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THEORETICAL STUDY ON LASER ANNEALING OF NON-STOICHIOMETRIC SiO_X FILMS

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The mathematical modeling of temperature distribution in SiO_x film was carried out. The use of laser annealing in SiO_x films is shown to be advisable and multi-pulse annealing being more effective than single-pulse one. The maximum temperature after the laser pulse in the center of the laser beam does not depend on the distance between the laser beams at simultaneous annealing with several laser beams.

***Keywords**: silicon oxide, nanocrystal, laser annealing, thermoconductivity equation*

INTRODUCTION

Structures with silicon nano-particles (nc-Si means nano-crystallized silicon) that are grown inside SiO_2 draw researchers' attention from the point of view perspectives of creation of functionally new nano-electronic devices on their base. On the base of SiO_2/Si-nc/SiO_2/Si structures created by ion plating of silicon in SiO_2, light-emitting diodes (LED) are made and investigated successfully [1–4]. Similar structures are made using high-temperature annealing that improves SiO_x layers (x<2) as it described in [5, 6]. Last time, for creating structures with silicon nano-clusters a laser irradiation is used. With its help, crystalline silicon can be nano-structured, as well as laser annealing can be realized for non-stoichiometric SiO_x films [7–9].

The relatively larger amount of silicon than it is necessary for stoichiometric SiO_2 phases can causes the additional Si atoms and the formation of Si-nanoparticles. The rate of Si atoms migration in the dielectric matrix significantly affects the formation of boundary state between Si nano-particles and SiO_2, making possible the formation of multiple insertions of individual Si atoms in the SiO_2 matrix [10]. Thermal annealing of SiO_x films leads to the formation of nanoparticles of different chemical composition, namely with excess silicon in the film [11]. The formation of silicon phase is accompanied by restoration of the stoichiometry of surrounding oxide matrix. The annealing temperature determines the structure of nanoparticles [12].

High-temperature annealing in the furnace (above 1270 K) is the necessary process for the formation of nc-Si in SiO_x. Nevertheless, the processing of SiO_x film with the typical thermal annealing is not localized process and can lead during annealing to the destruction of the electronic circuits components that are on the same substrate. Only recently, for the formation of nc-Si in SiO_x film, the laser annealing was first used [13].

For efficient use of nanostructures in silicon electronics it is necessary to perform the comprehensive theoretical and experimental study of the laser annealing process of non-stoichiometric SiO_x films.

In this paper, advancement of temperature profiles is analyzed in a non-stoichiometric SiO_x film. Annealing was carried out in several modes: one-pulse regime, many-pulse regime and one-pulse regime, but simultaneously the two laser beams.

THEORY

In the capacity of a specimen studied SiO_x film is used with thickness 138 nm and stoichiometry index 0.8.

Distribution of temperature field on the solid body surface after heating with laser pulse can be described by equation [14]:

$$\rho c_p \frac{\partial T}{\partial t} - \nabla[k(T)\nabla T] = \alpha I_0(t)(1-R)\exp(-\alpha y), \tag{1}$$

where $\alpha = \frac{2\omega n_1}{c} = \frac{4\pi n_1}{\lambda} = \frac{1}{\delta}$, $I_0(t)$ is intensity distribution of laser beam, T is absolute temperature of the specimen, $\rho(T)$ is a density, $c_p(T)$ is a heat capacity at constant pressure, $k(T)$

is a coefficient of thermal conductivity, τ is a laser pulse duration, R is a surface reflectance, α is a surface absorption factor for laser irradiation, λ is a wave-length of laser radiation, n_1 is a damping factor, c is light velocity, ω is a cyclic frequency, δ is a depth of laser radiation penetration into the substance.

To find a temperature distribution in a solid body at any time, it is necessary to know this distribution at initial moment of time (starting condition), the body geometry, and the law of interaction between environment and the body surface (boundary conditions).

Boundary conditions on the upper and lower facet-edges are expressed by the third–kind condition characterizing convective heat transfer between the body surface and environment at constant heat flow. The condition can be used for analysis of heating or cooling bodies, taking Stephan-Boltzmann law into consideration. According to it, a heat flow between two media is [15]:

$$-n\cdot q = h\left(T - T_{amb}\right) + \sigma\sigma_{SB}\left(T^4 - T_{amb}^4\right), \qquad (2)$$

where σ is a coefficient of the surface emission, $\sigma_{SB} = 5.67\cdot 10^{-8}\,\frac{W}{m^2\cdot K^4}$ is Stephan-Boltzmann constant, n is a normal vector, h is a heat transfer coefficient, T_{amb} is an environment temperature. To express the energy flow unambiguously, it is necessary to assign a pulse character of the laser radiation in Gauss form (inner heat flow in Gauss form [W/m^2]:

$$I_0\left(t\right) = \frac{I_0}{\tau}\cdot e^{-\frac{4\left(t-\tau\right)^2}{\tau^2}} , \qquad (3)$$

where I_0 is the initial intensity of a single laser pulse.

