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Theoretical and Experimental Investigations of Laser Annealing Non-Stoichiometric SiO_x Films

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In this work, spreading of temperature profiles and influence of a temperature on forming silicon nanoparticles in non-stoichiometric SiO_x films after laser annealing is investigated. Using parabolic thermal conductivity equation, mathematical simulation of temperature profiles is realized in a non-stoichiometric SiO_x film after laser annealing. It is shown that temperature 1800 K on a SiO_x surface is sufficient for separating the film material on silicon dioxide and its nanoparticles. IR-investigations confirm this separating.

Keywords: silicon oxide, nanocrystal, laser annealing, thermal conductivity equation.

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Introduction

Last years, a need is aroused appreciably for elaborating physical foundations for creation of composite materials on silicon base [1, 2]. In particular, investigation begins of structures with nanoparticles of silicon brought up inside SiO_2 with attributes that make it possible to use them for creating new generation of opto-, micro-, and nano-electronic equipment facilities (light-emitting diodes, lasers, solar cells, memory elements, and so on).

As a result of a thermal annealing, non-stoichiometric SiO_x film becomes reconstructed into nano-composite film SiO_2(Si) containing Si nanoparticles. It means that a high-temperature annealing is necessary to form silicon nanoparticles inside SiO_x [3-5]. Treatment of SiO_x using thermal annealing appears to be not a local process; it can produce destruction of electronic schemes' components disposed on the same wafer. Some time ago, for creation of Si nanoparticles in the volume of the SiO_x film, laser annealing localized in the space began to use [6, 7]. Realization of this method is connected with difficulties of taking into account non-homogeneities of the temperature distribution in SiO_x film and with estimation of dimensions and density of nanoparticles created on different depths of the specimen. So, all-round investigation is stimulated of non-stoichiometric SiO_x films and processes taking place in them through interaction with a laser beam.

I. Theory

As a specimen studied, SiO_x film with the thickness 138 nm and the stoichiometry index 0.8 is used.

The distribution of temperature field on a solid body surface after the heating with a laser pulse can be described with a differential parabolic equation (Fourier equation) [8]:

$$\frac{\partial T}{\partial t} = \chi\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{1}{\rho c_p}\left(\frac{\partial Q}{\partial t}\right), \qquad (1)$$

where $\chi = \frac{k}{\rho c_p}$ is the temperature conductivity, T is the sample temperature, Q is the quantity of heat received by the specimen volume per square unit of the surface, r is the substance density, k is the coefficient of thermal conductivity, c_p is the heat capacity at constant pressure. For the problem analyzed, the equation may be expressed in form [9-11]:

$$\rho c_p \frac{\partial T}{\partial t} - \nabla[k(T)\nabla T] = \alpha I_0(t)(1-R)\exp(-\alpha y), \quad (2)$$

where $a = \frac{2wn}{c} = \frac{4p n_1}{l} = \frac{1}{d}$, $I_0(t)$ is the intensity distribution of a laser beam, T is the absolute temperature of the specimen, $r(T)$ is the density, $c_p(T)$ is the heat capacity at constant pressure, R is the surface reflectance, a is the absorption factor for surface under laser irradiation, l is the wave-length of laser radiation, n_1 is the extinction coefficient, c is the light velocity, w is the cyclic frequency, d is the depth of penetration of laser radiation into the substance.

To find the temperature distribution in a solid body at any time, it is necessary to know the distribution at initial moment of time (starting condition), the body geometry, and the law of interaction between the 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 a constant heat flow. Taking Stephan-Boltzmann law into consideration, the condition can be used for analysis of heating or cooling bodies. According to Stephan-Boltzmann law, a heat flow between two media is:

$$-n\cdot q = h\left(T - T_{amb}\right) + s\,s_{SB}\left(T^4 - T_{amb}^4\right), \qquad (3)$$

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

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

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

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

$$\frac{\partial T}{\partial n} = 0, \qquad (5)$$

The initial conditions are taken in form

$$T_0 = T_{amb}, \qquad (6)$$

The system of equations (2-6) 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 using finite element method.

When modelling multi-pulse annealing regime, the equation of heat transfer is solved first of all for a one-pulse regime using equations (2-6). After that, the results obtained are taken as initial equations, and equations (2-6) are solved again, this time with new initial conditions.

II. Experiment

Laser irradiation is used in this work to trace the process of a phase transformation and changes in the film properties.

On the first stage, the SiO_x (x < 2) film enriched by silicon is deposited on the wafer. Later, in time of a high-temperature annealing on the second stage, the SiO_x film is transformed into a nano-composite film SiO_2 (Si) that contains nano-crystals Si inside the dielectric film SiO_2.

