Formation of SiO$_x$ nano-films at laser ablation of Si and composite SiC-ceramic

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By methods of electron microscopy, atomic force microscopy, X-ray microanalysis the influence of continuous IR laser irradiation ($\lambda = 1064$ nm, $P = 240$ mW, 175 W and 210 W) on Si, SiC, and SiC-Cr$_3$Si$_3$ ceramics is investigated. It is established that the basic product of ablation is silicon. Depending on capacity of radiation, time of irradiation and composition of the gas environment on a surface of collection plate films of SiO$_x$ and SiO$_x$:N, where $x \leq 2$, are precipitated. At various stages of an irradiation (from a mode of evaporation up to plasma formation) a nano-films of various morphology are formed.

**Keywords:** Laser irradiation; ablation; Si; SiC; SiC-Cr$_3$Si$_3$; SiO$_x$-films.

Por métodos de microscopía electrónica, de fuerza atómica, and microanálisis de rayos X se investigó la influencia de la irradiación de un láser IR continuo ($\lambda = 1064$ nm, $P = 240$ mW, 175 W and 210 W) en cerámicas compuestas Si, SiC, and SiC-Cr$_3$Si$_3$. Se establece que el producto básico de la ablación es el Silicio. Dependiendo de la potencia de la radiación, tiempo de la irradiación y la composición del gas en el cual se lleva a cabo el experimento se precipitarán películas de SiO$_x$ y SiO$_x$:N, donde $x \leq 2$ en una superficie colectora. En diferentes etapas de la irradiación (desde la evaporación hasta la formación del plasma) se forman nano-películas con distintas morfologías.

**Descriptores:** Irradiación Laser; ablación; Películas Si; SiC; SiC-Cr$_3$Si$_3$; SiO$_x$.

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1. Introduction

It is known that at the laser treatment of materials (metals, ceramics, polymers, etc.) different processes proceeds, which briefly can be described as a heating of surface layer. In this case occurs vaporization, a melting, ejection of melted droplets, exfoliation and decomposition [1-4]. In dependence on purposes and conditions of irradiation (modification of surface, a cutting of work materials, an obtaining of films; continuous or pulse regime of irradiation, different capacity of laser beam; different gas environment and others) by contribution of mentioned above processes in the certain frameworks can operate.

The goal of this work is the investigation of precipitation of films on quartz collection plate at laser irradiation of Si, SiC and SiC-Cr$_3$Si$_3$ ceramics in different modes of continuous irradiation: at low capacity of beam, at middle capacity and at high capacity.

Let’s note that the majority of works on an irradiation of silicon and silicon carbide are executed in modes of the pulse irradiation, characterizing by the big capacity in an impulse. At these modes the processes of the melting, ablation, ejection of liquid drops due to development of hydrodynamical effects are realized simultaneously. Therefore, for an establishment of evolutionary connection between a temperature state of a surface of a target and peculiarities of formation of clusters in a zone of a flying, morphology and phase composition of a precipitated film the regimes of a continuous irradiation of various capacity are chosen.

The Si, SiC and composites on the basis of SiC are materials with various heat conductivity, thermostability, resistance oxidation and reactionary ability [5,6]. It means that the process of ablation for these materials must be different. Among Si $\rightarrow$ SiC$\rightarrow$ SiC-Cr$_3$Si$_3$ ablative processes most actively should pass for silicon, because the silicon carbide and its composites are refractory high-temperature materials. As known, basic elements of precipitation are clusters [7-9], which sizes substantially depend on a mode of an irradiation. At the flying of clusters through the reactionary-active gas environment (oxygen, nitrogen, etc.) on their basis can be formed the new stable and metastable compounds [10,11]. Reasons, conditions and properties of such precipitated on collective plate nano-films practically are not studied.

2. Methods preparation and investigation

The irradiation of samples was carried out in air and in (O$_2$ + N$_2$) gas mixture with an infrared lasers ($\lambda = 1064$ nm) at $P = 240$ mW (regime I), 175 W (regime II), and 210 W (regime III). The radius of the beam was 0.45 mm. The time of irradiation was varied from 5 to 150 min. Various modes of irradiation are chosen to initiate ablation of particles and clusters of the various size. The products of evaporation on quarts collection plate were precipitated. For the determination of phase composition from plates the precipitated product was scraped. For the definition of phase composition of the ceramic surface layer was cut away and investigated.