On the specimen's vertical surfaces symmetric conditions of thermal insulation are to be set

$$\frac{\partial T}{\partial n} = 0 \,. \qquad (4)$$

The initial conditions are taken in form

$$T_0 = T_{amb} \,. \qquad (5)$$

The system of equations (1–5) describes a process of a single pulse laser annealing of SiO$_x$ film.

Non-stationary heat transfer equation for the problem investigated is solved numerically by FE -method.

When modeling multi-pulse annealing regime, the equation of heat transfer is solved first of all for one-pulse regime using equations (1–5). After that, the results obtained are taken as initial equations, and equations (1–5) are to be solved again, but with new initial conditions.

RESULTS AND DISCUSSION

Fig. 1 shows that rising laser irradiation intensity produces temperature growing. After laser pulse action completes (τ = 10 ns) the temperature on the surface grows some time after. Further on, a cooling of the film takes place because heat flows away from the film surface, and also transfers into the silicon wafer. After 30 ns from the start of annealing the temperature of the film surface becomes stabilized (Fig. 1). A level of stabilized temperature depends on a laser irradiation intensity: the more intensity, the higher temperature. Temperature of the specimen at high irradiation intensity is big enough for stimulating phase transitions of SiO$_x$ film into nano-composite film SiO$_2$(Si) with silicon nano-crystals [16–18]. Analysis of laser annealing influence on nano-crystalic silicon films produced in environment of inert gas argon [17] shows that one- and many-pulsed laser annealing improves crystallinity in films.

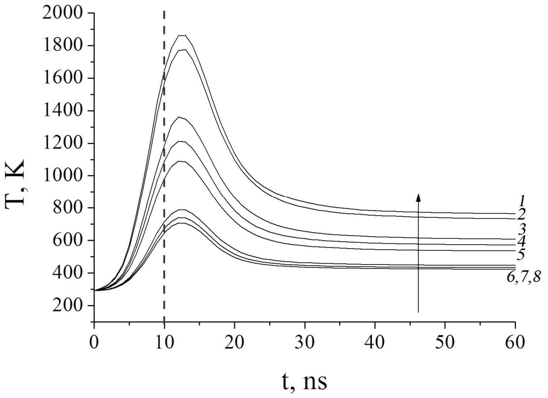


Fig. 1. Dependences of temperature on the specimen surface calculated on the basis of equation (1) versus time at various laser irradiation intensities (one pulse (duration 10 ns): 52, 49, 35, 31, 27, 17.2, 15.7 and 14.7 MW/cm^2 (*1–8*, respectively). Vertical dotted lines show a pulse prolongation

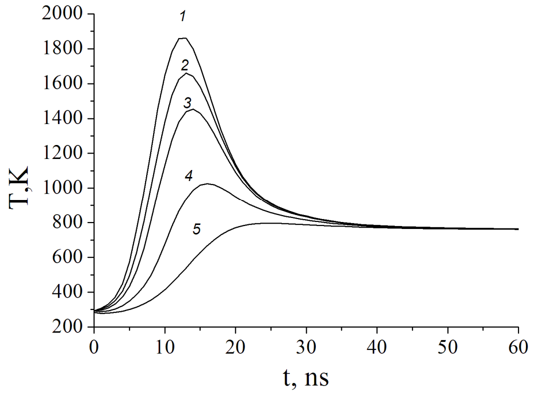


Fig. 2. Time dependences of the calculated temperature at different depths of the sample in the center of the laser beam: *1* – 0 nm, *2* – 18 nm, *3* – 38 nm, *4* – 80 nm, *5* – 138 nm. Laser pulse intensity is 52 MW/cm^2

The graphs of Fig. 2 show that maximum temperature is reduced with distance from the surface. But after 35 ns the temperature at each point becomes the same and doesn't change, indicating the establishment of thermodynamic equilibrium.

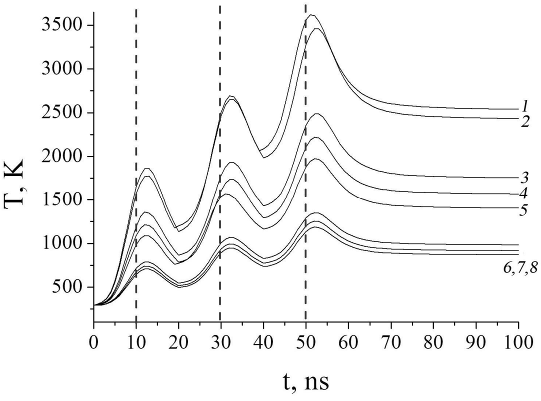


Fig. 3. Dependences of temperature on the specimen surface calculated on the basis of equation (1) versus time at various laser irradiation intensities (three pulses (10 ns duration, gap 10 ns between pulses): 52, 49, 35, 31, 27, 17.2, 15.7 and 14.7 MW/cm^2 (*1–8*, respectively). Vertical dotted lines show a pulse prolongation

