Optimization of metal-induced laser-stimulated crystallization of silicon films on a flexible substrate by varying the thickness of the aluminum layer

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The influence of the thickness of the aluminum layer on the degree of silicon crystallization after irradiation of a thin-film Al/Si structure on a flexible polyimide substrate by pulsed infrared laser radiation is studied.

Keywords: crystallization of amorphous silicon, metal-induced crystallization, laser-stimulated crystallization, infrared laser radiation, flexible electronics.

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Currently, there is great interest in the development of new methods for forming polycrystalline silicon (poly-Si) films on low-melting substrates [1–3]. The use of polymer substrates makes it possible to create flexible electronic devices based on Si, which will expand the range of applications of these devices. To simplify and to reduce the cost of the crystallization process an original method was developed, i.e. metal-induced laser-stimulated (MILS) crystallization of a-Si on polyimide films [4]. The essence of the method is to use a laser with a wavelength of 1064 nm to effect a thin layer of metal deposited on a layer of a-Si. The use of IR laser makes it possible to eliminate direct heating of the Si layer and the polyimide substrate, since they practically do not absorb in this range. The metal layer, in turn, absorbs the laser radiation energy and transfers it to the Si layer through heat transfer, causing its crystallization. To reduce the formation temperature of c-Si, the mechanism of aluminum-induced crystallization [5–6] is used, which led to the use of Al as the material of the absorbing metal layer. The goal of this paper was to determine the optimal thickness of the Al layer for MILS crystallization of a-Si films 1 μm thick on a polyimide substrate.

To study the effect of the Al layer thickness on the degree of Si crystallization, a series of samples with Al thicknesses of 50, 100, 200, 300, 400 and 500 nm were created. Layers of amorphous silicon and aluminum were sequentially sputtered onto a polyimide substrate using magnetron sputtering without devacuuming the chamber using Nexdep unit (Angstrom, Canada). On each sample five sections of size 10×10 mm were processed using MiniMarker 2 unit (Laser Center, Russia) with a laser beam moving speed of 100−300 mm/s with increment of 50 mm/s. Other parameters of laser processing were constant: radiation power 0.2 W, pulse frequency 99 kHz, pulse width 100 ns.

The structure of the samples was studied by Raman scattering spectroscopy (RSS) using InVia microscope (Renishaw, UK). A laser with a wavelength of 532 nm was used for the study. Measurements were carried out in 16 points on each sample, the distance between neighboring points was 15 μm. The degree of crystallinity for each sample was assessed by the proportion of points at which a peak of the crystalline phase was confidently detected. Additional evaluation criteria were the position of the crystalline phase peak averaged over each sample and its width at half maximum. Based on the peak position the size of silicon crystallites was estimated in accordance with the paper [7].

When the Al layer thickness was 50 nm, the energy transferred to Si turned out to be so great that Si evaporated from the substrate. At a thickness of 500 nm, the energy turned out to be insufficient to remove the entire Al layer, which made it impossible to record RSS. At a thickness of 400 nm (Figure 1, a) the presence in the sample of both crystalline component (a narrow peak in the region of 520 cm^{-1}, corresponding to crystalline TO mode) and the amorphous component (broad peaks around 312 cm^{-1} — LA mode and 480 cm^{-1} — TO mode were detected [8]).

The best degree of crystallization was shown by samples 100 nm thick (Figure 1, b) at processing rates of 150−300 mm/s. The chemical composition of this series was studied by energy dispersive analysis at three points on each sample; at each point, the area $500 \times 500\,\mu$m was integrally analyzed. The results obtained are presented in the Table in the form of values averaged for each sample, indicating confidence intervals.

The Table shows that as the speed of the laser beam increases, the Al content tends to increase. This can be explained by the smaller fraction of Al ablated by laser radiation at high laser speeds. Somewhat surprising is the complete absence of crystallized points on samples processed at a laser speed of 200 and 250 mm/s.

