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Monitoring of the Morphologic Reconstruction of Deposited Ablation Products in Laser Irradiation of Silicon**M. Vlasova^{1*)}, P. A. Márquez Aguilar¹, M. C. Reséndiz-González¹,
M. Kakazey¹, V. Stetsenko², T Tomila², A Ragulya²**¹ The Autonomous University of the State of Morelos, Av. Universidad, 1001, Cuernavaca, Mexico² Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3, Krzhizhanovsky St., Kyiv, 252680, Ukraine**Abstract:**

Using electron microscopy, atomic force microscopy, X-ray microanalysis, and IR spectroscopy, it was established that, in the regime of continuous laser irradiation of silicon at $P = 170$ W in different gaseous atmospheres with an oxygen impurity, SiO_x composite films with a complex morphology form. The main components of ablation products are clusters that form during flight of ablation products and as a result of separation of SiO_x -clusters from the zone of the irradiation channel. The roughness and density of the films depend on the heating temperature of the target surface and the type of deposited clusters.

Keywords: Silicon, Laser irradiation, Argon, Nitrogen, Oxygen, SiO_x films.

1. Introduction

It is known that, in laser treatment of different materials, a number of processes, the main of which are the heating-up and melting of the surface layer, occur. In this case, vaporization, ejection of melted droplets, exfoliation, and decomposition take place [1-5]. Depending on the aims and irradiation conditions (surface modification, cutting of articles, deposition of films, continuous or pulse irradiation of different power in various atmospheres, etc.), the contributions of the indicated products can be controlled to a certain extent [6, 7].

In recent years, considerable attention has been given to the technology of deposition of thin films. The reasons of this are as follows. On the one hand, properties of film-like structures (particularly, two-component oxide compounds) are close to properties of massive materials. On the other hand, such films, as a rule, have a number of unique properties, which are absent in massive materials. Note that the laser synthesis of thin films provides the highest power density on the "atomized" surface. The most adequately studied objects are SiO_2 and SiO_x films obtained in the regime of pulse irradiation of Si on a silicon surface [7]. A large amount of work has been devoted to structures in the laser treatment of silicon [7]. They describe both the transformation of silicon surfaces and features of ablation in different gaseous atmospheres [8-12].

The aim of this work is to investigate the morphologic features of films formed by ablation products on collective plates (substrates) depending on the conditions of laser irradiation, namely the composition of the gaseous atmosphere. The data of the investigation

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may be useful in deposition of films with certain morphologic properties and a metastable phase composition, specifically SiO_x and $\text{SiO}_x\text{:N}$, where $x < 2$. It is precisely these films that are of interest in applied problems of microelectronics [13-15].

2. Method of Preparation and Investigation

As a target, a monocrystalline silicon plate with a diameter of 30 mm and a thickness of 10 mm was used. Irradiation was performed with continuous-action lasers with a wave length $\lambda = 1064$ nm and a power $P = 170$ W in argon, nitrogen atmosphere with traces of oxygen. For this purpose, an irradiation chamber was preliminarily blown through with gases at an excessive pressure of 4 atm for 15 min. Then the chamber was closed. With such a method of gas feed, residual oxygen was present in the chamber. We used argon with a purity of 99.93% and nitrogen with a purity of 98.5%.

The diameter of a laser spot was 0.3 mm. The irradiation scheme is shown in Fig. 1. The traverse speed of a coordinate table was 0.1 mm/s. Such a regime was chosen to rule out the possibility of large contributions of hydrodynamic effects, accompanied by the ejection of large drops of silicon melt. Ablation products were deposited on quartz plates. The distance between a target and a collective plate was 20 mm, and the angle between them was 30° .

An electron microscopy study of deposition products was performed with a HU-200F type and a LEO 1450 VP (EDS) scanning electron microscope. An X-ray microanalysis of samples was performed in "Comebax SX50" and LEO 1450 VP (EDS) units. To determine components in a deposited film, the substrate was cut, and measurements were performed of the end face of the substrate in the region of the film. Atomic force microscopy (Digital Instruments Nanoscope IV in tapping mode with a silicon nitride tip) was used in the height (topography), phase, and amplitude regimes. A cross-section analysis was also performed. IR spectra were obtained for ablation products deposited in the chamber and on collective plates (to exclude the superposition with the IR spectrum of the quartz plates) with an M 80 spectrometer.

