Quantum Electronics **30** (8) 710 – 714 (2000)

PACS numbers: 42.62.Hk; 61.80.Ba; 81.10.h
DOI: 10.1070/QE2000v030n08ABEH001795

Formation of conic microstructures upon pulsed laser evaporation of solids

V V Voronov, S I Dolgaev, S V Lavrishchev, A A Lyalin, A V Simakin, G A Shafeev

Abstract. **The appearance and development of large-scale self-organising microstructures on the surface of monocrystalline Si and several other materials (Ge, Ti) are studied upon their evaporation by 20-ns pulses from a copper vapour laser at 510.6 nm. The structures were formed upon repeated pulsed laser irradiation ($\sim 10^4$ pulses with an energy density of $1-2$ J cm^{-2}) in the absence of optical breakdown of the medium above the target surface in the $1-10^5$ Pa pressure range in a wide range of angles of laser radiation incidence on the surface. The structures are cones with an apex angle of $\sim 20-25°$, which grow towards the laser beam. It is shown that the spatial period of the structures developing during laser evaporation is determined by the period of the waves arising on the melt surface and is equal to 10 – 20 μm. The x-ray diffraction analysis showed that the modified substrate region has a polycrystalline structure and consists of crystallites with dimensions ranging from 40 to 70 nm, depending on the pressure of the ambient atmosphere.**

1. Introduction

The action of pulsed laser radiation on the surface of solids is, as a rule, an essentially nonequilibrium process, which stems from inherently high temperature gradients and short surface-heating times as compared with the relaxation times of the system. Nonequilibrium processes can also be observed upon continuous laser heating because of the appearance of a feedback between the thermal and 'chemical' degrees of freedom of the system [1]. This results in the specific features in the growth of structures on the modified surface of a solid such as the formation of dendritic V_2O_5 crystals [2] or a rapid growth of Cu_2O crystals towards the laser beam [3].

Pulsed laser heating of a solid allows a significant increase in the vapour density above its surface in comparison with continuous laser heating. A characteristic feature of pulsed laser action on a solid is the formation of large-scale periodic structures on its surface. The formation of such structures upon irradiation by nanosecond laser pulses was reported in papers [4 – 7]. Periodic structures were observed on the surface of such materials as Ge, Ni, Sn, Al, Cu, HTSC ceramics, and also brass and bronze upon pulsed laser irradiation when a breakdown occured in the medium above the target. The mechanism of structure formation was related in the papers [8, 9] to the interaction of the melt of a solid with the plasma of the optical breakdown in the medium.

The periodic structures are formed in response to exposure of a surface to tens or hundreds of laser pulses with an energy density high enough to melt the surface. The structure period depends on the pressure of gas above the surface and also on the size of the laser spot. The structures arise owing to the development of instabilities at the interface between the melt and the plasma of the optical breakdown, such as the Kelvin – Helmholtz or Rayleigh – Taylor instabilities [9].

Several papers relate the formation of large-scale periodic structures to the displacement of the melt material by the target vapour, which results in a spatial redistribution of the molten material (see, e. g., Ref. [10]). The nonlinear optical processes responsible for the formation of ordered surface structures under intense laser irradiation of a solid surface were reviewed in Ref. [11].

In experiments [12], the surface of monocrystalline Si was exposed to several thousand radiation pulses of an excimer KrF laser at an energy density of $1-5$ J cm^{-2}. The authors [12] observed a growth of silicon microcolumns with a large height-to-diameter ratio, which extended over the initial surface by 10 – 15 μm. The column growth took place in gaseous media containing oxygen and also in SF_6 at a pressure of ~ 1 bar. The crystal growth mechanism referred to as 'vapour – liquid – crystal' [13], which is realised in the growth of whisker single crystals was proposed as the mechanism for growing silicon microcolumns. The authors of [12] also assumed that the chemical interaction between the substrate material and the gas medium may be responsible for the growth of the structures.

In this paper, we study the formation of periodic microstructures in Si, Ge, and Ti, irradiated by a copper vapour laser in a broad pressure range ($1-10^5$ Pa) in the absence of breakdown in the gaseous medium above the target surface. Under these conditions, microstructures are formed that are morphologically different from those arising upon plasma formation. The structure growth occurs in a broad pressure range of the ambient atmosphere and is supposedly unrelated to the chemical interaction with it. Since the target surface solidifies in the interpulse period, the morphological surface changes may accumulate and develop from pulse to pulse.

