Hydrogenation of Laser-crystallized a-Si:H Films

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Ultrafast laser processing of semiconductors is a rapidly developing field of material science at the moment. In particular, femtosecond laser crystallization of amorphous hydrogenated silicon thin films has a big potential in photovoltaics. However laser treatment causes dehydrogenation process which decreases materials' photosensitivity and thus limiting its application for optoelectronics. In present paper we studied photoelectric properties of laser-modified amorphous silicon films. Two different hydrogenation procedures were employed to restore films' hydrogen content: keeping in hydrogen plasma and in high-pressure hydrogen atmosphere. The effectiveness of applied procedures for increasing materials' photosensitivity is discussed.

Keywords: Amorphous hydrogenated silicon, Nanocrystalline hydrogenated silicon, Laser crystallization, Femtosecond laser pulses, Hydrogen concentration, Post-hydrogenation.

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1. INTRODUCTION

Laser processing of semiconductor materials during the last two decades has received a new impetus in development associated with distribution of commercially available laser systems which use ultrafast laser pulses. Duration of these pulses lying in the pico- and femtosecond range does not exceed the electron-phonon interaction time that causes in some cases unique properties of irradiated materials. In particular, femtosecond laser processing of the amorphous hydrogenated silicon (a-Si:H) films opens new possibilities for creating materials optimal for photovoltaics and optoelectronics [1-4].

The a-Si:H films have attracted attention in the 70s of the 20th century, when it was shown that hydrogenation (introduction of hydrogen atoms into the structure of amorphous films) allows to reduce the defect concentration in the amorphous matrix by several orders of magnitude, and, as a consequence, to make the material photosensitive and able to change its properties when doping. Improvement of the production technology of this material and structure of solar cells on its basis allowed to create solar batteries with efficiency up to 9.5 % (Un. Neuchatel). Currently, tandem structures of amorphous and nanocrystalline hydrogenated silicon (nc-Si:H) are applied to produce solar cells. The use of 2 active layers allows to significantly extend their absorption spectrum and also to increase the stability of the characteristics. Ultimately, this leads to the increase in the efficiency up to almost 12 % (Kaneka).

Nanocrystalline hydrogenated silicon used in the described tandem structure represents an amorphous silicon matrix with inclusion of some fraction of silicon nanocrystals. At that, as a rule, in order to produce nc-Si:H they use the plasma-enhanced chemical vapor deposition (PECVD) method, which is also applied for a-Si:H deposition, but in the case of nc-Si:H with an increased hydrogen content in the mixture of gases-precursors. Thus, deposition of the a-Si:H/nc-Si:H tandem requires, as minimum, two successive stages of deposition. Laser crystallization of a-Si:H films is an alternative approach to the nc-Si:H production. In recent years, it was shown the possibility of the controlled film crystallization by femtosecond laser pulses under simultaneous texturing of the material surface. Surface texturing is necessary for the "light retention" inside the active layer of a solar cell and is implemented almost in all modern solar cells. Also, the use of a laser beam, if necessary, allows to achieve high processing locality (from this point of view, utilization of ultrafast pulses has an advantage over the traditional laser processing [5]). In this case, fitting of the radiation wavelength allows to target the penetration depth of radiation into the material and, as a result, the thickness of the structurally modified layer [3, 6].

At the same time, photoelectric properties of nc-Si:H obtained by laser crystallization of amorphous hydrogenated silicon currently do not allow to create solar cells with high efficiency [7]. One of the supposed reasons of low quality of the obtained material consists in release of hydrogen from its structure when the films are heated by laser irradiation [8]. In both nc-Si:H and a-Si:H films, hydrogen is necessary for passivation of dangling bonds (inside the amorphous matrix and at the boundaries of nanocrystals) and removal of the associated with them electronic states in the forbidden band of the material. Since the states associated with defects of the type of dangling bonds are the primary recombination centers in the material, then the increase in their concentration induced by laser irradiation leads to a sharp decrease in the carrier lifetime and film photosensitivity. The below study is devoted to solution of this problem. We have used two procedures of post-hydrogenation of laser-modified a-Si:H films: exposure of the films in high-pressure hydrogen atmosphere and exposure in hydrogen plasma. In the work, we have studied the influence of the performed procedures of post-hydrogenation on the properties of the films with different structure modified using laser crystallization, and also compared the effectiveness of the utilized procedures for increase in the photosensitivity of the material obtained during laser processing.

