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Laser-stimulated tin-induced crystallization of silicon on flexible nonwoven substrates

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Abstract. The work is devoted to the formation of polycrystalline silicon coatings on electrospinned nonwoven polyacrylonitrile mats using a metal layer absorbing laser radiation. The results of experimental studies confirming the presence of crystallized silicon structures on nonwoven polymer substrates are presented. The efficiency of tin films with different thicknesses is compared when using them as upper laser-absorbing layers during laser-stimulated metal-induced crystallization of silicon. It was found out that during laser processing, the metal does not ablate completely and the remaining part of it is collected into particles, the size of which depends on the initial thickness of the metal film. It has also been established that during the laser annealing process expansion or glass transition of fibers can occur.

Keywords: nanofibrous nonwoven material, magnetron sputtering, laser-stimulated silicon crystallization, metal-induced silicon crystallization

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Лазер-стимулированная олово-индуцированная кристаллизация кремния на гибких нетканых подложках

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Аннотация. Работа посвящена получению поликристаллических кремниевых покрытий на нетканом нановолокнистом полимерном материале при помощи поглощающего лазерное излучение слоя олова. Приведены результаты экспериментальных исследований, подтверждающие наличие кристаллизованных кремниевых структур на нетканых полимерных подложках.

Ключевые слова: нановолокнистые нетканые материалы, магнетронное распыление, лазер-стимулированная кристаллизация кремния, металл-индуцированная кристаллизация кремния

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Introduction

Silicon (Si) is an affordable and well-studied material used in many fields of science and technology, for example, in micro- and nanoelectronics or solar energy harvesting. Devices using its polycrystalline (pc-Si) form are among the most promising. Recent research shows that pc-Si combines advantages such as efficiency close to that of crystalline Si (c-Si) and a relatively low cost of production [1]. Si films can be crystallized in various ways, but most of them are realized at sufficiently high temperatures. Metal-induced [2] or laser-stimulated [3, 4] crystallization methods are used to lower the crystallization temperature. However, both of these methods reduce the crystallization temperature of Si insufficiently for use bendable polymers as substrates. Combining the two approaches mentioned above allows minimizing the thermal effect on the substrate and opens up the possibility of using a larger range of materials [5]. Electrospinned nonwoven substrates are a unique basis for the production of nanostructures, since the diameter of their fibers initially lies in the range of hundreds of nm's.

Materials and Methods

Nonwoven nanofiber substrates were obtained by electrospinning from a solution of polyacrylonitrile (PAN) in dimethylformamide (0.661 g of dry matter and 5.046 ml of solvent). When the solution was ready, it was poured into a syringe fixed in a syringe pump. The distance from the end of the needle to the collector was set to 25 cm. The process lasted 15 minutes, while the voltage on the high-voltage power supply FUG HCP 140-65000 was equal to 53 kV, and the rate of extrusion of the solution from the syringe was set to 1 ml/h.

Thin films of Si and tin (Sn) were sequentially deposited to the obtained nonwoven substrates by magnetron sputtering using the Angstrom Nexdep setup. Four samples were obtained, differing in Sn thickness: I – 21 nm, II – 49 nm, III – 57 nm, IV – 76 nm. The Si thickness for all samples was equal to 190 nm.

On the obtained samples, 2×2 mm^2 squares were annealed with a pulsed laser (MiniMarker 2) with a wavelength of 1064 nm. Laser processing mode: laser radiation power 0.2 W; pulse duration 4 ns; frequency 60 kHz; laser beam scanning speed 1600 mm/s for samples I and II and 2700 mm/s for samples III and IV. The difference in the velocities of the laser beam for the samples is due to the different thicknesses of the Sn.

Crystallization was verified using Raman spectroscopy. The spectra were taken at the inVia (Renishaw) Raman microscope using a laser with a wavelength of 532 nm. The signal accumulation time was 10 s at each point at a radiation power of 1.25 μW; the laser spot size was 1.3 μm. The spectra were recorded at 16 points at distance of 15 μm.

Scanning electron microscopy (SEM) studies were carried out to observe changes occurring with nonwoven fibers and layers of Si and Sn after laser treatment.

Results and Discussion

Three of the four samples showed the evidence of crystallization, but even the peak of amorphous Si (a-Si) is missing from the spectra obtained from the sample with the thinnest Sn layer (Fig. 1, I). The absence of a-Si peak in the spectra of sample I indicates that not only metal, but also semiconductor ablation occurred during laser surface treatment. According to the remaining graphs (Fig. 1, II-IV), it can be seen that there is a clearly distinguishable peak in the spectra, close to the peak of c-Si (520 cm^{-1}).

Figure 2 shows the SEM images for each of the samples, as well as a snapshot of the original PAN fibers and deposited, but not yet laser-treated fibers.