V V Voronov, S I Dolgaev, S V Lavrishchev, A A Lyalin, A V Simakin, G A Shafeev General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 117942 Moscow, Russia

Received 26 January 2000
Kvantovaya Elektronika **30** (8) 710 – 714 (2000)
Translated by E N Ragozin; edited by M N Sapozhnikov

Microstructure formation and growth take place only when the number of pulses is high enough (above 10^3). From this point of view, the high repetition rate of a copper vapour laser — about 10 kHz — is undeniably an advantage over other laser sources. For this reason, it is the use of the copper vapour laser that enables the easy realisation of the conditions for microstructure growth, as regards to the energy density and to the number of laser pulses. The x-ray diffraction analysis was used to study the crystal structure of the modified Si surface and the dependence of the morphology of the structures on the angle of the laser beam incidence on the solid surface.

2. Experimental

We used (100) and (111) monocrystalline Si plates as substrates for microstructure growth. Several experiments were performed with monocrystalline Ge and polycrystalline Ti. The substrates were irradiated in air at atmospheric pressure and in a low vacuum ($\sim$ 1 Pa). To increase the size of the region exposed to the laser radiation, the beam was scanned over the sample surface. To this end, a sample was placed on a computer-controlled stage. The typical scanning rate of the laser beam across the surface of a sample was about 0.1 mm s^{-1}.

In our experiments we used a copper vapour laser with a wavelength of 510.6 nm, a pulse repetition rate $f = 10$ kHz, and a pulse length $\tau = 20$ ns. The unpolarised laser radiation was focused with a lens with a focal length of 5 cm on the sample surface to a spot 40 μm in diameter. The angle of laser radiation incidence on the sample surface was variable from zero to 60°.

Under our experimental conditions for a laser energy density of about 1 – 2 J cm^{-2}, no optical breakdown plasma was formed in the gas medium above the sample surface in air or vacuum. The surface morphology after laser irradiation was studied with a JEOL scanning electron microscope. The crystal structure of silicon with the microstructures produced by laser irradiation was studied by x-ray diffraction employing DRON-2 and URD-63 diffractometers (the characteristic copper K_α radiation at 0.154 nm).

3. Experimental results

Repetitively pulsed laser irradiation of a solid surface with an energy density high enough to melt the material results in a significant change of its morphology. The silicon surface irradiated in vacuum turns out to be covered with cone-like structures spaced at 10 – 20 μm on the average (Fig. 1). The cone apex angles are equal to 20 – 25°. Similar structures are formed on germanium and titanium.

The energy density of laser radiation at 510.6 nm required to produce the structures is 1 – 2 J cm^{-2}, and the number of pulses is about 10^4. This number of pulses of the copper vapour laser is accumulated when the total exposure time of a given point on a sample is equal to 1 s. For a larger number of pulses and / or a higher energy density, ablation prevails; i.e., a cavity is formed whose depth increases with exposure time. In the photograph of a cleaved facet of a sample shown in Fig. 2, one can see structures that protrude above the sample surface by 20 – 30 μm. In this case, the silicon substrate beneath them lies below the level of the sample surface by about the same value.

The formation of microstructures on the Si surface is accompanied by the appearance of characteristic speckles in the laser radiation reflected from the sample. The microstructure-bearing portions of the Si surface appear perfectly black in the reflected light due to absorption resulting from multiple reflections from the side cone surfaces.

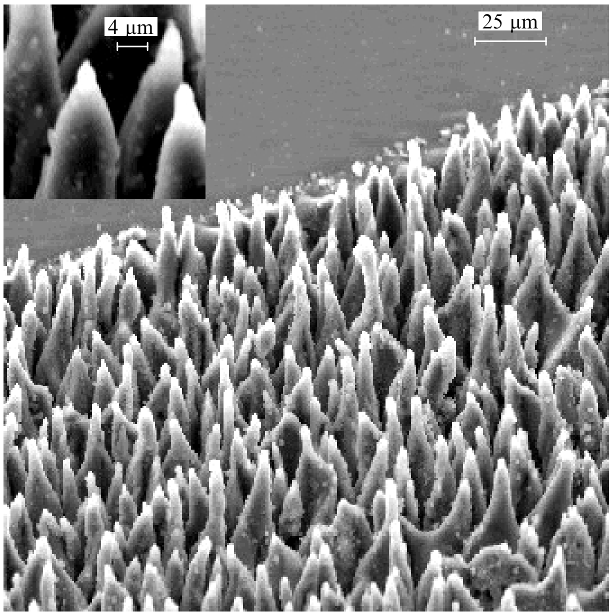

Figure 1. Morphology of monocrystalline Si after exposure of its surface to 10^4 laser pulses for an energy density of 1 J cm^{-2} in a vacuum and a magnified view of Si microcones (the inset).

