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Modification of Optical Properties of Surface Layers and Thin Films by Laser Treatment

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Optical conductivity of silicon wafer modified by femtosecond laser irradiation as well as an effect of laser treatment on the optical properties of surface layers of rapidly quenched multicomponent alloy ribbons have been investigated by ellipsometry. The samples of the nanostructured silicon as isolated cells were formed on the single crystal silicon wafers by method of laser ablation. Laser beam scanning modes provide in air atmosphere the synthesis of nanostructured silicon dioxide particles as well as silicon nanoparticles. It was established that ellipsometric parameters and optical conductivity σ of the cells of the nanostructured silicon are significantlly changes for two cell orientations relatively *p*-direction of the sample. This means that the formed silicon nanostructures possess essential optical anisotropy as a result of a deformation influence of laser ablation and an appearance of elastic stresses within the surface layer of the nanostructured silicon. The optical anisotropy was not found for silicon areas which were not subjected to laser action and located between the cells of the nanostructured silicon.

The obtained variations of the optical conductivity σ of rapidly quenched multicomponent alloy ribbons as functions of laser pulse energy E as well as a number of pulses N are nonmonotonic and reach a minimum at certain E and N values. Such behavior of their σ during the first phase of laser treatment is related to the so-called "laser-induced vitrification" effect owing to additional atomic disordering of the surface layers of ribbons which are not completely amorphous in the initial state but contain some amount of a crystalline phase. Then during the second phase of such treatment the current amorphous structure was continued to be formed and relaxed within surface layer. At the third phase of laser heat action the annealing of the surface ribbon was observed due to reaching some sufficient laser radiation dose which leads to the formation of the crystalline phase and, therefore, to an increase in σ.

Keywords: Nanostructured silicon, Rapidly quenched alloys, Laser treatment, Ellipsometry, Optical anisotropy.

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1. INTRODUCTION

Laser irradiation has various effects on the structure and optical properties of materials, depending on factors such as the radiation density, duration of treatment and atomic and electronic structure of irradiated materials. There are several stages of thermal effects of laser radiation on solid nontransparent materials (metals, semiconductors, dielectrics), namely, heating without changing the phase state, melting, evaporation, laser ablation. The laser ablation is a promising technique to produce various kinds of nanoparticles (clusters, droplets or solid fragments) [1, 2]. Nanostructured materials have a number of unique properties that are not observed in bulk matter. In particular, during recent years the laser ablation is widely used for the preparation of silicon nanocomposite materials for electronic devices [3].

In addition, short-time laser treatment of a material causes so-called "laser-induced vitrification" of its surface, which consists in disordering or amorphization of the surface layers, since heat exchange with the bulk of the sample provides high cooling rates. Long-term laser treatment of the material may cause "laser-induced devitrification" or "laser annealing" of its surface, resulting in a relaxation of the surface layer structure to its equilibrium state (for example, the formation of crystalline phases in the initially amorphous material) [4]. For study of such effects, amorphous metallic multicomponent alloy ribbons are well-known base [5].

The changes in the atomic and electronic structure of various materials after laser irradiation are revealed in the behavior of their optical properties [6]. Therefore, the purpose of this work is to study the optical and the conductivity properties of the nanostructured silicon derived from the irradiation by fiber laser of the monocrystalline silicon wafer as well as an effect of laser modification of optical properties of the surface layers of the rapidly quenched alloys for the samples which are not completely amorphous in the initial state but contain small amount of a crystalline phase due to technological conditions of their preparation.

2. SAMPLES AND RESEARCH METHODS

Nanostructured silicon was formed on the surface of single-crystal silicon (100) orientation wafer with the natural oxide layer by laser ablation. Irradiation was performed in an air atmosphere. The nanostructured silicon was formed by Yb-doped fiber laser which generates pulses with energies up to 1 mJ at a frequency of 1 MHz with a wavelength of 1060 nm. The power of laser irradiation on the surface of the monocrystalline silicon ranged from 100 mW to 1 W [3]. Scan modes of laser beam provide a synthesis of nanostructured particles of silicon dioxide or silicon nanoparticles. On the surface of silicon wafer the nanostructured layers in the form of separate cells were created. Wave structure as rowing along the short side of a rectangular cell was formed on the surface of cells.

