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Femtosecond pulse crystallization of thin amorphous hydrogenated films on glass substrates using near ultraviolet laser radiation

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Femtosecond laser treatments (second harmonic of Ti-sapphire laser, $\lambda \approx 400$ nm wavelength, < 30 fs pulse duration) were applied for crystallization of thin hydrogenated amorphous silicon films on glass substrates. The concentration of atomic hydrogen in the films was varied from 10 to $\approx 35\%$. The energy densities (laser fluences) for crystallization of the films with thicknesses from 20 to 130 nm were found. Assumedly, non-thermal processes (plasma annealing) take place in phase transition caused ultra-fast pulses. The developed approach can be used for creation of polycrystalline silicon films on non-refractory substrates.

The interest in amorphous silicon films on non-refractory substrates and their crystallization is constantly stimulated by demands of giant microelectronics. For example, enlargement of sizes of flat panel displays with active thin film transistor matrix can be described as "reverse Moor's low". Modern techniques of deposition allow producing of hydrogenated amorphous silicon (a-Si:H) films on substrates with plasticity temperature as low as 100 °C. For some applications the polycrystalline silicon films have many advantages comparing with a-Si:H films. So, the development of low thermal budget technology of crystallization of a-Si:H films is actual, and is of interest up today, especially for femtosecond laser crystallization [1–5]. Femtosecond laser treatments also used for creation of nanocrystals in dielectric films [6, 7] and for silicon nanostructuring [8]. But near-infrared laser radiation was mainly used for crystallization [1–7]. Near ultra-violet radiation has higher absorption for a-Si:H films, so, lesser laser fluence will be need to crystallize the films, and lesser radiation can reach substrate, what important for crystallization of very thin films.

Thin a-Si:H films were deposited on non-refractory glass substrates (temperature of plasticity ≈ 300 °C) using low-temperature plasma enhanced chemical vapor deposition (PECVD) technique. The growth temperature was varied from 200 to 280 °C, the thickness of the films was varied from 20 to 130 nm. It is known, that optical gap of a-Si:H depends on hydrogen concentration [9]. According to optical gap measurements from light transmission and reflection data, the films grown at temperature 280 °C contain 10–15 atomic % of hydrogen (optical gap ≈ 1.5 eV); the films grown at temperature 200 °C contain 30–35% of hydrogen (optical gap ≈ 2 eV).

A Ti-Sapphire laser (FemtoPower Compact Pro, Femtolasers Produktions GmbH) with a central wavelength of 800 nm, pulse duration of < 30 fs, pulse energy of up to 0.8 mJ and pulse repetition rate of 1 kHz was used for laser treatments. The pulse energy was set using a computer controlled polarization rotating LCD device in front of the laser's prism based pulse compressor. To make laser treatments in near ultraviolet range, the non-linear optic crystal for generation of second harmonic of this laser was used. The pulse energy of second harmonic can be varied up to 10 μJ. The laser beam was focused onto the sample surface using an achromatic lens. The radius of the laser spot was changed in a range from 50 to 500 micrometers by defocusing. The distribution of the laser energy in the laser spot has the Gaussian form:

$$E(r) = E_0 \exp(-2r^2/r_0^2), \tag{1}$$

where E_0 is the maximal laser energy and r_0 is the radius of the laser spot. Scanning treatments using x–y-sample translation by computer-controlled stages were carried out. The overlapping of the laser spots during scanning treatments was about 90%. From eq. (1) one can define the maximal surface laser energy density (laser fluence) as: $F_0 = 2E_{\text{pulse}}/\pi r_0^2$, where E_{pulse} is the laser pulse energy. We used laser fluences in a range from 5 to 50 mJ/cm^2. The scheme of laser treatments is shown in Fig. 1 (upper case), the results of scanning (optical microscope image) is shown in Fig. 1 (bottom case).