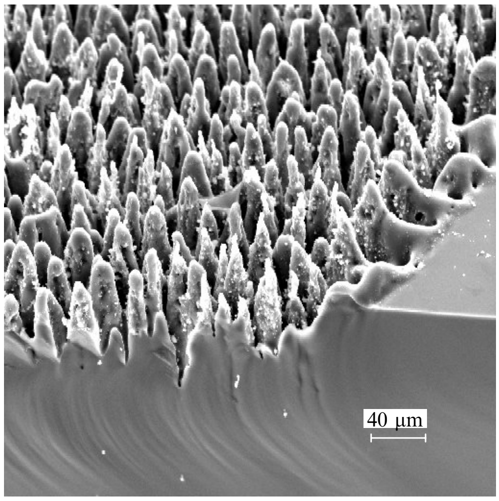

Figure 2. Cleaved facet of a silicon plate showing the depth of the modified region after laser irradiation in air (the oxide layer was removed by etching in an aqueous solution of HF).

The exposure of Si to laser radiation in air is accompanied by the formation of a thick oxide layer protruding above the surface of a sample. Etching this layer in an aqueous solution of hydrofluoric acid (HF) reveals a structure similar to that produced under irradiation in vacuum. One can see from the photographs presented, that the microstructure formation brings about a manyfold increase in the surface area. According to simple geometric estimates, the surface area increases by about a factor of five when microcones with an apex angle of 25° are formed on a surface. This is confirmed indirectly by the fact that release of gas bubbles, which accompanies the dissolution of Si oxide in an aqueous solution of HF, continues for several days.

As the angle of radiation incidence on a sample is altered, the inclination of the microstructures changes: They grow towards the laser beam, as shown in Fig. 3. The emergence of structures growing towards the laser beam is a specific feature of this work, because structures of this kind were not observed for oblique beam incidence in earlier works [4, 6].

The laser irradiation of a silicon surface is accompanied by modification of its crystal structure. X-ray diffraction patterns of the areas exposed to the laser radiation in air or in vacuum exhibit peaks of all possible Si reflections, in addition to a strong peak from a single crystal (Fig. 4). The Si oxide produced by laser irradiation in air is x-ray-amorphous and does not give rise to peaks in the diffraction pattern.

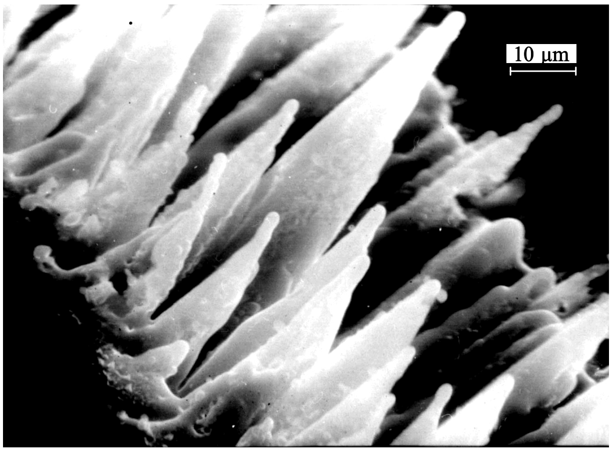

Figure 3. Microstructures growing upon oblique incidence of laser radiation on the silicon surface in vacuum at an angle of 60°.

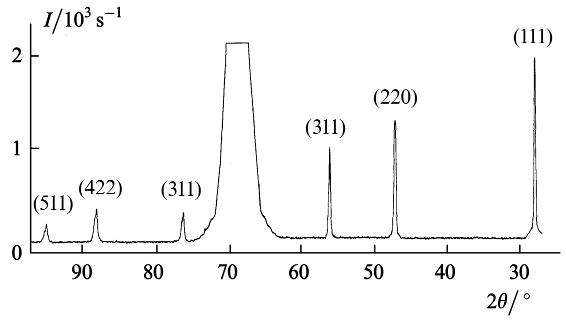

Figure 4. Diffraction pattern of (100)-oriented monocrystalline silicon with microstructures produced by irradiation in air, obtained in the $\theta/2\theta$-scanning mode.