3. Experimental Results and Discussion

3.1. Irradiation in an argon+oxygen atmosphere

According to the electron microscopy data, upon passing the laser beam, a channel forms on the surface of the target (Fig. 2 a, b). Arcs are clearly seen inside the channel. The formation of a large-scale periodic structure with a step $d \sim 3\text{-}20$ μm is caused, according to [8], by the pulse regime of melting of the material in the channel. The pulse regime is initiated by the variations in temperature caused by the oscillatory character of displacement (ablation) of the melt from the channel. On the tops of the arc and on the edges of the channels, combs from melted and repeatedly deposited silicon and solidified drops form. On the bottom of the channel, regions of a pure surface and regions of accumulations of spherical particles extended above the surface are seen (see Fig. 2 b).

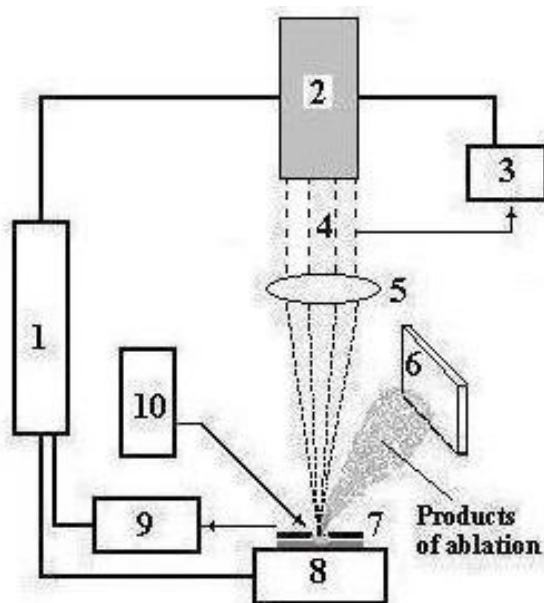
According to the X-ray microanalysis data, on the surface which was not irradiated, silicon is dominant. The oxygen content increases as the distance to the channel decreases and in the channel itself, particularly in the zones of accumulation of spherical particles (Tab. I).

The ablation products of silicon form a film (Fig. 3 aa'). On the surface of the film, particles of different size are seen. The formed film is practically homogeneous.

The X-ray microanalysis data show that, along with silicon, an insignificant amount of oxygen is present. In large particles, silicon prevails, and in the regions of accumulation of small particles, the oxygen content is the largest (see Tab. I).

Tab. I. Contents of elements at different places of targets and collective plates in laser irradiation in different mediums.

Atmosphere of irradiation	Place of analysis	Element content, wt. %		Value of x in SiO _x
		Si	O	
Argon + oxygen	Target: the surface of a target far from the irradiation zone	100	no	0
	the surface near the channel of irradiation	68.66	31.34	1.176
	inside the channel	54.86	45.14	1.69
	Collective plate: place 1 place 2 place 3	81.88 66.87 60.1	18.12 33.13 39.90	0.68 1.24 1.46
Nitrogen + oxygen	Target: the surface of a target far from the irradiation zone	100	no	0
	inside the channel of accumulation of spherical particles	48.5	51.5	1.82
	Collective plate: place 1 place 2	53 40	47 55 (N~5%)	2 1.5

**Fig.1.** Simplified scheme of irradiation of a Si target. (1) programmer (2) laser; (3) sensor of irradiation parameters; (4) laser beam; (5) optical system; (6) collective plate; (7) treated specimen; (8) device for fixing and displacement of a treated component; (9) sensor of process parameters; (10) device for feeding a process atmosphere.

