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SILICON SINGLE CRYSTAL SURFACE MODIFICATION BY COMPRESSION PLASMA FLOW ACTION

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Abstract. Modification of silicon single crystal surface by the action of nitrogen quasistationary compression plasma flow (CPF) generated by magnetoplasma compressor is studied. It was found that during single pulse surface treatment regular fracture features are obtained on the Si (100) surface in the target central part. Some of these regular structures can become free from the underlying bulk, formed as blocks ejected from the surface. Also, oriented silicon periodic structures are produced in the target periphery part. These surface phenomena are results of specific conditions during CPF interaction with silicon surface. High plasma flow energy density, large dynamic pressure, thermodynamic parameters gradients and induced magnetic field on treated surface cause rapid heating and melting of surface layer, as well as surface fracturing, long existence of molten layer and fast cooling and recrystalisation.

1. INTRODUCTION

High-power pulsed energy streams interaction with material surfaces results in surface modification, as well as the material removing from surface in the form of vapor, liquid droplets, or solid flakes due to evaporation, sputtering, ablation, exfoliation etc.

During surface treatment rapid melting and resolidification of surface layer is occured. High temperatures and consequent thermal stresses, as well as mechanically strained surface during treatment, result in significant deformation and fracture of the layer, induced defects, cracking and exfoliation of the coating. Also, cracks being characteristic of a molten material which is resolidified very quickly.

Material surface modification by pulsed energy beams such as pulsed laser, ion beams and plasma flows are of great importance, especially for grating-like patterns formation, i.e. wave-like periodic structures. The interplay between sputtering and surface diffusion smoothing processes is responsible for the creation of ripple structures, i.e. wave-like surface morphologies, when the direction of the ion beam is tilted to the surface normal [1,2]. On non-metal surfaces, including silicon, at normal incidence ripples are not observed [2]. Laser induced periodic surface structures (LIPSS) due to the incident laser light, have a period which coresponds to laser wavelenght [3]. Laser induced periodic structures with period which is much higher than laser wavelenght are described as laser induced capillary waves [3,4]. In the case of plasma surface interaction, the formation of periodical structures was not observed so far. In several types of plasma sources [5-7] rapid melting and solidification have occurred, but wave-like structures have not been yet observed.

Surface and interface properties are very important for semiconductor devices and their engineering applications. Supersonic compression plasma flow (CPF) is using for silicon single crystal surface modification. In central part of treated silicon surface regular fracture features are obtained. It was found that some of these structures as blocks can be ejected from the surface. In the periphery part of silicon samples surface highly oriented periodic cylindrical shaped structures are obtained. Surface cleavage and exfoliation phenomena, as well as ripple structures formation, as the results of specific conditions during CPF interaction on silicon surface are, also, observed and studied.

2. EXPERIMENTAL SETUP

Si (100) surface of single crystal were treated with quasistationary compression plasma flow produced by magnetoplasma compressor (MPC). MPC is a plasma source firstly designed, developed and investigated by group led by Prof. Morozov. This quasistationary plasma accelerator (plasma gun) is described elsewhere [8-12], therefore only a few details are given here for the sake of completeness.

The MPC consists of the specially designed electrode system [8]. Conically shaped cathode of MPC defines the profile of acceleration channel. Using nitrogen as working gas at 500 Pa pressures and 800 μF, 4 kV capacitor bank, the obtained current maximum was up to 100 kA and time duration up to 150 μs with current half period ~70 μs. In the MPC inter electrode region the plasma is accelerated due to the Ampere force. The plasma flow is compressed due to interaction between longitudinal current component and intrinsic azimuth magnetic field (pinch effect) [8]. The stable CPF is formed 20 μs after the beginning of the discharge. During a quasistationary phase the plasma flow parameters are slowly changing in time within certain volume. It is a consequence of an ion-drift acceleration of magnetized plasma realized using the specially shaped accelerating channel [13]. Namely, the continual ionization processes take part in working gas introduced in interelectrode region. The plasma is steadily accelerated and permanently compressed. Time development of CPF was observed using IMACON 790 high speed camera operating in streak mode, using parallel positioned slit along CPF axis. In Fig. 1 discrete plasma structures of CPF, seen as light and dark regions, are observed. These structures occur with ~5 MHz frequencies.