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2. EXAMINED SAMPLES AND MEASURING TECHNIQUE

The a-Si:H films of 300 nm thickness were deposited on quartz glass at plasma-chemical decomposition of a mixture of gases: monosilane (SiH_4) and argon (Ar) in a glow discharge plasma. A complex based on Yb:KGW laser was used to irradiate the films by femtosecond laser pulses. Film irradiation was performed by laser pulses with the wavelength of 515 or 1030 nm and duration of 300 fs. Laser processing was conducted in the scanning mode; the laser spot was focused using cylindrical lens in such a way that the size of the elliptical spot on the film surface was equal to 50×8 µm. Scanning was carried out along the direction perpendicular to the major axis of the spot (50 µm). The distance between the centers of adjacent bands was 25 µm, thus, they were intersected on half of the spot major axis. The laser beam velocity along the film surface was equal to 5 mm/s. Laser pulse repetition frequency was 200 kHz. Average irradiation power varied in the range from 40 to 160 mW to obtain the films with different volume fraction of the nanocrystalline phase. For the post-hydrogenation procedure, the films were placed for 48 hours into the chamber with hydrogen under the pressure of 135 atm. (at that, substrate temperature made 70 ºC) or for 1 hour into hydrogen plasma (at the substrate temperature of 240 ºC).

Film structure was determined from the analysis of the Raman scattering (RS) spectra. To study the electrical and photoelectric properties of the films, aluminum electrodes were sprayed on their surface. All the measurements were performed in a vacuum cryostat under the residual gas pressure of 10^{-3} Pa after pre-annealing of the films at the temperature of 170 ºC. This allowed to get rid of the influence of the Staebler-Wronski effect [9] and air atmosphere [10] on the parameters of the studied films. Spectral dependences of the absorption coefficient in the region of absorption edge were measured using the constant photocurrent method (CPM) [11].

3. RESULTS AND DISCUSSION

As noted above, the Raman scattering spectroscopy method was utilized to determine the film structure. In Fig. 1a we show the evolution of the RS spectra obtained for the a-Si:H films with increasing average power of laser pulses used for their irradiation. The results presented in Fig. 1a are obtained for the films processed by laser pulses with the radiation wavelength of 515 nm and not underwent post-hydrogenation. Radiation with the wavelength of 515 nm is strongly absorbed in a-Si:H that leads to a small penetration depth of a modifying radiation into the film. This, in turn, causes the formation of a two-layer structure with a nanocrystalline silicon layer formed on the layer surface of unmodified a-Si:H. A wide maximum with the center nearby 480 cm^{-1} on the RS spectra corresponds to the vibrations of the transverse optical (TO) phonons in a-Si:H, while a narrow peak near 520 cm^{-1} is associated with the appearance of silicon nanocrystals and corresponds to the TO phonons in them (see Fig. 1a). Decomposition procedure of the RS spectra of two-phase films of hydrogenated silicon into the constituent phonon modes and analysis necessary for the calculation of the crystalline phase fraction in the films (f_C) are described in more detail in [12]. Analysis of the

RS spectra presented in Fig. 1a using the technique described in [12] allowed to calculate the dependence f_C on the average power of laser pulses used for the film irradiation (see Fig. 1b). As seen from the figure, the volume fraction of silicon nanocrystals monotonously increases with increasing intensity of laser processing achieving the maximum value of 78 %. A partial exfoliation of the material from the substrate with subsequent removal of the delaminated film regions is observed with further increase in the pulse power.

