SURFACE AND VOLUME DIFFUSION OF NIOBIUM ATOMS ON WOLFRAM SURFACE (110)

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ABSTRACT

Diffusion properties of niobium atoms at the surface (110) of tungsten monocrystall were studied measuring electron work function φ and Auger-electron spectroscopy. Hurst-Gauss model which considers "traps" capturing for short time the diffusing atoms was taken for description of volume diffusion of Nb atoms in W subsurface. Based on the determined coefficient D_Δ for Nb volume diffusion into W, surface diffusion has been described within Fisher model in terms of "suction" of migrating atoms perpendicularly to the surface of interest.

1.INTRODUCTION

There were determined the coefficients for volume and surface diffusion of Nb atoms over the edge (110)W. Changes in emission properties of electrodes can lead to worsening of yield characteristics in a nuclear-to-electric energy thermal emission transformer. This may happen due to migration of atoms from the emitter-collector commutation bridge towards the work zone of the emitter. Niobium is conventionally used as the material for this commutation bridge to link the tungsten emitter and niobium collector. So, investigation of Nb diffusion over W surface is of interest.

Diffusion of Nb atoms was studies at the edge (110)W employing Auger-electron spectroscopy completed with measurements of the work function φ.

Main experimental data were those related to measurements of the Nb coating rates as functions of time and annealing temperature at Nb dilution in W. In order to determine the volume diffusion coefficient for Nb, D_Δ, we controlled changes in surface concentration for the coated layer, and in order to determine the surface diffusion coefficient D_s, we measured the Nb concentration distribution profiles at monocrystal surface along the [110] direction at various times and temperatures.

Determination of diffusion coefficients was based on the solution of Hurst-Gauss equations [1, 2] which take into account presence of the "traps" in the bulk which capture and extrude diffusing atoms. In case of volume diffusion, the system of Hurst-Gauss differential equations takes the following form:

$$\frac{\partial c}{\partial t} = D_\Delta \frac{\partial^2 c}{\partial x^2} - k_1 c + k_2 m \qquad \frac{\partial m}{\partial t} = k_1 c - k_2 m$$

where c,m – concentration of free and captured Nb atoms; k_1,k_2 – constants for trap capture velocity and trap escape velocity for atoms; t – time; D_Δ - volume diffusion coefficient for subsurface area; x – coordinate motion of Nb is considered along.

Boundary and initial conditions take the following form:

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = 0, \left(\frac{\partial m}{\partial x}\right)_{x=0} = 0, \quad c(x,0) = c_м, \quad H(h-x) = \begin{cases} c_м \; at \; x \le h \\ 0 \; at \; x > h \end{cases}, \quad m(x,0) = 0.$$

where $c_м$ – Nb monolayer concentration at the edge (110)W; h – thickness of sputtered Nb layer; H – mirror image of Heaviside function.

In case of surface diffusion, the system of differential equations can be considered within Fisher's model [3]. This model is based on the supposition that "suction" of migrating atoms takes place in the direction perpendicular to the surface of interest:

$$\frac{\partial c}{\partial t} = D_{\Delta}\frac{\partial^2 c}{\partial x^2} - k_1 c + k_2 m \qquad \text{at } x > a, \qquad \frac{\partial c}{\partial t} = D_s\frac{\partial^2 c}{\partial y^2} + \frac{D_{\Delta}}{a}\frac{\partial c}{\partial x} - k_1 c + k_2 m \qquad \text{at } x = a$$

$$\frac{\partial m}{\partial t} = k_1 c - k_2 m \qquad\qquad \frac{\partial m}{\partial t} = k_1 c - k_2 m$$

here a – thickness of the layer where surface diffusion takes place; D_s – surface diffusion coefficient; y – coordinate parallel to the surface.

