Formation of crystalline silicon structures on nanofibrous nonwoven materials using laser-stimulated metal-induced crystallization

© A.A. Serdobintsev, A.M. Kartashova, P.A. Demina, L.D. Volkovoynova, I.O. Kozhevnikov

Saratov National Research State University,
Saratov, Russia

E-mail: SerdobintsevAA@sgu.ru

Received May 12, 2023
Revised July 22, 2023
Accepted October 30, 2023

A technique for the crystallization of an amorphous silicon coating deposited on a nonwoven polymer material has been developed and tested. The results of experimental studies are presented, confirming the formation of sub-micron crystallized silicon structures on nanofibrous polymer substrates.

Keywords: crystallization of amorphous silicon, nanofibrous nonwoven materials, laser-stimulated crystallization, submicron particles, flexible electronics.

DOI: 10.61011/PSS.2023.12.57660.5111k

1. Introduction

Currently, microelectronics is actively developing, one of the main materials used is silicon. In this regard, the development of technological approaches for the formation of silicon structures on new types of substrates does not lose its relevance [1]. The formation of structures on flexible polymer substrates can be the basis for the implementation of biosensors or devices for converting solar energy, which can easily take the required shape and have low weight and thickness. The formation of nanoscale and submicron structures based on polycrystalline silicon is of particular interest [2]. An example of such developments is presented in the paper [3]. It used a polyimide film as a substrate, and surface treatment was carried out with an excimer laser. In this paper, non-woven nanofibrous material is used as a substrate; the amorphous silicon coating is crystallized by a pulsed infrared laser using a metal absorbing layer.

2. Experimental part

In this paper, submicron crystalline silicon structures were formed on nanofibrous nonwoven materials obtained by electrospinning from a solution of polyacrylonitrile (PAN) in dimethylformamide. The use of nanofibrous material as substrate makes it possible to obtain a silicon coating spatially limited by the diameter of the fiber. Then the resulting structure was subjected to laser annealing, and a pulsed laser with a wavelength of 1064 nm was used to minimize the effect of annealing on the substrate, since PAN is practically transparent at this wavelength [4]. Silicon also practically does not absorb in this range, so for its crystallization it is necessary either to increase the laser power or to use an additional absorbing layer. The second option seems more promising, as it reduces energy costs and preserves the life of the laser source. Within the framework of the concept of absorbing layer, a method for laser-stimulated metal-induced crystallization was developed and successfully tested [5], it was also used in this paper. Besides, the phenomenon of silicon autocrystallization was previously discovered during joint sputtering of Si and Al from two magnetron sources [6]. This approach will also be tested in this paper.

3. Discussion of results

Aluminum was used as an absorbing material in this paper, as it is a well-known metal that stimulates silicon crystallization [7]. Three types of samples were obtained and studied: sample of pure amorphous silicon (reference sample); sample consisting of a mixture of silicon and aluminum (obtained by joint sputtering of Si and Al from two magnetron sources); sample consisting of a layer of silicon coated with a layer of aluminum (sequential deposition of Si and Al). All layers on nonwoven substrates were obtained by magnetron sputtering in an argon environment. Sputtering was carried out in Angstrom Nexdep unit (Canada), equipped with two magnetron sources with disk targets with a diameter of 76 mm. The thickness of the coatings was 220−280 nm.

Laser treatment of the obtained samples was carried out on „MiniMarker 2“ unit (Russia), equipped with a pulsed laser with wavelength of 1064 nm and a galvanic scanner. At the preliminary stage the most preferred laser annealing modes were determined. As a result, three modes were identified, which were then used for laser annealing of various sections of each of three samples (Table 1). In this case, the repetition rate (99 kHz) and width of laser pulses (4 ns) were identical for all modes. In each mode, an area of size 10×10 mm was treated on each sample. The modes were selected in such a way that destruction of the nanofibrous substrate or peeling of the silicon coating did not occur.

Table 1. Parameters of laser treatment of structures

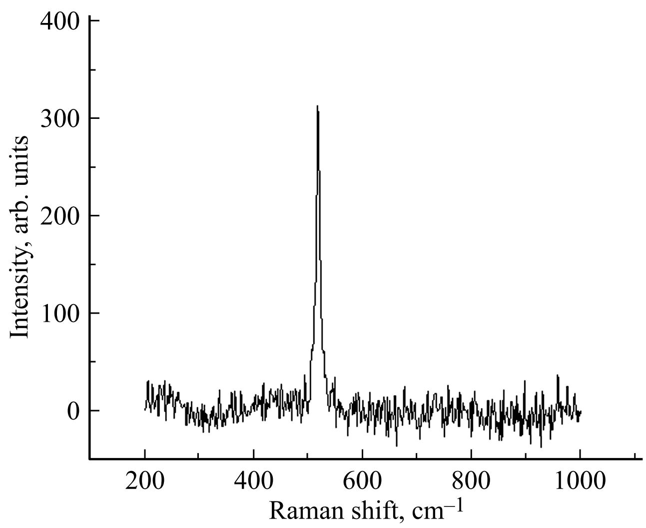
Mode No	Best of crystallization	Power, W	Speed, mm/s
I	Two-layer structure	0.2	400
II	Mixture of silicon and aluminium	0.6	1100
III	Pure silicon	0.8	1100