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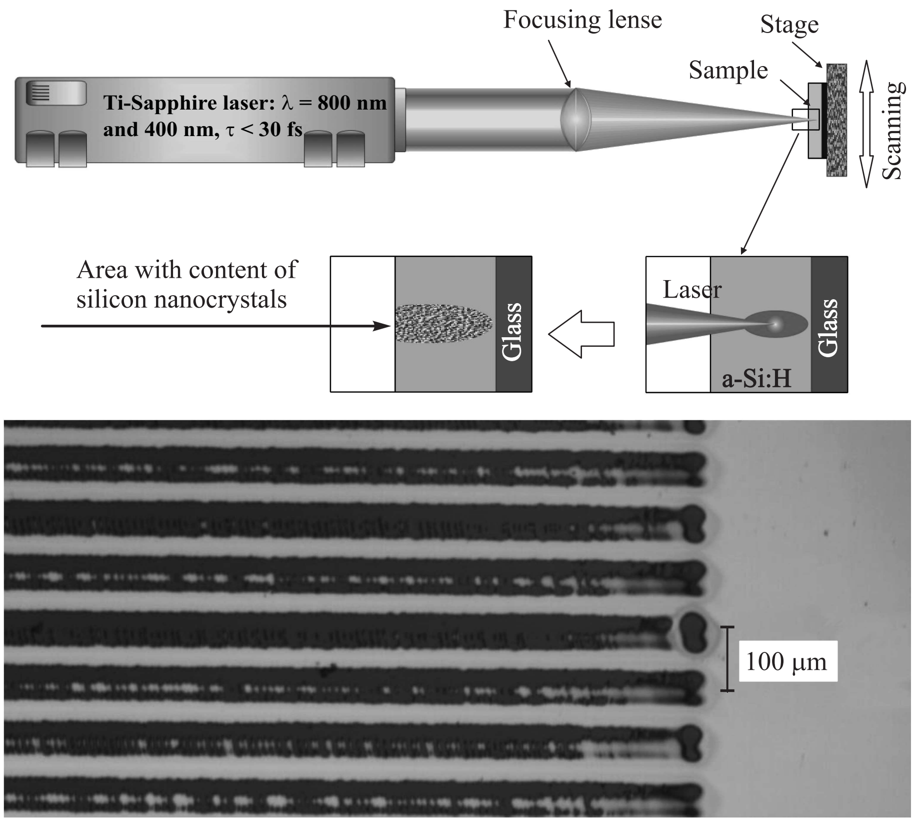

Fig. 1. Upper case: scheme of laser treatments; bottom case: optical microscope image of laser scanned sample, darker areas are polycrystalline Si

Raman spectroscopy technique was used to identify the structure (amorphous or crystalline) of the films. The Raman spectra were recorded in the back-scattering geometry. The 514.5 nm Ar^+ laser line was used as a source. Triple spectrometer (T64000 Horiba Jobin Yvon) with a micro-Raman setup was used. All Raman spectra were measured at room temperature. To avoid heating of the films, the laser beam was slightly defocused leading to a spot diameter of about $6\,\mu$m at a laser power reaching the sample of 2–3 mW.

The Raman spectrum of amorphous silicon contains broad peaks at approximately $480\,\mathrm{cm}^{-1}$ appearing as result of effective density of transversal optical (TO) vibration modes [10]. Due to scattering on optical phonon modes localized in the nanocrystals, the Raman spectrum of nanocrystals is characterized by narrow peak at position between $500–520\,\mathrm{cm}^{-1}$. The position and the width of the peak strongly depend on size and structure of the nanocrystals according to dispersion of the localized modes [11]. The peak width is mainly determined by size dispersion of the nanocrystals. The intensity of the "nanocrystal" peak depends on the contents of nanocrystal phase. So, one can determine the volume part of nanocrystal phase:

$$V_{\mathrm{nano-Si}}/V_{\mathrm{full}} = I_{NC}/(I_{NC} + \sigma I_A), \qquad (2)$$

where I_{NC} and I_A are integral intensities of nanocrystalline and amorphous peaks, and σ is relation between the integral Raman cross sections of nanocrystal Si and a-Si. According to literature data, σ can change from 0.1 for large grain polycrystalline silicon up to 1.1 for nanocrystalline Si [12].

According to Raman spectroscopy data, the femtosecond laser treatments (second harmonic of Ti-sapphire laser, $\lambda \approx 400$ nm wavelength, < 30 fs pulse duration) with fluence less than $20\,\mathrm{mJ/cm}^2$ have not changed the structure of the a-Si:H films. As one can see in Fig. 2 the femtosecond laser impacts with fluence higher than $20\,\mathrm{mJ/cm}^2$ lead to dramatic changes in structure of the a-Si:H film with 10–15% of hydrogen. For laser impact with fluence $25\,\mathrm{mJ/cm}^2$ one can see amorphous peak ($480\,\mathrm{cm}^{-1}$) and appearing of nanocrystalline peak with maximum at $515\,\mathrm{cm}^{-1}$. In the case of laser impact with fluence $30\,\mathrm{mJ/cm}^2$ the amorphous

