

A.M. CHAPLANOV\*, M.I. MARKEVICH\*  
and F.A. PISKUNOV\*

*Laser-stimulated oxidation of Cr films*

ABSTRACT

Further oxidation is controlled by diffusion, which requires thermal activation. The overall oxidation rate depends on the interplay of particular oxidation steps. At pulse duration's between  $10^{-5}$  and  $10^{-3}$  s, oxide growth continues for  $8 \cdot 10^{-6}$  to  $2 \cdot 10^{-5}$  s after the maximum temperature was reached; this process is favored by high concentrations of nonequilibrium vacancies.

1. INTRODUCTION

The wide spectrum of laser-induced chemical reactions can be divided into resonance and nonresonance processes, which are studied,

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\* Institute of Electronics BAS, 22 Logoiskii tract, 220-841 Minsk, Belarus.

respectively, by photochemistry and thermochemistry [1, 2]. The chemistry of laser-induced resonance processes deals with selective effects of monochromatic radiation on atoms and molecules. Thermochemical, non-selective processes are related to the dissipation of adsorbed energy through excitation of thermal degrees of freedom. One of these processes is laser-induced oxidation of metal surfaces. Pulsed irradiation of a film gives rise to surface chemical reactions accompanied by generation and quenching of point defects [3, 4]. These processes affect both the electrical properties of the metallic film and the growth of the surface oxide layer.

## 2. THEORY

Vacancy redistribution and oxidation processes in metallic films depend strongly on laser radiation parameters such as power density and pulse duration, as well as on gaseous environment. Pulsed irradiation raises the temperature in the near-surface region, thus activating metal oxidation via chemisorption of atmospheric oxygen. Interaction between the metal and the adsorbed oxygen results in electron transfer from metal to oxygen atoms. In this process, an oxide film a few angstroms in thickness is formed. In the initial stage, oxide-film growth is controlled by electronic processes associated with electron tunnelling from the metal bulk to the oxide surface, giving rise to a spacecharge field. After a layer about 100 Å thick is formed, the effect of tunnelling weakens, and further reaction is controlled by mass transport to the reaction front. These general features of surface oxidation apply to chromium films, as well. To simulate oxidation kinetics and vacancy profiles, we integrated a heat conduction equation and equations describing oxidation kinetics and vacancy redistribution, with appropriate initial and boundary conditions:

$$\rho(z) \cdot c_p(z) \cdot \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \lambda(z) \cdot \frac{\partial T}{\partial z} + N(t) \cdot q(z), \quad (1)$$

$$\begin{aligned} q(z) &= E \cdot k_1 \exp(-k_1 \cdot (z - z_0)), & z < z_1 \\ q(z) &= 0, & z \geq z_1 \end{aligned} \quad (2)$$

$$N(t) = \begin{cases} 1, & t \leq \tau; \\ 0, & t > \tau; \end{cases} \quad (3)$$

$$\frac{dC}{dt} = \frac{v_0 \left( C - \exp\left(-\frac{E_f}{kT(t)}\right) \right)}{n} \exp\left(-\frac{E_M}{kT(t)}\right) \quad (4)$$

$$C = C_0, \text{ by } t = 0$$

$$\frac{dh}{dt} = U_0 \cdot \exp\left(-\frac{E_d}{KT}\right) \cdot \left[ \exp\left(\frac{h_1}{h}\right) - \exp\left(-\frac{h_1}{h}\right) \right] \quad (5)$$

$$T = T_0$$

$$h = h_0 \text{ by } t = 0$$

where  $C_p$  is capacity,  $\rho$  is density,  $\lambda$  is thermal conductivity,  $t$  is time,  $C$  is the relative vacancy concentration,  $\tau$  is the pulse duration,  $E$  is power density of laser radiation,  $k - r$  is the absorption coefficient,  $T$  is the absolute temperature,  $h$  is oxide-layer thickness,  $E_d$  is the total activation energy for chromium diffusion in the oxide layer,  $n$  is the average number of hops regard for vacancies to reach a sink, and  $E_m$  is the energy of vacancy migration.

Figures 1a, 2, and 3a show the time dependencies of the chromium film temperature, nonequilibrium vacancy concentration, and oxide-layer thickness, respectively (pulse duration,  $10^{-3}$  s; pulse power, 1.54 W). These data demonstrate that the oxide layer grows during both heating to the maximum temperature of 1484 K and subsequent cooling. As one can expect, the major fraction of the oxide-film thickness ( $\sim 8.4$  nm) grows during the laser pulse; in the course of cooling, the oxide-film thickness

