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LETTER TO THE EDITOR

On the activation energy in radiation enhanced diffusion of silver in nickel

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Abstract. Coupled continuity equations for silver-atom and vacancy fluxes are solved to obtain theoretical fits to the Ag auger profiles in Ag–Ni layered systems, measured at different temperatures. It is observed that silver atoms are trapped by vacancies at higher temperatures. This phenomenon sharpens the Ag profile measured at 603 K. It is argued that the sharpening of Ag profile at higher temperatures cannot be interpreted as being due to a negative activation energy of atomic transport processes.

Recently, Marton *et al* [1] reported a decrease in the radiation-enhanced diffusion coefficient D of Ag following an increase in temperature, for ion-bombarded Ag–Ni layered systems. From the positive slope of the Arrhenius plot they deduced that the activation energy of atomic transport processes in this system is negative and they suggested a microscopic mechanism for Ag diffusion, in which they assumed the presence of complex defects having long lifetime at low temperature. In their analysis the diffusion coefficient D was treated as a free parameter in an equation similar to Fick's law. Cascade mixing effects, surface roughness and inelastic mean free path of the Auger electrons were also included in the analysis. (The Auger technique was employed for the experimental analysis.) However, they did not make any attempt to separate out the effects of vacancy–atom correlation on the transport of silver atoms. In such a case their parameter D becomes an 'effective' diffusion coefficient, since the effects of copious number of vacancies present in the radiation environment and their correlation with atoms are included in the same parameter D. Such a decrease of the effective diffusion coefficient is misleading, implying that the activation energy of the atomic transport processes can be negative, as proposed by Marton *et al* [1]. In the present work a more general analysis of their results is carried out, in which the coupling between the flux of vacancies with the flux of silver atoms is also considered, and it is indeed observed that the proposed negative activation energy is fictitious.

There are various theories that relate the transport of atoms to the flux of vacancies [2, 3, 4]. According to our previously reported formalism [4], the silver-atom–vacancy

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correlation effects are included using the following expressions for the silver-atom and vacancy fluxes:

$$\begin{aligned} J_c &= -D_c\,\delta c/\delta x - D_{ij}\,\delta v/\delta x \\ J_v &= -D_v\,\delta v/\delta x - D_{ji}\,\delta c/\delta x \end{aligned} \tag{1}$$

where $c = c(x, t)$ is the concentration of silver atoms at time t and depth x ($x = 0$ is the actual surface position), v is the vacancy concentration created by Ar^+ ion bombardment, D_c and D_v are the silver atom and vacancy diffusion coefficients, and D_{ij} and D_{ji} are the c–v and v–c correlation coefficients respectively. The coupled continuity equations for J_c and J_v are obtained using the following relations:

$$\begin{aligned} \delta c/\delta t &= -\operatorname{div} J_c \\ \delta V/\delta t &= -\operatorname{div} J_v + f(x) \end{aligned} \tag{2}$$

where $f(x)$ is the vacancy generation rate during Ar^+ ion bombardment. Silver-atom preferential sputtering effects are considered using the following boundary condition:

$$-D_c(\delta c/\delta x)|_{x=0} - D_{ij}(\delta v/\delta x)|_{x=0} = \varphi \Delta x_0 Ic \tag{3}$$

where φ is the sputtering cross-section, I is the incident particle flux and Δx_0 is the depth from which the sputtering may occur ($\Delta x_0 < 1$ nm). Such a preferential sputtering of Ag was not included in the analysis of Marton *et al* [1]. The Auger profile is computed using the following relation:

$$C_{\mathrm{A}}(t) = \int_0^\infty c(x, t) \exp(-x/\lambda_{\mathrm{e}})\, \mathrm{d}x \tag{4}$$

where $\lambda_{\mathrm{e}} = 0.5$ nm is the electron inelastic mean free path for silver at 375 eV [5]. All the above equations are numerically integrated in a moving frame whose velocity is the erosion speed. The vacancy source term $f(x)$ is obtained using a computer code available from Implant Science Corp., USA. The chosen vacancy profile is realistic, unlike the constant one chosen by Marton *et al* [1] in their analysis. Equations (1) to (4) are solved using a numerical procedure described in [4], for a chosen set of parameters D_c, D_v, D_{ij}, D_{ji} and Φ to fit the experimental data (where $\Phi = \varphi \Delta x_0 I$). Although on the face of it the number of parameters looks large, the most relevent parameter is only D_{ij} in the present case, as can be seen later.

