ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 11, No. 3. 2005

“Black Box” Approach for Studying High-Flux, High-Fluence Implantation Effects

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Received 26 January 2005; accepted 09 June 2005

A published “Black box” model, designed to study high-flux, high-fluence and low-energy ion irradiation effects in materials, in this paper is developed for continuously expanding altered layer. It enables to introduce diffusion into equations. The altered layer is considered as a “black box” with input and output parameters, such as sputtering rate, flux and fluence of incident atoms and supply rate of matrix atoms arriving from the bulk due to continuous movement of the interface boundary of the altered layer. Analysis of new rate equations is carried out and the role of the sputtering, diffusion and flux effects on the kinetics of incident atoms accommodation is studied.

Keywords: hydrogen, implantation, diffusion, magnesium alanate.

INTRODUCTION

There is currently a great interest [1, 2] in understanding of mechanisms and driving forces which cause diffusion of implanted atoms towards the bulk or the surface. Ion implantation process is widely used for modification properties of materials and production of new alloys. However deeper understanding of physics is essential for production of new materials.

It is suggested, that the difference in chemical potentials between activated surface, bulk and grain boundaries is established under ion irradiation [3]. The excess of the surface chemical potential relative to the grain boundaries produces a net flow of surface atoms into the grain boundaries that generate compressive stress in grains. If stress exceeds the limit of plasticity, stress relaxation occurs through the emission of dislocations, formation of sub-grains within the original grain structure [4]. Processes of long-range diffusion and localized motion can coexist, and the diffusivities may be quite different for atoms in the crystalline grains and in the grain boundaries.

A simplified model to study high-flux, high-fluence, low-energy ion irradiation of materials, enabling to establish links between processing parameters, such as ion energy, ion flux and fluence of irradiation, and the concentration of accommodated incident atoms in the altered layer was presented by Milčius et al. [5] and Pranevičius et al. [6] In this paper the model is developed for continuously expanding altered layer, analysis of new rate equations and calculations are presented.

THEORETICAL MODEL

For the analysis, the target is divided into three layers: (1) emission layer; (2) altered layer; and (3) unperturbed bulk material. The balance equation for i atoms of the altered layer written by [5, 6] is:

$$\frac{d\hat{N}_i^{(A)}}{dt} = -w_i \hat{N}_i^{(E)} + N_i \frac{dx_2}{dt} + \beta_i I_i \,, \tag{1}$$

where $< N_i^{(A)} >$ is the mean concentration of i atoms in the altered layer, w_i is the sputtering frequency probability of i atoms. The first term of the Eq. (1) defines the removal rate of i atoms from the altered layer by sputtering and thermal desorption; the second term defines the increase rate of i atoms in the altered layer as the result of i atoms arrival from the bulk as the back boundary of the altered layer x_2 is continuously moving, where N_i is the concentration of i atoms in the bulk; and the third term defines the accommodation rate of incident ions in the altered layer, where β_i is the retention probability and I_i is the flux of incident i atoms. If the flux of incident ions is equal to I and $\hat{N}^{(E)}$ is the number of atoms in the emission layer, the frequency probability of sputtering of i atoms is equal to $w_i = (Y_i I)/\hat{N}^{(E)}$, where Y_i is the sputtering yield of i atoms.

The recession rate of surface is defined by the flux of atoms leaving the emission layer and is equal to:

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = \frac{1}{N^{(E)}} \sum_j w_j \hat{N}_j^{(E)} \,, \tag{2}$$

where $N^{(E)}$ is the concentration of atoms in the emission layer.