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Ribbon samples of $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ alloys (12 nm in width and 30-35 μm in thickness) for this study were prepared by rapidly-quenched method. Laser treatment of the sample surfaces was performed in air using a YAG free-running pulse laser (wavelength λ = 1.06 μm, pulse duration 4 ms, and frequency 1 pulse per second). The diameter of the incident beam was equal to 14 mm. The pulse energy E and the number of pulses N ("dose") varied from 1 to 25 kJ/m^2 and from 20 to 400, respectively. In order to provide uniform irradiation of the surfaces, the samples, which were placed on a bulk heat-removing substrate, were scanned by laser beam which was normally incident on the surface. The thermal effect ΔT during the laser treatment was measured at the untreated face of the sample and did not exceed 50 K at the maximum irradiation dose.

Optical polarimetric measurements of silicon wafer and $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ ribbons were carried out using a laser ellipsometer LEF-3M-1 at a wavelength λ = 632.8 nm. The angular dependences of the ellipsometric parameters such as the phase shift Δ between the orthogonal components of the polarization vector and the azimuth Ψ of the restored linear polarization were obtained for the investigated samples [7]. All angular dependencies of ellipsometric parameters $\cos\Delta(\varphi)$ and $\mathrm{tg}\,\Psi(\varphi)$ of the samples were analyzed and the principal angle φ_p of light incidence ($\cos\Delta = 0$) and $\mathrm{tg}\,\Psi_p$ (the value $\mathrm{tg}\,\Psi$ at φ_p) were obtained.

Optical polarimetric measurements were carried out within the several cells on the silicon wafer and areas located between the cells for two mutually perpendicular directions (azimuthal angles $\alpha = 90^o$ and $\alpha = 0^o$, respectively) in own plane of the sample. For estimation of electronic properties of the surface layers, the optical conductivity σ for different areas of silicon sample surface is calculated according to the semi-infinite medium approximation.

$$n = \sin\varphi_p \mathrm{tg}\varphi_p \cos 2\Psi_p,$$
$$k = \sin\varphi_p \mathrm{tg}\varphi_p \sin 2\Psi_p,$$
$$\sigma = nkc/\lambda,$$

where n is the refractive index, k is the absorption index and c is the light speed, σ is the optical conductivity, φ_p is the principal angle, Ψ_p is the azimuth Ψ at φ_p.

3. RESULTS AND DISCUSSION

The obtained ellipsometric parameters φ_p, $\mathrm{tg}\,\Psi_p$ and the calculated optical conductivity σ for different areas of the silicon sample surface, namely areas which are located between two neighboring cells (1) and placed in one of the cells of the nanostructured silicon specimen (2) are given in Table 1.

Table 1 – Ellipsometric parameters φ_p, $\mathrm{tg}\,\Psi_p$ and σ for two different areas of the silicon wafer

Sample's area	direction	φ_p,°	$\mathrm{tg}\,\Psi_p$	σ, 10^{15} s^{-1}
1	$\alpha = 90^o$	75.42	0.0384	0.49
	$\alpha = 0^o$	75.44	0.0391	0.51
2	$\alpha = 90^o$	54.37	0.1032	0.12
	$\alpha = 0^o$	63.57	0.4731	0.74

One can see from the Table 1 that changes of the ellipsometric parameters φ_p and $\mathrm{tg}\,\Psi_p$ for two mutually perpendicular directions in own plane of the sample do not exceed the measurement errors, namely $\delta\varphi_p = 0.01°$ and $\delta\mathrm{tg}\,\Psi_p = 0.0010$ for area located between the cells of silicon wafer (1). For cell of the nanostructured silicon specimen (2) there are significant differences in the values φ_p and $\mathrm{tg}\Psi_p$ for two cell orientations ($\alpha = 90^o$ and $\alpha = 0^o$) relatively p-direction of the sample. For the calculated optical conductivity similar changes are observed. In comparison to almost unchanged data for area 1, the values of optical conductivity within area 2 are changed six times relatively to each another for two mutually perpendicular directions in own plane of the sample relatively its p-direction. Similar results were obtained for other investigated nanostructured silicon cells.