As target was the Si (001)-wafer with 2 mm thickness. SiC and 90 wt.% SiC + 10 wt. % Cr$_3$Si$_3$ ceramic were obtained at $T = 2073$ K and $P = 5$ GPa during 2 min. The size of samples constitutes: $d = 5$ mm, $l = 10$ mm.

For the support of a certain gas medium in the chamber of an irradiation a preliminary expulsion by gas mixture at superfluous pressure in 0.4 MPa during 15 min. was carried out. Then camera was closed. The purity of nitrogen and oxygen...
was 99.8%. The mixture of gases consisted their equal parts of nitrogen and oxygen.

An X-ray analysis of samples was performed in a Siemens D-500 diffractometer using Cu Kα radiation. Scanning electron microscopy studies were carried out with an HU-200F unit. An X-ray microanalysis of samples was performed in a “Comebax SX50” unit. Atomic force microscopy (AFM) measurements were performed on a Digital Instruments Nanoscope IV in tapping mode with a silicon nitride tip in regimes of height (topography) with cross-section-profile, phase and amplitude. Infra-red spectra obtained on spectrometer M 80.

3. Results and discussion

3.1. Irradiation of Si

The main product of silicon ablation at different capacity of irradiation is the Si. According to X-ray diffraction the precipitated products are roentgen amorphous. Their research by a method of IR-spectroscopy has shown (see Fig 1a and Table I) that during the passing through the air the silicon is converted into SiO$_x$, where $x = 2$ on a stage of the heating-evaporation (clusters/particles of little size). And for on a stage of the evaporation-melting of Si, when from a zone of an irradiation large clusters and drops of silicon are ejected, $x \leq 2$. This conclusion was supported by data of x-ray microanalysis (see Table II).

![Figure 1](image-url)

**Figure 1.** The IR-spectra of precipitated films at laser irradiation of Si in air (a) and in O$_2$-N$_2$ medium. (a) is the typical spectrum of silica, and (b) is the spectrum of silicon oxynitride. By * is marked bands for “pure SiO$_2$”.

<table>
<thead>
<tr>
<th>Medium of irradiation</th>
<th>Type of cluster</th>
<th>Content of elements, wt.%</th>
<th>SiO$_x$, where x</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong></td>
<td>Little cluster (~ 100 nm)</td>
<td>Si: 46.66, O: 53.34, N: not</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Big cluster (~ 1500 nm)</td>
<td>Si: 54.86, O: 45.14, N: not</td>
<td>1.69</td>
</tr>
<tr>
<td><strong>N$_2$ + O$_2$</strong></td>
<td>Little cluster (~ 100 nm)</td>
<td>Si: 45.9, O: 52.6, N: 1.5</td>
<td>~ 2</td>
</tr>
<tr>
<td></td>
<td>Middle cluster (~500 nm)</td>
<td>Si: 51.2, O: 46.37, N: 2.43</td>
<td>~ 1.74</td>
</tr>
<tr>
<td></td>
<td>Big cluster (~ 1700 nm)</td>
<td>Si: 61.62, O: 35.64, N: 2.74</td>
<td>~ 1.34</td>
</tr>
</tbody>
</table>

**Note:** s is strong; m is middle; w is weak; sh. is shoulder; v is very. The bold font marks the basic band, on which the bands given in the column settled down.

<table>
<thead>
<tr>
<th>TABLE I.</th>
<th>IR bands of absorption in films on the base of Si, O, N elements.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium of</td>
<td>The position of IR-bands of absorption in region $\nu \sim 400$–2000 cm$^{-1}$</td>
</tr>
<tr>
<td>precipitation</td>
<td></td>
</tr>
<tr>
<td>of films</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>471m, 600v.w, 808w, 1105s, 1381v.w, 1642v.w.</td>
</tr>
<tr>
<td>N$_2$- O$_2$</td>
<td>465m, 798wd.w, 1100s, 1381v.w, 1555w, 583sh, 960sh, 1647m, 1739w.</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>466s, 778w, 1084s.</td>
</tr>
<tr>
<td>SiO$_x$</td>
<td>620w, 880w, 980w, 1130w.</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>480w, 950wd.s.</td>
</tr>
<tr>
<td>Si$_x$N$_y$O$_z$</td>
<td>448m, 820w, 1099s, 1035sh.</td>
</tr>
<tr>
<td>SiC</td>
<td>910 s.w.</td>
</tr>
</tbody>
</table>