As implantation is maintained at the same conditions the implantation range is constant and the thickness of the altered layer is equal to about the mean penetration depth of ions. The boundary x_2 moves with the same velocity as x_1 if diffusion is neglected. In this study it was assumed, the boundaries are moving with different velocities $\mathrm{d}x_2 / \mathrm{d}t = \mathrm{d}x_1 / \mathrm{d}t + v(t)$, where $v(t)$ is the additional movement velocity of the altered layer’s interface due to diffusion. $v(t) = 0$, if the thickness of the altered layer is constant. After introduction dimensionless units as $n_j^{(E)} = N_j^{(E)}/N^{(E)} = c_j$, $w_i \varepsilon = w_i'$ and $< n_i^{(A)} >= \hat{N}_i^{(A)} /(N^{(A)} \cdot \delta(t))$, the Eq. (1) may be rewritten as:

$$\frac{d}{dt}(< n_i^{(A)} > N^{(A)} \cdot \delta(t)) = -w_i' N^{(E)} c_i + N n_i \sum_j w_j' c_j + \\ + N n_i v(t) + \beta_i I_i \;. \tag{3}$$

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After the summation (index i) the equation is obtained which defines the relationship between the concentration of atoms in the altered layer $N^{(A)}$; the emission layer $N^{(E)}$ and in the bulk N as:

$$\delta(t)\frac{\mathrm{d}N^{(A)}}{\mathrm{d}t} = (N - N^{(E)})\sum_i w_i' c_i + \sum_i \beta_i I_i + \left(N - N^{(A)}\right) v(t)\,. \tag{4}$$

The steady-state concentration of atoms in the altered layer is equal to:

$$N^{(A)}_{t\to\infty} = N + \frac{(N - N^{(E)})\sum w_i' c_i + \sum \beta_i I_i}{v}\,. \tag{5}$$

If $v = 0$ (case analyzed in Ref. [5, 6]), when boundaries are moving with the same velocity and the thickness of altered layer is a constant, the $N^{(A)}_{st.st.} \to \infty$. If $v \to \infty$, it means the x_2 boundary moves much faster then the x_1 and the altered layer is rapidly expanding. In that case $N^{(A)}_{st.st.}$ approaches the concentration of the bulk (N).

The steady-state concentration of atoms in the emission layer is equal to:

$$N^{(E)}_{t\to\infty} = N + \frac{\sum \beta_i I_i + \left(N - N^{(A)}\right) v(t\to\infty)}{\sum w_i' c_i}\,. \tag{6}$$

For $v \to 0$ and $v \to \infty$, the concentrations of atoms in the emission layer is equal to:

$$N^{(E)}_{t\to\infty} = N + \frac{\sum \beta_i I_i}{\sum w_i' c_i}\,. \tag{7}$$

Kinetics of incident atoms accommodation in the altered layer can be calculated using Eq. (3) which can be rewritten as:

$$\begin{aligned}\frac{\mathrm{d}<n_i^{(A)}>}{\mathrm{d}t} = \Big(&-w_i' N^{(E)} c_i + (Nn_i - <n_i^{(A)}> \times \\ &\times (N - N^{(E)}))\sum_j w_j c_j + d_i - \\ &- <n_i^{(A)}> d + \left(n_i - <n_i^{(A)}>\right)\times \\ &\times v(t)N\Big)\frac{1}{N^{(A)}\delta(t)},\end{aligned} \tag{8}$$

where $d_i = \beta_i I_i$ and $d = \sum \beta_i I_i$. If the concentrations of atoms in the emission and the altered layer are equal $N^{(E)} = N^{(A)}$; and $c_i \approx <n_i^{(A)}>$, using notations $\eta = N^{(A)}/N$, $\omega_i = \beta_i I_i / N^{(E)}$ and $\omega = \Sigma\omega_i$, Eq. (8) and Eq. (4) give the system of equations for calculation of the surface composition kinetics and kinetics of incident particles accommodation:

$$\begin{aligned}\frac{\mathrm{d}c_i}{\mathrm{d}t} = &\frac{\left(n_i + c_i(\eta - 1)\right)\sum w_j' c_j + (\omega_i - c_i\omega - w_i' c_i)\eta}{\eta\delta(t)} + \\ &+ \frac{\left(n_i - c_i\right)v(t)}{\eta\delta(t)}\end{aligned}\,, \tag{9}$$

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = \frac{(1-\eta)\left(\sum w_j' c_j + v(t)\right) + \omega\eta}{\delta(t)}\,. \tag{10}$$

These dimensionless equations have been used for quantitative analysis of the accommodation kinetics for implanted atoms.