Moreover, the angle dependencies of parameter cosΔ for one of the cells of silicon sample measured at four angle positions of the wafer in its own plane due to rotations by step of 45 degrees are presented in Fig. 1. It is seen that optical properties of the diagnosed cell are also significantly different for azimuthal measurements of nanostructured silicon sample due to formed therein surface structure after the action of the powerful laser.

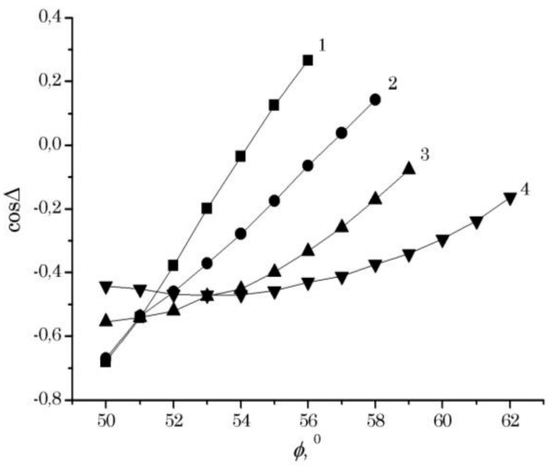


Fig. 1 – Dependencies of $\cos\Delta(\varphi)$ for one of the cells of the irradiated monocrystalline silicon sample at orientations $\alpha = 90^o$ (1), 45° (2), 0° (3) and – 45° (4)

So, optical properties for each cell formed on the silicon surface after laser action are anisotropic. This feature indicates the presence of strain and the appearance of the elastic stresses inside the silicon layer subsurface within the sample areas subjected to laser processing. Such stress distribution within the skin layer probed by polarized light affects the atomic and electronic structure of this layer as well as variations in its optical response to the light excitation which are clearly recorded by ellipsometric diagnostics in two perpendicular azimuthal directions as well as in four α angle orientations.

Amorphous metallic alloys in their optical and electronic properties are between semiconductors and classical metals [8, 9]. For comparison, in Fig. 2 the reflectance spectra of ribbons of typical amorphous alloys $Fe_{67}Cr_{18}B_{15}$, $Fe_{75}Ti_5B_{20}$ and $Fe_{70}Ni_{20}(GeSiB)_{10}$ in the infrared region of 50-450 cm^{-1} measured using Fourier spectrometer are shown.

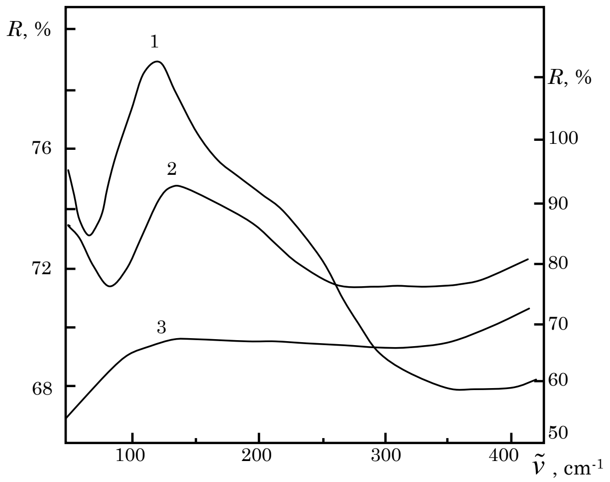
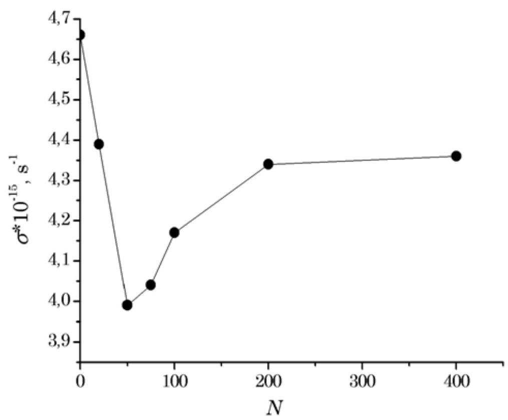
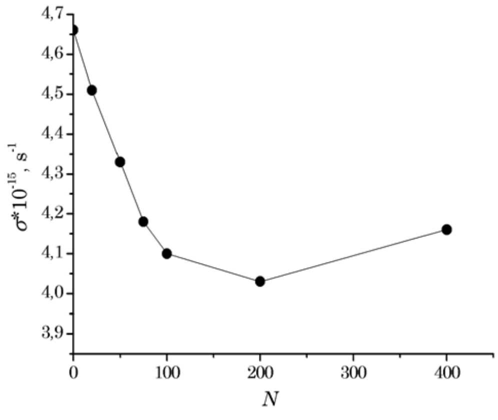