The Si diffraction pattern after laser irradiation in vacuum differs from that after laser irradiation in air by a lower intensity of polycrystalline peaks. The intensity ratio of the polycrystalline peaks is indicative of the absence of any texture. The peaks are significantly broadened in comparison with the peaks of a reference polycrystalline Si sample. The peaks for the sample irradiated in air are broader than those for the sample irradiated in vacuum.

A calculation of the dimensions of the regions of coherent scattering by the Scherrer formula [14] yields 46 nm for the sample irradiated in air and 72 nm for that irradiated in vacuum. The dimensions of coherent scattering regions correspond to the dimensions of particles arising in the condensation of the evaporated material. The high integrated intensity of polycrystalline peaks shows that a substantial fraction of the material in the irradiated region of Si converts to the polycrystalline state.

The nanoparticles in a laser-irradiated region may facilitate a further increase in the specific surface of a sample. The appearance of waves on the melt surface is the initial stage of microstructure development. It is these waves that determine the microstructure period. When the number of laser pulses and/or the radiation energy are monotonically increased, the origination of these waves precedes the formation of conic structures. Fig. 5 gives an example of the waves generated on the Si surface after laser irradiation in vacuum. One can see a transition from waves to conic structures. As the number of laser pulses increases, valleys begin to develop at the troughs of the waves and the cones appear at the crests of the waves.

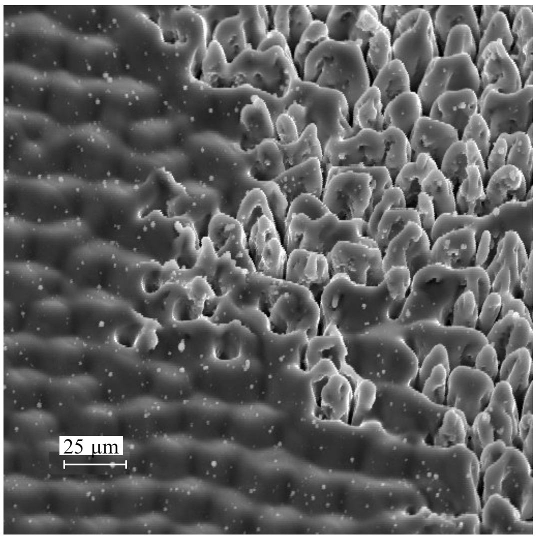

Figure 5. Structures arising on the Si surface upon pulsed laser irradiation in vacuum for a laser energy density of 1 J cm^{-2}.

4. Discussion

The growth of the structures on the surface of a solid upon laser evaporation takes place owing to a redistribution of the target material evaporated under the action of each laser pulse. Estimates show that approximately 10^{12} Si atoms are evaporated per one laser pulse. Taking the vapour diffusion length to be equal to the average structure height (20 μm) and the vapour temperature to be 2000 K, the pressure of this vapour as an ideal gas may be estimated at 30 bar. In this case, the silicon vapour density is 10^{20} cm^{-3}. Such a high vapour density ensures the fast growth of the structures.

The material evaporated from the target areas between the cones condenses primarily at the cone apexes, which rise above the surface. This redistribution takes place because a feedback appears between the structure morphology and its absorptivity. When the radiation absorption length is small compared to the characteristic vertical size of the structure, the regions of the microstructure surface that are irradiated at an angle close to the normal incidence will have the highest temperature in a laser beam of the uniform intensity. Direct measurements show that the reflectivity of a Si surface at the wavelength of a copper vapour laser is 0.38 at normal incidence and 0.72 for an angle of incidence of 78° (the angle of radiation incidence on the side surface of the cone).

For a laser energy density close to the Si melting threshold, an increase in the reflectivity with the increase in the angle of radiation incidence ensures survival of the cone-like structures from pulse to pulse. The laser radiation is reflected from the side surface in the direction of the valleys between the cones, thereby increasing the local radiation energy density in them. In the presence of cones on the surface, the temperature distribution over the surface becomes nonuniform even when the radiation intensity distribution is uniform, with the effect that vapour condenses primarily on relatively 'cool' cone surface areas. In this sense, the evolving structures are self-organising. During laser evaporation of the structure, evaporation from the cone apex proceeds faster than from the side surface owing to a larger radius of curvature of the latter, which favours structure sharpening. Similarly, for oblique incidence of the laser radiation, structures directed at the laser beam are highest in reflectivity.

