THE MODELING OF OXIDE GROWTH PROCESS ON THE SURFACE DURING THE DIFFUSION IN THIN FILMS UNDER CONDITIONS OF “OXYGEN PUMP” ACTION

A.I. OLESHKEVYCH,[1] A.M. GUSAK,[2] S.I. SIDORENKO,[1] S.M. VOLOSHKO[1]

[1]**National Technical University of Ukraine “Kyiv. Politekh. Inst.”**
(37, Prosp. Peremogy, Kyiv 03056, Ukraine)

[2]**B. Khmel’nyts’kyi Cherkasy National University**
(81, T.G. Shevchenko Blvd., Cherkasy 18031, Ukraine)

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We propose models which allow one to predict the growth kinetics for an oxide on the surface of thin films. It is assumed that, in a two-layer system, a material of the “lower” layer diffuses on the boundaries of grains of a material of the “upper” layer, and the reaction of its oxidation on the external surface creates an additional motive force of the diffusion. The amount of a diffusate spent on the formation of an oxide takes no participation further in the process of mass transfer. Therefore, the concentration gradient does not decrease. Under conditions of an additional influence of the “oxygen pump” on the surface of thin films, the motive force of the process caused by the concentration gradient continues to act for a sufficiently long time. We consider the process of growth of copper oxide on the nickel surface layer in the two-layer system Cu/Ni with regard for different mechanisms of diffusion of copper such as the volume diffusion through the oxide, the surface diffusion along the metal–oxide interface and the triple joints of the boundaries of grains, and the combined mechanism including the surface and volume diffusions. It is established that the mechanism of diffusion affects significantly the shape and size of the oxide layer and its effective thickness. We analyze the influence of parameters of the mass transfer on the effective index of growth of the oxide.

1. Introduction

The experimental data for a number of multilayer systems obtained by the condensation in vacuum such as Cu–Me (Me–Ni, Mn, Sn, Cr, Co), Cu–Mn–Sn, Cu–Cr–Al, Cu–Ni–Au, Cr–Cu–Ni, Cr–Cu–Ni–Au, Al – Me (Me – Ti, Ni, V, Cr, Ta, Mo, Co), $YBa_2Cu_3O_{7-x}$ – Me (Me – Ni, V, Ti, Mo, Nb, Al), Me–Si (Me – Mo, Ti, Cr, W, Ni, Pt), Pt–Ni–Si, Ni–Ti–Si, Ti–W–Si, Au–Co–Si, Al–Ti–W–Si, Au–Ni–Me–Si (Me – Mo, W, Ti), Au–Me–Mo–Si (Me – Co, Ni, Pt, Pd), and Au–Pd–Me–Ti–Si (Me – Mo, Cr) testify that the rate and the direction of migration of atoms turn out to depend on a physico-chemical state of the external surface in the case where the thicknesses of layers can be comparable with a size of the diffusion zone [1–3]. The processes of oxide formation running on the external surface at high temperatures cause thermodynamically the processes of diffusion in bulk. In multilayer systems, the external surface plays the role of “oxygen pump” which pumps a material of the “lower” layer through the “upper” one by the grain-boundary mechanism without the penetration of atoms of a diffusate in the bulk of grains of the upper layer. The processes on the surface are an additional (to the concentration gradient) motive force of the mass transfer.

The motive force of the mass transfer of atoms of a material of the “lower” layer to the surface is the concentration gradient. If a diffusate appearing on the surface is taken away (by the mechanism of surface diffusion) in the direction from the “grain boundary – surface” joint or is oxidized, then the concentration gradient does not decrease, and the motive force of the process caused by the concentration gradient continues to act over a sufficiently long time interval. The thermodynamical analysis indicates that the Gibbs energy of the reaction of oxidation of copper, manganese, nickel, tin, chromium, and aluminum is negative, which can be also considered as a motive force of the process of redistribution of components in the specimen by means of the mass transfer, in which the system passes to the state with a less energy.

We indicate the following fact which confirms the general character of the role of the surface as an additional motive force of the mass transfer in thin-film systems: the surface acts as the “oxygen pump” in the case of the inversion of materials of the layers, i.e., if Me_1 and Me_2 are, respectively, the lower and upper layers of a two-layer structure and if Me_2 is the lower layer, whereas Me_1 is the upper one [4].

The motive force of such a kind is quite clearly manifested for the two-layer system “copper (100 nm) – nickel (100 nm)”. On the initial stages of the diffusion (at temperatures of the order of 0.3 T_{melt}, the formation of oxide

Cu_2O on the external surface creates the "oxygen pump": atoms of copper from the "lower" layer diffuse onto the boundaries of grains of the "upper" layer without the entry to the bulk of grains of Ni.

Earlier under the assumption that the oxide formation reaction in the Cu-Ni system plays the role of an "oxygen pump" which presents an additional motive force of diffusion, we proposed a mathematical description of the given process [5]. Its idea consisted in the introduction of the reaction of oxidation into the Fick's system of equations which describe the mass transfer of Cu atoms on the boundaries of grains and on the Ni layer surface. It was assumed that the atoms of copper which are consumed in the formation of the oxide take no participation further in the diffusion. Therefore, a certain part of Cu atoms diffusing on the nickel surface layer is taken off for the formation of the oxide. As a result, we obtained a distribution of the concentration of Cu in the Ni layer with thickness H with regard for the formed oxide. In this case, taking the oxidation reaction constant into account allowed us to vary the rate of formation of the oxide and to describe the process of accumulation of the diffusate in the near-surface layer. By using this quite simple model which fits well the experimental data on the whole, we succeeded to corroborate the idea of the stimulating effect of the oxide which is formed on the external surface on the grain-boundary diffusion in bulk. At the same time, the oxidation within the model was considered as a homogeneous (in the limits of the surface layer) reaction which was characterized by a certain fitting value of the reaction rate. In this case, it was implicitly assumed that the formed layer of the oxide does not influence the process of surface diffusion.