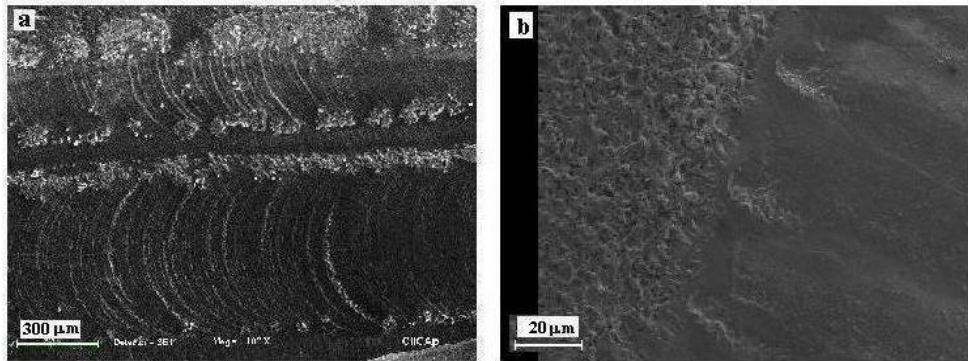


Fig. 2. Micrograph of a silicon surface after a pass of a laser beam (a). Surface near the edge of a channel. Irradiation in an Ar-O atmosphere (b).

In IR spectra of the deposition products, weak absorption bands of Si–Si bonds and more intensive absorption bands of Si–O bonds are present (see Tab. II).

Tab. II. IR absorption bands of deposited films

Atmosphere of deposition of films	IR absorption band, cm^{-1}	References
Argon + oxygen	515w. 600w. 900w. 1100m. 1165w. 1220w.	This work
Nitrogen + oxygen	465m. 798wd.w. 1100s. 1381v.w. 583sh. 960sh.	This work
SiO_2	466s. 778w. 1084s.	[16]
SiO_x	620w. 880w. 980w. 1130w.	[17]
Si_3N_4	480w. 950wd.s.	[18]
$\text{SiN}_x\text{:H}$	830s. 1175v.w.	[19]
$\text{Si}_x\text{N}_y\text{O}_z$	448m. 820w. 1099 1035sh.	[20]

Note: s is strong; m is middle; w is weak; sh is shoulder; wd is wide and v is very. The bold font designates basic bands, on which bands arranged in columns are located.

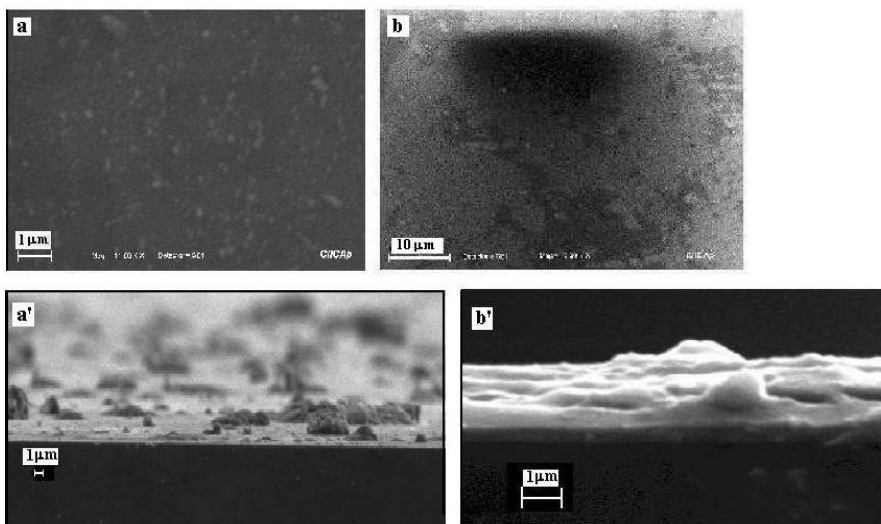


Fig. 3 Micrograph of a film formed during ablation of silicon in an Ar-O atmosphere (a,a') and a N-O atmosphere (b, b'). Top view of the film (on a plane) (a, b); side view of the film (from the side of a section) (b, b').