RESULTS AND DISCUSSIONS

The made evaluations were compared with the experimental results presented in publications of Wang et al. [7], Alimov et al. [8] and Miyagawa et al. [9]. In many articles [10 – 15] it is shown that implanted atoms diffuse according to Fick's law, however, radiation enhanced diffusion may be also considered [14, 15]. The diffusion could be enhanced by defects and dislocations or by contaminants of other elements. A classical diffusion model is used in this modeling. It is assumed that the boundary x_2 moves with the velocity equal to:

$$\frac{\mathrm{d}x_2}{\mathrm{d}t} = \frac{\mathrm{d}x_1}{\mathrm{d}t} + \sqrt{\frac{D}{t}}\,, \tag{11}$$

where D is the diffusion coefficient. The diffusion coefficient was the parameter extracted from experimental results. The alloy Ti225 with three components: titanium (95 at.%), aluminum (3 at.%) and vanadium (2 at.%) was studied. The sputtering yield (Y) was calculated using the program SRIM 2003 written by James F. Ziegler. Only the retention probability (β) was the free parameter. Fig. 1 shows comparison of experimental and calculated results. Parameters used in the calculations are presented in Table 1. Qualitative agreement has been obtained.

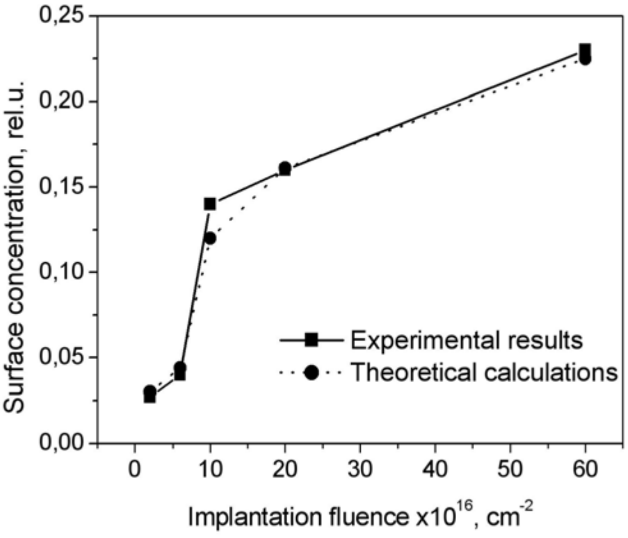

Fig. 1. Surface concentration of the implanted hydrogen (25 keV), in titanium vs. implantation fluence. Experimental results from Wang et al. [7]

Table 1. Calculation parameters for hydrogen implantation into alloy Ti225

Fluence (cm^{-2})	Diffusion coefficient	Retention probability – β	Altered layer thickness (nm)
$2\cdot10^{16}$	0.1	0.3	300
$6\cdot10^{16}$	0.1	0.15	300
$1\cdot10^{17}$	0.9	0.4	400
$2\cdot10^{17}$	0.9	0.3	400
$6\cdot10^{17}$	5	0.25	750

The implanted hydrogen is in a quasi-mobile state and in a chemically bonded state. Hydrogen in a quasi-mobile state diffuses easily to the low hydrogen concentration region e.g. the surface. In this model diffusion to the surface can be evaluated only with the parameter β (retention probability).

The diffusion increases with the increase of the fluence, and the retention probability decreases with the increase of fluence. This is seen in the ranges of the fluence from $2 \cdot 10^{16}$ to $6 \cdot 10^{16}$ cm^{-2} and from $1 \cdot 10^{17}$ to $6 \cdot 10^{17}$ cm^{-2}. At high fluences surface layer saturates and part of the implanted hydrogen diffuses towards the surface and is sputtered. For the fluence higher than $1 \cdot 10^{17}$ cm^{-2} the dihydrogenation process starts. Thus, the retention ratio has increased and became larger than for the lower fluences [7]. In calculations for this range of the fluence the retention probability had the highest value. It agrees with the experimental results quite well.