The further development of the model ideas requires an answer to the question about the mechanism of formation of the oxide layer on the surface of thin films. Therefore, the goal of the present work is the mathematical description and prediction of the kinetics of growth of copper oxide on the surface layer of Ni in the Cu/Ni system with regard for various mechanisms of diffusion of copper atoms: the volume diffusion through the oxide, the surface diffusion along the metal–oxide interface, *etc.*

2. Formation of Oxide due to the Volume Diffusion of Cu

Let us consider a bicrystal with the boundaries of grains with width δ and with length l (Fig. 1). The atoms of copper from the lower layer diffuse along boundaries through the layer of Ni and form the surface oxide Cu_2O. In the present model, we consider the formation of the oxide only by the mechanism of the volume diffusion of Cu through Cu_2O (case of the cylindrical symmetry). We assume that Cu atoms diffuse through the oxide more rapidly than oxygen. In other words, the diffusion of the metal outside and the growth of the oxide on the surface occur more intensively than the oxidation of boundaries of microcrystallites. In this case, we take the condition of quasistationarity for fluxes along the boundaries of grains and through the oxide volume. This allows us, in particular, to avoid the necessity to solve the equation of Fick's second law for the grain-boundary diffusion. Instead of this, we determine the flux along the boundaries of grains in terms of the difference of chemical potentials on "ends" (the joints of the boundary with copper and with the oxide) and the Onsager grain-boundary coefficient [6].

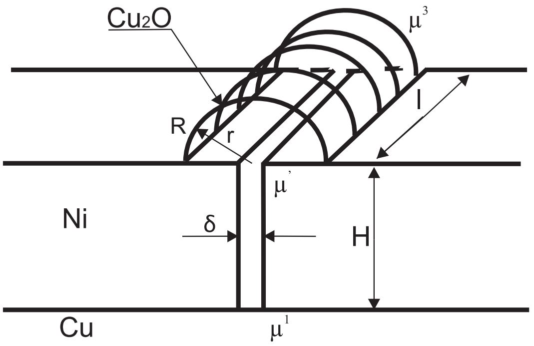

Fig. 1. Formation of Cu oxide on the Ni film surface under conditions of the volume mechanism of diffusion (the oxide has form of a half-cylinder)

In the present model, all copper atoms which have passed along the grain boundary migrate further to the external surface through a half-cylindrical oxide layer (whose axis passes along the joint of the boundaries of grains with the surface and whose radius $r \in [r_0, R]$). Therefore, we can use the condition of "sewing" in the form of the conservation law for the total flux of a diffusing substance:

$$n^{gb} L^{gb} \frac{\mu_1 - \mu'}{H} \delta l = n^{\mathrm{Cu_2O}} j_{\mathrm{Cu}}(R) \pi R l. \tag{1}$$

Here, n^{gb} and $n^{\mathrm{Cu_2O}}$ is the number of atoms per unit volume on the boundaries of grains and in the bulk of Cu_2O, respectively; L^{gb} – the Onsager coefficient for the grain-boundary diffusion:

$$L^{gb} = \frac{c^{gb} D_{gb}}{kT}, \tag{2}$$

c^{gb} – the grain-boundary concentration of copper; D_{gb} – the coefficient of diffusion of copper along the boundaries of grains; μ_1 – the chemical potential of pure copper; μ' – the chemical potential of copper in Ni on the boundary with Cu_2O; H – the Ni layer thickness; $j_{Cu}(R)$ – the density of the flux of Cu atoms through the external boundary of the half-cylindrical layer of oxide Cu_2O.

We determine the flux density from the condition of quasistationarity (it is almost obvious for the oxide: since the oxide is practically stoichiometric, the concentration in it must be invariable in time):

$$\frac{\partial c_{\mathrm{Cu}}}{\partial t} = -\mathrm{div} j_{\mathrm{Cu}}(r) = -\frac{1}{r}\frac{\partial}{\partial r}\left(r j_{\mathrm{Cu}}(r)\right) \approx 0. \tag{3}$$

Hence (see also [7]),

$$r j_{\mathrm{Cu}}(r) = -r L^{\mathrm{Cu_2O}} \frac{\partial \mu}{\partial r} = \mathrm{const}. \tag{4}$$

Condition (3) means simply that the total flux through any cylindrical cross-section is the same. The standard solution of the differential equation (4) with the boundary conditions $\mu = \mu'$ at $r = \delta/2$ and $\mu = \mu_3$ at $r = R$ takes the form

$$\mu(r) = \mu' + (\mu_3 - \mu')\frac{\ln(2r/\delta)}{\ln(2R/\delta)}. \tag{5}$$

This yields

$$r j_{\mathrm{Cu}}(r) = R j_{\mathrm{Cu}}(R) = L^{\mathrm{Cu_2O}} \frac{\mu' - \mu_3}{\ln(2R/\delta)}, \tag{6}$$

where μ_3 – the chemical potential of copper in Cu_2O on the boundary with the atmosphere at a steady pressure, $L^{\mathrm{Cu_2O}}$ – the Onsager coefficient of diffusion of copper in the bulk of Cu_2O,

$$L^{\mathrm{Cu_2O}} = \frac{2}{3}\frac{D_{\mathrm{bulk}}}{kT}, \tag{7}$$

D_{bulk} – the coefficient of volume diffusion of copper, and $2/3$ is the molar concentration of copper in the oxide.

Substituting (6) in the conservation law (1), we obtain

$$n^{gb} L^{gb} \frac{\mu_1 - \mu'}{H} l\delta = n^{\mathrm{Cu_2O}} L^{\mathrm{Cu_2O}} \frac{(\mu' - \mu_3)}{R\ln(2R/\delta)} \pi R l. \tag{8}$$

This relation yields the "intermediate" chemical potential μ' (taking $n^{gb} \approx n^{\mathrm{Cu_2O}}$):

$$\mu' = \frac{L^{gb}\frac{\mu_1}{H}\ln(2R/\delta) + L^{\mathrm{Cu_2O}}\mu_3(\pi/\delta)}{(\pi/\delta)\cdot L^{\mathrm{Cu_2O}} + \frac{L^{gb}\ln(2R/\delta)}{H}}. \tag{9}$$

We now write the equation of balance of fluxes on the movable boundary:

$$\left(\frac{2}{3}n^{\mathrm{Cu_2O}} - 0\right)\frac{dR}{dt} = n^{\mathrm{Cu_2O}} \frac{L^{\mathrm{Cu_2O}}(\mu' - \mu_3)}{R\ln 2R/\delta} - 0\ . \tag{10}$$

The coefficient $\frac{2}{3}$ stands for the number of Cu atoms in unit volume of the compound Cu_2O, i.e., the number of Cu atoms is $\frac{2}{3}$ of the total number of atoms.