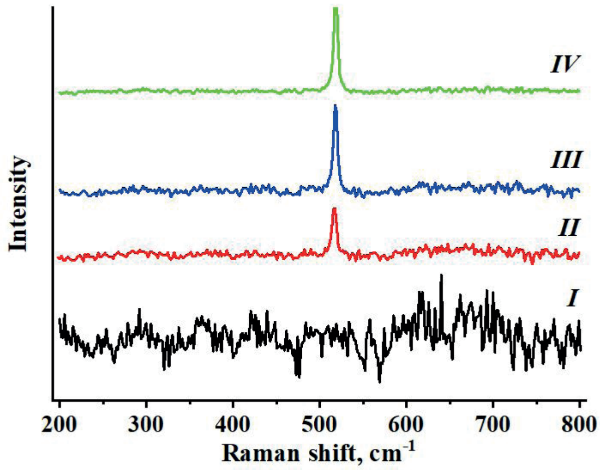

Fig. 1. Averaged Raman spectra of the samples

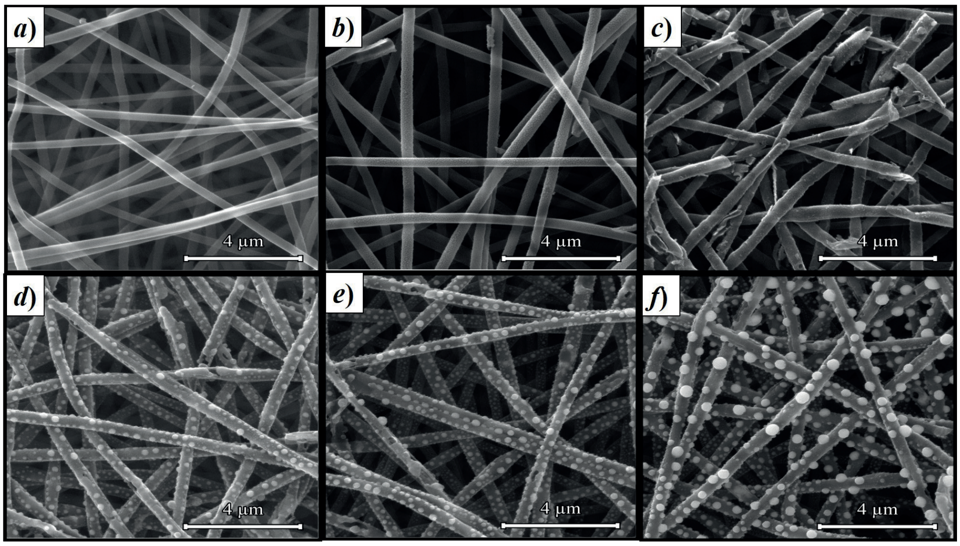

Fig. 2. SEM images of samples: (*a*) – initial PAN fibers; (*b*) – PAN fibers with deposited layers of Si and Sn that have not been subjected to laser treatment; (*c*) – I; (*d*) – II; (*e*) – III; (*f*) – IV

Initial PAN fibers and fibers with deposited layers of Si and Sn before laser treatment do not have much difference. For sample I besides the ablation of Sn and Si, the destruction of the substrate fibers also occurred. The fibers received enough heat for the glass transition (377 K [6]), and they lost their flexibility, becoming brittle. The images of samples II, III, IV also show damaged fibers, but their number is much smaller. The images clearly show also that after laser treatment, Sn is collected into particles, the size of which enlarges with increase of the thickness of the metal layer. In addition to the particles, the diameter of the filaments also grows (Table).

Initial PAN fibers have the smallest average diameter. It is then increased after deposition of Si and Sn layers. A further increase in the fibers diameter can be explained by their thermal expansion. It can be assumed that substrate heating rate slows down with increase of the thickness of the Sn, so the fibers do not have time to heat up to the glass transition temperature, but they manage to expand.

Additionally, the composition of samples II, III, IV was analyzed by the EDX before and after laser treatment. During laser treatment, an average of 13.5 at.% of Sn is removed, the remaining metal melts and collects into particles that are clearly visible in Figure 2.

Table

Data obtained during the investigation of samples by scanning electron microscopy

Sample	Average diameter of the fibers, nm	Average particle diameter, nm	Chemical composition				% of evaporated Sn
			Before laser treatment		After laser treatment		
			Sn, at.%	Si, at.%	Sn, at.%	Si, at.%	
Initial PAN	350.74 ± 0.49	–	–	–	–	–	–
PAN after deposition	389.30 ± 0.75	–	–	–	–	–	–
I	420.28 ± 0.75	–	–	–	–	–	–
II	465.03 ± 0.55	220.97 ± 0.45	15.71 ± 0.01	84.29 ± 0.01	13.29 ± 0.03	86.71 ± 0.03	15.40
III	450.51 ± 0.78	263.55 ± 0.48	21.02 ± 0.05	78.98 ± 0.05	18.45 ± 0.01	81.55 ± 0.01	12.23
IV	483.43 ± 0.84	415.29 ± 0.74	26.43 ± 0.01	73.57 ± 0.01	22.94 ± 0.01	77.06 ± 0.01	13.20

Conclusion

pc-Si structures on nonwoven nanofiber substrates using Sn as the upper absorbing layer were formed by laser-stimulated metal-induced crystallization. The effect of Sn layer thickness to the pc-Si formation was studied. For this purpose, Raman spectroscopy and SEM were used. It was found that the thinnest layer of Sn leads to full ablation of deposited layers and destruction of substrate fibers. Other samples exhibit a different behavior: Sn not only ablates during laser treatment, but also collects into particles. An average of 13.5 at.% of the Sn evaporates from the surface of the samples. Also it was found out that PAN fibers undergo thermal expansion during laser processing and the greater the thickness of the Sn, the more the fibers expand.

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