In Fig. 2 we illustrate the temperature dependences of the dark conductivity of the films after hydrogenation in high-pressure hydrogen atmosphere (Fig. 2a) and in hydrogen plasma (Fig. 2b). Most of the measured dependences have an activation behavior. Increase in the conductivity of the films obtained with increasing laser processing power associated with the film crystallization is typical for both series; at that, this increase is exhibited more significantly for the samples hydrogenated in plasma. In both series, it should be also noted the films with non-activation temperature dependences of the conductivity. These films were obtained using transition values of the average power of laser pulses. One can suggest that the absence of a unified activation energy for these films is associated with the change in the contribution to the dark conductivity from amorphous and crystalline phases of the films in different temperature ranges. We note that the transition to such non-activation temperature dependences occurs substantially earlier for the films hydrogenated in hydrogen plasma.

To estimate the contribution of the crystalline phase formed under laser irradiation of the films to the photosensitivity of the material, we used the CPM. This method allows to measure the spectral dependences of the absorption coefficient in the small absorption area. At that, CPM is sensitive only to that absorption which contributes to the generation of non-equilibrium charge carriers, i.e. to the measured photocurrent. Thus, by the form of the spectral dependences, which have different characteristic forms for amorphous and nanocrystalline silicon, one can conclude about phases contributions of the film with a complex structure to its total photoconductivity.

Our measurements showed that for all the films subjected to laser processing and not underwent post-hydrogenation one can observe the "amorphous" shape of the CPM spectra, namely, the absorption arm in the region of $h\nu < 1.4$ eV, associated with absorption on dangling bonds, and the exponential growth in the range of 1.4 eV $< h\nu < 1.8$ eV reflecting transitions with participation of the states in the band tails [13]. The difference in the shape of the CPM spectra of nanocrystalline silicon films and spectra of "amorphous" type consists in a significant increase in the absorption in the energy range of 1.2-1.7 eV. The absence of the contribution of the nanocrystalline phase to the CPM spectra and, consequently, to the photoconductivity (in the case of its substantial fraction in the film structure) is the result of hydrogen release from the crystallized under laser irradiation regions of the film.