This yields

$$\frac{dR}{dt} = \frac{3}{2}\frac{L^{\mathrm{Cu_2O}}(\mu' - \mu_3)}{R\ln(2R/\delta)}\ . \tag{11}$$

Substituting μ' from (9) and solving the differential equation, we get the following solution presenting the dependence of the radius on time:

$$\frac{H}{L^{gb}(\mu_1 - \mu_3)}\left(R^2 - \left(\frac{\delta}{2}\right)^2\right) + \frac{2}{3}\frac{1}{L^{\mathrm{Cu_2O}}(\mu_1 - \mu_3)(\pi/\delta)} \times$$

$$\times \left[R^2\left(\frac{\ln(2R/\delta)}{2} - \frac{1}{4}\right) - \left(\frac{\delta}{2}\right)^2\frac{1}{4}\right] = t. \tag{12}$$

The difference $(\mu_1 - \mu_3)$ is proportional to the thermodynamic moving force (per 1 atom) in the formation of Cu_2O from copper and oxygen.

In the Visual Basic 6 software, we constructed a model which allows one to analyze the time dependence of the distance from grain boundary, on which Cu oxide is formed. The results of calculations are presented in Fig. 2. We used the following data: $H = 100$ nm, $\mu_1 - \mu_3 = 2.1 \times 10^{-19}$ J/atom, $\delta = 5$ Å, $T = 873$ K, $t_{\max} = 1000$ s, $r_0 = 1$ nm.

If $D_{gb} = 10^{-14} \div 10^{-12}$ cm^2/s, a $D_{\mathrm{bulk}} = 10^{-17} \div 10^{-15}$ cm^2/s, then the oxide size varies insignificantly for 1000 s as compared with the initial value of r_0. Further, as the coefficients of diffusion increase by one order of magnitude, the maximum radius increases approximately trice. On the whole, the increase in the coefficients of diffusion by 4 orders of magnitude leads to the increase in the radius by 10 times. In other words, the growth of the oxide on the surface of the system by the volume mechanism can occur efficiently at the rather high coefficients of the volume and grain-boundary diffusions ($10^{-10} \div 10^{-13}$ cm^2/s).

By using the logarithmic dependence of the radius on time (Fig. 2,*b*), we determined the effective oxide growth index $K = d\ln R/d\ln t$ at the end of the time interval of measurements which is equal to 0.01, 0.09, 0.29, 0.4, and 0.43 for cases 1, 2, 3, 4, and 5, respectively. It is worth noting that the value of K varies in the process of annealing and tends to 0.5.

Let us introduce the effective thickness of the equivalent oxide interlayer

$$H_{\mathrm{eff}} L_{\mathrm{Ni}} l = \frac{1}{2}\pi R^2 l.$$

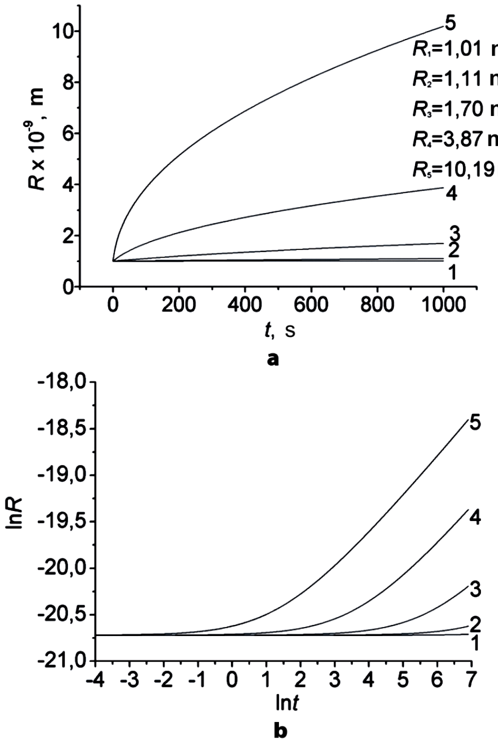

Fig. 2. Growth kinetics for the oxide (a) and the logarithmic dependence of the radius on time (b) at the following parameters: *1* – $D_{gb} = 10^{-14}$ cm^2/s, $D_{\rm bulk} = 10^{-17}$ cm^2/s; *2* – $D_{gb} = 10^{-13}$ cm^2/s, $D_{\rm bulk} = 10^{-16}$ cm^2/s; *3* – $D_{gb} = 10^{-12}$ cm^2/s, $D_{\rm bulk} = 10^{-15}$ cm^2/s; *4* – $D_{gb} = 10^{-11}$ cm^2/s, $D_{\rm bulk} = 10^{-14}$ cm^2/s; *5* – $D_{gb} = 10^{-10}$ cm^2/s, $D_{\rm bulk} = 10^{-13}$ cm^2/s

Then

$$H_{\rm eff} = \frac{\pi R^2}{2L_{\rm Ni}},$$

where $L_{\rm Ni}$ is the Ni grain size ($L_{\rm Ni} = 20$ nm).

Values of $H_{\rm eff}$ obtained in cases 1, 2, 3, 4, and 5, are 0.08, 0.1, 0.22, 1.2, and 8.15 nm. The growth index K for the effective thickness is obviously twice greater than that for the cylinder radius.

