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Femtosecond laser modification of amorphous silicon films for photovoltaic and polarization optics applications

D.V. Shuleiko [1], O.I. Sokolovskaya [1] ✉, M.N. Martyshov [1], A.A. Serdobintsev [2], L.D. Volkovoynova [2], S.B. Venig [2], P.P. Pakholchuk [1, 3], E.V. Kuzmin [1, 3], S.V. Zabotnov [1], P.K. Kashkarov [1, 4]

[1] Lomonosov Moscow State University, Faculty of Physics, Moscow, Russia;
[2] Saratov State University, Saratov, Russia;
[3] P.N.Lebedev Physical Institute of the RAS, Moscow, Russia;
[4] National Research Centre "Kurchatov Institute", Moscow, Russia
✉ sokolovskayaoi@my.msu.ru

Abstract. Femtosecond laser structuring is a promising method for obtaining amorphous-crystalline silicon (*a*-Si/*c*-Si) heterojunction in *a*-Si thin films, as well as surface structures with optical anisotropy. Depth-resolved Raman spectroscopy of an *a*-Si film irradiated at laser fluence of 0.1 J/cm^2, which is below *a*-Si ablation threshold, revealed its surface crystallization with the crystallized layer characteristic depth of 45 ± 5 nm. As a result of such laser irradiation, the electric current rectification coefficient in the film, determined from electrophysical measurements, increased from 2.7 to 13.6 indicating possible formation of an *a*-Si/*c*-Si heterojunction. The presence of 10-nm-thick Al coating decreases the number of pulses per unit area required for *a*-Si crystallization by 2.5 times. Optical anisotropy of the laser-crystallized *a*-Si films is manifested in their optical retardance of 280 ± 40 nm, caused by the formation of one-dimensional surface relief with the period of 1100 ± 50 nm.

Keywords: femtosecond laser pulses, amorphous silicon, heterojunction, laser-induced periodic surface structures, optical retardance

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Фемтосекундная лазерная модификация пленок аморфного кремния для приложений фотовольтаики и поляризационной оптики

Д.В. Шулейко [1], О.И. Соколовская [1] ✉, М.Н. Мартышов [1], А.А. Сердобинцев [2], Л.Д. Волковойнова [2], С.Б. Вениг [2], П.П. Пахольчук [1, 3], Е.В. Кузьмин [1, 3], С.В. Заботнов [1], П.К. Кашкаров [1, 4]

[1] Московский государственный университет им. М.В. Ломоносова, физический факультет, Москва, Россия;
[2] Саратовский национальный исследовательский государственный университет им. Н.Г. Чернышевского, г. Саратов, Россия;
[3] Физический институт имени П.Н. Лебедева РАН, Москва, Россия;
[4] Национальный исследовательский центр «Курчатовский институт», Москва, Россия
✉ sokolovskayaoi@my.msu.ru

Аннотация. Фемтосекундное лазерное структурирование является перспективным методом получения гетероперехода «аморфный-кристаллический кремний» (*a*-Si/*c*-Si) в тонких пленках *a*-Si, а также поверхностных структур с оптической анизотропией. Методом спектроскопии комбинационного рассеяния света с разрешением по глубине в пленке *a*-Si, облученной лазерными импульсами с плотностью энергии ниже порога абляции (0.1 Дж/см^2), обнаружено формирование поверхностного кристаллизованного слоя с характерной толщиной 45 ± 5 нм. Электрофизические измерения показали, что в результате подобного облучения пленки коэффициент выпрямления электрического тока в ней увеличился с 2.7 до 13.6, что указывает на возможное образование гетероперехода *a*-Si/*c*-Si. Наличие алюминиевого покрытия толщиной 10 нм уменьшает количество импульсов на единицу площади, необходимое для кристаллизации *a*-Si, в 2.5 раза. Оптическая анизотропия лазерно-кристаллизованных пленок *a*-Si проявляется в виде оптического запаздывания до 280 ± 40 нм за счет формирования одномерного поверхностного рельефа с периодом 1100 ± 50 нм.