**Note:** s is strong; m is middle; w is weak; sh. is shoulder; v is very. The bold font marks the basic band, on which the bands given in the column settled down.
FORMATION OF $\text{SiO}_x$ NANO-FILMS AT LASER ABLATION OF Si AND COMPOSITE SiC-CERAMIC

**Figure 2.** The AFM images a part of $\text{SiO}_2$-film obtained after laser irradiation in regime III. By arrow on Fig. 2 b is shown zone of CVD growths.

**Figure 3.** The AFM image of a part of film with pyramidal particles obtained in regime of topography (height) (a) and cross-section profiles in direction A and B (b,c).

**Figure 4.** The electron micro photo of film in the form of cloud.

At the passing through the $\text{O}_2$-$\text{N}_2$ medium takes place transformation $\text{Si} \rightarrow \text{SiO}_x$-$\text{N}$, where $x \leq 2$. On Fig 1b and in Table I IR-spectra of such films and theirs positions are presented. From the Table II it is visible that a film, basically, is formed by silicon oxide. The content of nitrogen in film is insignificant. This is caused that the diffusion of oxygen in silicon is more preferable than nitrogen [6].

At comparison with literary data (see Table I) it is possible to conclude that a precipitated films represent an assemblage of products of oxidation-nitriding of silicon particles (clasters). The degree of oxidation-nitriding should be defined by a number of factors: composition of the gas environment, the size of Si particles, time of flight, etc.

It is established that at different regimes of irradiation (capacity of beam, time of irradiation, etc.) the nano-films of different morphology are formed. It is caused by a degree of development and overlapping of processes of an evaporation-sublimation, a melting, ejection of liquid silicon drops and formation of plasma.
Figure 5. The AFM image in regime of topography (height) (a), phase (b) of cloud film and it profile (c).

Figure 6. The common schema of different stages of films formation at laser irradiation of silicon. (a – d) are different stages of the heating of target surface accompanied by ablation and precipitation of particles and clusters of various morphology.
According to AFM data at irradiation in regime I during 15 min. or on initial stage of the heating in regime II and III the layer of silicon oxide or silicon oxynitride consists from the nano-clusters. The size of clusters is $3 \div 176$ nm. At their precipitation the relief of collection plate becomes more smoothly. With the increasing of capacity of irradiation (regimes II, III) or time of irradiation in all regimes the heating of surface of target is accompanied by intensification of evaporation of silicon. At that the size of the evaporating clusters increases and makes: $250 \div 515$ nm (for regime II) and $1.23 \div 2.60 \mu m$ (for regime III). The formation of big clusters can be as result of detachment of clusters from a surface of a target, and also association of small clusters at their flyby [18]. On Fig. 2 a it is visible that in a mode III clusters of the various sizes are simultaneously deposited. For brevity on Fig. 2 a the most typical morphology of a surface of films, which is inherent at initial stages of irradiation at regimes I-II is noted.

In regimes II- III or long time of irradiation in regime I in the clusters on the particles appear the zones of the growth (Fig. 2b), which indicate on development of CVD mechanism (chemical vapor deposition). The intensive evaporation of Si from surface of target, the occurrence of the plasma and formation of nano-particles and nano-clusters in zones of cooling of the plasma intensify the mechanism CVD. As a result, a fundamentally new type of film is formed, which consists of pyramidal particles (Fig. 3a). The size of such individual pyramidal particles lays in region $0.8 \div 1.6 \mu m$. With an increase of time of irradiation they form regions, inside of which pyramids form rows. The distance between rows is $60 \div 130$ nm (see Figs. 3b, c). It is possible to assume that at longer irradiation in a mode III a deposited film will have a greater roughness.

For regime III the formation of additional type of precipitation products in the form of clouds is observed (Fig. 4). AFM data show that clouds consist from chains of nano-clusters, organized into ripples (Fig. 5). The distance between ripples changes from $\sim 2$ to $10$ nm. Inside of ripples the congestions of particles (nano-clusters) are visible. The size of this clusters changes from $\sim 16$ to $60$ nm. It is possible to assume that the sizes of other particles in ripples are less on some orders of magnitude. Forms of similar type are registered at laser irradiation in pulse modes. Theirs attribute to fractal low-dimensional structures. The formation of fractal structures take place on the periphery of the laser plume in the zones of the cooling of plasma [19].