From AFM images one can see (Fig. 4) that the film consists of a mixture of clusters and particles of different size. In lower layers of the film, smaller particles and clusters are located. Large clusters are present on the surface of the film and confirm coalescence of smaller clusters in the stage of cooling of drops of different size. The size of clusters and particles ranges from 625-2149 nm. The size of large clusters is to 4 μm .

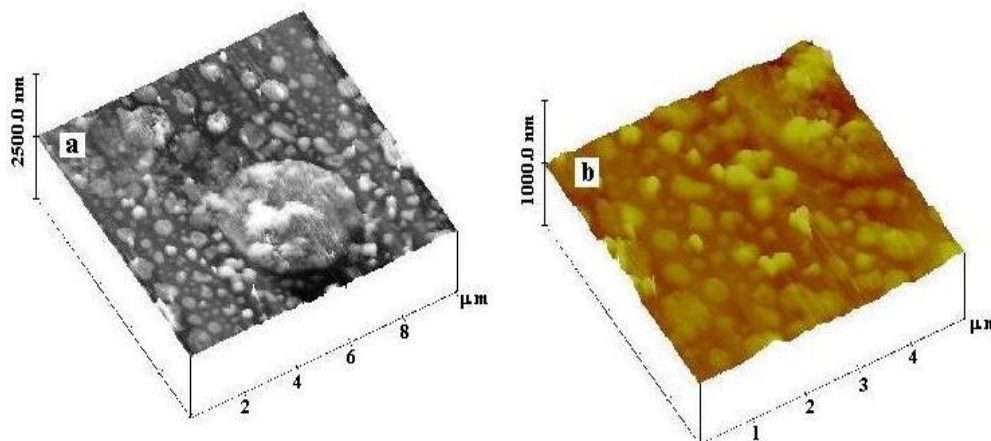


Fig. 4 AFM image of a fragment of a film deposited in irradiation of Si in an Ar-O atmosphere in the height regime at different resolution.

Taking into account the melting point and the boiling point of silicon (1420°C and 2620°C, respectively) [21] and product formation on the channel boundary, we can assume that the temperature on the surface of the target is above 2600°C. In flying in argon, the ablation products begin to cool, merge in clusters of different size and deposit on the collective plate. The presence of large clusters on the surface of the film indicates that they form in the final stage of irradiation (in a longer irradiation time). The presence of oxygen both on the surface of the target and in the film is explained by the diffusion of retaining oxygen from the gaseous atmosphere into silicon.

Since the oxygen content in different regions of the film does not correspond to the oxygen content in the silica, the film can be considered as a SiO_x film, where $x < 2$.

3.2. Irradiation in a nitrogen+ oxygen atmosphere

In passing of the laser beam on the surface of a silicon target, a channel forms, as in the previous case (Fig. 5 a). Outside the irradiation zone, on the surface of the target, a porous layer is deposited. On the boundary of the irradiation zone, solidified drops of the melt are present (Fig. 5 b). On the bottom of the channel, a loose layer is located (Fig. 5 c). It consists of conglomerates and individual spherical particles of different size (Fig. 5 d), that extend over the surface. Regions of a “pure” surface are also present.

According to the X-ray microanalysis data, (see Tab. I), on the surface that was not irradiated, silicon prevails. In the channel, along with silicon, oxygen is detected. The oxygen content is larger in the accumulations of spherical particles. However, nitrogen was not detected.

Thus, as the laser beam passes, in the zone of the forming channel, the following processes occur: melting and evaporation of silicon; diffusion of silicon into the surface layer of the channel and formation of SiO_x silicon oxides; sublimation (evaporation) of formed compounds. Taking into account the melting point and the evaporation (sublimation) temperature of Si and SiO_2 [22, 23], that cover the range 1400-2600°C, it can be concluded that, in the used irradiation regime, the silicon surface is heated in a narrow zone to a temperature $\geq 2600^\circ\text{C}$. The inhomogeneity of the coating of the surface of the channel with newly formed particles indicates that the separation (removal) of assemblies of particles of different size takes place. The formation of a deposit on the surface of the target and the ejection of melted silicon from the channel are caused by intensive propagation of the evaporation products and the development of hydrodynamic effects.