3. Formation of Oxide due to the Surface Diffusion along the Metal–Oxide Interface

In this case, we consider the appearance of Cu atoms on the Ni layer surface on the boundaries of grains with length l and with width δ which form a two-dimensional plate of oxide Cu$_2$O with height h_0 (Fig. 3). We assume that the motion of Cu atoms occurs along the Ni - Cu$_2$O interface in the near-surface layer $\delta_{\rm int}$ in the direction of the x axis. Thus, the oxide "is completed" from both sides of the plate due to the surface diffusion of Cu (the oxide size in this direction ie equal to X).

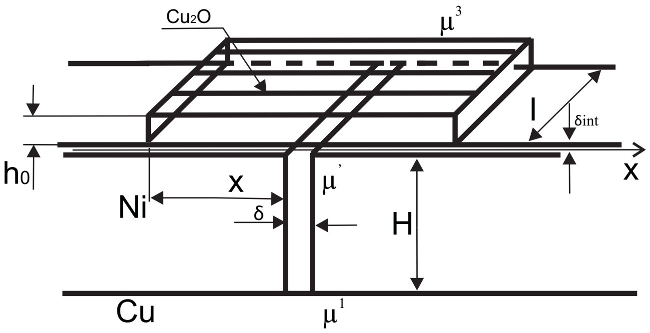

Fig. 3. Formation of the oxide on the Ni film surface due to the surface diffusion of copper

We now write the equation of balance of two fluxes

$$n^{gb}L^{gb}\frac{\mu_1-\mu'}{H}\delta l = 2n^{\rm int}L^{\rm int}\frac{\mu'-\mu_3}{X}\delta_{\rm int} l, \qquad (13)$$

where $L^{\rm int}$ – the Onsager coefficient of diffusion along the interface:

$$L^{\rm int} = \frac{c^{\rm int}D_{\rm int}}{kT},$$

$c^{\rm int}$ – the concentration of copper on the interface; $D_{\rm int}$ – the coefficient of diffusion of copper along the interface, $n^{\rm int}$ – the number of atoms on the interface, $n^{\rm int} \sim n^{gb}$.

We will determine the oxide growth rate from the equation of balance (the flux which comes to the external edge is spent for the completion of the oxide layer by dX)

$$n^{\rm int}L^{\rm int}\frac{\mu'-\mu_3}{X}\delta_{\rm int} l dt = \frac{2}{3}n^{\rm Cu_2O}dXh_0 l, \qquad (14)$$

where μ_3 is the chemical potential of copper in Cu$_2$O on the boundary with the atmosphere at a steady pressure.

The quantity h_0 is the asymptotic thickness of islands at the lateral growth and is determined in the general case by the kinetic parameters, rather than the thermodynamic ones. The formation of islands by the lateral growth was explained by P. Gas in France and C. Lavoie in the USA (islands increased to a thickness of about 10 nm and then grew laterally). Models of the formation of such islands were developed in [8–10]. The thickness is defined as a certain ratio of the coefficient of diffusion and the reaction rate on the boundary.

Thus,

$$\frac{dX}{dt} = \frac{3}{2}L^{\rm int}\frac{(\mu'-\mu_3)\, n^{\rm int}\delta_{\rm int}}{Xn^{\rm Cu_2O}h_0}. \qquad (15)$$

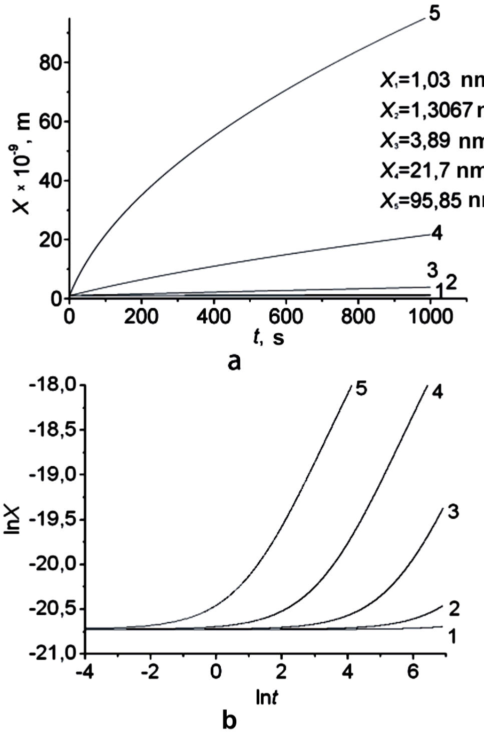

Fig. 4. Dependence of the distance, to which the oxide is spread, on time (*a*) and the corresponding logarithmic dependence (*b*): *1* – $D_{gb}=10^{-14}$ cm^2/s, $D_{\rm int}=10^{-15}$ cm^2/s; *2* – $D_{gb}=10^{-13}$ cm^2/s, $D_{\rm int}=10^{-14}$ cm^2/s; *3* – $D_{gb}=10^{-12}$ cm^2/s, $D_{\rm int}=10^{-13}$ cm^2/s; *4* – $D_{gb}=10^{-11}$ cm^2/s, $D_{\rm int}=10^{-12}$ cm^2/s; *5* – $D_{gb}=10^{-10}$ cm^2/s, $D_{\rm int}=10^{-11}$ cm^2/s

From Eq. (13), we obtain

$$\mu' = \frac{L^{gb}\mu_1 X\delta + 2L^{\rm int}\delta_{\rm int}\mu_3 H}{2L^{\rm int}\delta_{\rm int}H + L^{gb}X\delta}. \tag{16}$$

Substituting relation (16) in (15) and solving the differential equation for the coordinate x as a function of time, we get the solution

$$t = \frac{3\delta_{\rm int}^2\delta {L^{\rm int}}^2 L^{gb} H}{h_0\left(\mu_1-\mu_3\right)}\left(X-\left(\frac{\delta}{2}\right)\right)+$$

$$+\frac{3n\delta_{\rm int}\delta^2 L^{\rm int}{L^{gb}}^2 H}{4h_0\left(\mu_1-\mu_3\right)}\left(X^2-\left(\frac{\delta}{2}\right)^2\right). \tag{17}$$

Results of the modeling are presented in Fig. 4. Values of the coefficients of diffusion were chosen in the same limits as those in model 1. But, instead of the coefficient of volume diffusion, we used, in this case, the coefficient of diffusion of Cu atoms along the interface, $D_{\rm int}$.

