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Structural Rearrangement of $a\text{-SiO}_x\text{:H}$ Films with Pulse Photon Annealing

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Abstract

Amorphous SiO_x films with silicon nanoclusters are a new interesting material from the standpoint of the physics, technology, and possible practical applications, since such films can exhibit photoluminescence due to size quantization. Moreover, the optical properties of these structures can be controlled by varying the size and the content of silicon nanoclusters in the SiO_x film, as well as by transforming nanoclusters into nanocrystals by means of high-temperature annealing. However, during the annealing of nonstoichiometric silicon oxide, significant changes can occur in the phase composition and the structure of the films. The results of investigations on the crystallization of silicon nanoclusters in a SiO_x matrix have shown that, even a very fast method of annealing using PPA leads to the formation of large silicon crystallites. This also causes the crystallization of at least a part of the oxide phase in the form of silicon hydroxide $\text{H}_6\text{O}_7\text{Si}_2$. Moreover, in films with an initial content of pure silicon nanoclusters $\leq 50\%$, during annealing a part of the silicon is spent on the formation of oxide, and part of it is spent on the formation of silicon crystals. While in a film with an initial concentration of silicon nanoclusters $\geq 53\%$, on the contrary, upon annealing, there occurs a partial transition of silicon from the oxide phase to the growth of Si crystals.

Keywords: silicon nanoclusters, silicon nanocrystals, silicon suboxides, pulse photon annealing, PPA, ultrasoft X-ray emission spectroscopy, USXES.

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1. Introduction

Dielectric SiO_2 , Si_3N_4 , and Al_2O_3 films with nanoclusters and silicon nanocrystals are of great interest as, due to size quantization, such films can exhibit photo- and electroluminescence. Moreover, if low-temperature processes (such as ion-plasma, plasma-chemical, etc.) are used to create a silicon structure, it is possible to form [1–4] amorphous $a\text{-SiO}_x\text{:H}$ films with nanoclusters (*ncl*-Si), whose size will determine the luminescence region. In case of high-temperature processes at $T \geq 1000$ °C, as this occurs during radiation annealing of ion-implanted samples with large doses of silicon [5] or during annealing of non-stoichiometric oxides [5–8] it is possible to form silicon nanocrystals in the dielectric film matrix. The size and concentration of nanocrystals will also determine the luminescent properties of these films [9–11].

It was shown in [1,3,4] that by using the modulated plasma of a DC-magnetron in a chamber containing 80 % Ar + 20 % SiH_4 , it is possible to set the number of *ncl*-Si nanoclusters in amorphous $a\text{-SiO}_x\text{:H}$ films over a wide range, and thus it is easy to control the optical properties of the films. Therefore, it can be interesting to transform amorphous $a\text{-SiO}_x$ films with nanoclusters into films with silicon nanocrystals by high-temperature annealing. However, during the high-temperature annealing of SiO_x films, silicon is reduced from nonstoichiometric oxide [8]. The appearance of excess Si in the $a\text{-SiO}_x$ + *ncl*-Si film will lead to an increase in the size of the nanocrystals as a result of their coalescence and due to photoluminescence quenching. Therefore, this work proposes to carry out short-term pulse photon annealing of $a\text{-SiO}_x$ films with silicon nanoclusters to form small-sized silicon nanocrystals (*nc*-Si).

2. Experiment

This work involved studying samples of $a\text{-SiO}_x\text{:H}$ + *ncl*-Si films (400 nm in thickness) of three compositions with a silicon nanoclusters content of about 15, 50, and 53%. The studied films were grown using modulated DC-magnetron plasma at the temperature of Si (100) substrate $T_s = 265$ °C. A mixture of 80% Ar + 20 % SiH_4 with added oxygen ~15.5 mol % was used as a plasma-forming gas [4]. These samples were annealed in

vacuum (10^{-5} Torr) using pulsed photon annealing (PPA) [12]. The PPA was performed using the UOLP-1M irradiation system containing three gas discharge xenon lamps with a working wavelength range of $\lambda = 0.2\text{--}1.2$ μm and operating in the pulse mode with the duration of the pulses being 10^{-2} s. The samples were annealed from the side of the silicon substrate, since the optical radiation of a xenon lamp passes through the SiO_x layer almost without absorption, and all the energy is absorbed in the silicon substrate. This can lead to the SiO_x film snapping due to the high stresses arising at the SiO_x film – Si substrate interface.