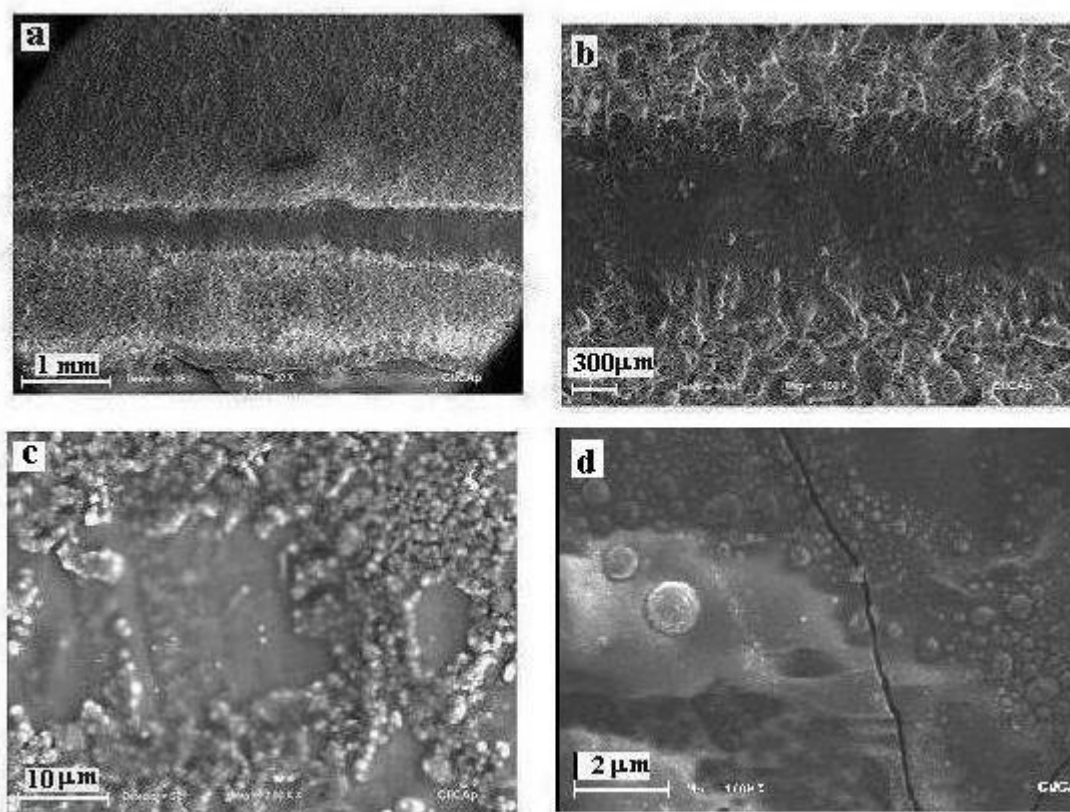


Fig. 5 A micrograph of a silicon surface after passing a laser beam (a-c) and a surface inside a formed channel (c-d). Irradiation in N-O atmosphere.

On the collective plate, the ablation products form a film. From Fig. 3 b, b' it is seen that the film is inhomogeneous and loose in comparison with that obtained in argon. According to the X-ray microanalysis data, the main components of the film are silicon, oxygen, and nitrogen (see Tab. I).

From AFM images (Fig. 6), it is also seen that the film consists of a mixture of clusters and particles of different size. As in the case of irradiation on an argon atmosphere, particles and clusters of smaller size are located in the lower layers of the film. The size of clusters ranges from 65 to 360 nm.

In IR spectra of such films, absorption bands (see Tab. II) that are assigned to Si-O and Si-N bonds are present. That is why it can be concluded that this obtained spectrum is a

superposition of ablation products, namely SiO_2 , Si_3N_4 and metastable intermediate compounds based on them.