In Fig. 3 we show the results of the influence of hydrogenation on the CPM spectra of the films crystallized by laser irradiation. As seen, CPM spectra of laser-modified films, underwent post-hydrogenation in high-pressure hydrogen atmosphere, remain amorphous shape even for
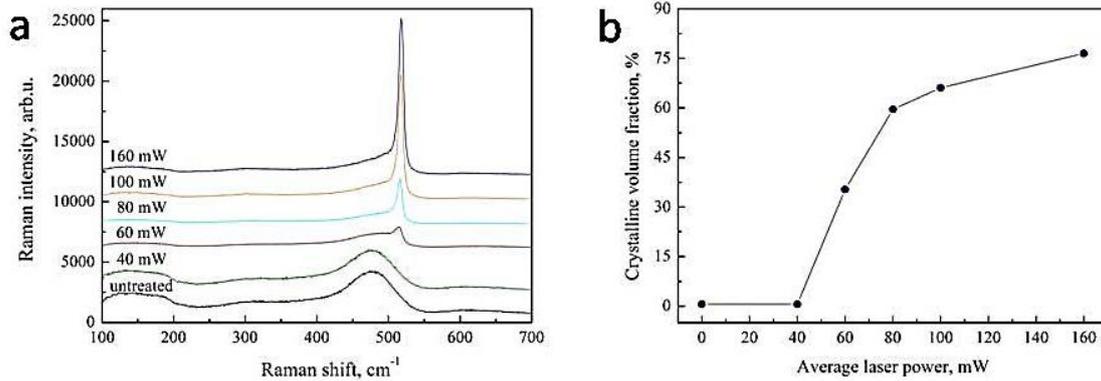
Fig. 1 – RS spectra of the studied films (a) and volume fraction of the crystalline phase in them calculated from processing of the spectra (b). Average power of laser irradiation is given in the figure; the spectra are dispersed along the vertical axis for clarity
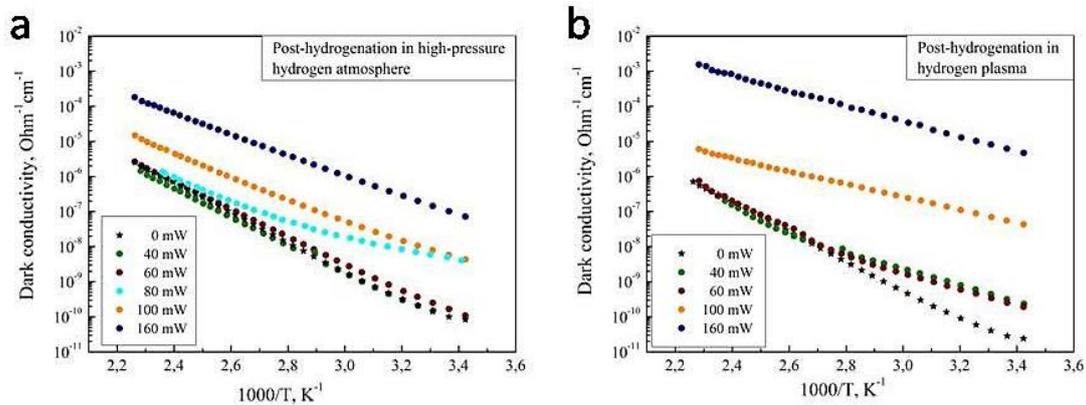
Fig. 2 – Temperature dependences of the dark conductivity of the a-Si:H films irradiated by laser pulses and underwent post-hydrogenation procedure in high-pressure hydrogen atmosphere (a) or in hydrogen plasma (b)
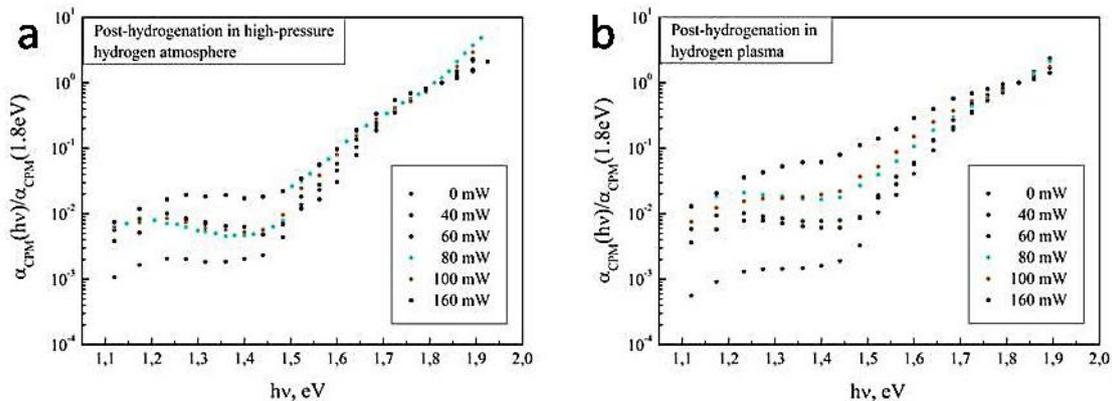

Fig. 3 – Spectral dependences of the absorption coefficient of the a-Si:H films irradiated by laser pulses and underwent post-hydrogenation procedure in high-pressure hydrogen atmosphere (a) or in hydrogen plasma (b)

the samples with a high fraction of the crystalline phase. At the same time, for the films hydrogenated in hydrogen plasma one observes a gradual absorption growth in the range of 1.2-1.7 eV indicating a growing contribution of the crystalline phase to the total film photoconductivity with increasing concentration of crystallites in the film structure. However, total transformation of the spectra is not observed even in this case.