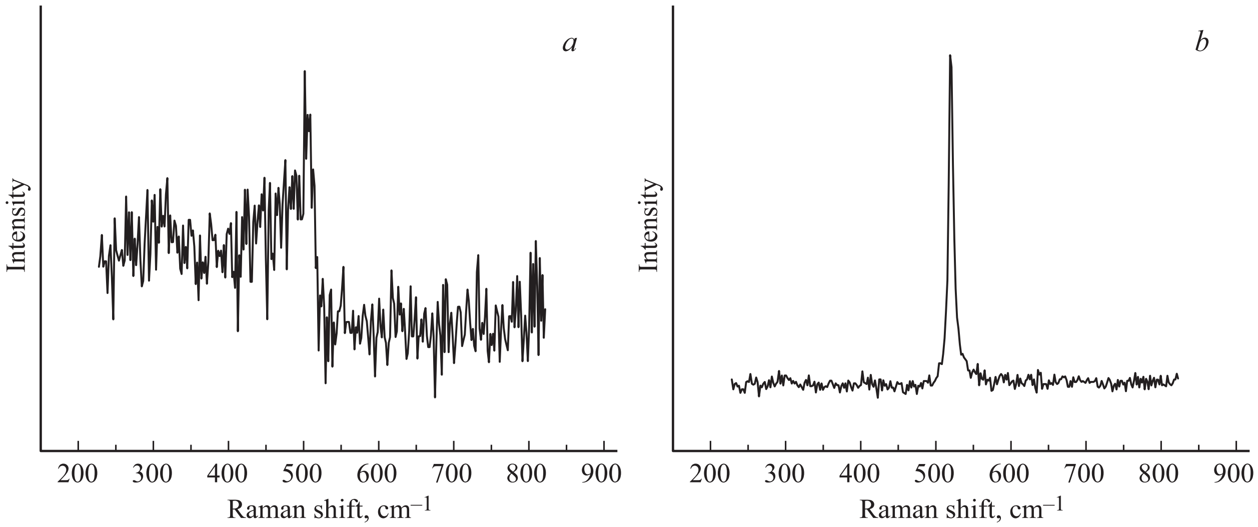

Figure 1. Characteristic RSS spectra: *a*) spectrum corresponding to a sample containing the components *a*-Si and *c*-Si (layer thickness Al 400 nm, beam movement speed 250 mm/s); *b*) spectrum corresponding to crystallized Si (layer thickness Al 100 nm, beam speed 150 mm/s).

Chemical composition and results of RSS studies of samples with Al layer thickness of 100 nm

Movement speed of laser, mm/s	Content Si, at.%	Content Al, at.%	Content O_2, at.%	Position poly-Si of peak, cm^{-1}	Width of the peak on its half-height, cm^{-1}	Proportion of crystallized points, %
150	79.47 ± 0.22	7.35 ± 0.19	13.18 ± 0.36	519.87 ± 0.16	6.69 ± 0.48	100
200	86.71 ± 0.32	7.24 ± 0.07	6.05 ± 0.26	–	–	0
250	76.94 ± 0.29	16.79 ± 0.12	6.26 ± 0.19	–	–	0
300	76.09 ± 0.89	16.67 ± 0.32	7.24 ± 1.00	517.69 ± 0.69	12.36 ± 2.58	81.25

To clarify this point, the surface morphology of samples with Al layer 100 nm thick was studied using scanning electron microscopy (Tescan Mira II LMU microscope, Czech Republic). The study results are shown in Figure 2.

In the image of the sample surface processed at laser speed of 150 mm/s (Figure 2, *a*), one can distinguish faceted dark areas, which most likely correspond to areas *c*-Si. Despite the visual heterogeneity of the surface, no cracks or chips are observed, the film remains continuous. Since the Al content in this sample was 7.35 ± 0.19 at.%, it can be assumed that the lighter areas correspond to residual Al on the Si surface. This is confirmed by the data of local energy dispersive analysis, which revealed decrease in the Al content in dark areas by 1.5 times. Considering that 100% of the studied points on the surface of the sample showed the presence of crystalline phase, we can conclude that the thickness of the residual Al, which is most likely in oxidized state, is small. Such a virtually transparent layer does not prevent RSS measurements.

For samples processed at laser speeds of 200 and 250 mm/s (Figure 2, *b, c*), the surface looks much more uniform, which suggests the presence of a continuous layer of unoxidized Al on surface. As a result, RS spectrometry does not detect the crystalline phase, since the probing laser does not reach the Si surface. However, with increase in the processing speed, the signal of the crystalline phase reappears, which is accompanied by the appearance of small (100–200 nm) formations both light (Figure 2, *c, d*), and dark (Figure 2, *d*). Most likely, these are Al crystallites (light) formed during laser annealing and containing some Si impurity. Dark crystallites can be identified as *c*-Si that came to the surface as a result of Al-induced layer exchange [9].

It should be noted that in our previous papers [10,11] related to the study of amorphous silicon films crystallized by similar method on glass substrates, in some of the measurements the position of the RSS peak of the crystalline phase was recorded, shifted towards higher frequencies relative to the peak of single-crystal silicon . This effect may indicate the presence of compressive mechanical stresses in crystallized films [12]. In the present paper, for all measurements, the peak of the crystalline phase is shifted only to lower frequencies. Thus, most likely, the mechanical stresses in the film on a flexible substrate are lower due to the greater plasticity of the latter.