One can see from Fig. 5, that the microstructures develop from the waves on the melt surface, which are the source of initial nonuniformity of the surface absorptivity. The nature of the initial surface relief (of the waves), which serves as the initial nonuniformity for the development of microcones, calls for further investigation. Capillary waves may be a possible mechanism for the formation of the initial periodic structure. The dispersion relation for capillary waves on the liquid surface has the form [15]:

$$\omega^2 = \frac{\sigma}{\rho} h k^4,$$

where ω is the wave frequency; σ, h, and ρ are the surface tension coefficient, the depth, and the density of the melt, respectively; $\boldsymbol{k}$ is the wave vector of the capillary wave; $k = 2\pi/\lambda$; and λ is the wavelength.

Since silicon solidifies in the period between pulses, the lifetime of the liquid phase should be taken as the wave period $T = 2\pi/\omega$. In general, this time depends on the excess of the melt temperature over the melting temperature. When the energy density of the laser beam is close to the melting threshold, this time may be taken to be equal to the laser pulse length τ, i.e., $T = 20$ ns in the case under consideration. Assuming that the melt depth is $h \sim 1$ μm (of the order of the heat diffusion depth in silicon during the laser pulse) and that $\sigma = 850$ mN m^{-1} for $T = 1550$°C [16], we obtain a wavelength of ~ 1 μm, which is well below the observed structure period.

However, under our experimental conditions, the above dispersion relation is invalid, because it was obtained for the waves on a free melt surface. The final dimensions of the melt cell produced by the laser beam of size $a \times b$ impose limitations on the spectrum of capillary waves. In this case, the possible moduli of the wave vector $\boldsymbol{k}$ of the capillary wave become discrete and are determined by the relation: $k^2 = \pi^2(m^2/a^2 + n^2/b^2)$, where m and n are integers [15].

The Benard cells, the defect-deformation instability [17], and the Rayleigh–Taylor and Kelvin–Helmholtz instabilities [9] represent other factors that ar responsible for the nonuniformity of the melt surface. The two latter effects, however, seem to be highly improbable owing to a low density of the environment under our experimental conditions.

Note that the surface tension coefficients for Ge and Ti are of the same order of magnitude as for silicon: $\sigma = 558$ and 1558 mN m^{-1} for 1550 and 1670°C, respectively. The observed structure periods prove to be close and are about 10 μm.

The silicon evaporated during a laser pulse again deposits on the cooled crystal in the form of clusters measuring tens of nanometres in size. The microcones, containing such clusters which have formed on a monocrystal, have, unlike the substrate, a polycrystalline structure. Their appearance differs noticeably from that of the microstructures produced in the case of a laser-induced breakdown of the medium. In the latter case, a microstructure ends with a sphere-like swelling whose diameter is close to the cone diameter at the structure tip or even exceeds it [12].

Note that the microcolumns formed by the radiation of an excimer laser on the surface of Si in Ref. [12] do not contain the oxide layer, which is probably explained by the action of the shock wave generated upon the optical breakdown of the medium. Pedraza et al. [12] did not point out the occurrence of a UV radiation-induced breakdown in the medium, but its presence is indirectly evidenced by the absence of structure growth at below-atmospheric pressures, when the breakdown of the medium is significantly facilitated. It seems that under our experimantal conditions, the breakdown of the medium did not occur in the operating pressure range, which is associated with a lower energy of the radiation quantum and a longer duration of the laser pulse compared to that of the excimer laser. The Si surface evaporated by the radiation of a copper vapour laser in air is covered with a thick layer of noncompact silicon oxide, as in the case of SiC ceramics ablation in air [18]. Note that the structure growth toward the obliquely incident laser beam does not take place in the presence of a breakdown plasma [9] because the pressure of a plasma cloud, which expands normally to the surface, results in the mechanical disruption of these structures.

5. Conclusions

Therefore, in the absence of breakdown of the medium upon pulsed laser evaporation of solids, there arise self-organising structures on their surface. These structures are cones extending over the surface by 20–30 μm, with axes directed along the laser beam axis. The structures develop when the number of laser pulses is high enough ($\sim 10^4$) and the energy density in the laser beam exceeds the melting threshold of the material. The initial nonuniformity for the structure development, which determines their spatial period, is the waves on the melt surface of a solid. The structures contain polycrystalline silicon whose particles measure tens of nanometres. The formation of a cone-like profile proves to be possible because the reflectivity increases with increasing angle of incidence of the laser radiation. The melting and evaporation take place primarily in the valleys between adjacent cones while the cones themselves do not melt due to reflection of the laser radiation from their side surface.