Table 2. Results of sample studies using RSS method

Structure	Mode	Position of peak, cm^{-1}	Full width at half maximum, cm^{-1}	Fraction of crystallized of points, %	Size of crystallites, nm
Two-layer	I	517.7 ± 0.009	9.7 ± 0.0327	93.75	4.4
	II	–	–	0	–
	III	519.3 ± 0.0091	8.7 ± 0.0207	93.75	10.1
Mixture	I	–	–	0	–
	II	516.2 ± 0.0199	12.5 ± 0.0771	50	3.1
	III	515.6 ± 0.0354	18.2 ± 0.3258	50	2.8

The presence of crystallized phase was verified using Raman scattering spectroscopy (RSS). RSS spectra were recorded using Renishaw inVia spectrometer (UK) equipped with a microscope using a laser with wavelength of 532 nm, the incident radiation power was 0.025 mW. In each laser-treated region RSS spectra were recorded at 16 points, next the percentage of crystallized points was calculated. A typical RSS spectrum of the crystallized point is shown in the Figure. The average parameters of the crystalline phase peak for each „mode-sample" combination are given in Table 2.

The highest content of the crystalline phase (more than 93%) was found in a sample consisting of two layers, and this result was achieved in two of the three annealing modes. It is also worth noting that the position of the peak c-Si on



Typical RSS spectrum of crystallized point.

this sample is closest to the value 520 cm^{-1} characteristic of single-crystal silicon. The peak width at half maximum is also minimal for this particular sample, which indicates better ordering of the crystal structure.

The sample, which is a mixture of silicon and aluminum, is only 50% crystallized, also in two annealing modes. But the peak parameters in this case are worse: the peak position is shifted to lower wave numbers, which indicates smaller sizes of the crystallized regions. This is confirmed by calculation in accordance with the paper [8], the results of which are also given in Table 2. Note that the obtained sizes of nanocrystals are in good agreement with the improved model presented in the paper [9]. The peak width at half maximum is approximately by 1.5 times greater than for a two-layer structure. Thus, we can state the worst parameters of the crystal structure. The pure silicon sample did not crystallize at all: the silicon either remained amorphous or the nonwoven substrate was destroyed.

4. Conclusion

Thus, the use of aluminum as a separate absorption layer appears to be the most effective approach to the formation of crystalline silicon structures on nanofibrous nonwoven substrates. During laser radiation absorption the metal layer transfers energy to silicon through heat transfer and partially evaporates. The energy obtained in this way is sufficient for the silicon crystallization, and the destruction of the nanofibrous substrate does not occur. In the case of mixing silicon and aluminum in one layer, the degree of crystallization is reduced by approximately two times compared to individual layers. Pure amorphous silicon without an absorbing metal layer does not crystallize in modes that do not destroy the nanofibrous substrate.

Funding

This study was supported by grant No. 23-22-00047 from the Russian Science Foundation, https://rscf.ru/project/23-22-00047/.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y. Do, D.Y. Jeong, S. Lee, S. Kang, S. Jang, J. Jang. Adv. Eng. Mater. **22**, 1901430 (2020). DOI: 10.1002/ADEM.201901430.

[2] A.A. Nastulyavichus, S.I. Kudryashov, N.A. Smirnov, R.A. Khmelnitsky, A.A. Rudenko, N.N. Melnik, D.A. Kirilenko, P.N. Brunkov, A.A. Ionin. Optika i spektroskopiya **7**, 897 (2020). (in Russian). DOI: 10.21883/OS.2020.07.49558.61-20.

[3] M.D. Efremov, V.A. Volodin, L.I. Fedina, A.A. Gutakovsky, D.V. Marin, S.A. Kochubey, A.A. Popov, Yu.A. Minakov, V.N. Ulasyuk. Pis'ma v ZhTF **29**, 13 (2003). (in Russian). http://journals.ioffe.ru/articles/12925.

[4] E.L. Alexandrova. FTP **38**, *10*, 1153 (2004). (in Russian). https://journals.ioffe.ru/articles/5630.

[5] A.A. Serdobintsev, I.O. Kozhevnikov, A.V. Starodubov, P.V. Ryabukho, V.V. Galushka, A.M. Pavlov. Phys. Status Solidi A **216**, 1800964 (2019). DOI: 10.1002/PSSA.201800964.

[6] A.A. Serdobintsev, V.V. Galushka, L.D. Volkovoynova, I.O. Kozhevnikov, E.S. Prikhozhdenko, D.I. Artyukhov, N.V. Gorshkov, A.M. Pavlov, A.V. Starodubov. Vacuum **203**, 111304 (2022). DOI: 10.1016/J.VACUUM.2022.111304.

[7] A. Tankut, M. Karaman, E. Ozkol, S. Canli, R. Turan. AIP Advances **5**, *10*, 107114 (2015). DOI: 10.1063/1.4933193.

[8] Jian Zi, H. Büscher, C. Falter, W. Ludwig, Kaiming Zhang. Appl. Phys. Lett. **69**, 200 (1996). DOI: 10.1063/1.117371.

[9] V.A. Volodin, V.A. Sachkov. ZhETF **143**, *1*, 100 (2013). (in Russian). http://jetp.ras.ru/cgi-bin/r/index/r/143/1/p100?a=list.

Translated by I.Mazurov