MODEL FOR ION-ASSISTED FILM GROWTH

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A new model of growing film densification is proposed. The model takes into account the diffusional mobility of point defects and interaction between them. The film density as a function of ion flux, ion energy and substrate temperature is investigated.

1. Introduction

Vapor-deposited thin films have a lower density than the corresponding bulk material. This is caused by a low mobility of surface atoms thus vacancies and their complexes are formed [1]. It is possible to increase the density of vapor-deposited films by self or gas ions bombardment during growth [2]. Muller has proposed a model for ion-assisted film densification [3]. This model explains the experimentally observed increase in the film density for the low ion fluxes case, but it leads to unreasonable results for large ion fluxes: the film density exceeds the one of the bulk material. This discrepancy is mainly due to by neglecting of point defects mobility.

We present a model, where the diffusion of point defects is taken into account. Satisfactory description of experimental data is obtained in the frame of our model.

2. Diffusion model of densification

Let us denote the fluxes of condensing atoms and gas ions as J_n and J_g respectively and the film growth rate as V. Ions penetrate into the film and produce interstitials and vacancies. In moving coordinate system, connected with surface (x = 0), the concentrations of interstitials C_i, vacancies C_V, implanted gas atoms C_g and gas-vacancy complexes C_c can be described by the following diffusion equations:

$$\frac{d}{dx}\left(D_i \frac{d}{dx} C_i\right) - V\frac{d}{dx} C_i - \alpha_{iv} C_i C_v - \alpha_{ic} C_i C_c + Q_i(x) = 0, \qquad (1)$$

$$\frac{d}{dx}\left(D_v \frac{d}{dx} C_v\right) - V\frac{d}{dx} C_v - \alpha_{iv} C_v C_i - \alpha_{gv} C_v C_g + \omega_c C_c + Q_v(x) = 0, \qquad (2)$$

$$\frac{d}{dx}\left(D_g \frac{d}{dx} C_g\right) - V\frac{d}{dx} C_g - \alpha_{gv} C_g C_v + \alpha_{ic} C_i C_c + \omega_c C_c + Q_g(x) = 0, \qquad (3)$$

$$\frac{d}{dx}\left(D_c \frac{d}{dx} C_c\right) - V\frac{d}{dx} C_c - \alpha_{ic} C_c C_i + \alpha_{gv} C_g C_v - \omega_c C_c = 0. \qquad (4)$$

Here, $D_{i,v,g,c}$ are the diffusion coefficients of interstitials, vacancies, gas atoms and complexes respectively, $D_\alpha = D_{0\alpha}\exp\left(-E_\alpha^m / kT\right)$, E_α^m are the migration energies, $\alpha = i, v, g, c$; T is the substrate temperature, $\alpha_{iv,gv,ic}$ and ω_c are the constant of reactions in the following processes:

recombination of interstitials and vacancies

α_{iv}: i + v = 0,

formation of gas + vacancy complexes

α_{gv}: g + v = c,

recombination of interstitials and vacancies in gas-vacancy complexes

α_{iv}: i + c = i + v + g = g,

thermal decaying of gas-vacancy complexes

$$\omega_c: c = g + v.$$

All of constants a have the following form

$$\alpha_{ab} = \frac{4\pi R_{ab}}{\Omega}\left(D_a + D_b\right), \tag{5}$$

where R_{ab}, are the reactions' radii, Ω is the atom volume, and

$$\omega_c = \omega_d \exp\left(-E_c^d / kT\right), \tag{6}$$

where ω_d is the vibration frequency factor for gas-vacancy complex, E_c^d is the dissociation energy of gas-vacancy complex. In Eqs. (1)-(4) $Q_{j,v,g}(x)$ are the generation rates of interstitials, vacancies and implanted gas atoms respectively.

Without irradiation, i.e. at $Q_{j,v,g} \equiv 0$, Eqs.(1)-(4) have to describe the film growth with atom density $\rho_0 < 1$. Therefore we choose assume the next boundary condition for vacancies

$$C_v(0) = C_v^0, \tag{7}$$

where $C_v^0 = 1 - \rho_0$. The boundary concentration C_v^0 depends on vapor flux and temperature.

Suppose that the surface is ideal sink for interstitials, implanted gas atoms and gas-vacancy complexes:

$$C_{i,g,c}(0) = 0. \tag{8}$$

At far distance from surface, i.e. with $x \to \infty$ the point defects fluxes are absent:

$$\frac{d}{dx} C_{i,v,g,c}(\infty) = 0 \tag{9}$$

Eqs. (1)-(4) should be complemented by an equation for determination of the surface velocity V. $J_n \Delta t \Delta S$ atoms fall on surface square ΔS during time Δt and $J_g Y \Delta t \Delta S$ atoms (Y is the sputtering coefficient) leave the surface. The total number of atoms in the film increase: $\Delta N = (J_n - J_g Y)\Delta t \Delta S$. From the other hand, ΔN can be written as $V \Delta t \Delta S \rho(\infty)\Omega^{-1}$, therefore

$$V = \frac{J_n - J_g Y}{1 - C_v(\infty) - C_c(\infty) + C_i(\infty)}\Omega. \tag{10}$$

Follow Ref.[3], let us describe the densification by the next way. The vacancies which are created in thin layer d refilled by arriving vapor atom or interstitials, so we change generation rates of vacancies and interstitials in this layer as

$$Q_v^{eff}(0 \le x \le \delta) = 0, \quad Q_i^{eff}(0 \le x \le \delta) = \max\left[0, Q_i(x) - Q_v(x)\right]. \tag{11}$$