Figures 1 and 2 show the theoretical fits to the experimental results (figures 1(*a*) and 1(*b*) of [1]) of Marton *et al*. In the figures, the normalised concentration $C_{\mathrm{A}}(t)$ against t curves are drawn and the time scales are not exactly the same as in [1], a conversion being made by a constant scaling factor (obviously same for both the cases). This was done because some experimental parameters such as the Ar^+ beam current, the incident angle and therefore the Ag sputtering rate and the erosion speed were unknown. However, this changes only the time scale. Also, the surface roughness may easily be included through a time-scaling factor. But by keeping all these conditions the same in both the cases considered, a comparison can be made between the two figures. All the parameters used for the fitting except D_{ij} are the same for both cases. The parameters are $\Phi = 1.5 \times 10^{-9}\ \mathrm{cm\,s^{-1}}$, $D_c = 1.0 \times 10^{-18}\ \mathrm{cm^2\,s^{-1}}$, $D_v = 4.1 \times 10^{-15}\ \mathrm{cm^2\,s^{-1}}$, $D_{ji} \leq 1.0 \times 10^{-20}\ \mathrm{cm^2\,s^{-1}}$ for both the cases. $D_{ij} = 1.0 \times 10^{-15}\ \mathrm{cm^2\,s^{-1}}$ for the 299 K case, whereas $D_{ij} = -8.5 \times 10^{-15}\ \mathrm{cm^2\,s^{-1}}$ for the 603 K case.

It can be seen that the parameter D_{ij} is negative for the high temperature (603 K) case, signifying that the vacancies trap silver atoms at higher temperatures, whereas for

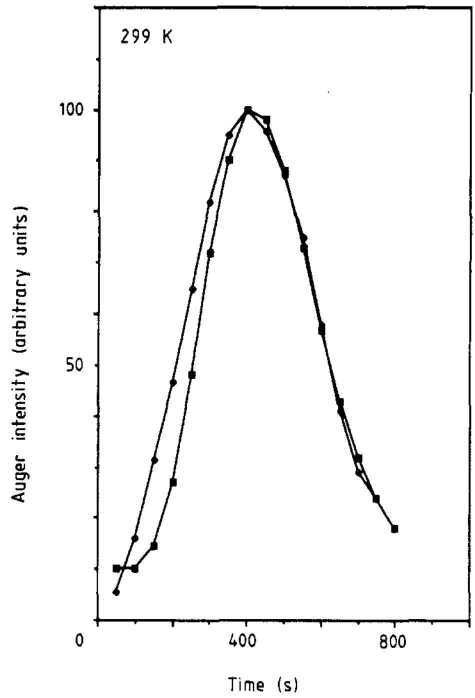

Figure 1. Theoretical (■) and experimental (◆) normalised Ag auger profiles recorded at 299 K. The experimental results are taken from [1].

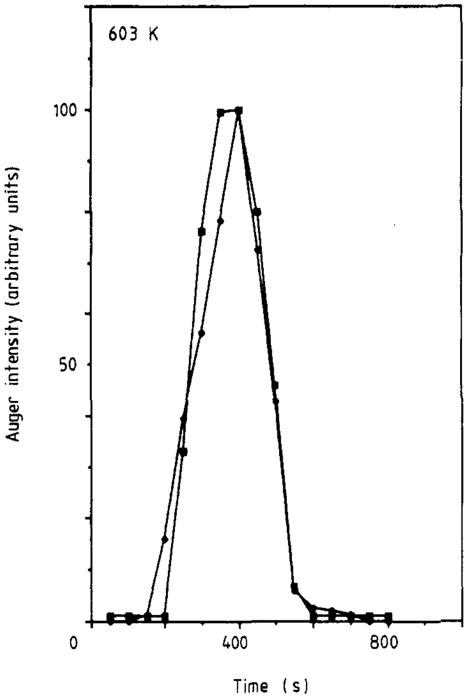

Figure 2. Theoretical (■) and experimental (◆) normalised Ag auger profiles recorded at 603 K. The experimental results are taken from [1].

the room temperature (299 K) case the vacancies try to repel silver atoms. These results are similar to our previous results for nitrogen implanted Cu, where the trapping was observed at higher temperatures [4]. The reason for the different trapping behaviour at different temperatures can be qualitatively understood using the model of Marwick [3], according to which the faster diffusing species move up the vacancy gradient and *vice versa*. Possibly the silver diffusion coefficient is higher (or lower) with respect to the nickel diffusion coefficient at higher (or lower) temperatures. Since the vacancy profile is Gaussian in nature, the effects of different relative diffusion coefficients is trapping (or repulsion) at higher (or lower) temperatures.

