

LETTERS

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Defect – deformation nanometer self-organisation upon laser recrystallisation of thin amorphous films on substrates

V.I. Emel'yanov, K.I. Eremin, A.A. Sumbatov

***Abstract*. A hidden hexagonal order in the arrangement of nanometer crystal grains formed upon laser recrystallisation of thin films of amorphous silicon on a substrate is experimentally found. The hexagonal ordering of the grains and the extremal dependence of the grain size on the laser pulse energy density are described within the framework of the cooperative defect – deformation mechanism of laser recrystallisation.**

Keywords: *defect – deformation self-organisation, laser recrystallisation, amorphous films.*

1. Recrystallisation of thin (10 – 100 nm) α-Si films on substrates produced by an excimer laser was extensively studied as a possible method for preparation of thin-film transistors and integrated circuits [1]. This process is characterised by the extremal dependence of the crystal grain size d on the laser pulse fluence F, which has three qualitatively different regions (Fig. 1). The crystallisation models [2 – 4], which are based on the concept of the individual nucleation and growth of each of the grains, can qualitatively explain only some of the parts of the experimental curve in Fig. 1. All these models assume a random spatial distribution of the grains. In this paper, we found experimentally for the first time that the arrangement of the crystal grains has a hidden long-range quasi-hexagonal order (Fig. 2). We proposed a new (cooperative) defect – deformation (DD) mechanism of nucleation of crystal grains upon laser recrystallisation, which explains this fact and describes all the three parts of the curve in Fig. 1.

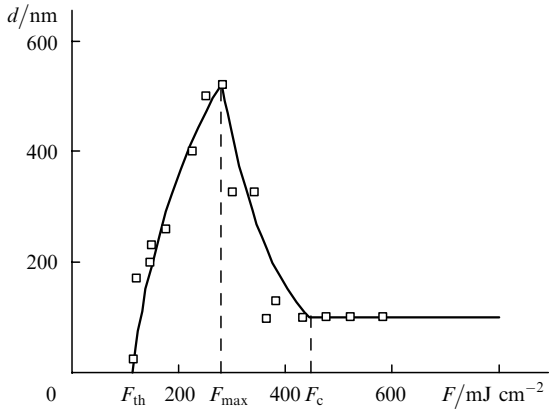

Figure 1. Experimental (squares) and theoretical (curve) dependences of the crystalline grain size d on the laser-pulse fluence F for $B = 40$ K cm^2 mJ^{-1}, $C = 20$ J mol^{-1} K^{-1}, $L_m = 5 \times 10^4$ J mol^{-1}, $C_1 = 350$ nm, $C_2 = 520$ nm, $T_{max} = 2.7 \times 10^3$ K (these and other parameters are defined in the text).

V.I. Emel'yanov, K.I. Eremin International Teaching and Research Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia; e-mail: emel@em.msk.ru;
A.A. Sumbatov State Scientific Centre of the Russian Federation 'L.Ya. Karpov Institute of Physical Chemistry', ul. Vorontsovo Pole 10, 103064 Moscow, Russia
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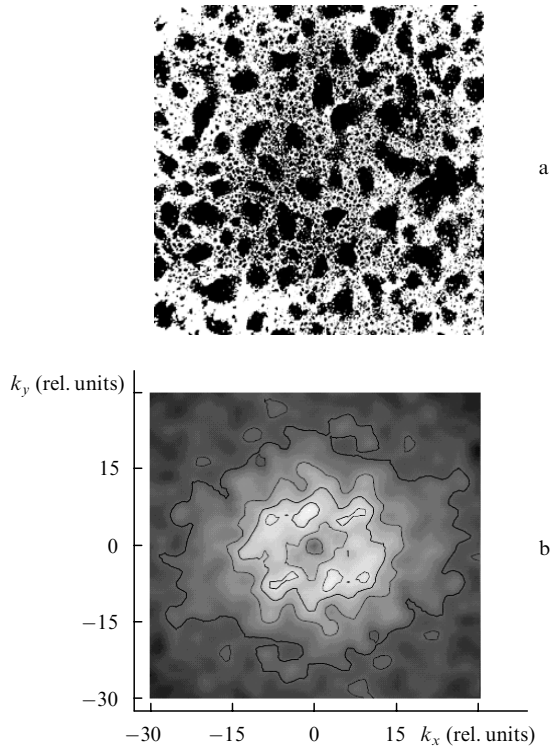

Figure 2. TEM photograph of a part of the α-Si film after irradiation by an obliquely incident laser pulse when a laser spot on the film surface has the shape of ellipsoid (the laser fluence is $F = 580$ mJ cm^{-2}) (a) and the smoothed amplitude $|F(k_x, k_y)|$ of the Fourier spectrum of this TEM photograph (b). The brighter regions correspond to the greater values of $|F(k_x, k_y)|$. The Fourier spectra of photographs obtained for other laser-pulse fluences are similar.