Ключевые слова: фемтосекундные лазерные импульсы, аморфный кремний, гетеропереход, лазерно-индуцированные поверхностные периодические структуры, оптическое запаздывание

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Introduction

Advances in the ultrafast laser-assisted fabrication technologies open up prospects for improvement of photovoltaic devices based on thin amorphous silicon (*a*-Si) layers with heterojunctions "*a*-Si – crystalline silicon (*c*-Si)", as well as polarization-sensitive optical elements for the near and middle infrared (IR) ranges, based on thin *a*-Si layers with submicron surface relief that possess optical and electrophysical anisotropy [1, 2]. Employing ultrafast laser

pulses leads to well-known phenomenon of laser-induced periodic surface structures (LIPSS) formation. The presence of optical anisotropy in the LIPSS allows fabricating optical elements that are sensitive to polarization, by direct femtosecond laser irradiation of thin films without photoresists and lithography. Such integrated optical elements may be of interest for polarization optical measurements, forming structured light beams, and for telecommunications, as selectors of polarized light signals in fiber-optic communication lines [3, 4].

Another femtosecond laser pulses application is laser-induced crystallization, being of interest for thin *a*-Si layers due to possibility of *a*-Si/*c*-Si heterojunction formation, which can increase Si-based solar cells efficiency. Primarily, this approach seems beneficial for HIT structures (Heterojunction with Intrinsic Thin-layer solar cells), where layers of amorphous silicon are deposited on a *c*-Si wafer by the PECVD method. The maximum efficiency for HIT solar cells is 26.7% [5], and the maximum thermodynamic efficiency limit for fully silicon solar cells is estimated at about 33% [6]. Thus, it is relevant to search for techniques of Si-based solar cells efficiency increasing. Employing laser pulses of femtosecond duration, compared to longer ones, for *a*-Si crystallization [7, 8], especially in context of heterojunction formation in thin *a*-Si layers seems beneficial due to more effective localization of laser action at sub-thermal timescale. Also, the additional *a*-Si/*c*-Si heterojunctions resulted from film laser-induced crystallization as well as higher charge mobility in *c*-Si compared to *a*-Si could contribute to efficiency increase of solar cells based on HIT structures.

Materials and Methods

To fabricate a *a*-Si/*c*-Si heterojunction by laser-induced *a*-Si crystallization, at the first stage, 1 μm-thick undoped *a*-Si film was magnetron-sputtered (Robvac VSM 300, 500W) at direct current on a glass substrate, covered by pre-deposited 500 nm-thick ITO layer, acting as a bottom contact for electrical measurements. On the second stage, laser radiation parameters required for *a*-Si thin surface layer crystallization to form a heterojunction, were determined. For that purpose, single scan lines were formed via irradiating the film by Satsuma femtosecond laser ($\lambda = 515$ nm, $\tau = 300$ fs, $\upsilon = 1$ kHz) with constant scanning speed $V = 300$ μm/s and laser spot diameter $D = 50$ μm, while the fluence E varied from 0.01 to 0.1 J/cm^2 from line to line.

To investigate the distribution of *c*-Si phase over the irradiated *a*-Si film depth, a uniformly deepening profile was etched (Perkin-Elmer PHI 4300, argon ions, 4 keV, 100 nA) with depth increasing by 10 ± 1 nm for each 100 ± 10 μm along the scan line, and the Raman spectra (Renishaw Raman spectrometer, excitation 532 nm) were measured in the mapping mode with 10 μm step along the etched profile. Then, *c*-Si phase volume fraction f_c for each point of Raman map was calculated using the integral intensities of Raman lines corresponding to TO phonon modes in *a*-Si (I_A, 480 cm^{-1}) and *c*-Si (I_C, 521 cm^{-1}) as $f_c = I_C/(\sigma I_A + I_C)$, where $\sigma = 0.1$ is an empirical ratio for the integral Raman scattering cross sections in *c*-Si and *a*-Si phases.