Initial and boundary conditions at that take the following form:

$$c(x,0,0) = \begin{cases} c_м \ при \ x = a \\ 0 \ при \ x > a \end{cases}, \qquad c(x,y,t) = c_м \quad \text{at } y = 0.$$

Wipple [4] used the Fourier and Laplace transformations and obtained a precise solution for the problem; later, Suzuoka [5] solved the problem for the case of instantly depleted source. Precise calculations in this case were close to those approximate of Fisher. Considerable discrepancy of Fisher's model from that of (and Suzuoka) lies in the supposition about zero diffusion flux along Y-axis in the bulk at x > a. But in the case when the surface diffusion coefficient exceeds considerably that for volume ($D_S >> D_{\Delta}$), Fisher's approximate formula provides the numbers quite close to that obtained within Wipple's model. Most close solutions are provided by the models with x = a [6]. Since in our case we are interested in this particular region, it is possible to neglect the transverse component in the volume diffusion and solve the problem within Fisher's model. As it is known [7], diffusion coefficients in the bulk and in the subsurface zone are quite different. That is why, in calculations of the surface diffusion coefficient instead of the volume diffusion coefficient D_v determined in experiments with massive samples, one should use the volume diffusion coefficient for subsurface zone of the crystal D_{Δ} measured experimentally for that particular surface where we determine the surface diffusion coefficient D_s. Finding of D_{Δ} with known concentration profile for substance distribution in the subsurface represents quite a complex task; so, in our work we determine the volume coefficient in subsurface based on changes with temperature and annealing time in concentration of the source sputtered over the investigated surface directly at the material-vacuum interface. Quantitative measurements were based in this case on the control over the surface work function φ and Auger-measurements with preliminary calibration of changes in the work function with the rate of Nb coating θ.

Temperature dependencies of diffusion coefficients and capture/decay probabilities for various initial coating rates are presented at figure 1 and in table 1 and can also be presented in the following form:

For initial coating $\theta_0 = 0.62$

$D_{\Delta} = (8.5 \pm 2)\times 10^{-9}\cdot\exp(-\frac{3.57 \pm 0.04}{kT})$ cm²/s, $\quad k_1 = 1{,}2\cdot 10^{-3}$ 1/s, $k_2 = 5\cdot 10^{-4}$ 1/s.

For initial coating with $\theta_0 =$ 5 monolayers

$$D_{\Delta} = (8.5 \pm 22.5)\cdot 10^{-7}\cdot\exp(-\frac{3.8 \pm 0.4}{kT}) \text{ cm}^2/\text{s}$$

$$k_1 = (4.8 \pm 14.1)\cdot 10^{7}\cdot\exp(-\frac{3.7 \pm 0.4}{kT}) \text{ 1/s}, \qquad k_2 = (4.3 \pm 61.6)\cdot 10^{14}\cdot\exp(-\frac{6.6 \pm 2.1}{kT}) \text{ 1/s}.$$

For the multi-layer region ($\theta_0 = 1$) the points lie in the transitional region.
Surface diffusion coefficient for Nb at the edge (110)W takes the form:

$$D_s = (3.6 \pm 1.7)\cdot 10^{-2}\cdot\exp(-\frac{1.71 \pm 0.07}{kT}) \text{ cm}^2/\text{s}$$

Investigations showed that the obtained values of D_{Δ} for niobium in tungsten are considerably smaller than those, presented in literature [8] what agrees well with the data of [7] about inhibition of diffusion in

subsurface regions. At that, the diffusion coefficient at $\theta_0 = 0.62$ is much smaller than that at $\theta_0 = 5$ showing the difference for more than 10 times at T = 1,840K. The value D_Δ for $\theta_0 = 1$ lies in the transitional area.

Such behavior of D_Δ can be explained by the influence on the diffusion process from surface forces in form of segregation at heating of the component with lower melting point towards the surface what results in lower diffusion coefficient. Naturally, such influence is more noticeable for $\theta_0 = 0.62$ than for $\theta_0 = 1$ and for $\theta_0 = 5$.