Fig. 2 – Infrared reflectance spectra of the $Fe_{67}Cr_{18}B_{15}$ (1), $Fe_{75}Ti_{5}B_{20}$ (2) and $Fe_{70}Ni_{20}(Ge_{Si}B)_{10}$ (3) amorphous ribbons. The scale on the right refers to curve 3. Curve 1 is displaced up by 11 %



a



b

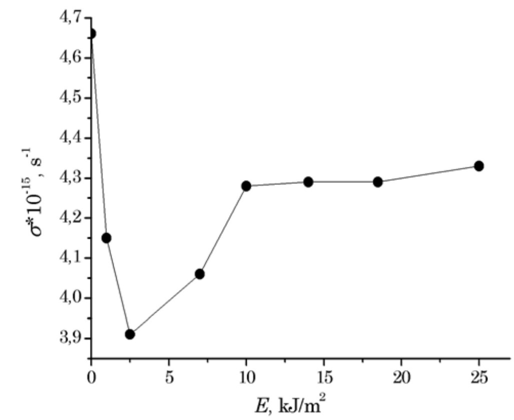
Fig. 3 – Optical conductivity dependencies $\sigma(N)$ of amorphous metallic ribbons $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ at a constant pulse energy $E = 25$ kJ/m² (a) and 7 kJ/m² (b)

It is seen that behavior of optical properties of these alloys is not Drude-like ones within the infrared region. But it is well-known that for metallic materials the spectral behavior in this range must be similar to $R \to 1$ (Hugen-Rubens relation [10]) as wave number $\tilde{\nu} \to 0$.

Therefore, it was interesting due to specific atomic and electronic structure of such materials to investigate the behavior of the optical properties of the amorphous ribbons after the action of laser radiation. In Fig. 3 the optical conductivity σ of $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ ribbons as a function of the number of laser pulses N at a constant pulse energy $E = 25$ kJ/m² (a) and 7 kJ/m² (b) is presented. At low irradiation doses, σ clearly decreases (by approximately $0.7 \cdot 10^{15}$ s^{-1}, that much more than the error $\delta\sigma = 0.1 \cdot 10^{15}$ s^{-1}) and reaches its minimum at $N = 50$ and 200. However, a further increase in the laser irradiation dose results in an increase of σ.

The curves $\sigma(E)$ at constant values $N = 200$ and 50 are similar (Fig. 4a, b). Consequently, the experimentally observed behavior of the optical conductivity σ is assumed to be related to the structure relaxation and transformation within the surface layers of ribbons subjected to laser treatment.

The obtained results may be interpreted as follows. In as-rapidly quenched alloys prepared by the spinning technique, the formation of crystal-like clusters or grains of crystalline phase is more probable near the free formed surfaces of ribbons in condition of air atmosphere than one near the contact surface, since the latter provides higher cooling rates due to direct contact during fabrication with the cooled rapidly rotating copper disk.



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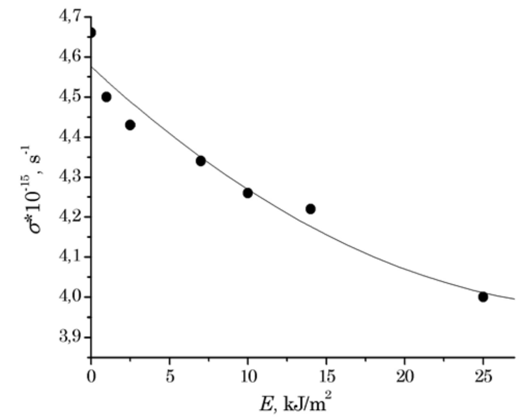

b

Fig. 4 – Optical conductivity dependencies $\sigma(E)$ of amorphous metallic ribbons $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ at constant number of pulses $N = 200$ (a) and 50 (b)

It is known [11] that the optical conductivity spectrum of crystalline bcc iron has a wide absorption band in the photon energy range of 2-2.6 eV. The photon energy of probing light in this study was equal to 2 eV. This means that the observed decrease of the optical conductivity σ at the operating wavelength for low N and E might be attributed to the decomposition of α-Fe-like crystalline grains in the surface layer of the ribbons upon the additional laser-induced quenching of the surface layer due to short-term laser heating of the surface and intensive heat removal through the bulk of the ribbon.

