Research on diffusion of Mo substrate atoms into Ti and Cr thin films by secondary ion-ion emission method

A. D. Abramenvok, Ya. M. Fogel’, V. V. Slyozov, L. V. Tanatarov, O. P. Ledenyov

National Scientific Centre Kharkov Institute of Physics and Technology,
Academicheskaya 1, Kharkov 61108, Ukraine.

The experimental research on the nature of diffusion by the Mo substrate atoms into the Ti and Cr deposited thin films is completed by the secondary ion-ion emission method. In [1], the initial stage of the Ti thin film on the Mo substrate deposition process, using the Ti evaporation technique in the vacuum, is researched. It was found that the Mo substrate atoms diffuse into the continuously deposited Ti thin film. The diffusion of Mo substrate atoms by the nodes of crystal grating in the deposited metallic Ti thin film with the continuously increasing thickness is theoretically considered in [2]. In this research, the diffusion coefficients of Mo substrate atoms into the Ti and Cr thin films are measured by the secondary ion-ion emission method in the Mo-Ti and Mo-Cr systems.

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**Introduction**

In [2], it was shows that in the two layered system substrate – deposited thin film (DTF), the concentration $C$ of substrate’s atoms at the boundary between the DTF and the vacuum at the big enough thicknesses of the DTF is expressed as in the time dependent eq. (1)

$$C(t) = At^{\frac{3}{2}} \exp\left(-\frac{k^2}{4D}t\right), \quad (1)$$

where $D$ is the diffusion coefficient of substrate’s atoms into the material of the DTF, $t$ is the time; $A$ is the constant.

Applying the secondary ion-ion emission method [1, 3], it is possible to register the changing of concentration magnitude of the Mo substrate’s atoms, diffused through the Ti or Cr DTFs with the continuously increasing thickness over some time period $t$. Since the second ions current $I$, corresponding to the Mo substrate’s atoms, which are situated on the Ti- or Cr-vacuum surface, is proportional to the concentration of Mo atoms, hence the dependence of the second ions current of the Mo$^+$ on the time $I(t)$ can be described by the formula (1). Going from this consideration, a new measurement method of diffusion coefficient’s magnitude $D$ in the solid states can be proposed. The essence of this method consists in the following things:

1) the research of dependence $I(t)$ for the ions of substrate’s substance;
2) the finding of value $k^2/4D$, using the tangent of the angle of tilt in the dependence $\ln I \cdot t^{\frac{3}{2}} = f(t)$; and
3) the measurement of velocity of growth of thin film thickness.

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In the present research, the diffusion coefficients of the Mo substrate’s atoms in the Ti and Cr thin films are measured by the secondary ion-ion emission method during the deposition on the Ti and Cr thin films on the Mo substrate. Since the Ti and Cr metals together with the Mo metal create the solutions of substitution, hence it is possible to use the formula (1) to describe the diffusion process in these metals. In [1], the measurement set up, and the method of mass-spectrometry research on the diffusion of the substrate’s atoms in the deposited thin film with the use of phenomena of secondary ion-ion emission, are described. The primary argon ions $Ar^+$ were used to irradiate the metal-vacuum surface in this research.

In Fig. 1, the dependence of the current of the secondary ions $Mo^+$ on the time $I(t)$ for the Mo - Ti system at the temperature of 1000°C is presented. This dependence was obtained during the continuous deposition of the Titanium thin film with the velocity of 0.5 monolayer per minute on the Molybdenum ribbon at the temperature $T=1000°C$. The computed curve $I(t)$, calculated with the use of eq. (1), is also shown in Fig. 1. As it can be seen, the experimental curve of the dependence $I(t)$ is well approximated by the computed curve at the big enough thicknesses of the Titanium thin film. The similar correlation is observed in the case of Molybdenum - Chrome system.
The value of expression $k^2/4D$ was calculated, using the obtained tangent of the angle of tilt in the dependence $\ln I \cdot t^{1/2} = f(t)$, created for the time period, when the experimental and computed curves $I(t)$ were coincided. The deposition velocity of the $Ti$ and $Cr$ thin films was determined by the weighting of the layer of thin film’s material, deposited per certain time. The diffusion coefficients of the $Mo$ substrate’s atoms in the deposited $Ti$ and $Cr$ thin films were determined with the help of the above described two measurements.