2.EXPERIMENTAL

Diffusion experiments with niobium films of $\theta_0 = 1$ or less, there was no atomic migration revealed over measurable distances that could allow us measuring the concentration profile for Nb distribution with required resolution. Higher annealing temperature in this case would only result in swift dissolution of Nb atoms preventing us from registration of surface diffusion. Sputtering relatively thick Nb film ($\theta_0 = 5$) results in more pronounced surface migration of Nb, particularly at low temperatures.

3.CONCLUSION

As the calculations with determined diffusion coefficients showed, proliferation of Nb over the edge (110) W in conditions of suction back to the bulk and capture/release reactions is quite negligible (see Table 2). At the same time the surface diffusion coefficient for Nb atoms at the edge (110) W represents a noticeable value.

Table 1

Initial rate of coating	Annealing temperature, K	Diffusion coefficient, cm^2/s	Capture coefficient, 1/s	Release coefficient, 1/s
0.62	1810	10^{-18}	$1.2x10^{-3}$	$5x10^{-4}$
	1875	$2.1x10^{-18}$	$1.2x10^{-3}$	$5x10^{-4}$
	1930	$4x10^{-18}$	$1.2x10^{-3}$	$5x10^{-4}$
	2000	$8.5x10^{-18}$	$1.2x10^{-3}$	$5x10^{-4}$
	2050	$1.45x10^{-17}$	$1.2x10^{-3}$	$5x10^{-4}$
1	1500	$3.5x10^{-20}$	$7x10^{-5}$	$3x10^{-8}$
	1525	$5x10^{-20}$	10^{-4}	$6x10^{-8}$
	1550	$2x10^{-19}$	$5x10^{-4}$	10^{-7}
5	1560	$6x10^{-19}$	$7.5x10^{-5}$	$1.9x10^{-7}$
	1660	$1.55x10^{-18}$	$1.7x10^{-4}$	$1.2x10^{-6}$
	1700	$5x10^{-18}$	$4.3x10^{-4}$	$1.2x10^{-5}$
	1780	$1.5x10^{-17}$	$1.5x10^{-3}$	$3.3x10^{-5}$
	1840	$4x10^{-17}$	$4.5x10^{-3}$	$9.5x10^{-5}$

Table 2

T,K	D_Δ, cm^2/s	D_s, cm^2/s	L, cm	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1600	$4.84x10^{-20}$	$1.17x10^{-7}$	θ	0.7	0.47	0.31	0.2	0.13	0.08	0.05	0.03	0.019	0.011
1800	$8.6x10^{-19}$	$4.79x10^{-7}$		0.7	0.47	0.31	0.2	0.13	0.08	0.05	0.03	0.019	0.011
2000	$8.59x10^{-18}$	$1.48x10^{-6}$		0.69	0.46	0.3	0.2	0.13	0.08	0.05	0.03	0.019	0.011