Input data are as follows: $H = 100$ nm, $\mu_1-\mu_3 = 2.1\times10^{-19}$ J/atom, $\delta=\delta_{\rm int}=5$ Å, $T = 873$ K, $t_{\max} = 1000$ s, and $h_0 = 2$ nm.

We may conclude that the character of the function $X = f(t)$ is significantly changed as compared with that in model 1. In this case, the oxide on the surface grows much more rapidly at the coefficients of diffusion $D_{gb} = 10^{-11}\div10^{-10}$ cm^2/s and $D_{\rm int} = 10^{-12}\div10^{-11}$ cm^2/s.

In the interval $D_{\rm int} = 10^{-15}\div10^{-13}$ cm^2/s, the oxide size varies slightly. At $D_{\rm int} = 10^{-12}\div10^{-11}$ cm^2/s, the rate of growth of the oxide increases step-wise, and X becomes 96 nm, which is larger by one order than the maximum radius in model 1. This is related to the larger rate of diffusion along the interface as compared with the volume mechanism which was considered dominant in model 1.

In cases 1, 2, 3, 4, and 5, the effective growth indices for the oxide are 0.03, 0.25, 0.69, 0.72, and 0.58, respectively, and exceed the values obtained within model 1. We note that the growth index increases firstly and then decreases.

In the given model, the effective thickness of the oxide layer is determined by the formula

$$H_{\rm eff} = 2X\frac{h_0}{L_{\rm Ni}}.$$

The values of $H_{\rm eff}$ at $L_{\rm Ni} = 20$ nm obtained in the cases 1, 2, 3, 4, and 5 are 0.2, 0.26, 0.78, 4.34, and 19.2 nm. The comparison indicates that these values are larger that those obtained in model 1.

We emphasize that the above-mentioned model stops to be adequate when X attains a half of the Ni grain size, because this means the fusion of oxide strips in the continuous oxide layer. After that, the oxidation should run by the different mechanism and, possibly, significantly slower. Therefore, the chosen values of $L_{\rm Ni}$ in cases 4 and 5 is not quite correct for calculations of $H_{\rm eff}$.

4. Formation of Oxide due to the Diffusion of Cu along Triple Joints of the Boundaries of Grains

In this case, we consider the diffusion of Cu atoms mainly along the triple joints of of the boundaries of grains. We assume that a joint has form of a pipe with width δ (Fig. 5). Oxide Cu$_2$O grows in the form of a hemisphere with radius r ($r\in[r_0,R]$). Hence, we can use the spherical symmetry.

The conservation law for a flux looks as

$$n^{\text{joint}} L^{\text{joint}} \frac{\mu_1 - \mu'}{H} \pi \left(\frac{\delta}{2}\right)^2 = n^{\text{Cu}_2\text{O}} j_{\text{Cu}}(R)\, 2\pi R^2, \qquad (18)$$

where n^{joint} – the number of atoms in a triple joint of the boundaries of grains; L^{joint} – the Onsager coefficient of diffusion over the triple joints of the boundaries of grains:

$$L^{\text{joint}} = \frac{c^{\text{joint}} D_{\text{joint}}}{kT},$$

c^{joint} – the concentration of copper in a triple joint of the boundaries of grains; D_{joint} – the coefficient of diffusion of copper over the triple joints of the boundaries of grains.

The condition of quasistationarity in a spherical specimen can be written as follows [7]:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 j_{\text{Cu}}(r)\right) \approx 0. \qquad (19)$$

The standard solution of the differential equation (19) with the boundary conditions $\mu = \mu'$ at $r^2 = \delta/2$ and $\mu = \mu_3$ at $r^2 = R^2$ reads

$$\mu(r) = \mu' + (\mu_3 - \mu') \left(\frac{1}{\delta/2} - \frac{1}{R}\right). \qquad (20)$$

This yields

$$r^2 j_{\text{Cu}}(r) = R^2 j_{\text{Cu}}(R) = n^{\text{Cu}_2\text{O}} L^{\text{Cu}_2\text{O}} \frac{\mu' - \mu_3}{\frac{1}{\delta/2} - \frac{1}{R}}. \qquad (21)$$

Substituting the formula for a flux in relation (18), we obtain

$$n^{\text{joint}} L^{\text{joint}} \frac{\mu_1 - \mu'}{H} \left(\frac{\delta}{2}\right)^2 = 2 n^{\text{Cu}_2\text{O}} L^{\text{Cu}_2\text{O}} \frac{(\mu' - \mu_3)}{\frac{1}{\delta/2} - \frac{1}{R}}. \qquad (22)$$

From this relation, we find μ' ($n^{\text{joint}} \approx n^{\text{Cu}_2\text{O}}$):

$$\mu' = \frac{\left(\delta^2 L^{\text{joint}} \mu_1\right)\left(\frac{2}{\delta} - \frac{1}{R}\right) + 8 L^{\text{Cu}_2\text{O}} \mu_3 H}{8 n^{\text{Cu}_2\text{O}} L^{\text{Cu}_2\text{O}} H + L^{\text{joint}} \delta^2 \left(\frac{2}{\delta} - \frac{1}{R}\right)}. \qquad (23)$$

We now write the equation of balance of fluxes determining the oxide growth rate with regard for the flux of Cu atoms given by formula (18):

$$\left(n^{\text{Cu}_2\text{O}} \frac{2}{3} - 0\right) \frac{dR}{dt} = j_{\text{Cu}}(R) - 0, \qquad (24)$$