2. We irradiated by a laser the $z = 0$ surface of a three-layer sample, which consisted of a α-Si : H film ($0 \leqslant z \leqslant h$, $h = 0.04$ μm), a buffer Si_3N_4 layer ($h \leqslant z \leqslant h + H$, $H = 0.15$ μm), and a glass substrate of thickness 0.5 mm ($z \geqslant h + H$). The size of a α-Si crystal grain before irradiation was of about 7 nm. The irradiation was performed under normal ambient conditions by single 248-nm pulses from an excimer laser. The pulse FWHM duration was 7 ns and the fluence was 50 – 700 mJ cm^{-2}. The cross section of the laser beam was 5×10 mm.

The extremal dependence of the grain size on the laser energy density obtained by us is shown in Fig. 1. It is described by the DD mechanism of laser recrystallisation of thin amorphous films, which consists in the following. Consider a fine-grained (amorphous) semiconductor film on a substrate, with grain boundaries formed by dislocation walls [5]. Irradiation by a laser pulse of duration τ_p with the fluence F causes the melting of a surface layer of thickness

$$h_m = l_T \ln\left[\frac{T(0) - L_m/C}{T_m}\right] < h,$$

where $l_T = (\chi_{eff}\tau_p)^{1/2}$ is the thermal diffusion length; χ_{eff} is the effective thermal diffusivity of a three layer substrate; T_m is the melting temperature of the α-Si film; L_m and C are the specific melting heat and the specific heat of α-Si, respectively; $T(0) = BF$ is the temperature on the $z = 0$ surface; and B is a coefficient.

The melting of dislocation walls results in the formation of local aggregates of excess mobile atoms, which are rearranged along the film to produce after solidification a spatially homogeneous concentration n_{i0} of interstices, which does not depend on F. A near-surface layer enriched with interstices can be treated as a 'film' of thickness h_m, which is rigidly attached to the lower part of a sample. It was shown in paper [6] that, when the concentration n_{i0} of interstices exceeded the critical concentration n_c, a DD instability was developed in the film accompanied by the formation of the relief modulation grating $\zeta(\boldsymbol{r}, t) = \zeta_q \times \exp(i\boldsymbol{qr} + \lambda_q t) + \text{c.c}$ (where $\zeta(\boldsymbol{r}, t)$ is the local displacement of the surface along the z axis, the condition $\zeta > 0$ corresponding to the relief trough; $\boldsymbol{q}$ is the grating vector; and λ_q is the grating growth rate). The interstices are accumulated in the projections of this relief, and the deformation grating

$$\xi(\boldsymbol{r}, t) = [z - (h/2)]q^2\zeta_q \exp(i\boldsymbol{qr} + \lambda_q t) + \text{c.c.} \qquad (1)$$

also appears.

3. The dependence of the growth rate λ_q of the DD grating on its wave number has a maximum at [6]

$$q = q_m = 3\nu\beta h_m^{-1} n_{i0}/n_c. \qquad (2)$$

Here, $\nu = (1 - 2\sigma)/(1 - \sigma)$; σ is the Poisson coefficient; $\beta = c_t^2/c_l^2$; c_l and c_t are the longitudinal and transverse sound speeds, respectively; $n_c = \rho c_l^2 k_B T/\theta_i^2$; ρ and T are the density and temperature of the α-Si film; and θ_i is the dilatation potential of the interstices in the film. The period of the dominating DD grating is $\Lambda = 2\pi/q_m$.