Electron microscopy results confirm the integrity of silicon films after MILS crystallization. The optimal thickness of the Al layer was established to be 100 nm for the thickness of the crystallized layer of Si 1 μm. For the laser

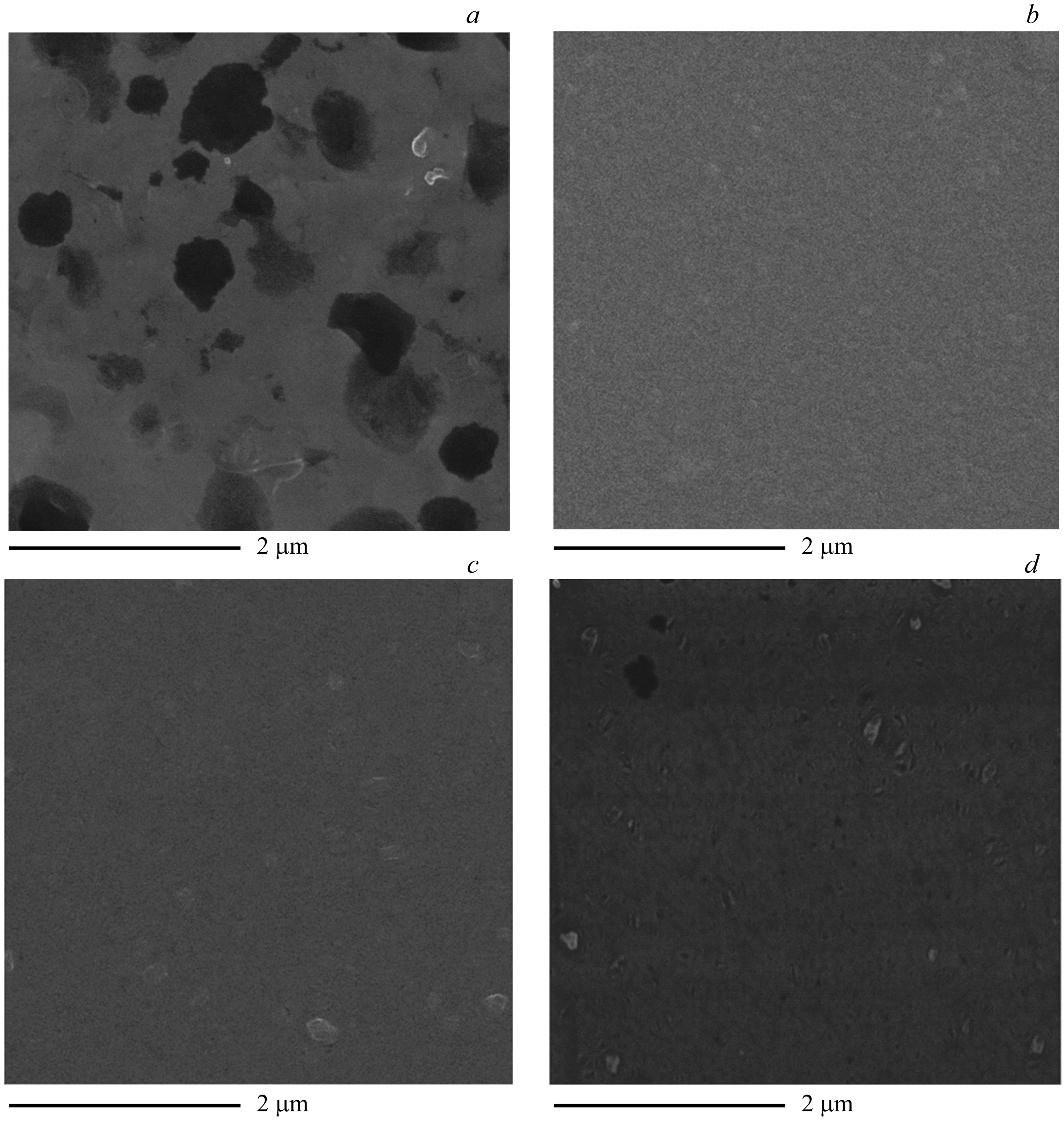

Figure 2. Morphology of samples with Al 100 nm thick and different laser processing speeds: *a*) 150 mm/s, *b*) 200 mm/s, *c*) 250 mm/s, *d*) 300 mm/s.

speed of 150 mm/s the crystalline phase was detected in all studied areas of the sample in the virtual absence of peaks of the amorphous phase, which indicates complete crystallization of at least the surface region of the silicon film. Thus, as a result of the studies carried out, the possibility of producing poly-Si films on flexible polymer substrate without its destruction was shown.

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Conflict of interest

The authors declare that they have no conflict of interest.

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