The advantages of MPC, as compared to other types of plasma accelerators, are high stability of generated CPF, size (CPF up to 6 cm in length and 1 cm in diameter), and high plasma parameters (electron density ~10^{17} cm^{-3} and temperature up to 3 eV), as well as the CPF time duration (quasistationary stable phase is 40-50 μs) and large flow velocity (40 km/s in nitrogen) sufficient for material surface modification. Beside that, the operation in the ion current transfer mode [13] with the minimization of the electrodes erosion represents an additional and very important advantage of the quasistationary plasma accelerators in comparison with the classical ones. The electrodes surfaces are protected of the erosion due to the magnetic field self-shielding. Magnetic flux conservation is a particular characteristic of CPF. During the action of CPF on a sample surface, due to CPF deceleration and frozen-in magnetic field, current loops (vortices) are formed.

For the studies of CPF interaction with silicon surfaces, commercial one-side polished n-type silicon wafers (100 orientation) 300 μm thick and 10 mm in diameter were used. The samples were glued to the cylindrical brass holder of the same diameter with conductive carbon paste, and mounted perpendicularly in front of the MPC cathode at the distance of 5 cm. Silicon samples are exposed to a single plasma pulse. A target surface is parallel to the direction of gravitation force and perpendicular to the plasma flow velocity. Therefore, the gravitation force has no influence on the surface wave's formation. To investigate the morphology of treated silicon surface, optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used.

3. RESULTS

OM and SEM micrographs of a treated Si (100) surfaces are given in Fig. 2 and Fig. 3, respectively. In central part of the treated surfaces two sets of fracture lines intersecting at 90º form a grid that divides the surface into rectangular blocks (Fig. 2). Some of the blocks are ejected from the surface, and large holes at the surface emerged. In this case development of subsurface fracture, parallel to the surface, is occured. A typical hole is shown in Fig. 2. At the bottom of arisen holes very small ripple structures are observed.

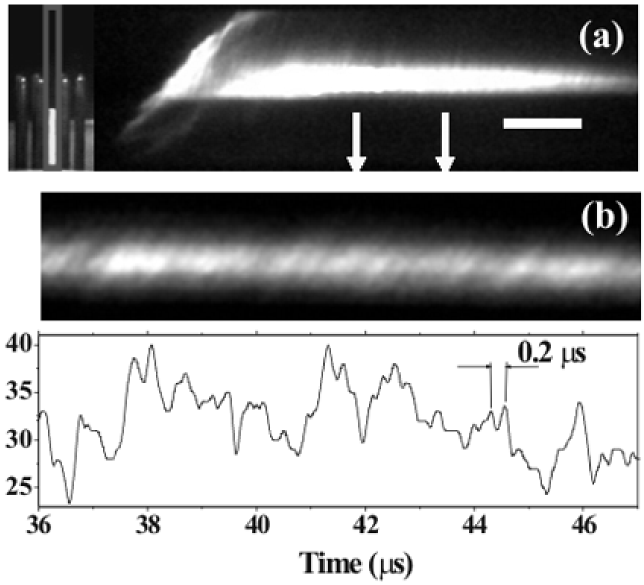

Fig. 1. The compression plasma flow intrinsic oscillations: a) Time and space development of CPF from the cathode onwards. Bar size is 10 μs. b) Enlarged time period indicated by arrows with its light intensity variation represented versus time.

Surface fracture and periodic cylindrical structures obtained by plasma pulse treatment of the Si (100) sample surface are shown in Fig. 3. Periodic silicon structures are obtained on the periphery part of the target surface. Wavelengths (hill-to-hill distances) of highly oriented periodical silicon structures are in the range from 100 nm up to 5 μm [14-18]. The lengths of these structures are in the range from 50 μm up to one millimeter (Fig. 2). Typical wavelength is about 2-3 μm and length 200 μm. The AFM micrographs were used for the periodical structures surface investigation (Fig. 4). Structures are smooth, homogenous and sinusoidally shaped with an amplitude (half hill-to-valley distance) of about 0.2-0.3 μm [17]. It is worth to emphasize that this structures are obtained by single plasma pulse treatment of the Si sample surface. The regular silicon surface structures can be obtained on the area region up to several square millimeters. They are covering up to 50 % of the whole surface. SEM micrographs of the obtained parallely oriented periodic structures on Si (100) surface are shown in Figs. 5-7.