Because the local crystallisation rate of α-Si depends exponentially on the local deformation [7], taking into account (1), we obtain that a spatially periodic distribution of crystal grains with the period $\Lambda/2$ is formed in the film of thickness h_m. Alternatively, such a distribution of grains can be formed because periodic aggregates of defects in the DD grating serve as the nucleation centres for crystal grains. The crystal grain size in this case is $d = \varepsilon\Lambda/2$, where the coefficient $\varepsilon \leqslant 1$. By substituting expression (2) into the expression for the period of the dominating DD grating, we obtain the dependence of the grain size on F:

$$d = l_T \frac{\varepsilon\pi n_c}{3\nu\beta n_{i0}} \ln\left[\frac{BF - L_m/C}{T_m}\right] \equiv C_1 \ln\left[\frac{BF - L_m/C}{T_m}\right],$$

where $C_1 \approx \text{const}$. This dependence well reproduces the experimental dependence in the region $F_{th} \leqslant F \leqslant F_{max}$, where $F_{th} = B^{-1}(T_m + L_m/C)$ is the threshold melting fluence for the α-Si film; and F_{max} is the fluence at which the dependence $d(F)$ has a maximum (Fig. 1).

For $F = F_{max}$, the regime of formation of the periodic DD structure in a three-layer sample drastically changes. This is caused by the achievement of the thermal decomposition temperature of Si_3N_4 ($T = 1900$ K) on the $z = h$ surface of the buffer film. Because the α-Si film is melted over its entire thickness to this instant, the thermal decomposition results in the efficient injection of an impurity from the Si_3N_4 surface ($z = h$) to the α-Si film. For $F > F_{max}$, the wave number q_m is still determined by expression (2), where now $h_m = h + H = \text{const}$, and the average concentration of defects (injected impurity) is determined by the expression $n_{i0} = n_{i0}(T) = \alpha n \exp(-E/k_B T)$, where n is the concentration of atoms in Si_3N_4; E is the activation energy of the thermal decomposition of the Si_3N_4 surface; $\alpha < 1$ is the coefficient taking into account a decrease in the average impurity concentration compared to its value at $z = h$. By representing the temperature on the $z = h$ surface in the form $T = T_{max} + B(F - F_{max})$ and expanding the exponent in the expression for n_{i0} into a series in powers of $F - F_{max}$, we find the dependence of the crystal grain size on the pulse energy density

$$d = \frac{\varepsilon\pi n_c(H + h)}{3\nu\beta n_{i0}(T_{max})} \exp\left[-\frac{EB(F - F_{max})}{k_B T_{max}^2}\right]$$

$$\simeq C_2 \exp\left[-\frac{EB(F - F_{max})}{k_B T_{max}^2}\right],$$

where C_2 is a constant. The latter equality is valid in the approximation $n_c = \text{const}$. For the value $E/k_B = 1900$ K corresponding to the activation energy of sublimation of Si_3N_4 [8], the obtained dependence $d(F)$ well reproduces the experimental dependence in the region $F_{max} \leqslant F \leqslant F_c$, where F_c is the fluence at which grains with a constant size d, independent of F, begin to form (see Fig. 1).

For $F = F_c$, the wave number q_m of the dominating DD grating achieves the limit value $q_c = \pi/(h + H)$ in the spectrum of bending modes [6]. For $F > F_c$, the maximum λ_q of the growth rate of the DD grating shifts to the region $q_m > q_c$, but for all $F > F_c$ the same DD grating is realised with $q = q_c$ and the period $2\pi/q_c = \pi/(h + H)$. According to the DD model, the grain size d in the region $F > F_c$ should remain constant and equal to $\varepsilon\Lambda/2 = \varepsilon(h + H)$. This prediction corresponds, for $\varepsilon = 0.5$, the experimental dependence $d(F)$ in the region $F > F_c$ (Fig. 1).

4. A nonlinear computer analysis [9] of the film DD model [6] showed that due to the DD instability a stationary hexagonal periodic DD structure is formed on an isotropic surface, which should determine the symmetry and perio-

dicity of the spatial arrangement of crystalline grains in the film.

To verify the prediction of a long-range hexagonal order in the grain arrangement, we performed the computer two-dimensional Fourier transform of the digitised image of the irradiated film morphology obtained with a transmission electron microscope (Fig. 2a). The smoothed amplitude $|F(k_x, k_y)|$ of the Fourier spectrum is shown in Fig. 2b. The most interesting feature of the spectrum is the presence of three pairs of intense maxima. Each of the pairs located symmetrically with respect to the centre of an ellipsoid on a line passing through its centre corresponds to a grating of the local surface brightness of the film image, i.e., to the grain grating. Therefore, the picture in Fig. 2a is formed by three groups of grain gratings with the wave vectors $\boldsymbol{q}$ that are approximately equal in modulus and are directed at certain angles to each other, which corresponds to the presence of the hidden long-range hexagonal order in the grain arrangement.

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