One-pulse annealing can easily damage a film, but low energy density of some pulses can realize the annealing process without several damages. So, it is useful to investigate multipulse annealing regime at such films (Fig. 3). As it seen from Fig. 3, using multipulse regime can guarantee the temperatures needed on the specimen surface in process of annealing a SiO$_x$ film applying lower laser irradiation intensity. It makes possible to realize annealing without a specimen damage. It is shown in [14] that in case of annealing the film using one laser pulse with intensity 52 MW/cm^2 there are phase transfers in a non-stoichiometric SiO$_x$ film and decomposition of the SiO$_x$ film on stoichiometric phase SiO$_2$ with nano-particles Si, and the temperature on the specimen surface can reach 2000 K. When multipulse regime is used, the necessary annealing temperature can be reached using less intensive laser sources applying necessary quantity of pulses. In our case, for three pulses the intensity is equal to 27 MW/cm^2.

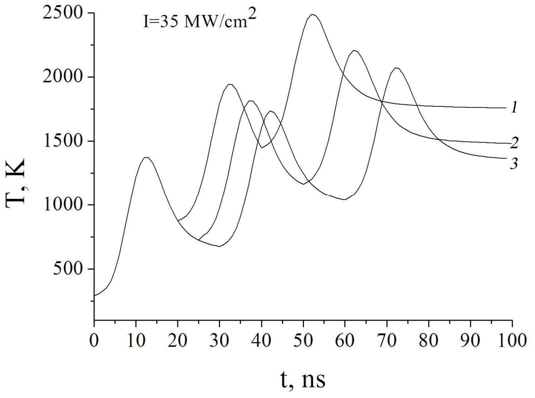
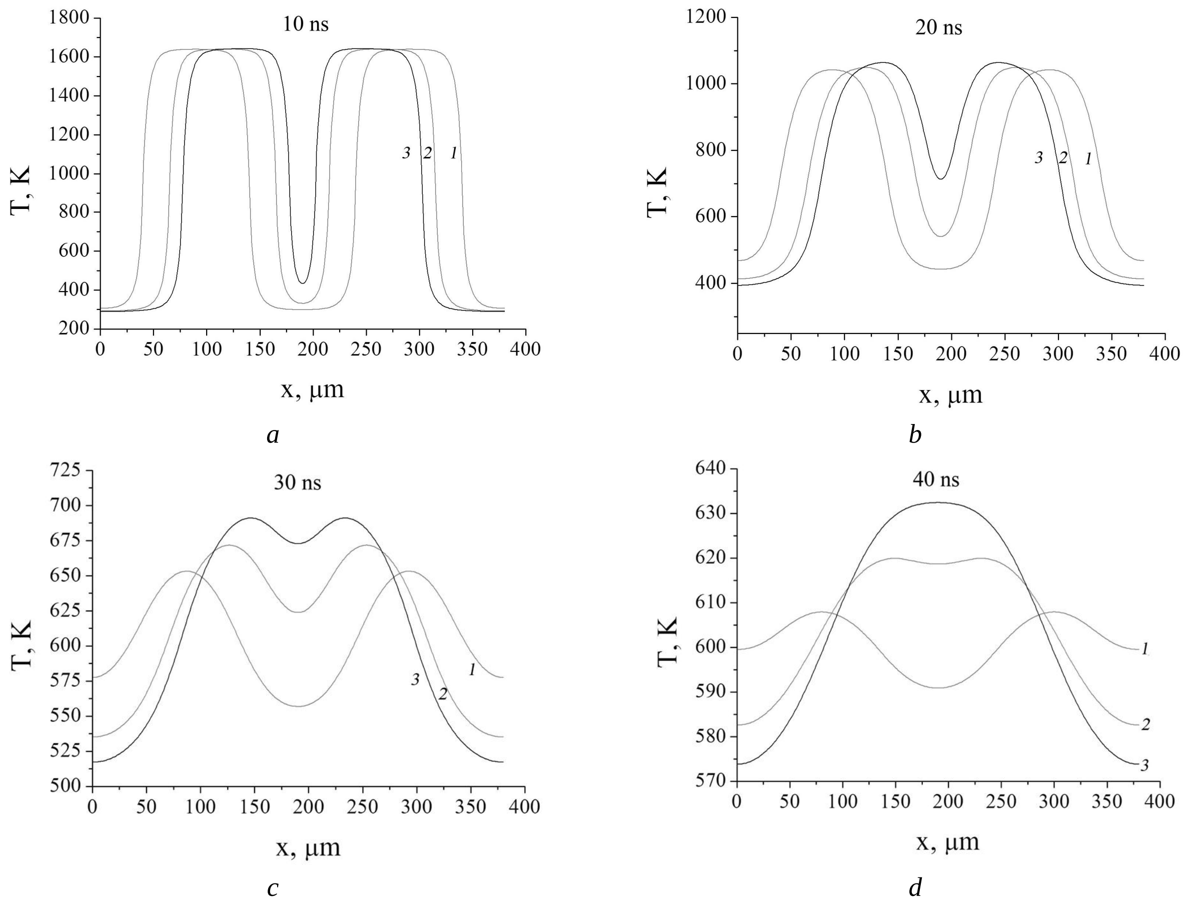