The study of the possibility to form silicon nanocrystals was carried out by X-ray diffraction (XRD) using a PANalytical Empyrean B.V. diffractometer with monochromatic $\text{Cu } K_{\alpha 1}$ radiation (Centre for Collective Use of Scientific Equipment of VSU). In addition, to simultaneously control both crystalline and amorphous phases based on silicon, the films were analysed by Ultrasoft X-ray Emission Spectroscopy (USXES) using a RSM-500 spectrometer [13, 14]. In this case, the film was irradiated with fast electrons (energy of 3 keV, which corresponds to an analysis depth of 60 nm [15]), and the characteristic Si $L_{2,3}$ X-ray radiation arising from electron transitions from the valence band to a vacancy at the Si $2p$ core level was analysed. As a result, we obtain information about the energy distribution of valence electrons throughout the valence band. Thus, USXES allows detecting the presence of Si-Si or Si-O bonds, regardless of the ordering degree of the film's atomic structure [13–16].

3. Results and discussion

3.1. XRD investigations

Fig. 1 shows the diffraction patterns of $a\text{-SiO}_x\text{:H}$ films annealed using PPA with two doses of $140 \text{ J/cm}^2 + 180 \text{ J/cm}^2$. Annealing at 140 J/cm^2 did not lead to crystallization of particles in the film. Additional annealing at 180 J/cm^2 led to the appearance of two reflections of the crystalline phases at $2\theta = 23.94^\circ$ and 28.9° . The reflection at 28.9° corresponds to d -spacing with $d = 3.13$ Å, and at 23.94° to d -spacing with $d = 3.71$ Å. A search in the international database of crystallographic data [17] showed that the plane with $d = 3.13$ Å can be easily attributed to crystalline silicon and the appearance of this reflection is associated with

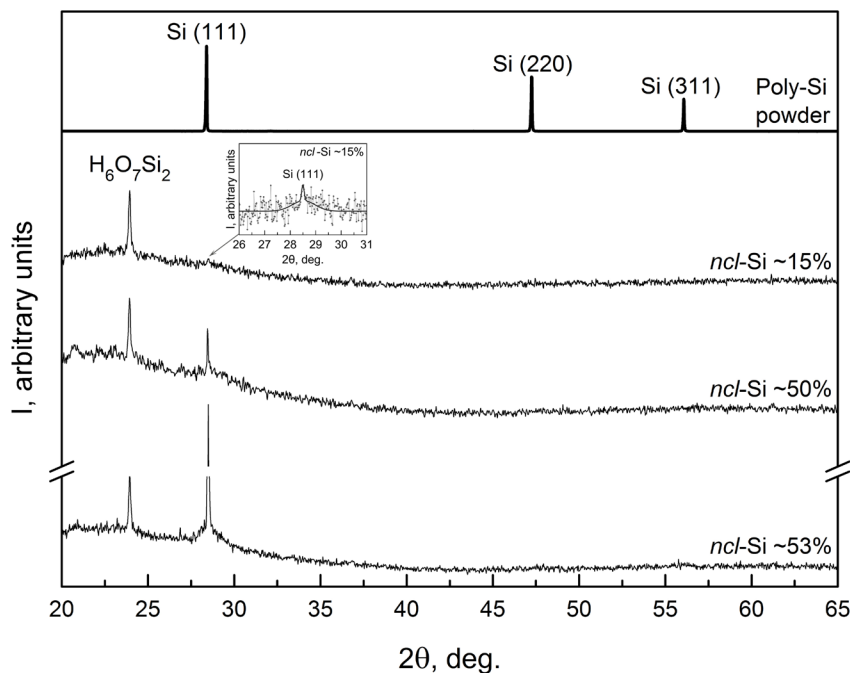


Fig. 1. XRD patterns of poly-Si powder and $a\text{-SiO}_x\text{:H}$ samples with a $ncl\text{-Si}$ content of about 15 %, 50 %, and 53 % after PPA 140+180 J/cm²