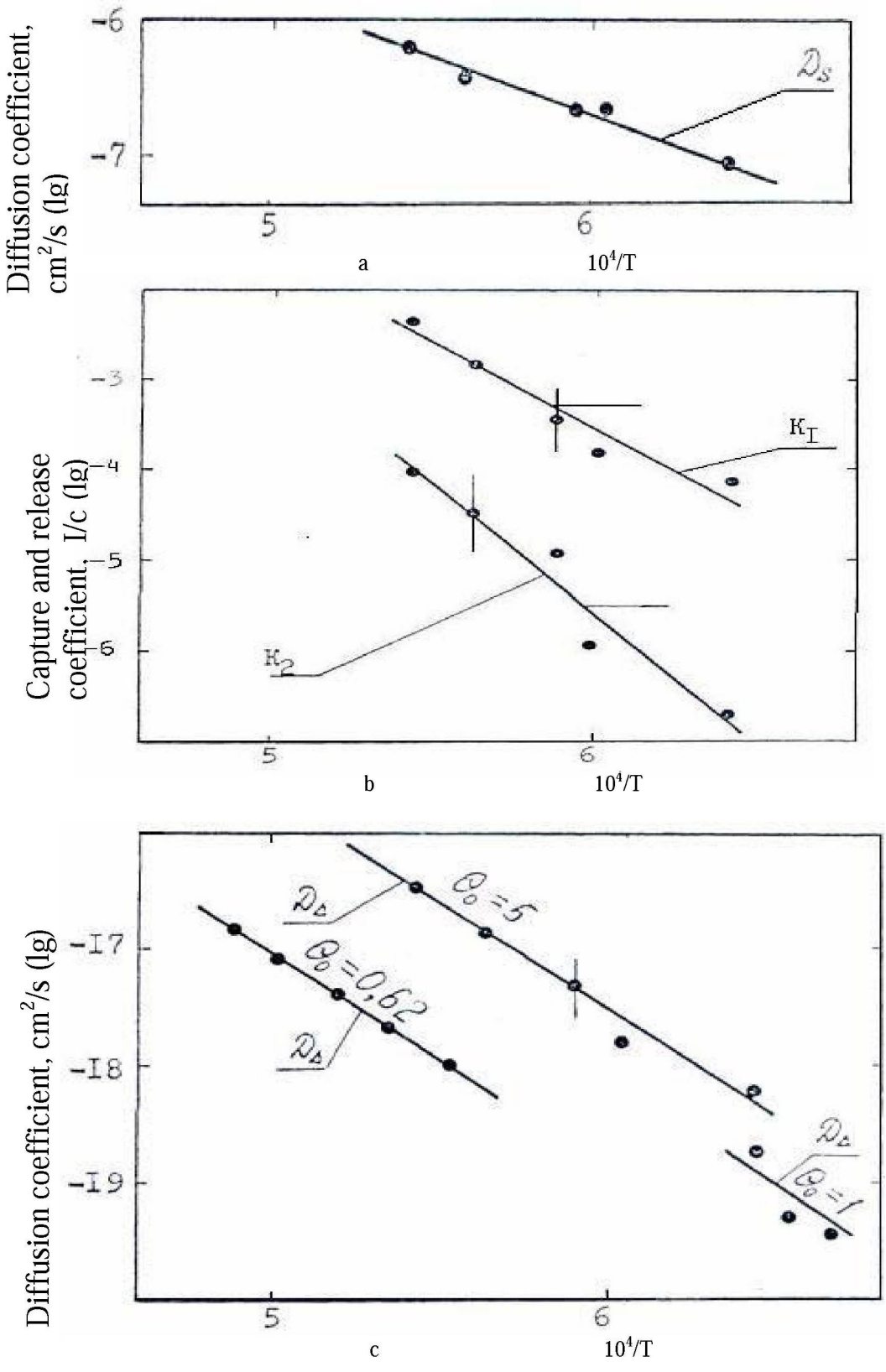
Diffusion coefficient, cm²/s (lg)
-6
-7
5
6
D_S
a
$10^4/T$
Capture and release coefficient, I/c (lg)
-3
-4
-5
-6
K_I
K_2
5
6
b
$10^4/T$
Diffusion coefficient, cm²/s (lg)
-I7
-I8
-I9
D_Δ
$Q_0=5$
$Q_0=0,62$
D_Δ
D_Δ
$Q_0=1$
5
6
c
$10^4/T$

Fig. 1.a, b, c- Arrhenius curves: D_s – surface diffusion coefficient, D_Δ - volume diffusion coefficient, K_1 and K_2 – capture and release coefficients, θ_0 – initial rate of coating with niobium.

4.REFERENCES

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TRANSLATION ITEM

1. Mishin Yu.M., Razumovsky I.M. – FMM, 1982, v.54, i.5, p.923.
2. Bokshtain S.Z., Gubareva M.A., Kishkin S.T., Moroz L.M. Peculiarities of diffusion in surface layers of metals – in the book Surface diffusion and diffluence. Moscow, "Nauka", 1969, pp. 264-270.