As result, it is possible schematically to present all process at laser irradiation of silicon (see Fig. 6).

### 3.2. Irradiation of ceramics

Laser irradiation of ceramics in different mediums was made at $P = 240$ mW. As target the $\alpha$-SiC and $\alpha$-SiC + Cr$_5$Si$_3$ ceramics were used. Phase composition was determined by method of XRD.

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**Figure 7.** The AFM image of surface of SiC-ceramic obtained in regime of phase (a-c) and precipitated film in regime height (d). (a) initial sample; (b) after 15 min of irradiation; (c), (d) after 30 min of irradiation.
On image of AFM we can see that after irradiation on surface of $\alpha$-SiC (which presented by micro plates of $\alpha$-SiC, Fig. 7a) appears loose deposit (Fig. 7b). Concerning data x-ray microanalysis under irradiation on air and in $(N_2 - O_2)$ medium the surface of silicon carbide ceramic is oxidized. With the increase of time of irradiation the surface of ceramics is purified (see Fig. 7c) and further again by layer of $SiO_2$ is covered, and etc. This means that along with the oxidation of surface of SiC-ceramic occurs evaporation-sublimation of $SiO_2$. In fact, on the surface of collection plate the film of $SiO_x$ or $SiO_x:N$ is forming. Theirs IR-spectra (see Fig. 8) are similar to spectra, presented on Fig. 1. And type of films similar to films, obtained at laser irradiation of $Si$. From Fig. 7d it is visible that the film consists from clusters of the various size.
According to XRD data, the composite ceramic is presented by $\alpha$-SiC and Cr$_5$Si$_3$ components. On electron micro photo (Fig. 9) and AFM image (Fig. 10a) non-uniform distribution of component is visible. With the using of x-ray microanalysis the regions of localization of chromium silicide in SiC matrix have been determined (see arrow on Figs. 9, 10). During irradiation the morphology of a surface of the ceramic sample changes essentially (Fig. 11a) and on surface of collection plate the film is forming (Fig. 11b). The IR spectra of films are similar to spectra presented on Figs. 1 and 8. This means that the films SiO$_x$ or SiO$_2$+N (depend on type of gas medium) are formed.

X-ray microanalysis has shown that on a surface of ceramics, basically, there is a chromium and oxygen. This means that the oxidation of Cr$_5$Si$_3$ takes place. The content of elements corresponds to formation of Cr$_2$O$_3$. On Fig. 10b and 11a it is visible that the given layer is porous. In this case the most probable source of the loosening should be Si and...
SiO$_2$, which as a result of sublimations of SiC and also oxidation of SiC and Cr$_5$Si$_3$ are formed [10,11]. The chromium oxide enrich the surface of sample as it is nonvolatile.

The morphology of precipitated film differs from the previous cases. Alongside with particles-clusters (Fig. 12a), typical for films obtained at ablation of silicon (see the Fig. 2), are present the “sockets” consisting of “petals” (Fig. 12b). They are visible and on Fig. 11b. It is possible to assume that two various mechanisms of growth of SiO$_x$ (or SiO$_x$:N) particles are simultaneously realized. Apparently, in formation of sockets take part fused clusters of SiO$_2$. However ascertainment of the given mechanism demands more careful study. The common schema of process on Fig. 13 is presented.

In consideration of the temperatures of the melting and evaporation-sublimation of investigated materials it is possible to conclude that at used modes of an irradiation on a surface of targets the temperatures nearby 3000 K and above develop.

4. Conclusion

The research of process of an irradiation in a continuous modes of silicon, silicon carbide and composite ceramics on the basis of SiC has shown:

1. Depending on capacity and time of an irradiation it is possible to receive films with different morphology (in the form of clusters, pyramidal particles and clouds or theirs mixtures).
2. Depending on gas medium it is possible to obtain films with different phase composition (from SiO$_x$, where $x \leq 2$, up to SiO$_x$:N).
3. The growth of precipitated particles is caused by different mechanisms. One of them is process of CVD.
4. In intensive regime of irradiation cloud-like films are formed. They have fractal structure, which similar to those, which at an intensive pulse irradiation is received.

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