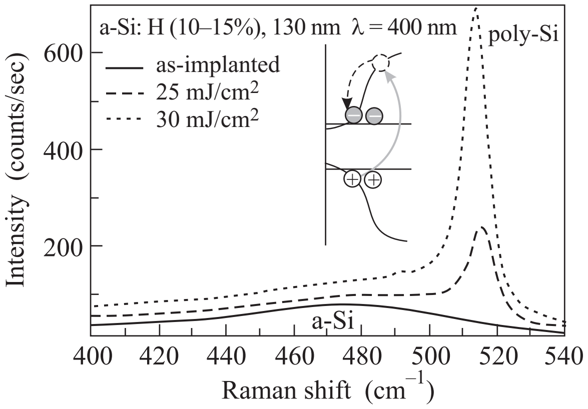

Fig. 2. Raman spectra of the films with relatively low hydrogen concentration: solid line – as deposited sample; dashed and doted lines poly-Si films (after femtosecond laser impact). Insert – schematic process of Auger generation

peak is small compared with nanocrystalline peak, so one can conclude that the film almost totally crystallized. As it was mentioned, from position of this peak one can estimate the average size of Si nanocrystals. In this case the average size is about 5 nm. The ablation threshold for femtosecond pulse treatments for near ultraviolet photons in this case was $35\,\mathrm{mJ/cm^2}$. Earlier, in the case of femtosecond laser pulse treatments near IR range the ablation threshold for a-Si:H film with 10–20% of hydrogen was found to be of about $65\,\mathrm{mJ/cm^2}$ [4].

In the case of a-Si:H film with 30–35% of hydrogen the crystallization threshold is much higher. As one can see in Fig. 3, laser treatment with fluence $40\,\mathrm{mJ/cm^2}$

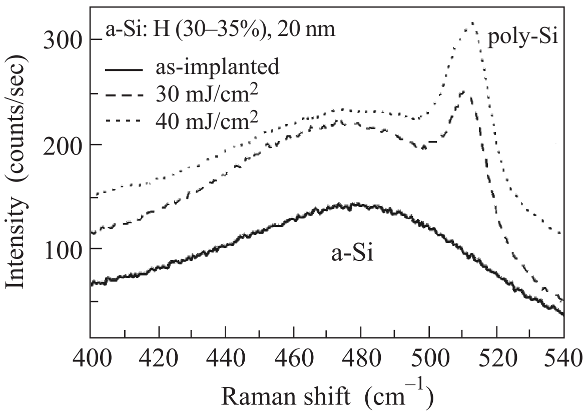

Fig. 3. Raman spectra of the films with relatively high hydrogen concentration: solid line – as deposited sample; dashed and doted lines poly-Si films (after femtosecond laser impact)

leads only to partly crystallization of the film. It should be noted, that the film thickness in this case was several times lesser (20 nm versus 130 nm in the case of a-Si:H film with 10–15% of hydrogen). When laser fluence was $25\,\mathrm{mJ/cm^2}$ and lower, no structural changes were observed in the highly hydrogenated films. Supposedly, the dependence of needed for crystallization laser fluence on concentration of hydrogen is caused by difference in absorbance coefficient owing to hydrogen [9].

For very short time of pulse, the absorbed energy cannot dissipate in substrate, so, knowing the heat capacity and specific heat of melting for a-Si, one can easy calculate the energy density needed for total melting of a film. According to data [4] the energy density needed for total melting of a-Si:H film with thickness 130 nm is $76\,\mathrm{mJ/cm^2}$. So, if assume the thermal mechanism of crystallization, the laser fluence $30\,\mathrm{mJ/cm^2}$ is not enough to melt this film. We assume some non-thermal effects. The pulse duration is much lower than time of electron-phonon interaction in semiconductors (about 1–2 picoseconds). So, hot electron-hole plasma can not excite vibration modes in material during pulse. The excitation of an electron from valence band to conduction band means a break of a valence bond. According to some theoretical calculations, when from 9 to 20% valence bonds are broken, silicon became unstable [3, 13]. According to estimations of Bok [14], when concentration of excited electron-hole pairs reaches $8 \cdot 10^{21}\,\mathrm{cm^{-3}}$, melting temperature of silicon falls down to zero. Let us assume that the energy of excitation of one electron-hole pair is equal to 2 eV (or $3.2 \cdot 10^{-19}$ Joules). Then, to excite this number of electron-hole pairs it takes about $33\,\mathrm{mJ/cm^2}$ for Si films with thickness 130 nm. It is lesser than takes for total melting of such film ($76\,\mathrm{mJ/cm^2}$) in the case of thermal melting. So, if one assumes not-thermal mechanism of phase transfer, some gain in energy takes place.