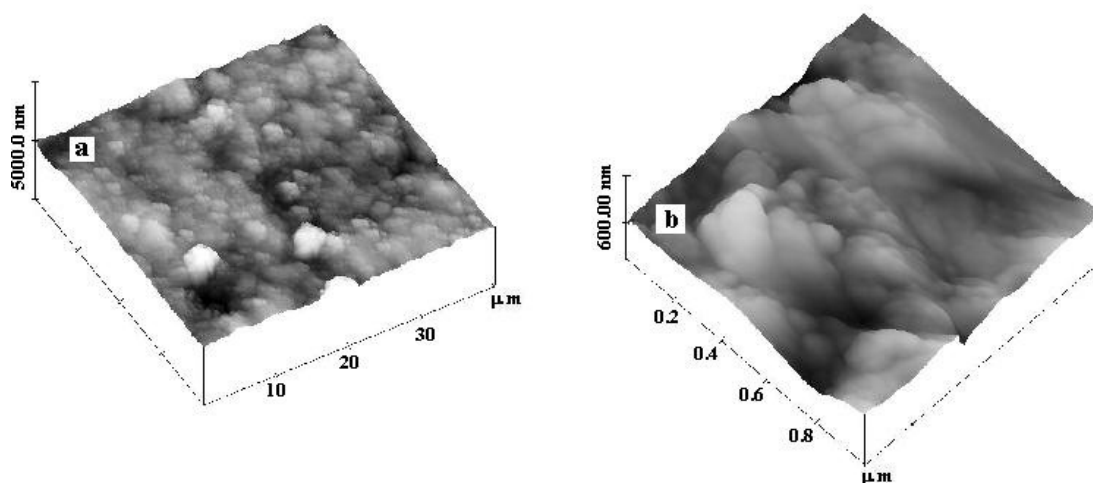


Fig. 6 AFM image of a fragment of a film deposited in irradiation of Si in N-O atmosphere in the height regime at different resolution.

The formation of silicon nitride and silicon oxide during the flight of ablation products in an argon atmosphere are easily explained, whereas the formation of SiO_x and silicon oxynitride can be associated with the incompleteness of the oxidation and nitration processes in the transfer of large clusters. Note that the detection of regions of “pure” surface and accumulations of spherical particles containing oxygen in the channel zone indicates that diffusion of gases into the liquid silicon layer occurs. In this case, not only silicon “clusters + particles”, but also newly formed intermediate compounds are ejected. The comparatively low melting point of silicon ($\sim 1420^\circ\text{C}$), its large affinity to oxygen, and the low mobility of nitrogen in silicon lead to the formation of a SiO_x film (where $x \leq 2$) on the surface of the target even at a low oxygen content.

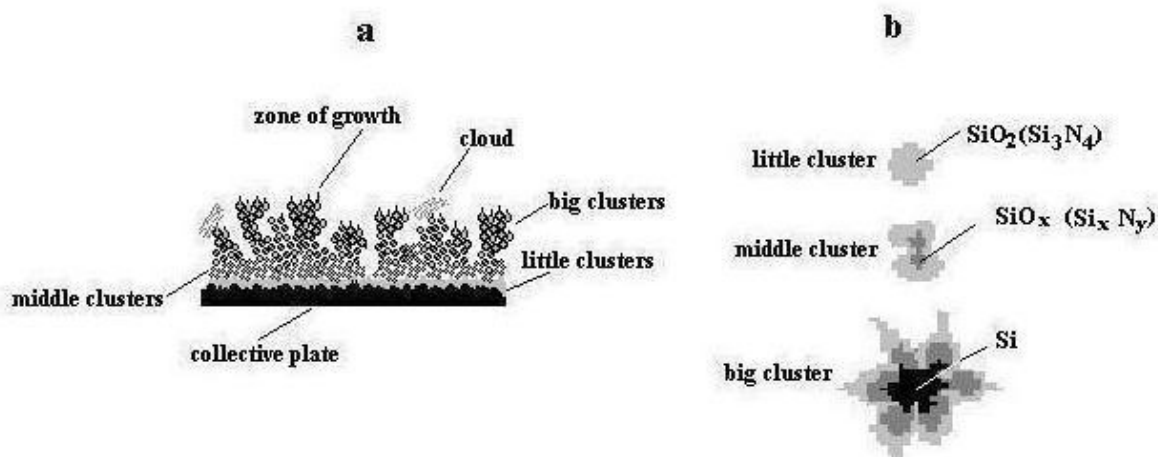


Fig. 7 Schematic representation of a film formed on a collective plate: (a) and (b) - composite structure of formed particles.