The self-organising structures considered above, which arise upon laser evaporation of solids, have a broad spectrum of potential applications. For instance, a modified silicon surface exhibits a high absorption coefficient in the visible range, which is undeniably of interest for solar battery production technology. The high absorption coefficient of the silicon surface permits raising the photocurrent generation efficiency and discarding the deposition of anti-reflection coatings, which are efficient only in a narrow range of angles of laser radiation incidence and are non-durable in service.

Conic sharpened microstructures are of interest as field electron emitters, which are easy to integrate into silicon microelectronic devices. Note that the previously observed structures arising upon the laser breakdown of a medium can hardly be used as emitters due to the spherical shape of their point. Finally, the structure formation results in a significant increase in the surface area of a solid, which can find application in catalysis and production of sensor devices.

Acknowledgements. The authors thank V P Ageev and V I Luchin for valuable discussions of the results of this study. This work was supported in part by the Russian Foundation for Basic Research (Grants Nos 98-02-16104 and 98-02-16207).

References

1. Bunkin F V, Kirichenko N A, Luk'yanchuk B S *Usp. Fiz. Nauk* **138** 45 (1982)
2. Bobyrev V A, Bunkin F V, Deli E, Kirichenko N A, Luk'yanchuk B S, Nanai L, Simakin A V, Hevesi I, Shafeev G A *Kvantovaya Elektron. (Moscow)* **9** 1943 (1982) [*Sov. J. Quantum Electron.* **12** 1267 (1982)]
3. Alimov D T, Atabaev Sh, Bunkin F V, Zhuravskii V L, Kirichenko N A, Luk'yanchuk B S, Omel'chenko A I, Khabibulaev P K *Pis'ma Zh. Tekh. Fiz.* **8**(1) 10 (1982)
4. Brailovskii A B, Dorofeev I A, Ezerskii A B, Ermakov V A, Luchin V I, Semenov V E *Zh. Tekh. Fiz.* **61**(3) 129 (1991) [*Sov. Phys. Technical Phys.* **36**(3) 324 (1991)]
5. Ageev V P, Gorbunov A A, Konov V I *Kvantovaya Elektron. (Moscow)* **16** 1214 (1989) [*Sov. J. Quantum Electron.* **19** 785 (1989)]
6. Ursu I, Mihailescu I N, Popa Al, Prokhorov A M, Ageev V P, Gorbunov A A, Konov V I *J. Appl. Phys.* **58** 3909 (1985)
7. Kautek W, Roas B, Schultz L *Thin Solid Films* **191** 317 (1990)
8. Golubev V N, Dorofeev I A, Libenson M N, Luchin V I *Pis'ma Zh. Tekh. Fiz.* **17**(24) 67 (1991) [*Sov. Tech. Phys. Lett.* **17**(24) 884 (1991)]
9. Brailovsky A B, Gaponov S V, Luchin V I *Appl. Phys. A* **61** 81 (1995)
10. Arutyunyan R V, Bol'shov L A, Dunaevskii N A, Reshetin V P *Dokl. Akad. Nauk SSSR* **316** 347 (1991) [*Sov. Phys. Dokl.* **316**(1) 82 (1991)]
11. Akhmanov S A, Emel'yanov V I, Koroteev N I, Seminogov V N *Usp. Fiz. Nauk* **147** 675 (1985)
12. Pedraza A J, Fowlkes J D, Lowndes D H *Appl. Phys. Lett.* **74** 2322 (1999)
13. Givargizov E I *Rost Nitevidnykh i Plastinchatykh Kristallov iz Para* (Filamentary and Scaly Crystal Growth from Vapour) (Moscow: Nauka, 1977)
14. Iveronova V I, Rivkevich G P *Teoriya Rasseyaniya Rentgenovskikh Luchei* (Theory of X-Ray Scattering) (Moscow: Izd. MGU, 1978)
15. Landau L D, Lifshits E M *Fluid Mechanics* (Oxford: Pergamon Press, 1987)
16. *Fizicheskie Velichiny (Spravochnik) (Handbook of Physical Quantities)* Grigor'ev I S, Meilikhov E Z (Eds) (Moscow: Energoatomizdat, 1991)
17. Emel'yanov V I *Kvantovaya Elektron. (Moscow)* **28** 2 (1999) [*Quantum Electron.* **29**(7) 561 (1999)]
18. Voronov V V, Dolgaev S I, Lyalin A A, Shafeev G A *Kvantovaya Elektron. (Moscow)* **23** 637 (1996) [*Quantum Electron.* **26** 621 (1996)]