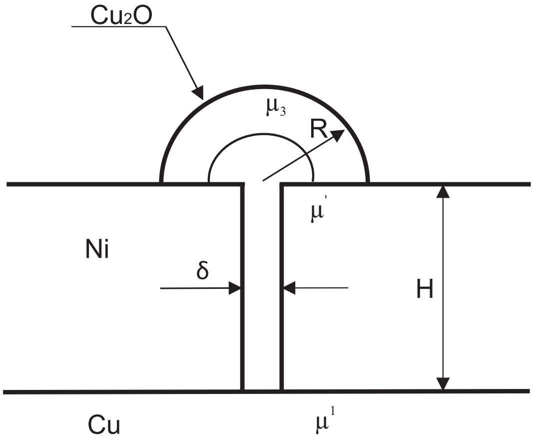

Fig. 5. Formation of the oxide on the surface near a joint of the boundaries of grains

$$\frac{dR}{dt} = \frac{3}{2} L^{\text{Cu}_2\text{O}} \frac{(\mu' - \mu_3)}{\frac{1}{\delta/2} - \frac{1}{R}} \frac{1}{R^2}. \qquad (25)$$

Substituting μ' in Eq. (25), we get the required solution

$$t = \frac{16 L^{\text{Cu}_2\text{O}} H}{9 \delta^2 L^{\text{joint}} (\mu_1 - \mu_3)} \left(R^3 - \frac{\delta^3}{8}\right) +$$

$$+ 2\delta L^{\text{joint}} \left(R^3 - \frac{\delta^3}{8}\right) - \delta^2 L^{\text{joint}} \left(R^2 - \frac{\delta^2}{4}\right). \qquad (26)$$

In cases 1–5, the effective indices of growth of the oxide are 0.02, 0.1, 0.24, 0.3, and 0.32, respectively (see Fig. 6,*b*).

The effective thickness of the oxide layer is given by the formula

$$H_{\text{eff}} = \frac{4\pi R^3}{6 {L_{\text{Ni}}}^2}.$$

In cases 1–5, the values of H_{eff} at $L_{\text{Ni}} = 20$ nm are, respectively, 0.005, 0.008, 0.03, 0.18, and 1.5 nm and are less approximately by one order than those obtained within the previous models.

Results of the modeling performed with the initial data analogous to those in model 1 (with the exception of the coefficient of diffusion over joints of the boundaries of grains which was taken by one order greater than the coefficient of diffusion on the boundaries of grains; moreover, a joint width was set 10 Å) are shown in Fig. 6,*a*. The value of R at $t_{\max} = 1000$ s is significantly less than that in model 2 and is approximately equal to the value taken in model 1, except for the case where $D_{\text{joint}} = 10^{-9}$

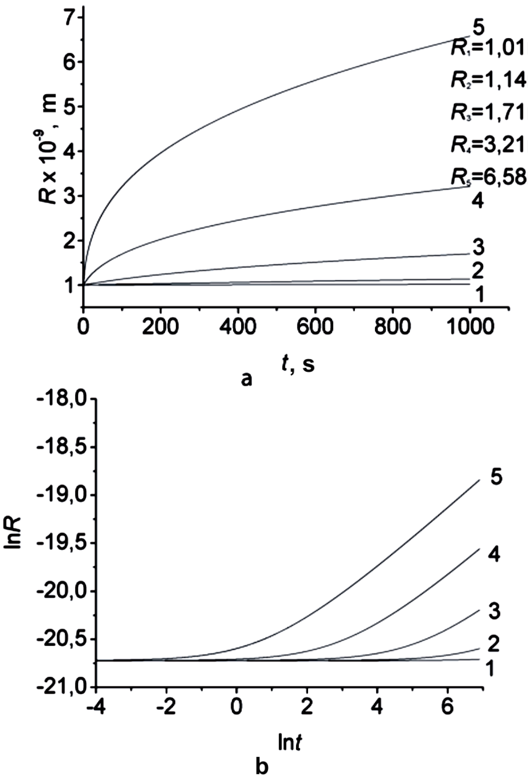

Fig. 6. Dependence of the radius of the oxide on time (a) and the corresponding logarithmic dependence (b): *1* – $D_{\text{joint}} = 10{-}13$ cm^2/s, $D_{\text{bulk}} = 10^{-17}$ cm^2/s; *2* – $D_{\text{joint}} = 10^{-12}$ cm^2/s, $D_{\text{bulk}} = 10^{-16}$ cm^2/s; *3* – $D_{\text{joint}} = 10^{-11}$ cm^2/s, $D_{\text{bulk}} = 10^{-15}$ cm^2/s; *4* – $D_{\text{joint}} = 10^{-10}$ cm^2/s, $D_{\text{bulk}} = 10^{-14}$ cm^2/s; *5* – $D_{\text{joint}} = 10^{-9}$ cm^2/s, $D_{\text{bulk}} = 10^{-13}$ cm^2/s

cm^2/s, $D_{\text{bulk}} = 10^{-13}$ cm^2/s. In this case, the oxide size calculated within model 1 is larger approximately by a factor of 1.5. Thus, under conditions of the accepted geometry of a triple joint of the boundaries of grains, the contribution of this mechanism to the oxide-forming is insignificant.

5. Formation of Oxide by the Combined Mechanism: Surface and Volume Diffusions of Cu

We now consider the growth of the oxide on the surface in the case where it grows along two directions, by completing on edges due to the diffusion along the metal–oxide interface and normally to the interface due to the volume diffusion of Cu through the oxide (Fig. 7). In this sense, the model is close to the Fisher model of grain-boundary diffusion [11] with the sucking off of a diffusate into the grain volume but takes additionally the movement of external interfaces into account.