The SiO_x films are deposited on n-type silicon wafer (ρ = 4.5 ohm×cm (100)) using an ion-plasma sputtering (IPS) method. The silicon target is sputtered by argon ions in the Ar + O_2 environment. The gas ratio during film deposition is Ar/O_2 = 5.25. Other deposition parameters are: pressure during deposition process P = 8×10^{-4} torr, substrate temperature T = 150 °C, heating cathode current I_C = 145 A, the anode voltage V_A = 50 V, the anode current I_A= 10 - 11 A, the voltage on the target V_T = 1.1 - 1.3 kV, deposition current I_S = 0.65 mA. The thickness of the deposited SiO_x films is ≈140 nm, and the stoichiometry indexes of the investigated initial SiO_x films are x = 0.80.

The laser irradiation is carried out at a room temperature and atmospheric pressure. The samples with the Si/SiO_x structures are irradiated on the SiO_x side using the fundamental (λ = 1064 nm, t = 15 ns) and the second harmonic (λ = 532 nm, t = 10 ns) frequencies of the YAG:Nd^{+3} laser in Q-modulation mode with the intensity in the range from 10 MW/cm^2 to 52 MW/cm^2. The SiO_x surface is irradiated by a single-mode focused laser beam with a computer-controlled scanning, with repetition frequency 25 Hz, and the adjustable degree of overlap of the laser spot, which is 0.3. The level of the laser beam intensity is governed by defocusing and/or by the neutral gray optical filters. The pulse laser energy and the duration are measured using conventional pulse energy meter and coaxial photo-element FC-19 with oscilloscope of C8-12, accordingly [11, 12].

IR- spectra of the films are measured in the diapason 800 - 1400 cm^{-1} using a Perkin – Elmer Furier-spectrometer Spectrum BX. Separation of a silicon phase is accompanied by renewal of a surrounded oxide matrix stoichiometry that can be successfully tracked using methods IR – spectrometry for fixing vibration frequency changes of atomic connections Si–O.

Minimum intensity of the IR spectrum position for SiO moves steadily from 980 cm^{-1} to high-frequency region when the contention of oxygen in the oxide composition rises. This wave range appears to be typical for Si–O valence bonds. Taking into consideration that in this region of IR – spectra only vibrations of silicon-oxygen phases are revealed, and presence of Si–Si connections is not registered, the method given can be used for determination of an oxide matrix composition in resulting as well us in annealed specimens containing a silicon phase.

III. Results and discussion

The temperature of annealing determines a closing structural condition of Si inclusions. In case of annealing absence, there is a great quantity of atoms with Si–Si connection which in case of rising temperature unite in

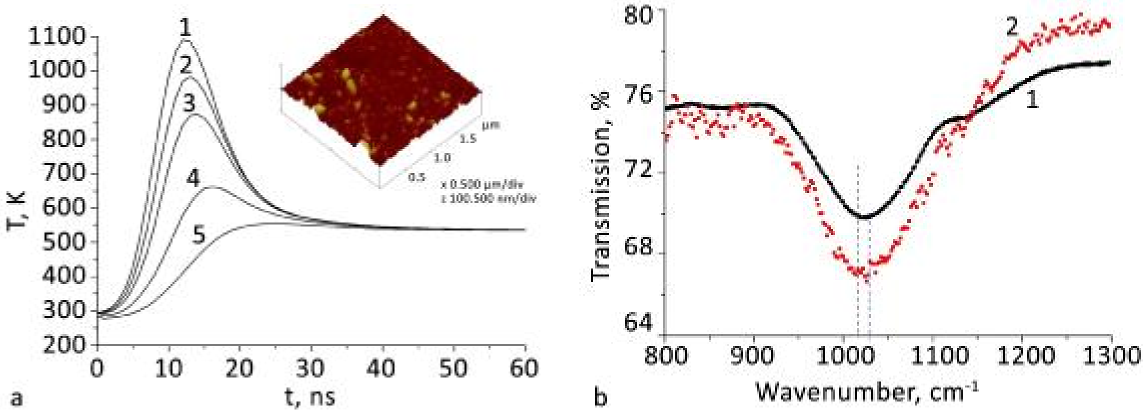

Fig. 1. (a) Distribution of calculated temperature on different depths of a SiO_x film (x = 0.8) in the centre of a laser beam activity (*1* – 0 nm; *2* – 18; *3* – 38; *4* – 80; *5* – 138 nm; on the inset, AFM – image is presented of the film surface after laser annealing); (b) IR-spectra before the laser annealing (1) and after laser annealing SiO_x film (I = 27 MW/cm^2, λ = 532 nm).