These periodical structures are not dependent on the crystal orientation. Similar structures were obtained, also, using hydrogen and argon plasma flow interaction with silicon samples. The shapes of obtained structures were not dependent on the working gas [15]. Also, after plasma flow exposure, the sample was treated by HF acid and has been concluded that the obtained cylindrical structures are made of pure silicon [14].

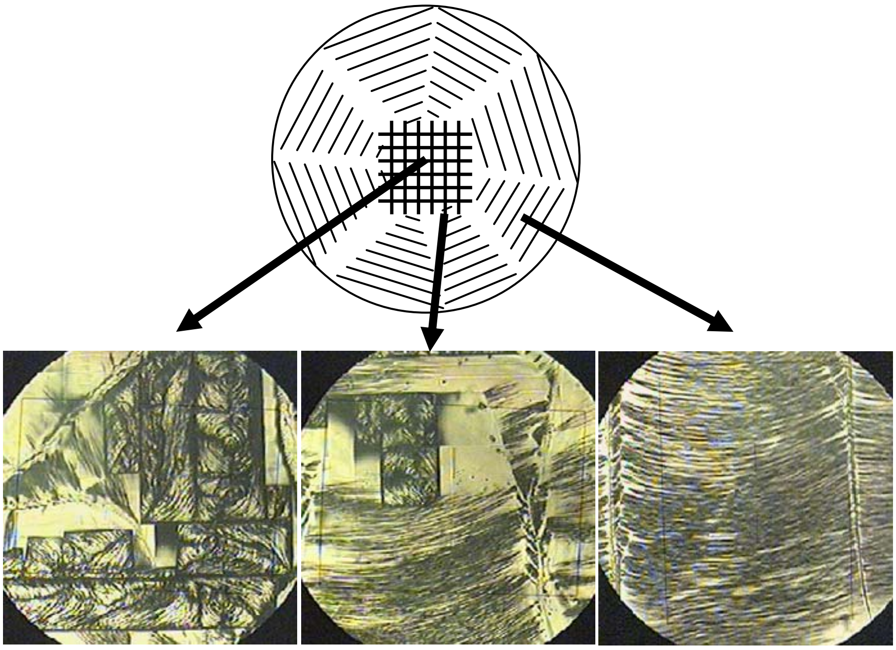

Fig. 2. Schematic diagram and optical microscopy micrographs of CPF treated Si (100) surface. Micrographs size are 1×1 mm^2.

4. DISCUSSION

The formation of observed surface features may be explained by energetic action of CPF on the surface (absorbed energy 10-15 J per pulse, flow power density ~$1 \cdot 10^5$ W/cm^2 [16]). The interaction of CPF with silicon sample surface causes the evaporation of a thin surface layer and formation of a shock-compressed plasma layer (SCPL) [14]. Formation of this cloud of dense target plasma results in the shielding of a processed surface from a direct action of a CPF and surface protection from further excessive evaporation. A thickness of this plasma plume is about 1 cm. Using the high speed camera, time of interaction was estimated to be 40-50 μs [14]. It may be taken that molten layer exists on the target surface during the interaction. By analyzing the cross section of treated silicon sample, thickness of near-surface molten layer is estimated at 6-10 μm.

Energetic action of CPF causes the fast heating and melting of the surface layer and the presence of high dynamic pressure of CPF of the order of several atmospheres [16]. Namely, CPF kinetic energy thermalization causes the heating of target surface and high gradient of thermodynamic parameters is occurred. Target surface is heated by convective and radiative heating. Beside that, deceleration of the CPF results in the formation of current loops (vortices), due to freezing of magnetic field into plasma, and magnetic field 1-10 mT is induced at the surface [16].

Formation of regular fracture features (Figs. 2,3) can be explained by considerable fraction of the absorbed plasma flow energy trapped into fractures rather than converted to heat energy [19,20]. Single crystal silicon is well known as a typical anisotropic material and it is very brittle at room temperature [21]. Low adhesion between blocks and silicon bulk, and eventual ejection of blocks from the CPF treated surface, can be explained by development of subsurface fracture, parallel to the surface. Cracking between the block and the bulk is growing due to local energy absorption.