the crystallization of silicon nanoclusters. While the reflection with $d = 3.71 \text{ \AA}$ can be explained by the formation of the silicon hydroxide $\text{H}_6\text{O}_7\text{Si}_2$ (Fig. 1) [18]. The formation of $\text{H}_6\text{O}_7\text{Si}_2$ hydroxide upon annealing can be explained by the fact that the initial $a\text{-SiO}_x\text{:H}$ films obtained in the magnetron plasma contain a large amount of hydrogen, which when heated easily reacts with SiO_x radicals.

A comparative analysis of the XRD patterns of samples with different silicon nanoclusters contents (from ~ 15 to 53 %) revealed that the changes in the diffraction pattern were of an expected character (Fig. 1). In the film with a content of silicon nanoclusters ~ 15 %, the most intense reflection is due to silicon hydroxide

$\text{H}_6\text{O}_7\text{Si}_2$, while the reflection from $c\text{-Si}$ is rather weak (Fig. 1). In the sample with a nanocluster content of about 50 %, the intensity of the silicon ($c\text{-Si}$) reflection Si (111) sharply increased. However, the intensity of the hydroxide reflection remained slightly higher. In the sample with the maximum concentration of silicon clusters (53 %), the $c\text{-Si}$ reflection became predominant after annealing (Fig. 1). Thus, an increase in the concentration of silicon nanoclusters in the initial SiO_x film upon PPA leads to an increase in the $c\text{-Si}$ content so that the Si (111) reflection intensity increases by an order of magnitude (Table 1).

However, a sharp increase in the phase of crystalline silicon cannot be explained only by an increase in the concentration of silicon

Table 1. Position and intensity of reflections in XRD patterns of $a\text{-SiO}_x$ films with different $ncl\text{-Si}$ content

Sample	Phase assignment	XRD line position 2θ , deg.	d -spacing, \AA	Intensity, cts	Rel. intensity, %
$ncl\text{-Si}$ 15 %	$\text{H}_6\text{O}_7\text{Si}_2$	23.9366	3.71461	396	100.00
	Si(111)	28.4907	3.13035	45	11.52
$ncl\text{-Si}$ 50 %	$\text{H}_6\text{O}_7\text{Si}_2$	23.9323	3.71525	282	100.00
	Si(111)	28.4663	3.13297	222	78.84
$ncl\text{-Si}$ 53 %	$\text{H}_6\text{O}_7\text{Si}_2$	23.9406	3.71399	331	9.47
	Si(111)	28.4924	3.13016	3496	100.00
Poly-Si powder (reference)	Si(111)	28.4020	3.1399	23365	100.00
	Si(220)	47.2600	1.922	14749	63.12
	Si(311)	56.081	1.6386	8159	34.92

nanoclusters in the initial film, since this increase is not large (50 % \rightarrow 53 %). Therefore, we carried out further studies to estimate the content of not only crystalline, but also amorphous silicon phases in these films by the USXES method [13–16].

3.2. Ultrasoft X-ray Emission Spectroscopy

Fig. 2 shows the X-ray emission Si $L_{2,3}$ -spectra of the films before (a) and after (b) PPA, obtained at an analysis depth of 60 nm (experimental spectra are shown by dots, spectra simulated using reference spectra are shown by a solid line). While Fig. 3 shows the reference Si $L_{2,3}$ -spectra of the $c\text{-Si}$, $a\text{-Si}$, $\text{SiO}_{1.3}$, $\text{SiO}_{1.7}$ and SiO_2 . The Si $L_{2,3}$ -spectra of $\text{SiO}_{1.3}$ and $\text{SiO}_{1.7}$ suboxides were obtained in [14]. As can be seen from Fig. 2, the spectra of the initial and annealed films clearly differ in the contribution to the fine structure components due to the presence of Si-O bonds (peaks at 89.5 eV and 94.5 eV), as well as Si-Si bonds (peaks at 92 eV and 89.6 eV) (Fig. 2). In the annealed film with a minimum initial amount of silicon \sim 15 %, the spectrum is close to that of pure SiO_2 (Figs. 2 and 3). A comparison with the spectrum of the initial film (Fig. 2a) indicated a decrease in the intensity in the region of 92 eV, i.e. in the region of the main maximum of the spectrum in $c\text{-Si}$, which indicates a decrease in the content of elemental silicon in the film

