Title: Nanostructural Transformation in Thin SiOₓ Layers Induced by Pulsed Laser Radiation

[1] Organization (10.5 points)
Project Leader: Leading Science Researcher
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[2] Research Progress (10.5 points)

Thin-film structures based on semiconductor and metallic oxides layers attract attention of researchers due to the possibility of their transformation into nanocomposite layers, containing single-crystalline nanoparticles. Nanocomposites layers are widely applied in advanced electronic and optoelectronic devices (light emitting diodes, single-electron transistors, resonant-tunnel diodes, memory cells, etc.). In this regard, the importance of studying the transformation of the amorphous - crystalline phase processes are greatly increased. In particular, this refers such structures with TiOₓ[1], and SiOₓ layers [2]. The latter are of interest both in terms of increasing the absorption coefficient and possible absorption spectral transformation to increase the efficiency of the solar energy converters [3], and also to improve of the sensoric sensitivity characteristics. All the well known developed methods of thin SiOₓ films formation make possible to realize the required index of stoichiometry x. As it was find in [4] x is determined from next relation: \( y \cdot \text{SiO}_x \rightarrow x \cdot \text{SiO}_y \cdot (y-x) \cdot \text{Si} \), where \( y \geq x \), and SiOₓ will be evidently consisted of SiO₂ and SiOₓ. Following SiO₂ decomposition with formation of Si nanoparticles in SiOₓ matrix is needed the next technology step – annealing of the structure. The contribution relation of the amorphous and single crystalline phases of the annealed structure depends on the temperature: annealing below 1000 °C favors an aggregation of Si atoms into amorphous clusters, at higher temperature silicon nanocrystals are formed. Traditionally used isothermal annealing improves the structure and modifying their properties. There are experiments using rapid annealing [5], which speeds up the process, but does not solve the problem of excluding the effect of the adjacent substrate layers or multilayer structure at temperatures of 950 °C – 1150 °C, especially if it consists of ultrathin layers. Moreover, the transformation of the amorphous phase into crystalline NPs in those technique modes is mainly due to the film melting. This mode does not provide a many cases, the more effective method of modifying the properties of films can be adiabatic laser annealing [6, 7]. This allows to control the heat level of the local area before the melting threshold, including not full but partial melting, limiting the melting of the inclusions only. However, there are not many papers that would detail the mechanisms of transformation of oxide films under the action of laser pulses. Therefore, the main purpose of our work was to study the structural transformations of SiOₓ films that occur under the influence of nanosecond laser pulses, depending on the radiation energy density and its wavelength, and to study the possibility of controlled influence on the SiOₓ inclusions, structural and topography properties.

In this study, the effect of laser-assisted phase transformation of the SiOₓ films from amorphous to crystalline were investigated with aim to show the possibility of transition from non-stoichiometry SiOₓ to nanocomposite layer contained the Si crystals in the SiOₓ matrix. AFM, FESEM images, Raman and IR spectra were used for determine the phase state changes before and after laser action. The SiOₓ / Si structures were irradiated by base frequency \( \lambda = 1064 \) nm and second harmonic, \( \lambda = 532 \) nm of Nd:YAG laser with pulse duration \( t = 10 \) ns, at intensity range up to \( I = 114.0 \) MW/cm².

[3] Results (10.5 points)
(3 - 1) Research results

We had to elaborate laser technology phase transition SiOₓ thin film in the structure of SiOₓ / Si nanoparticles with controlled crystallinity of the SiOₓ film.
This work is connected with medicine, biology and physics.

Samples preparation
Silicon enriched SiO$_2$ films were deposited on n-type Si substrate ($p = 0.01 \Omega\cdot cm$) by Low Pressure Chemical Vapor Deposition (LP CVD) method at the temperature of 660 °C. The samples were irradiated in ambient air atmosphere.

Results and discussion

![Image of SiO$_2$ film](image)

Fig. 1. AFM images of SiO$_2$ film before (a) and after (b, c) - laser irradiation: a) topography, b) phase, $\lambda = 0.532 \mu m$, $\tau_p=10$ ns, $I = 31$ MW/cm$^2$.

For the case of the action on the SiO$_2$ / Si structures by pulses with $\lambda_1 = 1.064 \mu m$, topography changes on its surface began at $I = 14$ MW/cm$^2$, and under the action of pulses with $\lambda_2 = 0.532 \mu m$, already at $I = 7$ MW/cm$^2$, Fig.1. In addition, for different wavelengths, the thresholds for visually detected damages also significantly differed: $L_1 = 114$ MW/cm$^2$ and $L_2 = 54$ MW/cm$^2$.

This is due to the large difference between the absorption coefficients in Si ($\alpha_1 = 10$ cm$^{-1}$, $\alpha_2 = 10^4$ cm$^{-1}$) for two laser wavelengths ($\lambda_1 = 1.064 \mu m$, $\lambda_2 = 0.532 \mu m$), respectively, at not very high levels of radiation intensity. The nanoparticle sizes were increasing from 6 to 65 nm at the variation of laser pulses intensity from 1 to 114 MW/cm$^2$ with $\lambda_1 = 1.064 \mu m$, and to 35 nm with $\lambda_2 = 0.532 \mu m$. The AFM image topography of the SiO$_2$ film surface are confirmed by the FESEM data (Fig. 2). It could be seen from FESEM images that the average size of Si nanoparticles on the SiO$_2$ surface after laser action at $\lambda_2 = 0.532$

![Image of SiO$_2$ film](image)

Fig. 2. SEM image of SiO$_2$ film irradiated by pulses of Nd$^3$; YAG – laser, $\tau_p=10$ ns, $\lambda = 0.532 \mu m$, $I = 31$ MW/cm$^2$ $\mu m$, intensity $I = 31$ was about $d = 40$ nm that close to the data from AFM average image $d = 35$ nm.