Sputtering being temperature independent, the parameter Φ is expected to remain the same for both the cases. As previously observed [4], the coefficient D_{ji} had no effect on the profile. The parameter D_v had no profound effect on the room temperature (299 K) profile, but the higher temperature profile required it to be higher. For the sake of reducing the number of parameters, it is kept the same for both the cases. But it is possible that vacancies are in the form of small clusters at low temperatures, which break at higher temperatures (which obviously implies an increasing behaviour of D_v with the increase in temperature).

The silver diffusion coefficient D_c remained the same for both the cases (but a slight increase of D_c at higher temperature cannot be ruled out). This result is in agreement with the results of other groups, that in this temperature range and in a radiation environment the diffusion coefficient remains almost constant [4, 6]. A closer examination of Arrhenius plots of Marton *et al* (figure 2 in [1]) also shows that their parameter

D/S cannot be described by a negative activation energy. We calculated the 'q-probability' values by performing the χ^2 test using the method described in [7]. These values give the goodness-of-fit of the model. The 'q-probability' values for their fits are equal to 0 and 10^{-11} for 1 keV and 4 keV results shown in figure 2 of [1], which are low by any standard. To increase the q-values it was necessary to increase the error in D/S [8], but in the case under consideration the uncertainty in the calculated activation energy (-0.04 eV) is greater than 30%. This means that the kinetic energy of atoms (kT) may exceed the activation energy, which makes it questionable to use the concept of the 'jumping process' (Arrhenius behaviour) and make connection to rate theory. On the other hand, the q-value increases if the same experimental results are fitted with the following non-exponential T-functions: $D/S = A + B/T$ or $D/S = A + BT$, where A and B are constants. A non-exponential behaviour signifies that the atomic transport processes are not governed by activation energy.

In conclusion, the increased sharpness of the Ag profile observed at higher temperature cannot be attributed to the negative activation energy as proposed by Marton *et al* [1]. A more realistic physical mechanism may be described as follows. Because of the preferential coupling of silver atoms with the vacancies, the silver atoms get trapped in vacancies at higher temperature. Since in the present case the vacancy profile is very close to the surface and the vacancies preferentially move towards the surface, the Ag atoms are segregated towards the surface. Once they are near the surface they are easily removed because of sputtering. The removal of segregated Ag atoms causes depletion of Ag atoms from the bulk layer, making it thinner. This mechanism requires that the area under the peak in the Auger profile should be less for the high temperature case than for the low temperature case. Apparently this is the case (see figures 1(*a*) and 1(*b*) of [1]): however, an experimental confirmation is required for this point. Fine *et al* [9] sought similar explanation for the sharpness of the Ag profile observed in their segregation experiments (see figure 5 of [9] and its explanation). In fact, using the experimental results of [9] one can easily argue that the time required to obtain the sharpness of the Ag profile in the segregation experiment [9] is considerably reduced in the high-temperature experiment [1], because of higher diffusion coefficients of both Ag atoms and vacancies (i.e. D_c and D_v), which is observed in the parameters obtained from the present theoretical fits. The flux of silver atoms towards the surface also causes the 50 nm nickel layer to be enriched in silver. This causes the erosion speed within this layer to increase, since the sputtering coefficient of silver is almost double that of nickel. Thus, in the Auger measurement, the silver profile should appear at a smaller sputtering time than for the high-temperature case, which is experimentally observed (compare figures 1(*a*) and 1(*b*) of [1] and see figure 5 of [9]).

The above theoretical results supported by the experimental data from literature [1, 9] show that the transport of silver atoms in a radiation environment is not governed by a negative activation energy, as proposed by Marton *et al* [1], but mainly by silver-atom–vacancy correlation effects.

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