An increase of the laser irradiation dose makes the conditions of heat removal from the surface insufficient to provide a high cooling rate. Moreover, the absorption efficiency of the laser pulse energy is improved due to both an increase in the surface temperature and the formation of an oxide film on it. Then the processes of structure relaxation and crystallization at the surface have become dominant in this case and the amount of new α-Fe-like crystalline grains increases whereas the laser pulse energy and the number of laser pulses rise. Such modifications of atomic and electronic structure in the surface layers of the ribbons should cause the increase of optical conductivity that observed experimentally.

4. CONCLUSIONS

The ellipsometric method is strongly sensitive to detect optical anisotropy of the surface layer structure of the nanocrystalline silicon sample formed by power laser processing.

In comparison to almost unchanged ellipsometric data for the unsubjected area of such sample, the values of the optical conductivity within the subjected area are changed six times relatively to each another for two mutually perpendicular directions in own plane of the sample relatively its p-direction.

Such behavior of the optical properties of nanostructured silicon is a consequence of the appearance of deformation and elastic stresses in the formed surface layer of single silicon sample within the areas subjected to laser processing.

At low number of laser pulses N and pulse energy E, the laser treatment of amorphous ribbon surface is characterized by dominant processes of decomposition of α-Fe-like crystalline grains in the surface layer of the ribbons, while an increase in the laser irradiation dose results in the formation of additional grains of the bcc α-Fe crystalline phase due to structural relaxation and surface crystallization inside the ribbons. The amount of these crystalline grains in this case grows as N and E increase.

Such modifications of atomic and electronic structure in the surface layers of the ribbons result in the behavior of the optical conductivity for the above-mentioned amorphous alloy as functions of values N and E used.

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Модифікація оптичних властивостей поверхневих шарів та тонких плівок лазерною обробкою

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Еліпсометричним методом досліджено оптичну провідність кремнієвої пластини, модифікованої фемтосекундним лазерним опроміненням, а також вплив лазерної обробки на оптичні властивості поверхневих шарів швидкозагартованих багатокомпонентних стрічок сплаву. Зразки наноструктурованого кремнію у вигляді окремих комірок було сформовано на монокристалічних кремнієвих пластинах методом лазерної абляції. Режими сканування лазерного променю забезпечують синтез у повітряній атмосфері наноструктурованих частинок діоксину кремнію та кремнієвих наночастинок. Встановлено, що еліпсометричні параметри та оптична провідність σ комірок наноструктурованого кремнію суттєво відрізняються для двох орієнтацій комірки відносно p-напрямку зразка. Це означає, що сформовані кремнієві наноструктури мають суттєву оптичну анізотропію внаслідок деформаційного впливу лазерної абляції та виникнення пружних напружень в поверхневому шарі наноструктурованого кремнію. Для ділянок кремнію, які не опромінювались лазером і розташовані між комірками наноструктурованого кремнію, оптичної анізотропії не виявлено.

Отримані залежності оптичної провідності σ швидкозагартованих багатокомпонентних стрічок сплаву від енергії лазерного імпульсу E та кількості імпульсів N є немонотонними і досягають мінімуму при певних значеннях E та N. Така поведінка σ під час першого етапу лазерної обробки пов'язана з так званим ефектом «лазерної вітрифікації» внаслідок додаткового атомного розупорядкування поверхневих шарів стрічок, які не є повністю аморфними у вихідному стані, а містять деяку кількість кристалічної фази. Під час другого етапу такої обробки наявна аморфна структура продовжувала формуватись і релаксувати в поверхневому шарі. На третьому етапі лазерної теплової дії спостерігався відпал поверхні стрічки за рахунок досягнення достатньої дози лазерного випромінювання, що призводить до утворення кристалічної фази і, отже, до збільшення σ.

Ключові слова: Наноструктурований кремній, Швидкозагартовані сплави, Лазерна обробка, Еліпсометрія, Оптична анізотропія.