Good agreement was obtained for deuterium implantation into tungsten. Experimental results were taken from article of Alimov et al. [8]. Calculated retention probability decreased monotonically from 1 for implantation fluence of $2.5 \cdot 10^{21}$ cm^{-2} to 0.35 for implantation dose of $9.8 \cdot 10^{22}$ cm^{-2}. As deuterium don't form chemical compound with tungsten, monotonous decrease of the retention probability can be explained by surface saturation for higher doses and enhanced diffusion towards the surface and evaporation.

It was not obtained good quantitative agreement between experimental and calculated results for nitrogen implantation into zirconium at 50 keV. For this calculation the retention probability has increased as the fluence increased (Fig. 2).

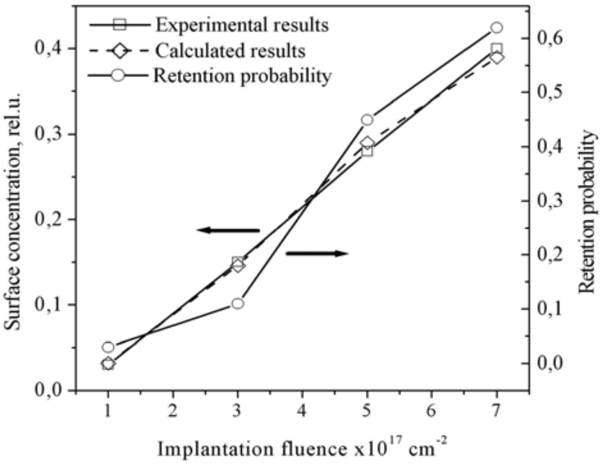

Fig. 2. Nitrogen surface concentration, as implanted into zirconium (50 keV), vs. implantation fluence. Experimental results from Miyagawa et al. [9]

Implantation process induces radiation damage, and the radiation enhanced diffusion is not introduced in the model, so variation of retention probability is understandable. The model is good for calculations of light ion's implantation, when radiation damage is low.

Fig. 3 illustrates kinetics of the surface concentrations, calculated according to the Eq. (9), as hydrogen is implanted into Mg and Al. In this modeling it was assumed that alloy is two-elemental with magnesium (33 at.%) and aluminum (67 at.%).

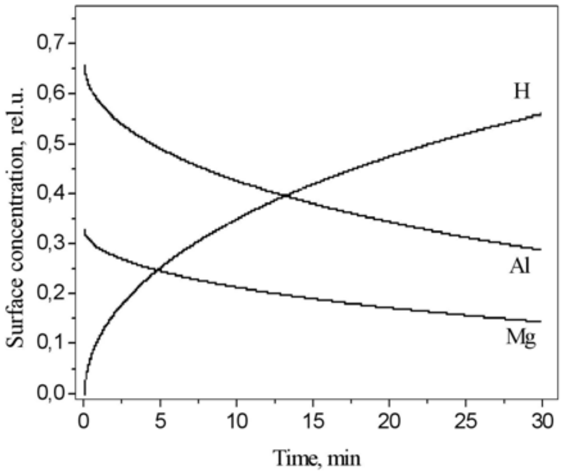

Fig. 3. Surface concentrations, as hydrogen is implanted into 2Mg-Al alloy at the fluence of $6.25 \cdot 10^{15}$ cm^{-2} and the energy of 500 eV

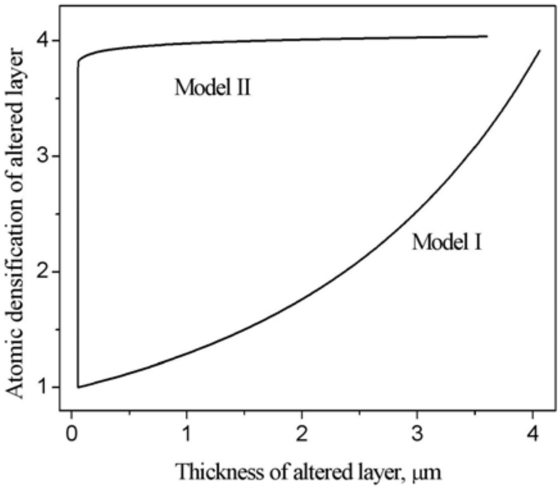

Fig. 4. Atomic densification vs. altered layer depth, as hydrogen is implanted into 2Mg-Al alloy at the fluence of $3.44 \cdot 10^{15}$ cm^{-2} and the energy of 500 eV