We also note that in the experiments with non-hydrogenated films (they are not shown in the figures) a monotonic absorption growth in the region of $h\nu < 1.4$ eV was observed with increasing laser processing power that implies a monotonic growth of the defect concentration

in the films. As noted above, this effect can be associated with a gradual release of hydrogen from the material's structure. In the series of samples subjected to post-hydrogenation, the change in the absorption coefficient in the specified range has a non-monotonic behavior. Ratio $\alpha(1.2\text{-}1.4 \text{ eV})/\alpha(1.8 \text{ eV})$ can be used as a measure of the defect concentration. This dependence is represented in Fig. 4. The reason of the observed reduction in the "defect" absorption is seemingly associated with the formation of a percolation chain under the processing power exceeding 80 mW (this is seen from an abrupt increase in the dark conductivity of the films, see Fig. 2). As known, the forbidden band of silicon nanocrystals is less than the

mobility gap width of the surrounding amorphous matrix (1.2 eV and 1.8 eV, respectively). This results in the formation of potential discontinuities in the conduction (0.15 eV) and valence (0.45 eV) bands [14]. Thus, the charge carriers generated in the amorphous matrix near the nanocrystals can be captured in them. If nanocrystals are not connected with each other, such capture will lead to the decrease in the observed photocurrent. If a percolation chain of nanocrystals is created in the film, then captured carriers will contribute to the photocurrent, at that moving with mobility higher than in a-Si:H. Since the presented CPM spectra are normalized to absorption at the quantum energy of 1.8 eV, the value of the defect arm can reflect the change in the material photoconductivity at an interband generation in a-Si:H. In non-hydrogenated films, there are additional barriers at the boundary of nanocrystals associated with a high concentration of dangling bonds and preventing capture of charge carriers from the amorphous matrix into the nanocrystal.
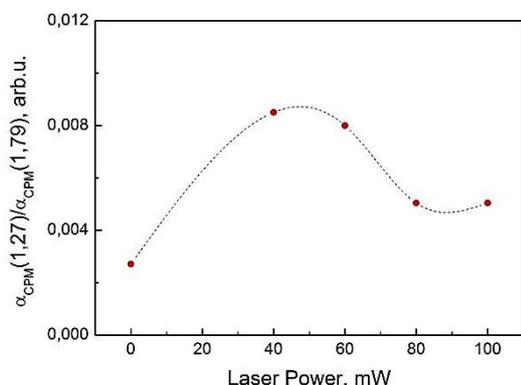
Fig. 4 – Dependence of $\alpha(1.27 \text{ eV})/\alpha(1.79 \text{ eV})$ ratio on the average power of laser pulses used for the films processing

We note that the mentioned peculiarity is clearly traced in the films hydrogenated in high-pressure hydrogen atmosphere and is only slightly traced for the films hydrogenated in hydrogen plasma (decrease in the absorption arm from 40 to 60 mW).

Thus, hydrogenation in hydrogen plasma is a more effective method for increasing the photoconductivity of nc-Si:H formed using femtosecond laser pulses. Hydrogenation in high-pressure hydrogen atmosphere also leads to the changes in the photoelectric properties of the films; however (in the conditions we utilized) these changes are less pronounced compared with the films hydrogenated in hydrogen plasma. In addition, hydrogenation in high-pressure hydrogen atmosphere does not allow to significantly increase the contribution of a crystallized part of the films to their photoconductivity.

The observed "incomplete" change in the CPM spectra for the spectra of the "nanocrystalline type" after their hydrogenation can be associated with both insufficient passivation of dangling bonds by hydrogen and features of a two-layer film structure formed during laser processing. To resolve this question, we compared the influence of hydrogenation of laser-modified films with different geometry of distribution of the crystalline phase over the sample thickness. The use of different wavelength of laser pulses allows to vary the penetration depth of radiation and, as a consequence, thickness of the structurally-modified layer. Thus, crystallization of the near-surface layer only occurs in the case when $\lambda = 515$ nm (that was done for the above described series of samples), while at $\lambda = 1030$ nm the film structure varies almost uniformly in the sample thickness, which in our case was 300 nm [6]. In the given experiment, we performed hydrogenation in hydrogen plasma, since this method showed greater efficiency in reduction of the hydrogen content in laser-modified a-Si:H films.