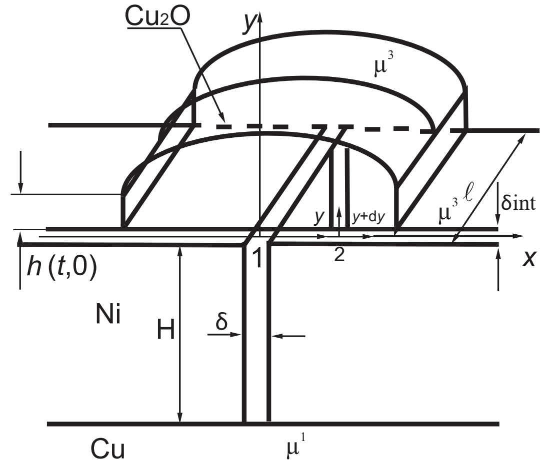

Fig. 7. Formation of the oxide on the surface due to the surface and volume diffusions of copper

Let the oxide growing on the surface have form shown in Fig. 7. We consider that the diffusion of Cu atoms occurs both along the interface, i.e. in the direction of the x axis (the oxide size in this direction is X) and into the volume of the formed oxide Cu$_2$O, i.e. in the direction of the y axis.

1. The substance conservation law for point 1 is as follows:

$$L^{gb}\frac{\mu_1-\mu'}{H}l\delta = -L^{\text{int}}\left.\frac{\partial\mu}{\partial x}\right|_{x\to 0}2\delta_{\text{int}}l. \tag{27}$$

In formula (27), we neglect the flux related to the diffusion of Cu atoms through the oxide layer, because this flux is insignificant under the condition $X \ll h\frac{L^{\text{int}}}{L^{\text{Cu}_2\text{O}}}$.

2. The substance conservation law for interval 2 with width dx in the approximation of quasistationarity is as follows:

$$\delta_{\text{int}}l\left[-L^{\text{int}}\left.\frac{\partial\mu}{\partial x}\right|_{x} - \left(-L^{\text{int}}\left.\frac{\partial\mu}{\partial x}\right|_{x+dx}\right)\right]n^{\text{int}} =$$

$$= n^{\text{Cu}_2\text{O}}L^{\text{Cu}_2\text{O}}\frac{\mu(x)-\mu_3}{h(t,x)}dxl; \tag{28}$$

$$n^{\text{int}}L^{\text{int}}\frac{\partial^2(\mu(x)-\mu_3)}{\partial x^2}dx =$$

$$= n^{\text{Cu}_2\text{O}}\frac{L^{\text{Cu}_2\text{O}}}{\delta_{\text{int}}}\frac{\mu(x)-\mu_3}{h(t,x)}dx; \tag{29}$$

Heights of the oxide layer h (in nm) for each of 5 diffusion channels and values of X at $t_{\max} = 1000$ s and the coefficients of diffusion in three cases (K_y and K_x are, respectively, the effective indices of growth of the oxide along the y and x) axes

Channel number	Case 1 $X = 6.7$ nm $K_x = 0.58$		Case 2 $X = 24.5$ nm $K_x = 0.51$		Case 3 $X = 69.8$ nm $K_x = 0.41$	
$n = 1$	$h = 1.37$	$K_y = 0.31$	$h = 4.35$	$K_y = 0.59$	$h = 16.8$	$K_y = 0.57$
$n = 2$	$h = 1.28$	$K_y = 0.26$	$h = 3.52$	$K_y = 0.54$	$h = 12.2$	$K_y = 0.52$
$n = 3$	$h = 1.19$	$K_y = 0.19$	$h = 2.76$	$K_y = 0.47$	$h = 8.3$	$K_y = 0.46$
$n = 4$	$h = 1.09$	$K_y = 0.11$	$h = 1.99$	$K_y = 0.38$	$h = 5.04$	$K_y = 0.39$
H_{eff}	0.99 nm		8.35 nm		71.5 nm	

$$\frac{\partial^2\left(\mu\left(x\right)-\mu_3\right)}{\partial x^2}=\frac{L^{\mathrm{Cu_2O}}n^{\mathrm{Cu_2O}}}{L^{\mathrm{int}}\delta_{\mathrm{int}}n^{\mathrm{int}}}\frac{\mu\left(x\right)-\mu_3}{h\left(t,x\right)},$$

$$0<x<X\left(t\right), \qquad (30)$$

where $\mu\left(x\right)$ – the chemical potential of copper in Ni on the boundary with $\mathrm{Cu_2O}$ at a point on the x axis; $h(t, x)$ – the height of the oxide layer at a point x at the time moment t.

We now write the equation for the oxide growth rate in the case where Cu diffuses along the interface:

$$-n^{\mathrm{int}}L^{\mathrm{int}}\left.\frac{\partial\mu}{\partial x}\right|_{x(t)}l\delta_{\mathrm{int}}dt=\frac{2}{3}n^{\mathrm{Cu_2O}}dxh(t,0)l, \qquad (31)$$

$$\frac{dx}{dt}=\frac{3\delta_{\mathrm{int}}n^{\mathrm{int}}}{2h(t,0)n^{\mathrm{Cu_2O}}}\left(-L^{\mathrm{int}}\left.\frac{\partial\mu}{\partial x}\right|_{x(t)}\right). \qquad (32)$$

The coefficient $\frac{2}{3}$ – the number of Cu atoms in unit volume of the substance $\mathrm{Cu_2O}$.

The equation for the oxide growth rate for the volume diffusion of Cu along the y axis reads

$$n^{\mathrm{Cu_2O}}L^{\mathrm{Cu_2O}}\frac{\mu\left(x\right)-\mu_3}{h\left(t,x\right)}dxldt=\frac{2}{3}n^{\mathrm{Cu_2O}}dh\left(t,x\right)dxl. \qquad (33)$$

We obtain

$$\frac{dh(t,x)}{dt}=\frac{3}{2}\frac{L^{\mathrm{Cu_2O}}(\mu\left(x\right)-\mu_3)}{h\left(t,x\right)}. \qquad (34)$$

The system of equations (27), (30), (32), (34) was solved by the method of shooting. The solution gives the dependences $h(t,x)$ and $x(t)$. The modeling was executed for the following data: $H = 100$ nm, $\mu_1-\mu_3 = 2.1\times10^{-19}$ J/atom, $\delta=\delta_{\mathrm{int}} = 5$ Å, $n = 5$ (n – the number of diffusion channels, by which the atoms of copper move into the bulk along the y axis, $n = 1$ – the central channel at the coordinate origin, $n = 5$ – the last channel at the point X), $T = 873$ K, $t_{\max} = 1000$ s, $h_0 = 1$ nm (h_0 – the height of the oxide layer at the initial time moment).