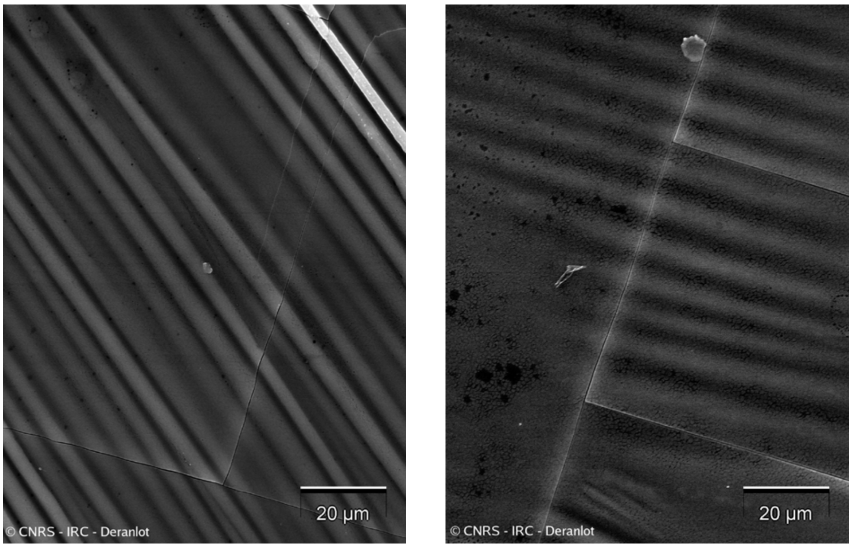

Fig. 3. SEM micrographs of silicon surface obtained after single pulse treatment by CPF.

An aim of this paper is to compare periodical structures obtained on CPF treated silicon surface with wave-like periodical structures obtained by laser, ion beam and plasma flow silicon surface treatment.

Laser induced periodic surface structures (LIPSS), theoretically and experimentally observed elsewhere [3], corresponds to a non-uniform energy input into the sample, modulated by the interference between the incident wave and an induced surface wave. Targets are made of intrinsic and extrinsic semiconductors, metals and dielectrics. At normally incident laser beam, periodical surface structures are perpendicular to the laser beam polarization and have a period which corresponds to laser wavelength. In some case, the structures have a period which is much higher than laser wavelength. These structures are described as laser-induced capillary waves [4].

Ripple structures on silicon surface, created by ion bombardment [1], are based on the interplay between the sputtering and surface diffusion smoothing processes. The sputtering yield depends on the local surface curvature. This dependency leads to a surface instability (negative surface tension) where the erosion velocity in depressions is greater than on mounds of the surface. On the other hand, surface diffusion tends to smooth the surface topography. The interplay between these two effects is responsible for the creation of cones, dots and holes on surfaces at normal ion incidence, and especially for ripple and wave-like surface morphologies, when the direction of the ion beam is tilted to the surface normal (off-normal incidence) [1,2]. In case of grazing-incidence sputtering geometries ($\theta \geq 70^\circ$) orientation of the surface structures is forced to be parallel to the ion beam orientation. For angles smaller then the critical incident angle, structures become perpendicular to the ion beam orientation. In non-metal substrates, including silicon, at normal incidence ripples are not observed [2]. The ripples can be created by bombardment at normal ion incidence in the case of some metals (Ag, Cu) due to anisotropic surface diffusion [2].