In Fig. 5 we present the CPM spectra of the a-Si:H films irradiated by laser pulses with the wavelengths of 515 and 1030 nm which underwent post-hydrogenation procedure in hydrogen plasma. Since processing intensities necessary for film crystallization by irradiation of various wavelengths differ substantially, then fractions of the crystalline phase in the films are shown in the figures for objective comparison. As seen from Fig. 5, the change in the shape of the CPM spectra occurs considerably earlier for the films irradiated with the wavelength of 1030 nm (a significant absorption growth in the range of 1.2-1.7 eV is noticeable at 30 % of crystallinity, and for the fraction of the nanocrystalline phase exceeding 42 % the CPM spectra have a typical "nanocrystalline shape"). Thus, the change in the shape of the CPM spectra of hydrogenated films is manifested much stronger for the films with a uniform structure. This result can be associated with the presence in the films irradiated with $\lambda = 515$ nm of a a-Si:H layer near the film substrate, the impact on which from laser pulses is negligible. This layer is photosensitive and contributes appreciably to the material photoconductivity, thereby
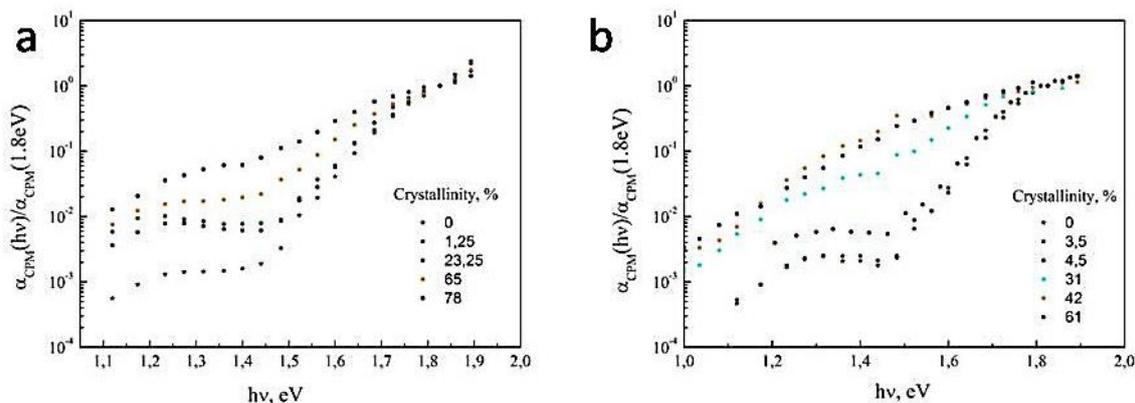
Fig. 5 – Spectral dependences of the absorption coefficient of the a-Si:H films irradiated by laser pulses with the wavelength of 515 nm (a) or 1030 nm (b)

slowing down the transition of the CPM spectra to the "nanocrystalline" type. The obtained results thus imply the effectiveness of passivation of dangling bonds in the structure of the studied films and increase in the photosensitivity of the crystalline phase in their composition.

4. CONCLUSIONS

The a-Si:H films crystallized by femtosecond laser pulses were studied in the work. The performed processing allowed to obtain films with the volume fraction of the crystalline phase from 0 to 78 %. At that, concentration of hydrogen atoms in the film structure significantly decreases. To our opinion, this explains a low photoconductivity of the nc-Si:H layer obtained at laser processing. To reduce hydrogen concentration in the films, they were placed in high-pressure hydrogen atmosphere or hydrogen plasma. Both procedures have an effect on the photoelectric properties of the films, however only the latter allowed to obtain the desired contribution of the crystalline phase to the material photoconductivity.

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