Fig. 4. Calculated temperature of the specimen surface in the centre of laser beam with intensity 35 MW/cm^2 versus different gaps between pulses (pulse time is 10 ns). Times between pulses are 10 ns (*1*), 15 ns (*2*), 20 ns (*3*) (three laser pulses)

As it seen from Fig. 4, changing gap value between pulses makes it possible to control temperature on the surface. As it was expected, with rose of time between pulses a temperature on the surface diminishes. So, the time between pulses appears to be one of parameters to corrugate temperature on the specimen surface.

The maximum temperature after the laser pulse in the center of the laser beam does not depend on the distance between the laser beams, which can be clearly seen in Fig. 5 *a*. When changing the distance between the laser beams, temperature changes in this region of the sample. Accordingly, the closer to each other are laser beams, the greater the surface temperature of the sample between the beams (Fig. 5). The temperature of the sample in the center of the laser beam at high intensity of laser irradiation is enough to stimulate the phase transition of SiO$_x$ film into nanocomposite SiO$_2$(Si) film with Si nanocrystals [14]. It was shown [17] that at the temperatures of 1470 and 1620 K the Si nanocrystals were formed during 1 s and 20 ms respectively.



a *b*

c *d*

Fig. 5. Dependences of the calculated surface temperature of the sample to the coordinate x for different distances between the laser radiation in the radiation intensity of 52 MW/cm^2 at different times: *a)* 10 ns, *b)* 20 ns, *c)* 30 ns, *d)* 40 ns. (*1* – 100 mµ, *2* – 50 mµ, *3* – 25 mµ)

Although the surface temperature of the sample between laser beams increases with decreasing distance between the beams but it is not enough to stimulate the phase transition of SiO_x film into nanocomposite SiO_2(Si) film with Si nanocrystals which agrees well with the experimental data obtained in [19]. As a result, silicon nanoparticles will be formed accurately at the positions of the peak intensity of the laser radiation.

CONCLUSIONS

The laser annealing can be used for the formation of Si nanocrystals in nonstoichiometric SiO_x film. Such annealing allows localizing the treatment process of the sample without destroying other items located on the same substrate with the film.

After laser annealing the sample bulk is heated but the temperature in the laser beam is higher compared to other parts of the sample that allows us to predict the formation of regions of silicon nanoparticles. One-pulse annealing can easily damage a film, but low energy density of some pulses can realize the annealing process without several damages, thus formed on the surface of the sample temperature needed for phase separation of SiO_x films into silicon oxide and silicon nanocrystals.

The maximum temperature after the laser pulse in the center of the laser beam does not depend on the distance between the laser beams. Silicon nanoparticles will be formed accurately at the positions of the peak intensity of the laser radiation.

Theoretical modeling makes it possible to select optimal parameters of laser annealing for the best partition of SiO_x film into SiO_2 and Si nanoparticles.

Теоретичне вивчення лазерного відпалу нестехіометричних плівок SiO_x

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Проведено математичне моделювання розподілу температури у плівці SiO_x. Показано, що доцільно використовувати лазер при відпалі плівок SiO_x, причому відпал декількома імпульсами ефективніший за одноімпульсний відпал. Максимальна температура, після завершення лазерного імпульсу, в центрі дії лазерного променя не залежить від відстані між лазерними променями при одночасному відпалі декількома лазерними променями.

Ключові слова: *оксид кременю, нанокристали, лазерний відпал, рівняння теплопровідності*

Теоретическое изучение лазерного отжига нестехиометрических пленок SiO_x

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Проведено математическое моделирование распределения температуры в пленке SiO_x. Показано, что целесообразно использовать лазер при отжиге пленок SiO_x, причем отжиг несколькими импульсами более эффективен чем одноимпульсный. Максимальная температура, после завершения лазерного импульса, в центре действия лазерного луча не зависит от расстояния между лазерными лучами при одновременном отжиге несколькими лазерными пучками.

Ключевые слова: *оксид кремения, нанокристаллы, лазерный отжиг, уравнения теплопроводности*

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