer simulation data allow us to conclude that the proposed model for calculating the concentration of components in layer modified as a result of stationary sputtering adequately describes the observed phenomenon. At low energies of the bombarding ions the surface of titanium carbide is depleted of carbon, and with increase in the energy of the ions the stoichiometric sputtering of the target is possible, i.e., sputtering which does not change the surface composition of the material. Moreover, using this model it is possible to estimate the thickness of the modified layer, which was impossible in principle using previously proposed methods. In the future, it is planned to carry out additional studies of changes in the component composition of the surface layer of other frequently used materials, such as WC, TaC, and SiC. The method for calculating the concentration of target components in the modified layer and the thickness of this layer can be used as the basis for the technology of creating the surface layer materials with specified properties.

Conflict of interest

The author declares that he has no conflict of interest.

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