To investigate the effect of additional thin aluminum (Al) coating on *a*-Si laser crystallization, 1 μm-thick *a*-Si films with or without Al coating were deposited on glass substrates and irradiated in scanning mode. The irradiation was performed by ytterbium solid-state femtosecond laser Avesta TEMA-DUO (1050 nm, 150 fs, 130 nJ, 78 MHz, laser spot diameter 25 μm) which was purchased within the framework of the Lomonosov Moscow State University Program of Development and the National Project "Science and Universities" No. DS/45-pr on 28.12.2023 under contract No. 0784-44-2024 on 12.07.2024. The scanning was realized by moving the sample using an Aerotech motorized translator system in a horizontal plane orthogonally to laser beam with constant speed, varying from 2 to 2000 mm/s from line to line, resulting in the variation of the acting laser pulses number N_p per unit area from 10^6 to 10^3.

On the third stage, a large area (5×10 mm^2) was irradiated on the surface of *a*-Si film in raster mode with a 40 μm step ($< D$) between the scan lines, using selected laser radiation parameters (see Results section). To conduct electrophysical measurements in the direction orthogonal to the sample surface plane, aluminum square-shaped 300×300 μm contacts were deposited by thermal evaporation in vacuum (VUP-5) on top of both initial and irradiated areas. The current-voltage characteristics of both initial and irradiated *a*-Si samples were measured in the range from -2 to 2 V in air at room temperature using a Keithley 6487 picoammeter with integrated power supply. The measurements were carried out in the dark and under illumination (white light, $I = 100$ mW/cm^2) from the downside through a transparent conductive ITO layer.

To analyze polarizing properties of LIPSS, the prototypes of 0.5×0.5 cm² *a*-Si films-based waveplates were fabricated. For this purpose, a 1 μm-thick *a*-Si film without pre-deposited contacts or Al coating was irradiated by femtosecond laser (Avesta, 1250 nm, 150 fs, 10 Hz) at fluence $E = 0.15$ J/cm², higher than ablation threshold. The irradiated surface was analyzed by scanning electron microscopy (SEM, Vega 3, Tescan). Optical delay measurements were performed in the near and middle IR ranges using a Bruker IFS 66v/S IR Fourier spectrometer in transmission geometry with varied polarization of the transmitted radiation.

Results and Discussion

Depth-resolved Raman spectroscopy of etched meanders demonstrated that the intensity of the narrow peak corresponding to *c*-Si TO mode (521 cm⁻¹) decreases rapidly along the etched meander, which indicates the presence of crystalline Si phase only in the thin surface layer (Fig 1, *a*). The dependence of f_c on the irradiated *a*-Si film depth determined from the Raman spectra has a sharp character (Fig. 1, *b*): at the film surface f_c is 86 ± 4%, remaining the same up to the depth of 20 ± 5 nm, and then decreases rapidly, reaching zero at a depth of 45 ± 5 nm.