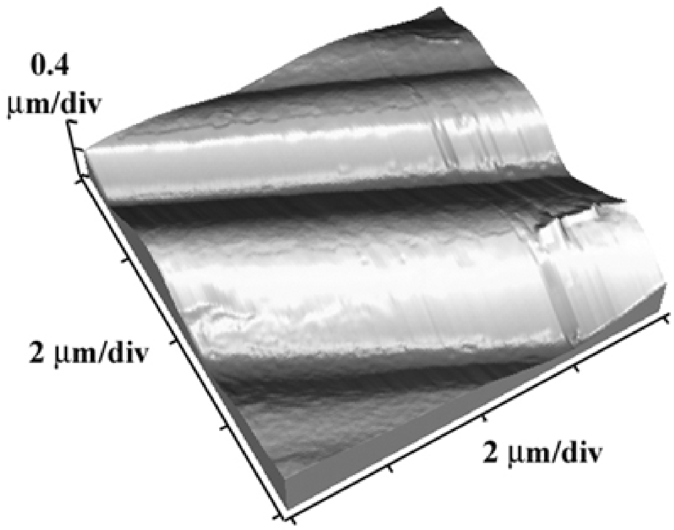

Fig. 4. AFM micrograph of CPF treated Si (100) surface.

In the case of plasma surface interaction experiments, the periodical silicon surface structure formation has not been observed so far, although the time of interaction varied up to 10 μs, and delivered plasma energy density was of the order of 10 J/cm^2, which is comparable to our experimental conditions. Using several types of plasma sources such as coaxial plasma gun [5], pulsed plasma beam [6] and thermal plasma jet [7], rapid melting and resolidification have occurred, but wave-like structures have not been observed.

However, in our experiment we have obtained silicon periodical surface structures. This can be attributed to specific property of compression plasma flow. The energy density delivered to the surface is about 10 J/cm^2 and surface is completely and uniformly melted. Due to the fast cooling of the melted surface layer, which is usually occurring in this kind of experiment, the surface structures formed during melt phase are freezing (quenched) at a particular moment during a process of the melt resolidification [15,17]. Therefore, the basic effects of the CPF action on solid target are surface melting, formation of different surface patterns and their freezing during fast cooling (quenching effect). This process may be compared with laser surface interaction. Three main similarities of CPF used here and laser beams of high fluences are: i) silicon surface uniform melting; ii) perturbation action on melted surface layer; and, iii) quenching of the produced surface wave structures. In the laser surface interaction at high fluences, the periodical structures results from freezing of capillary waves which are generated on the uniformly melted surface. In this case laser induced plasma plume adiabatically spreads in a direction normal to the treated surface which induces a very strong recoil impulse directed into the treated target [3,4]. Laser induced capillary waves are smooth and sinusoidally shaped structures [3] similar to those obtained by CPF treatment in this experiment.

If free surface of a liquid is put out of balance, waves are formed along the surface under the influence of gravitational pull and surface tension [22]. If the direction of gravitation force is such that it can not contribute to the creation of surface waves, the waves formed at the liquid surface are capillary waves. The dispersion of such capillary waves is given as [22]:

$$\omega^2 = \frac{\gamma}{\rho} k^3 \tag{1}$$

Here, γ is the surface tension, ρ is the density of the liquid, ω is the frequency and k is wave number of the capillary waves. When waves are driven by a periodical force applied on the free liquid surface their frequency has to be close to the frequency of the applied force. In the case of periodical radiation pressure of laser light to the liquid surface, the capillary waves with arbitrary waveform were generated by modulating the laser output [23]. This approach has been used for study of CPF induced capillary waves experimentally observed here. Namely, CPF treatment of the melted silicon surface is periodical perturbation due to CPF intrinsic oscillations.

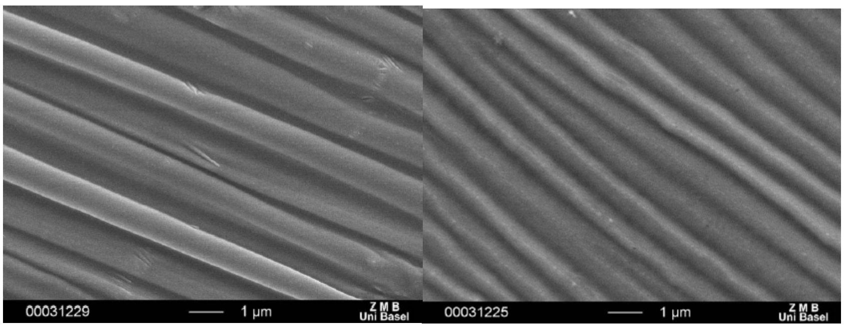

Fig. 5. SEM micrographs of highly oriented periodical structures on treated silicon surface.