becomes constant at 9.4 nm starting at 1249 K. As apparent from Figure 2, the irradiated chromium film contains a high concentration of non-equilibrium vacancies, which affect the activation energy of diffusion. In calculating the oxide-film thickness, we took into account the effect of nonequilibrium vacancies on the diffusion kinetics: high concentrations of point defects give rise to elastic strains, thus reducing the activation energy of chromium diffusion. According to the estimates reported in [5, 6], this reduction may amount to 10–20%. In our calculations, we took an activation energy of 2.9 eV, which is less than the value of 3.6 eV reported in the literature. Figures 1b and 3b display the time dependencies of chromium-film and oxide-layer thickness (pulse duration  $10^{-5}$  s; pulse power, 11 W). As in the above simulation, the relative concentration of non-equilibrium vacancies in the irradiated chromium film is fairly high, about  $4 \cdot 10^{-5}$ . The oxide-layer thickness is 4.5 nm at the maximum temperature of 1768 K and further increases to 7.6 nm during cooling. The oxide layer continues to grow down to 1260 K, and the increment in oxide thickness (3.0 nm) in this case is much greater than after irradiation for  $10^{-3}$  s, because at shorter pulse durations the cooling time is comparable to the heating time. Figure 3 also demonstrates that the effect of power density (which controls the maximum film temperature attained) on the final oxide-layer thickness is much stronger than that of pulse duration. For pulse durations differing by two orders of magnitude, the difference in oxide thickness is about 1–1.5 nm. Note, however, that the above features are only observed when chromium oxidation is not limited by oxygen chemisorption. Pulsed laser heating of metallic films produces high concentrations of nonequilibrium vacancies, amounting to  $C = 4 \cdot 10^{-5}$ . A substantial fraction of the vacancies concentrate at grain boundaries, thus facilitating intergranular adsorption and diffusion of oxygen and, hence, oxidation of grain boundaries. As a result, film oxidation proceeds both at the surface and in the interior. Therefore, if the grain size is comparable to the oxide-layer thickness, the calculation gives a notably underestimated oxide-layer thickness. Our

experimental studies with a pulse duration of  $2 \cdot 10^{-3}$  s and a power density of  $6 \cdot 10^4$  W/cm<sup>2</sup> showed that pulsed laser annealing causes recrystallization of chromium films, accompanied by an increase in grain size from 5–6 to 50–60 nm.

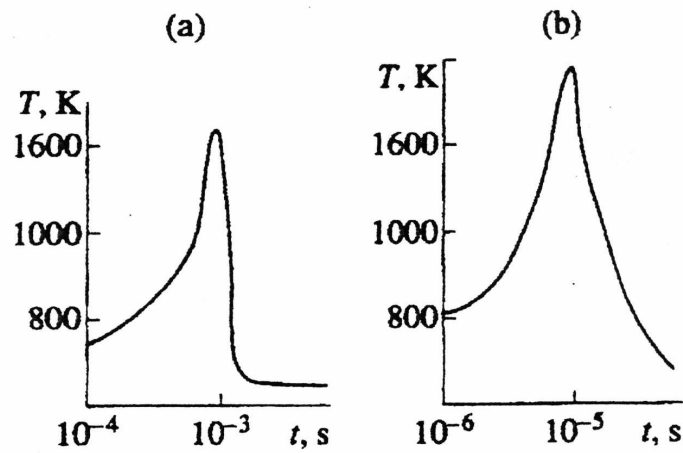


Fig. 1. Variation in the chromium film temperature during and after pulsed laser irradiation: (a)  $\tau_p = 10^{-3}$  s,  $P = 1.54$  W; (b)  $\tau_p = 10^{-5}$  s,  $P = 11$  W

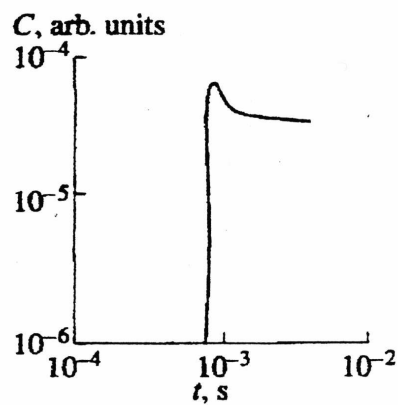


Fig. 2. Variation in vacancy concentration during and after pulsed laser irradiation: (a)  $\tau_p = 10^{-3}$  s,  $P = 1.54$  W

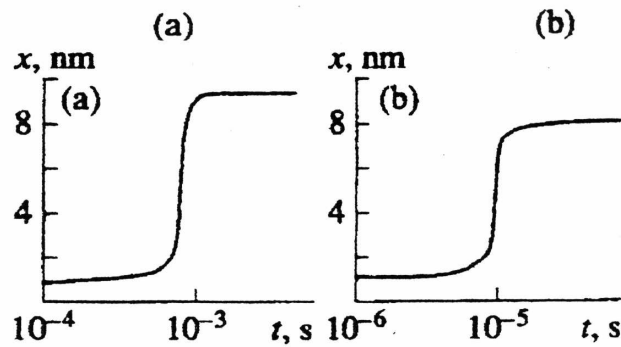


Fig. 3. Variation in the thickness of the oxide layer during and after pulsed laser irradiation: (a)  $\tau_p = 10^{-3}$  s,  $P = 1.54$  W; (b)  $\tau_p = 10^{-5}$  s,  $P = 11$  W

### 3. CONCLUSIONS

Computer simulations demonstrate that oxidation is controlled by diffusion, which requires thermal activation. The overall oxidation rate depends on the interplay of particular oxidation steps. At pulse durations between  $10^{-5}$  and  $10^{-3}$  s, oxide growth continues for  $8 \cdot 10^{-6}$  to  $2 \cdot 10^{-5}$  s after the maximum temperature was reached; this process is favored by high concentrations of nonequilibrium vacancies.

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