after annealing. In addition, an analysis of the films phase composition by modelling the Si $L_{2,3}$ -spectra (Table 2) did not detect crystalline silicon (with a precision of \sim 5 %), which was expected from the shape of the Si $L_{2,3}$ -spectrum of annealed SiO_x film ($ncl\text{-Si} \sim$ 15 %). At the same time, X-ray diffraction revealed a low amount of Si crystals in the SiO_2 film (Fig. 1). In the sample with a high Si initial content (\sim 50 %), if compared to the initial amorphous film (Figs. 2a and 2b), annealing also leads to a decrease in the fine structure intensity due to elemental Si, i.e. to a decrease in the silicon phase content in the composite film.

At the same time, in the film with a maximum content of silicon nanoclusters (\sim 53 %), annealing led to changes of different character in the ratio of oxide phases to elemental silicon. Namely, the main maximum (at 92 eV) in the Si $L_{2,3}$ -spectrum of annealed film was formed by $c\text{-Si}$ (Fig. 2a) and the oxide phase content decreased. Phase composition analysis by means of computer simulation of the spectra (the simulated spectra are shown in Fig. 3a and 3b with a solid line) and its results shown in Table 2 confirm our qualitative reasoning.

These results explain the unusual sharp increase in the intensity of silicon reflection after