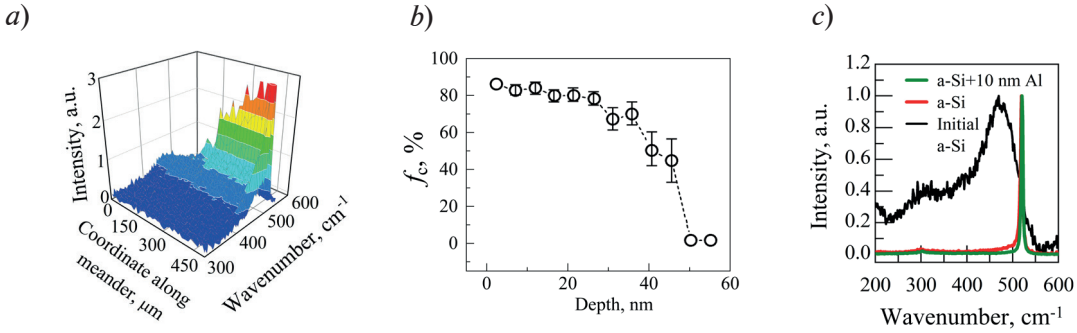

Fig. 1. Depth dependent Raman spectra of meander area (zero coordinate along meander corresponds to the center of ion etched crater) (*a*); crystalline silicon volume fraction dependence on *a*-Si film depth (*b*); Raman spectra for the *a*-Si with 10 nm Al layer irradiated with 80 000 laser pulses; *a*-Si without Al, irradiated with 200 000 laser pulses; and initial *a*-Si film (*c*)

Comparison of the Raman spectra for the irradiated *a*-Si films with and without Al coating (Fig.1, *c*) revealed that for the film without Al layer no crystallization is observed below laser pulses number $N_p = 200\,000$, while above this value almost complete crystallization of the film is achieved, with f_c up to 96 ± 1%. On the other hand, for the *a*-Si film with a 10 nm-thick Al coating, Raman spectroscopy data has shown that laser-induced crystallization begins to occur at $N_p = 80000$, which is 2.5 times less than that required for crystallization of *a*-Si without Al coating. Such results can be attributed to the higher absorption of Al compared to Si, and, consequently, more efficient laser-induced heating of the *a*-Si film with an Al coating. At $N_p = 80000$ and above the film is also almost completely crystallized with $f_c = 99 \pm 1\%$, while at lower N_p however, only Al layer melting is observed without Si film crystallization.

The obtained f_c distribution data allowed to set up the following optimal laser irradiation parameters for *a*-Si/*c*-Si heterojunction fabrication in the *a*-Si film: fluence 0.1 J/cm², repetition rate 1 kHz, scanning speed 300 μm/s.

The current-voltage characteristics both for the initial *a*-Si film and for *a*-Si/*c*-Si heterojunction, fabricated using the mentioned above laser irradiation parameters, demonstrate a pronounced diode character (Fig. 2, *a*, *b*), indicating the presence of a potential barrier in both structures. However, the resistance of the laser-irradiated *a*-Si film decreased about 500 times compared to the initial one, being the result of upper layer partial crystallization with crystalline Si (nanocrystalline, *nc*-Si) phase formation, which is known to have a lower resistivity compared to *a*-Si. Both samples' current-voltage characteristics demonstrate "rectifying" character with the rectification coefficient *k* calculated as the ratio of the current strength in the forward and reverse voltage bias increasing from 2.7 to 13.6 at a voltage of $U = 2$ V after laser irradiation. Increased rectification coefficient can be attributed to the laser-induced formation of an additional potential barrier for free charge carriers in the form of a *a*-Si/*nc*-Si heterojunction.

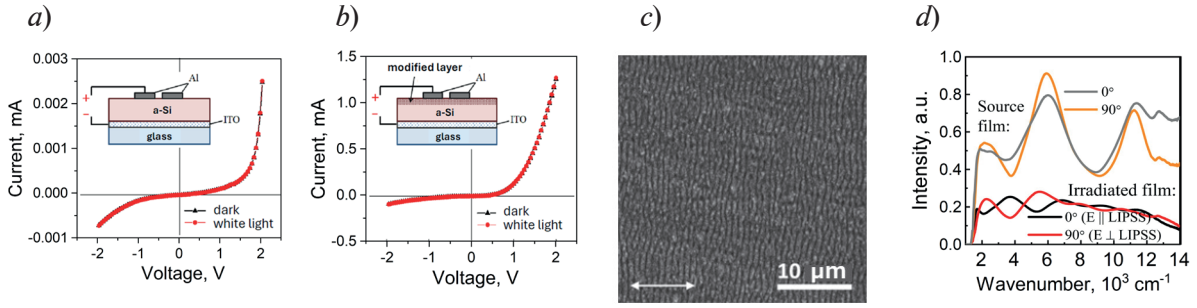

Fig. 2. The current-voltage characteristics of (*a*) initial and (*b*) laser-processed *a*-Si film with ITO contact, insets show its connection to the picoammeter; (*c*) SEM image of the irradiated region with LIPSS on *a*-Si surface, (*d*) IR transmission spectra for the initial *a*-Si film and the film irradiated in LIPSS formation mode