We analyzed 3 cases, for which the coefficients of diffusion were taken as follows:

1. $D_{gb} = 10^{-12}$ cm^2/s, $D_{\mathrm{int}} = 10^{-13}$ cm^2/s, $D_{\mathrm{bulk}} = 10^{-15}$ cm^2/s;
2. $D_{gb} = 10^{-11}$ cm^2/s, $D_{\mathrm{int}} = 10^{-12}$ cm^2/s, $D_{\mathrm{bulk}} = 10^{-14}$ cm^2/s;
3. $D_{gb} = 10^{-10}$ cm^2/s, $D_{\mathrm{int}} = 10^{-11}$ cm^2/s, $D_{\mathrm{bulk}} = 10^{-13}$ cm^2/s.

Results of the modeling (see Table) allow us to draw the following conclusion. The oxide grows in such a way that its size along the x axis is larger than that along the y axis. In addition, the maximum along the y axis is observed for that channel which is central, i.e. it coincide with the exit to the grain boundary surface.

Comparing with models 1–3, we may assert that the oxide grows to a larger size in model 4, which is caused by the simultaneous action of two mechanisms of diffusion.

We determine the effective thickness of the oxide layer by the formula

$$H_{\mathrm{eff}}=\frac{2}{L_{\mathrm{Ni}}}(\frac{X}{n}+\sum_{i=1}^{n}h_i).$$

Let us compare the effective coefficient of growth of the oxide K_x along the x axis with the values obtained within the previous models. In the case where $D_{gb} = 10^{-10}$ cm^2/s, $D_{\mathrm{int}} = 10^{-11}$ cm^2/s, and $D_{\mathrm{bulk}} = 10^{-13}$ cm^2/s, it is equal to 0.57, which is approximately equal to the value in model 2 at $D_{gb} = 10^{-10}$ cm^2/s and $D_{\mathrm{int}} = 10^{-11}$ cm^2/s. That is, the contribution of the volume mechanism of diffusion is insignificant. For $D_{gb} = 10^{-11}$ cm^2/s, $D_{\mathrm{int}} = 10^{-12}$ cm^2/s, and $D_{\mathrm{bulk}} = 10^{-14}$ cm^2/s, we have $K_x = 0.5$, which is less than that in model 2 but is larger than that in model 1 at $D_{gb} = 10^{-11}$ cm^2/s and $D_{\mathrm{bulk}} = 10^{-14}$ cm^2/s. This testifies that the diffusion runs by the volume mechanism and along the metal–oxide interface. Finally, in the case where $D_{gb} = 10^{-12}$ cm^2/s, $D_{\mathrm{int}} = 10^{-13}$ cm^2/s, and $D_{\mathrm{bulk}} = 10^{-15}$ cm^2/s, $K_x = 0.41$, which is approximately equal to the value calculated within model 1 at $D_{gb} = 10^{-10} - 10^{-11}$ cm^2/s and $D_{\text{bulk}} = 10^{-13}$–$10^{-14}$ cm^2/s and is larger than the value obtained in model 3. Thus, the diffusion runs by the volume mechanism and by the grain-boundary one.

We now analyze values of the effective coefficients of growth of the oxide K_y for the coordinate y in three cases at $L_{\text{Ni}} = 20$ nm (see Table). In the first case, the oxide grows most intensively in the region of the first channel which coincides with the exit of a grain boundary on the surface. In the second and third cases, the growth rate increases in all five channels with the maximum value at 1 and 2 channels. In addition, we observe a decrease in K_x simultaneously with an increase in K_y. In other words, the diffusion becomes faster along the y axis, which testifies to the enhancement of the role of the volume diffusion.

6. Conclusions

The above-proposed models allow one to develop the theoretic ideas of the mechanism and the growth kinetics for an oxide on the surface of thin films. Since we considered four different models of "oxygen pump", the question arises about which of the models or which of their combinations is realized at various temperatures of the annealing. This will be obviously depend on the morphology of a film (the lateral size of a grain) and on the ratio of the coefficients of grain-boundary diffusion, volume diffusion, and diffusion along the metal–oxide interface. Judging from the above-obtained regularities of the oxide growth, we may expect the pump mode at low temperatures which is determined by the diffusion along triple joints of the boundaries of grains, as well as the diffusion in the oxide bulk at high temperatures.

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МОДЕЛЮВАННЯ ПРОЦЕСУ РОСТУ ОКСИДУ НА ПОВЕРХНІ ПРИ ДИФУЗІЇ В ТОНКИХ ПЛІВКАХ В УМОВАХ ДІЇ "КИСНЕВОГО НАСОСА"

А.І. Олешкевич, А.М. Гусак, С.І. Сидоренко, С.М. Волошко

Резюме

Запропоновано моделі, які дозволяють прогнозувати кінетику росту оксиду на поверхні тонких плівок. Вважають, що у двошаровій системі матеріал "нижнього" шару дифундує по границях зерен матеріалу "верхнього" шару і реакція його окислення на зовнішній поверхні створює додаткову рушійну силу дифузії. Кількість дифузанта, яка витрачається на утворення оксиду, не бере далі участі у процесі масоперенесення, тому градієнт концентрації не знижується. За умов додаткового впливу "кисневого насоса" на поверхні тонких плівок рушійна сила процесу, зумовлена градієнтом концентрації, продовжує діяти достатньо довго. Процес росту оксиду міді на поверхні шару нікелю в двошаровій системі Cu/Ni розглянуто з урахуванням різних механізмів дифузії міді – об'ємної крізь оксид, поверхневої вздовж міжфазної границі "метал–оксид", по потрійних стиках границь зерен, а також за комбінованим механізмом – поверхневої та об'ємної дифузії. Встановлено, що механізм дифузії суттєво впливає на форму та розмір оксидного шару, а також на його ефективну товщину. Проаналізовано вплив параметрів масоперенесення на ефективний показник росту оксиду.