According to experimental data [4] the reflectance coefficient of light with photon energy for a-Si:H films with similar hydrogen concentration can reach 35–40%. So, the absorbed energy density for near whole crystallization of the film is about $20\,\mathrm{mJ/cm^2}$ (laser fluence 30 mJ/cm2, Fig. 2). But, supposedly, in our case near ultraviolet photons (about 3 eV) can generate not only one, but two electron-hole pairs due to Auger generation like processes (see inset in Fig. 2). Taking into account so low fluence for crystallization of the film, the non-thermal mechanism of phase transfer looks more justified.

Anyway, metastable stage of ultra dense electron-hole plasma relaxes to more stable crystalline phase. Because the initial stage was amorphous, the generation of latent heat of crystallization takes place. So, this process is similar to "explosive" crystallization [15], or, theoretically predicted as-called "plasma annealing" [16]. Den-

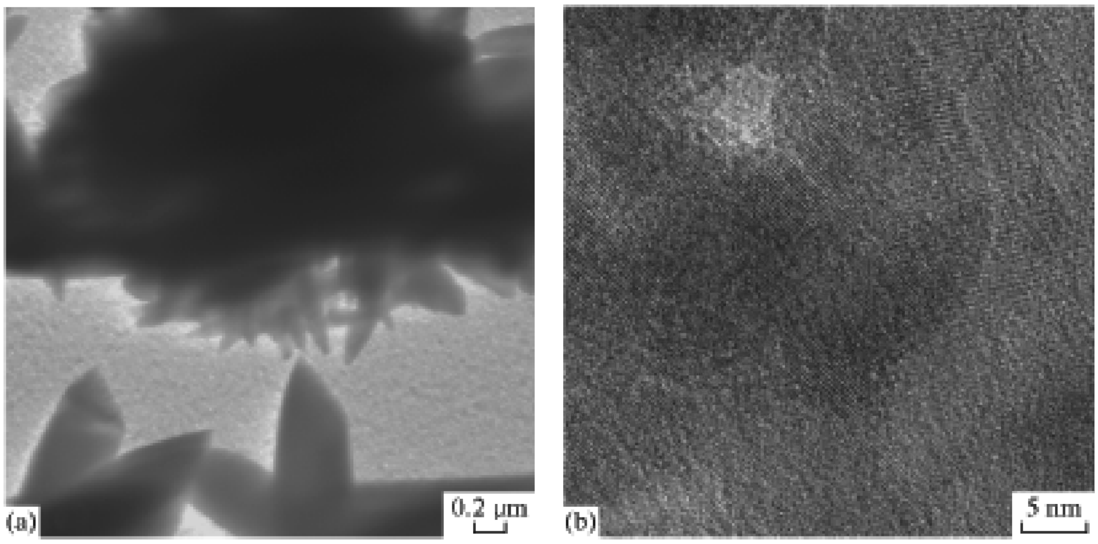

Fig. 4. Electron microscopy image of poly-Si film (crystallized by femtosecond laser treatments with fluence $30\,\mathrm{mJ/cm^2}$): upper case – bright field TEM-image (darker areas are polycrystalline silicon); bottom case – HRTEM image

drite (or star-like shaped) form of polycrystalline areas (Fig. 4, upper case) confirms the assumption about "explosive" crystallization. It should be noted, that "explosive" crystallization can take place also in thermal phase transfer processes. The big crystalline areas are consisting from small nanocrystals with size about 5 nm (Fig. 4, bottom case) what is in very good agreement with Raman data. The Fig. 4 show crystallized film with thickness 130 nm. The initial (as-deposited) film contains 10–15% of hydrogen. For high-resolution transmittance electron microscopy (HRTEM) studies the film was thinned down to 50 nm. Due to more effective absorbance of near ultraviolet photons compared with near IR photons, the threshold for crystallization for the first case is lower – $30\,\mathrm{mJ/cm^2}$ compared with $63\,\mathrm{mJ/cm^2}$ for near IR photons [17]. It was mentioned above, that for case of a-Si:H film with 30–35% of hydrogen the crystallization threshold is much higher. It can be due to wider optical gap in this case (≈ 2 eV), what makes Auger generation impossible, because one photon with energy 3 eV can not generate two electron-hole pairs, each pair have minimal energy ≈ 2 eV.

In conclusion, femtosecond laser treatments in near ultraviolet range were applied for crystallization of hydrogenated amorphous silicon films. The laser fluences for crystallization were found for the films of various concentration of atomic hydrogen. Non-linear effects and non-thermal "explosive" impacts may play some role in pulse femtosecond treatments. The developed approach can be used for the creation of very thin (down to 20 nm) polycrystalline Si films on non-refractory substrates.

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