The diffusion coefficients of the $Mo$ substrate’s atoms in the deposited $Ti$ and $Cr$ thin films were measured at a number of the temperatures $T$ of the $Mo$ substrate. The same $Mo$ substrate was used to perform a series of measurements. Every subsequent experiment was performed, when the deposited $Ti$ or $Cr$ thin film layers, created on the surface of the $Mo$ ribbon at the previous experiment, was evaporated due to the $Mo$ ribbon heating up to the temperature of $1400° C$. The value of the diffusion coefficient $D$ was determined as an average value among a number of the values, obtained in several experiments. The deviation among the values of the diffusion coefficient $D$ was in the range of 10-12%.

In Fig. 2, the dependences $\ln I \cdot t^{1/2} = f(t)$ are created, using the results of diffusion coefficients measurements during the diffusion by the $Mo$ atoms into the $Ti$ and $Cr$ deposited thin films. As it can be seen in Fig. 2, the dependences $\ln I \cdot t^{1/2} = f(t)$ are linear in the cases of the $Mo-Ti$ and $Mo-Cr$ systems. Going from the tangent of the angle of tilt of the direct lines in Fig. 2, the activation energies of diffusion by the $Mo$ substrate atoms into the $Ti$ and $Cr$ thin films are calculated. The values of activation energies are $2.76 eV$ ($Mo-Ti$) and $2.9 eV$ ($Mo-Cr$). The diffusion coefficients for the $Mo-Ti$ and $Mo-Cr$ systems can be calculated, using the following formulas

$$D = 5.3 \cdot 10^{-3} e^{6400/4T}; \quad D = 1.6 \cdot 10^{-2} e^{67000/4T}.$$

In the case of the diffusion of the $Mo$ substrate atoms into the $Ti$ thin film, the measurement of diffusion coefficient was completed, using the $Mo^{99}$ radioactive isotope in [4]. At the diffusion of the $Mo$ substrate atoms into the $Ti$ thin film, the value of diffusion coefficient is $1.7 \cdot 10^{-9} cm^2/sec$, and the activation energy is $1.4 eV$. The big difference between the present research results and the early reported research [4] can be attributed to the fact that the diffusion of the $Mo$ substrate atoms into the $Ti$ thin film was mainly realized through the defects (the grain boundaries, dislocations) in the $Ti$ thin film’s crystal structure in [4]. At the deposition of the $Ti$ thin film on the $Mo$ substrate by the evaporation technique in the vacuum, the created $Ti$ thin film has a small concentration of defects [5], and the diffusion by the $Mo$ substrate atoms into the $Ti$ thin film has place through the crystal grating. As far as the $Mo-Cr$ system is concerned, it is necessary to emphasis that the experimental results, obtained by the secondary ion-ion emission method, are in good agreement with the data in [6, 7].

**Conclusion**

The experimental research on the nature of diffusion by the $Mo$ substrate atoms into the $Ti$ and $Cr$ deposited thin films is completed with the application of the secondary ion-ion emission method. The diffusion coefficients of $Mo$ substrate atoms into the $Ti$ and $Cr$ thin films are measured. The comparative analysis on the obtained research results is provided.

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*E-mail: ledenyov@kipt.kharkov.ua*

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Fig. 1. Dependence of current of secondary ions $Mo^+$ on time $I(t)$ for $Mo - Ti$ at temperature of $1000° C$: 1 - experimental curve; 2 – computed curve, calculated with the use of eq. (1).

Fig. 2. Dependence of $\ln D$ on $1/T$ for $Mo - Ti$ (curve 1) and $Mo - Cr$ (curve 2).
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