Raman spectra of SiO$_2$ films on the silicon substrate are shown in Fig. 3 before, curve 1 and after, curves 2-5, laser processing with different power density. An intensive band from a silicon substrate with a frequency of $\approx 520$ cm$^{-1}$ [8] appears in all spectra. At the same time on the spectrum with the SiO$_2$ initial film, in addition to the aforementioned band from the silicon substrate, a low frequency shoulder appears due to the contribution to the spectrum of amorphous silicon clusters and Si nanocrystals with dimensions smaller than 10 nm [9]. Raman strips that coincide with the frequency band of bulk silicon are inherent to nanocrystals with dimensions of $\approx 10$ nm or more. To estimate the average sizes of nanocrystals, the experimental Raman spectrum was divided into three components: a broad band of amorphous Si with a maximum of $\approx 475$ cm$^{-1}$, a band of silicon nanocrystals described by an asymmetric curve and a band in the form of symmetric Lorentzian, from a silicon substrate (Fig. 3b). The parameters that varied during the fitting of the simulated spectrum to the experimental one were the frequency of the asymmetric band, its asymmetry and its half-width. All these values are related to each other and correlate with the average size of nanocrystals, the experimental Raman spectra were divided into three components: a broad band of amorphous Si with a maximum of $\approx 475$ cm$^{-1}$, a band of silicon nanocrystals described by an asymmetric curve [9] and a band in the form of symmetric Lorentzian, from a silicon substrate (Fig. 3b). The parameters that varied during the fitting of the simulated spectrum to the experimental allows us to estimate them. The results of Raman spectra are in good agreement with the deconvolution of the IR spectra data of optical density obtained in our previous study [10], where the coefficient of non-stoichiometry $x$ was changing in the range from 0.98 to 1.75 with increase of the laser intensity up to 100 MW/cm$^2$.

At this place could be inserted part of EPR and XRD results
SiO₂ film when the threshold of melting is exceeded. Since the melting temperature for Si NPs with \( d > 6 \text{ nm} \) is approximately the same as for Si, and the temperature of laser heating (\( t_0 = 10 \text{ ns} \), \( \lambda = 0.532 \text{ microns} \)) at \( I = 12 \text{ MW/cm}^2 \) does not exceed \( T = 800 \text{ K} \), then the role of the second factor can be significant only for the smallest NPs with \( d < 3 \text{ nm} \), which is inherent in the initial state of the SiO₂ film.

The dissociation energy for the Si-Si and Si-O bonds is 3.29 and 8.26 eV, respectively, which causes in the first place the breaking of Si-Si atoms interconnections bonds. Since, under the action of laser pulses with \( \lambda = 532 \text{ nm} \) on SiO₂ film, the depth of its heating (\( L_0 \)) is \( L_0 = 10^{-4} \text{ cm} \), the temperature gradient \( dT/dx \) can reach \( dT/dx \sim 10^5 \text{°C/cm} \). This ensures the effect of the laser thermal shock [11]. These processes explain the structural transformation of SiOₓ film into nanocomposite one containing Si nanocluster.

**Conclusions**

The possibility of laser-induced nanostructural transformation of non-stoichiometric thin SiOₓ-amorphous films containing Si NPs with initial averaging values of \( d \leq 6 \text{ nm} \) in a SiO₂-like nanocomposite layer with increased NPs sizes, \( d \sim 35 \text{ nm} \) was shown based on the analysis of AFM images, Raman spectra, SEM, and X-ray energy dispersive spectra (EDS).

The physical model that explains the increase in the size of Si NC in thin SiO₂ films due to two mechanisms has been proposed:

a) as a result of the LTS effect, when laser pulses act on SiO₂ film, breaking the bonds in the SiO₂ grid occurs with subsequent redistribution of Si atoms, their attachment to the nucleuses of existing silicon nanocrystals, or agglomeration of them in new NPs in case of exceeding their limit of solid phase solubility (before the melting threshold);

b) the partial recrystallization of silicon NPs occurs when laser pulses act on SiO₂ film, with exceeding of the melting threshold. This applies, first, to the smallest size of NPs, which merge and form the NPs with larger sizes in the process of sharp cooling at the end of the laser pulse.

The possibility of regulated influence on the structural and morphological properties of SiO₂ films in order to obtain the required characteristics has been demonstrated.

Before submitting the manuscript text to the high-ranking edition, comprehensive additional arguments in favor of increasing the Si crystalline phase in the SiO₂ film will be added from the EPR and XRD data shortly.

(3-2) Ripple effects and further developments

Exchange of scientific expertise between the participants was very helpful for coordination of experimental work towards the goal of this project. Also,
it has contributed to strengthening of domestic and international collaboration at Research Institute of Electronics. Joint work and discussions between the participants of this project have broadened the scope of existing domestic and international research collaborations at RIE, as well as opened new venues for collaboration in the future.

(2)
Traveling Report (Mention each travel by CRP budget.)

Name: Prof. Leonid L. Fedorenko
Affiliation: V. Lashkaryov Institute of the Semiconductor Physics NAS of Ukraine
Destination: Shizuoka University, Japan
Purpose: To carry out a joint research, plan the future collaboration, participate at the workshop and report previously obtained results.
Name of receiver: Prof. Hidenori Mimura

1. A. K. Al-Kamal, Synthesis of Ag-doped TiO2 NPs by Combining Laser Decomposition of Titanium Isopropoxide and Ablation of Ag For Dye-Sensitized Solar Cells. Thesis Submitted to the Graduate School-New Brunswick Rutgers. The State University of New Jersey. 2015. 42P.