For the 1 μm-thick *a*-Si film on a glass substrate fabricated as waveplate prototype, low spatial frequency LIPSS (LSFL) presence with a period of 1100 ± 50 nm was confirmed by SEM (Fig. 2, *c*). Formed as a result of femtosecond laser irradiation with fluence above the ablation threshold, these structures possess high regularity. The IR transmission spectra (Fig. 2, *d*) demonstrate alternating maxima and minima in the spectra of both the initial and irradiated films, emerging as interference in the layered structure of the samples. The decreased transmittance and lower interference amplitude for the laser-irradiated sample is associated with the formation of a crystalline phase in it, as well as diffuse scattering on the formed surface relief. More importantly, the interference maxima at 0° polarization of the transmitted light in the laser-irradiated film are shifted significantly, compared to the initial film. Based on this shift in the interference maxima positions, a difference in refractive indices of ordinary and extraordinary waves was determined as 0.47 ± 0.07. The anisotropy axis orientation was also determined to be parallel to the ridges of the formed LSFL. Thus, the fabricated waveplate prototype based on *a*-Si demonstrates an optical retardance value of 280 ± 40 nm, which can be attributed to the anisotropic surface relief of LSFL in the form of alternating *nc*-Si/air micron-scale ridges.

Conclusion

In this study, for a thin surface layer (45 ± 5 nm) of *a*-Si film exposed to femtosecond laser pulses the crystallization with a high crystalline Si volume fraction of $86 \pm 4\%$ was achieved Moreover, employing Al coating on *a*-Si film not only decreases the number of pulses required for its effective crystallization due to more effective light absorption, but also leads to almost complete crystallization of the film thin surface layer, with volume fraction reaching up to $99 \pm 1\%$. The formed structures are showing increased rectification coefficient due to formation of *a*-Si/*c*-Si heterojunction, which is promising for photovoltaic cells improvement. Irradiation of *a*-Si films by femtosecond laser pulses with the fluence higher than *a*-Si ablation threshold leads to LIPSS formation. This surface relief, in a form of LSFL, possesses the optical retardance of up to 300 nm. Such optically anisotropic structures could be used as a basis for creating polarization-sensitive optic elements, for example, quarter-wave plates for the near-infrared range.

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THE AUTHORS

SHULEIKO Dmitrii V.
shuleyko.dmitriy@physics.msu.ru
ORCID: 0000-0003-3555-6693

VENIG Sergey B.
Sergey.Venig@gmail.com
ORCID: 0000-0002-4759-5828

SOKOLOVSKAYA Olga I.
sokolovskayaoi@my.msu.ru
ORCID: 0000-0001-8017-9984

PAKHOLCHUK Petr P.
petr.pakholchuk@mail.ru
ORCID: 0000-0002-2608-7621

MARTYSHOV Mikhail N.
martyshov@physics.msu.ru
ORCID: 0000-0002-6363-4970

KUZMIN Evgeny V.
kuzmine@lebedev.ru
ORCID: 0000-0002-6322-6838

SERDOBINTSEV Alexey A.
alexas80@bk.ru
ORCID: 0000-0003-3281-8352

ZABOTNOV Stanislav V.
zabotnov@physics.msu.ru
ORCID: 0000-0002-2528-4869

VOLKOVOYNOVA Larisa D.
loris.volkoff@gmail.com
ORCID: 0000-0001-6780-9865

KASHKAROV Pavel K.
p.kashkarov@mail.ru
ORCID: 0000-0001-6889-001X

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