From Eqs. (1)-(4), (10) with boundary conditions (7)-(9) one can find the film density ρ_f, i.e. density with $x \to \infty$:

$$\rho_f \equiv \rho(\infty) = 1 - C_v(\infty) - C_c(\infty) + C_i(\infty). \tag{12}$$

3. Calculations

Let us consider the growth of vapor-deposited Cr films which is bombarded with low-energy Ar^+ ions. The parameters of irradiation and material constants, which are used in Eqs.(1)-(4), (10) are shown in Table. The profiles of generated point defects, implanted gas atoms and the sputtering coefficients are calculated by the code SPURT [4], which is similar to the cascade code TRIM [5]. Nonlinear Eqs.(1)-(4), (10) are solved by finite element method.

Figure 1 shows the film density versus ion flux at different temperatures. The curve obtained at T=0 K corresponds to the Muller's model [3]. One can see that taking into account the diffusional mobility of interstitials limits the growth of film density and it does not exceed the density of bulk material.

Figure 2 shows the film density versus ion energy at different ratios ion-to-vapor fluxes.

4. Conclusion

The proposed model of ion-assisted growth of vapor-deposited films correctly describes the film densification at high ion fluxes at the temperature, when interstitials are mobile.

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Table. Material parameters used for calculation.

Interstitial diffusivity pre-exponential	0.015 cm^2 s^{-1}	Interstitial migration energy	0.15 eV
Vacancy diffusivity pre-exponential	0.300 cm^2 s^{-1}	Vacancy migration energy	1.10 eV
Argon diffusivity pre-exponential	0.075 cm^2 s^{-1}	Argon migration energy	0.30 eV
Gas-vacancy diffusivity preexponential	10^ cm^2 s^{-1}	Migration energy of gas-vacancy complex	4.50 eV
Vibration frequency factor for gas-vacancy complex	1.3x10^{13} s^{-1}	Dissociation energy of gas-vacancy complex	1.30 eV
Recombination radius, R_{iv}	0.580 nm	Trapping radius, $R_{gv} \sim R_{ic}$	0,75 nm
Atom volume	12x10^{-24} cm^3	Vapor flux	3.75x10^{16} cm^{-2} s^{-1}
Depth of δ-layer	0.410 nm	Constant lattice	0.29 nm

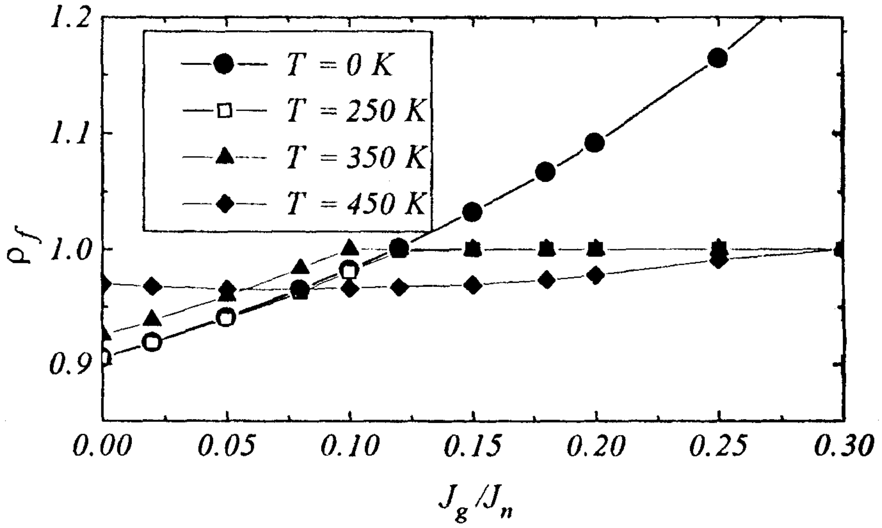

Fig. 1. Relative density as a function of ratios of ion-to vapor fluxes

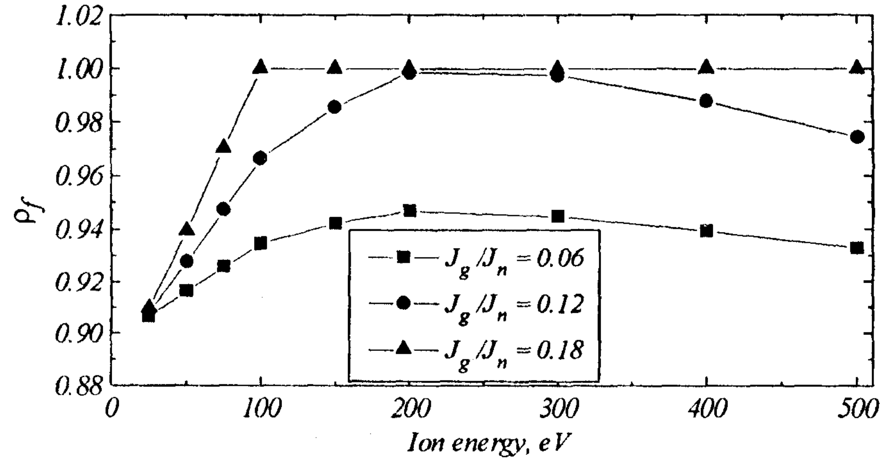

Fig. 2. Relative density as a function of ion energy at T=300 K