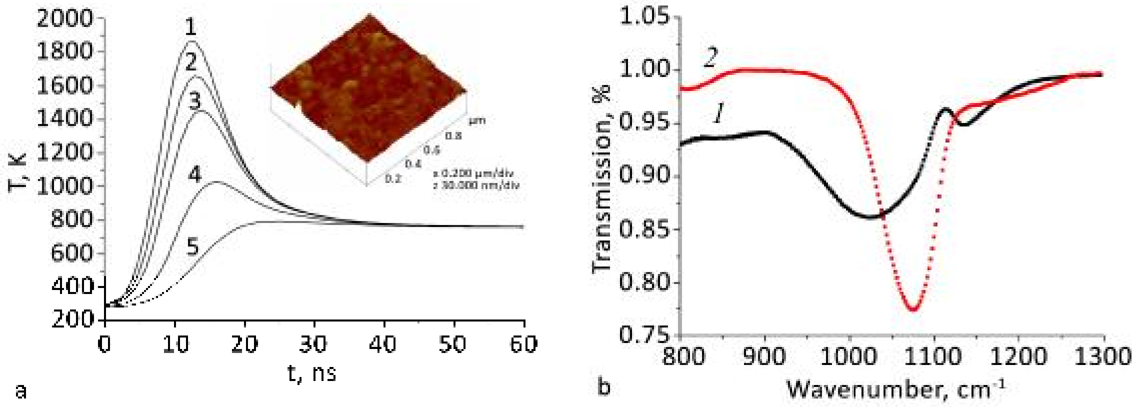

Fig.2. (a) Distribution of calculated temperature on different depths of a SiO_x film (x=0.8) in the centre of a laser beam activity (*1* – 0 nm; *2* – 18; *3* – 38; *4* – 80; *5* – 138 nm; on the inset, AFM – image is presented of the film surface after laser annealing); (b) IR-spectra before the laser annealing (1) and after laser annealing SiO_x film (I = 52 MW/cm^2, λ = 532 nm).

chains, rings composed from Si atoms, and in scattered fractal-like compositions. Such inclusions are called "non-phase" ones, because the clear border of dividing phases is absent. Compact phase inclusions-clusters of amorphous Si are formed at temperatures over 900 K and are crystallized at temperatures over 1300 K.

Dependence of temperature distribution from time in the centre of laser beam on different depths is shown in Fig. 1, a, 2, a. This dependence keeps its resemblance on different depths, but the temperature maximum diminishes with the remoteness from the surface.

In IR –spectra with stoichiometry index x = 0.8 after laser annealing SiO_x films with laser beam intensity 27 MW/cm^2 it is not observed a displacement of the minimum position (n_{M1}= 1026 cm^{-1}) into high-frequency region, but intensity of absorption band decreases (Fig. 1, b). Such a nature of IR-spectrum changes points on insufficient transformation of the oxide matrix. It corresponds well with theoretic calculations (fig. 1, a) of a temperature distribution through the SiO_x film depth being evidence that the temperature on a depth more then 80 nm at such intensity of laser irradiation is insufficient for transformation SiO_x film into a nano-composite film with silicon nanoparticles.

To transform a SiO_x film into nano-composite SiO_2(Si) film, it is necessary to use a laser irradiation with a greater intensity. After annealing the film with using a laser of higher intensity, minimum of IR-spectrum makes higher, and it moves to the higher frequency region (Fig. 2, b).

Location of the minimum in diapason 1050–1100 cm^{-1} is typical for stoichiometric films SiO_2. Such a shift of an intensity minimum in direction of high-frequency region shows on a phase separation and transformation of the SiO_x film substance into a SiO_2 film with silicon nano-cristals. The results adjust satisfactorily with the theoretical calculations (Fig. 2, a), that appears to be an evidence that at intensity 52 MW/cm^2 the temperature of SiO_x film rised through all its depth for transforming a SiO_2 film into nano-composite film SiO_2(Si). As a result of the transformation, the structure and properties of the film were changed appreciably.

Using this result, assumption can be done that at big intensities of laser annealing crystallized particles will be created on the depth up to 50 – 80 nm where the temperature is sufficient for creation of silicon crystallized nanoparticles, but on greater depths 80 – 100 nm amorphous nanoparticles of silicon can be created. The temperature 800 K [10] is sufficient to produce them.

Conclusion

Laser annealing can be used for settling the Si nano-crystals in non-stoichiometric SiO_x film, which makes it possible to realize the localized processing of a specimen without destroying other elements deposited on the same wafer with the annealed film.

At the low intensity of laser annealing (10 - 25 MW/cm^2) non-stoichiometric SiO_x film, displacement of the minimum position of IR –spectrum into the high-frequency region is not fixed, but the value or its depth roses. Such a character of changing IR-spectrum shows on insufficient transformation of an oxide matrix. It corresponds well to theoretic analysis of temperature distribution through the SiO_x film depth which shows that a temperature in the volume at the given laser irradiation intensity is insufficient for transformation of SiO_x film into a nano-composite film with silicon particles. To reach a full transformation of SiO_x film with the thickness 138 nm into nano-composite film SiO_2(Si) with silicon nanoparticles, it is necessary to radiate it with laser beam of higher intensity.

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Теоретичні та експериментальні дослідження лазерного відпалу нестехіометричних плівок SiO_x

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В даній роботі було досліджено розповсюдження температурних профілів та вплив температури на формування наночастинок кремнію в нестехіометричних плівках SiO_x після лазерного відпалу. З залученням параболічного рівняння теплопровідності було проведено математичне моделювання формування температурних профілів в нестехіометричній плівці SiO_x після лазерного відпалу. Показано, що температура 1800 К на поверхні SiO_x достатня для розділення речовини плівки на діоксид кремнію і його наночастинки. ІЧ-дослідження підтвердили таке розмежування.