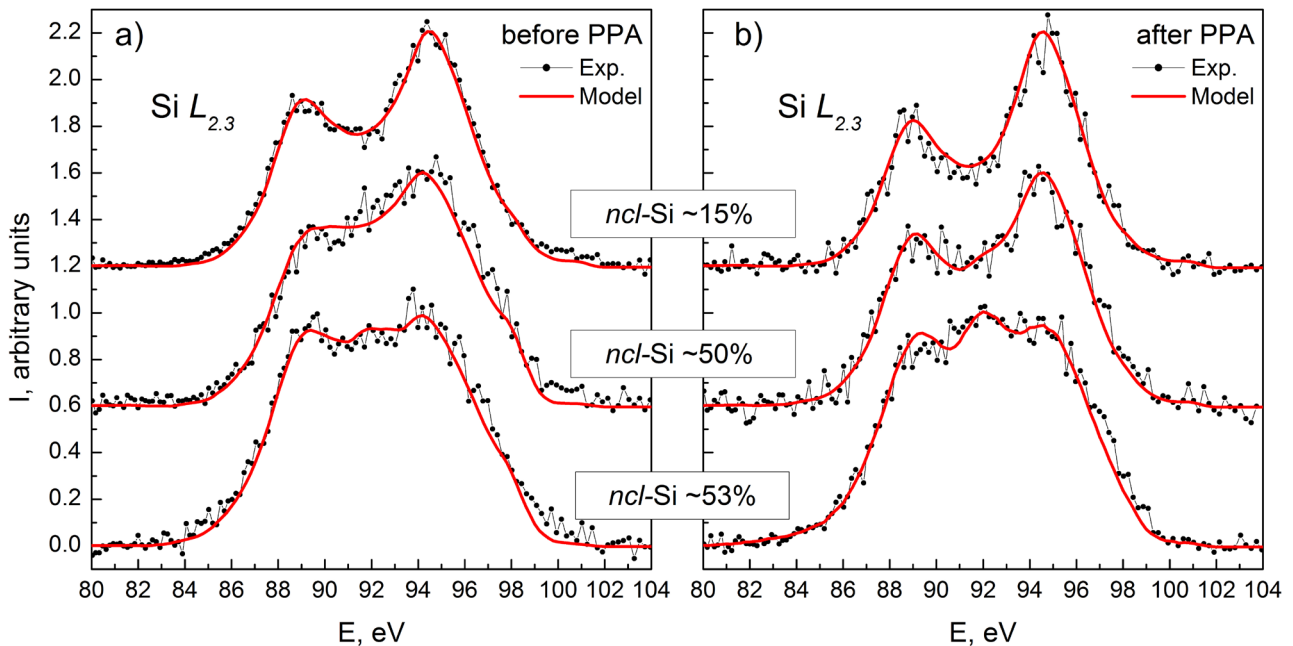


Fig. 2. Ultrasoft X-ray emission Si $L_{2,3}$ -spectra of $a\text{-SiO}_x\text{:H}$ films with different $ncl\text{-Si}$ content before PPA (a) [4] and after PPA (b). Experimental spectra are shown by dots, spectra simulated using reference spectra are shown by solid lines

Table 2. Phase composition of SiO_x films with different *ncl*-Si content after PPA by USXES data

Sample	<i>c</i> -Si, %	$\text{SiO}_{1.7}$, %	SiO_2 , %	Error, %
<i>ncl</i> -Si ~15 %	–	30	70	~10
<i>ncl</i> -Si ~50 %	25	15	60	
<i>ncl</i> -Si ~53 %	60	–	40	

annealing of the film with the initial content of *ncl*-Si nanoclusters ~53 %. That is, if the *ncl*-Si content in the films is < 50 %, during annealing some of the silicon is oxidised and does not participate in the formation of silicon crystals. While with an *ncl*-Si content of ≥ 53 %, when silicon atoms predominate in the structural network, some of the Si atoms are reduced from SiO_x , i.e. $\text{SiO}_x \xrightarrow{t^o} \text{Si} + \text{O}_2$ and participates in the formation of silicon crystals [8]. As a result, we observe a sharp increase in the intensity of the silicon reflection in the XRD patterns of SiO_x films with a high initial *ncl*-Si content.

4. Conclusions

Thus, the results of investigations on the silicon nanoclusters crystallization in a SiO_x matrix have shown that even a very fast method of annealing using PPA leads to the formation of large silicon crystallites. This also causes the crystallization of at least a part of the oxide phase in the form of silicon hydroxide $\text{H}_6\text{O}_7\text{Si}_2$. Moreover, in films with an initial content of pure silicon nanoclusters ≤ 50 %, during annealing part of the silicon is spent on the formation of oxide, and part of it is spent on the formation of silicon crystals. While in a film with an initial concentration of silicon nanoclusters ≥ 53 %, on the contrary, upon annealing, there occurs a partial transition of silicon from the oxide phase to the growth of Si crystals.

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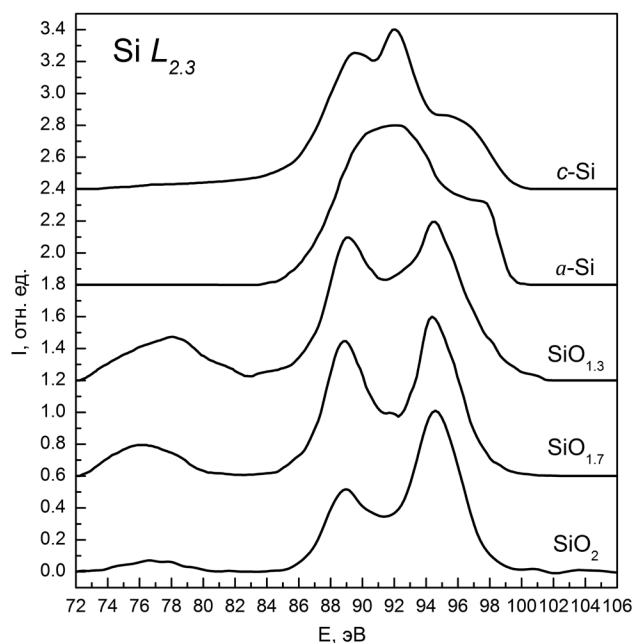


Fig. 3. Ultrasoft X-ray emission $\text{Si } L_{2,3}$ -spectra of crystalline silicon *c*-Si, amorphous silicon *a*-Si, nonstoichiometric silicon oxide $\text{SiO}_{1.3}$ and $\text{SiO}_{1.7}$ [14], and silicon dioxide SiO_2

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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