Thus, the films formed in the irradiation of silicon in an argon atmosphere or a nitrogen atmosphere containing an oxygen impurity are composite. Small clusters deposit first on the surface of the collective plate. As the target is heated and melts, larger clusters deposit on the surface of the collective plate. In this stage, large clusters form not only in flying, but also as a result of their separating from the irradiation zone (channel).

When particles are flying in gaseous atmospheres (oxygen, nitrogen, carbon dioxide, etc.) that are able to interact with silicon at high temperatures, compounds, including metastable ones, can form [8, 24]. The diffusion of atoms of surrounding gases into the subsurface layer of the target also occurs. Taking into account that, in a gaseous atmosphere, clusters of different size can be present, the degrees of development and the degrees of completeness of diffusion processes over the whole volume of clusters during their flight will be different. For instance, nanoclusters can be silicon oxide or silicon nitride. Larger clusters will be characterized by the incompleteness of the diffusion process. In this case, the surface layer of clusters must be characterized by the stoichiometric composition (SiO_2 , Si_3N_4) or by a more complex composition if they fly in a mixture of gases. In the subsurface layer, metastable compounds (SiO_x , Si_xN_y , etc.), characterized by an excessive silicon content, must form. In the core of a cluster, silicon must be located. In such a model, the thickness of layers depends on the size of a cluster, its fly time, and the diffusion rate of gas atoms.

Thus, the film formed on the collective plate appears rather inhomogeneous in the phase composition as well. In Fig. 7, such a film is shown schematically.

Changes in the homogeneity and density of the film with changing composition of the gaseous atmosphere are determined to a large degree by the temperature of the deposited product. Actually, in deposition at $T \geq T_{\text{melt}}$, the melt is deposited. In this case, a more homogeneous, denser film forms. If “particles + clusters” deposit in the solid state, a loose multilayer film with different morphology of layers is obtained.

The established features of the formation of films in the ablation of silicon in different gaseous atmospheres enable us to come closer to the solution of the problems of synthesis of thin films (nanofilms) of predetermined morphology and phase composition.

4. Conclusions

Investigations performed in the regime of continuous laser irradiation of a silicon surface in a gaseous atmosphere of complex composition showed the following.

1. The morphologic features of a formed film deposited on a collective plate reflect the multistage process of heating of the surface of a silicon target and passing from the initial stage of evaporation of individual particles to the stage of ablation of clusters from the surface of the target, which is accompanied by the formation of clusters from individual particles as they fly in a gaseous atmosphere.
2. The composition of a gaseous atmosphere and the diffusibility of gases entering its composition predetermine the composition of a deposited film.
3. The reactivity of used gaseous atmospheres with respect to irradiated silicon grows in the order oxygen \rightarrow nitrogen \rightarrow argon.
4. While particles and small clusters fly through a reactive gaseous atmosphere, new compounds (SiO_2 , Si_3N_4) form.
5. The flight of large clusters through a gaseous atmosphere is accompanied by the diffusion of gas molecules from them and the formation of composite clusters of a complex composition.

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Садржај: *Коришћењем електронске микроскопије, атомске микроскопије, рентгенске микроанализе и инфрацрвене спектроскопије утврђено је да се композитни филмови SiO_x са комплексном морфологијом формирају у режиму континуалног ласерског зрачења силикона на $P\ 170\ W$ у различитим гасовитим атмосферама са примесама кисеоника. Кластери који се формирају током прелета аблационих продуката и као резултат сепарације кластера SiO_x од зоне канала зрачења су основне компоненте аблационих продуката. Финоћа и густина филмова зависи од температуре загревања површине мете и врсте нанетих кластера.*

Кључне речи: *Силикон, ласерско зрачење, аргон, азот, кисеоник, филмови SiO_x .*