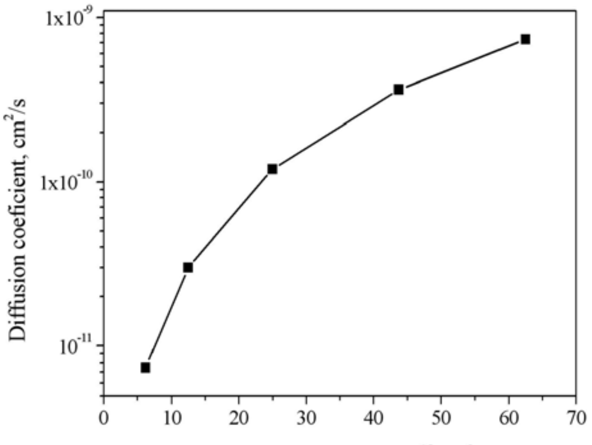

Fig. 5. Diffusion coefficient, calculated according to the model II, vs. implantation fluence

It was shown [4], that using plasma-enhanced magnetron-sputtered deposition (PMD) technique for hydrogen implantation into Mg and Al film it is possible to get magnesium alanate. However, the magnesium alanate formation mechanisms, using PMD technique, are not well understood. Two different models are considered. **Model I** – hydrogen from surface diffuses into the bulk and magnesium alanate is formed when sufficient amount of hydrogen is implanted. **Model II** – implanted hydrogen forms $Mg(AlH_4)_2$ instantly. When monolayer is converted to the new phase, hydrogen diffuses into the deeper monolayers. The mathematical difference between these two models in equations is only the value of diffusion coefficient in Eq. (11). In the model I diffusion coefficient is constant. In the model II the value of the diffusion coefficient increases starting from zero and is changed in such a way, that atomic densification would be equal to desired value. In this calculation hydrogen is implanted into 2Mg-Al alloy and it was assumed, that magnesium alanate is formed, when atomic densification, calculated using Eq. (10), in the altered layer increases 4 times. Physical difference between these two models is clearly illustrated in Fig. 4. In the model I, implanted hydrogen diffuses into the bulk, but expansion of the altered layer is proportional to the $\sqrt{D/t}$ (Eq. (11)). Densification gradually increases while the altered layer expands. Hydrogen concentration reaches formation of magnesium alanate value, $Mg(AlH_4)_2$ is formed, only at the end of the implantation.

In the model II hydrogen forms magnesium alanate straight after the implantation incase a monolayer is converted to the new phase, then hydrogen diffuses into the bulk. In this model the $Mg(AlH_4)_2$ phase is present from the beginning of the implantation. In the model II diffusion coefficient is not an arbitrary constant. As shown in Fig. 5 the diffusion coefficient increases as the implantation fluence increases.

Calculations are in the qualitative agreement with experimental results [16], so even such a simple approximation can give estimated results.

CONCLUSIONS

1. The model presented by Milčius et al. [5] and Pranevičius et al. [6] is developed for continuously expanding altered layer. This enables to introduce diffusion into equations and make quantitative analysis. The model is simple and enables us to study the kinetics of incident atoms accommodation in the altered layer as function of the incidents energy, the fluence and the intensity of irradiation.
2. Retention probability dependence on fluence for various implantation cases is discussed. From comparison with experimental results it was observed, the model fits better for the light ions implantation than for the heavy ions implantation.
3. Two models were proposed for the hydrogen diffusion in 2Mg-Al alloy and formation of the magnesium alanate.

Acknowledgments

Author expresses special gratitude to professor L. Pranevičius for his encouragement and help.

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