On the completely molten silicon surface, in the presence of high dynamic pressure of CPF, perturbation occurs [16]. The obtained periodical cylindrical structures on the surface are liquid structures frozen during fast cooling and recrystallization (quenching effect).

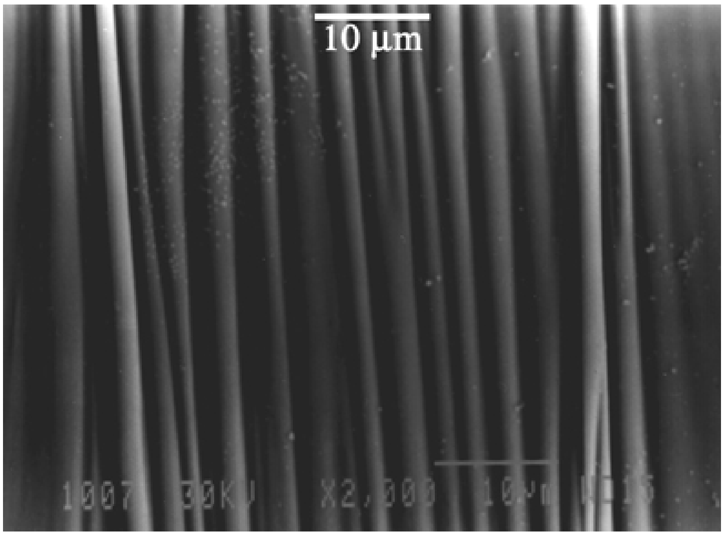

Fig. 6. SEM micrograph of CPF treated silicon surface.

Supposing that the periodical cylindrical structures are frozen surface capillary waves quenched at a particular moment during a process of the melt resolidification, main wave parameters can be estimated using dispersion equation. Taking $\gamma \sim 0.75$ N/m and $\rho \sim 2.5$ g/cm^3 for molten silicon [ref. 24 and references therein], with typical ex situ measured wavelength of periodical structures equal to ~4 μm (Figs. 2-7), calculated capillary wave frequency is found to be ~5 MHz. This value corresponds to the in situ measured frequency of discrete plasma structures, i.e. frequency of perturbation of ~5 MHz (Fig. 1). About 200 plasma pulses delivered to treated silicon surface during 40 μs of plasma flow quasistationary phase. This is a clear indication that the CPF interaction with molten silicon surface can be regarded as a periodical driven force of the induced surface capillary waves.

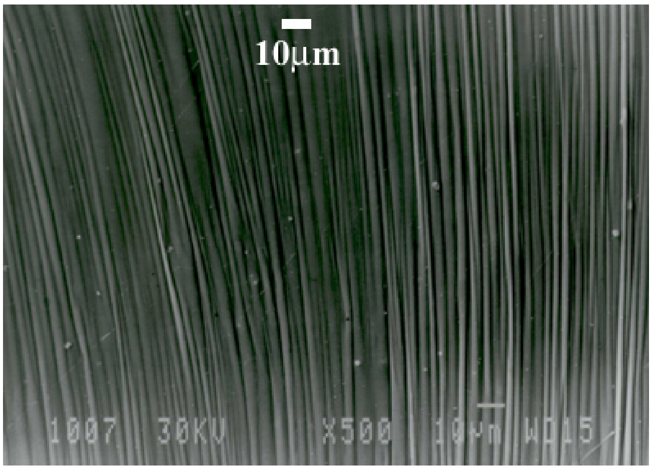

Fig. 7. Silicon surface cylindrical structures obtained by single plasma pulse treatment of the Si (100) sample.

The surfaces of periodical structures are found to be smooth, homogenous and sinusoidally shaped (Fig. 4), as would be expected from frozen capillary waves [3]. Besides the freezing of capillary waves, a rapid solidification can also produce serious cracking problems due to differential stresses. An example of the surface regular fracture together with frozen capillary waves, obtained by single plasma pulse treatment of the Si (100) sample surface, is shown in Fig. 3. During cooling and unloading of treated surface, the residual stresses created in the subsurface region can produce surface fracturing [21]. From Fig. 3 one can conclude that crackings occurre after solidification of periodic cylindrical structures and may be explained with the emerging of residual stresses. Recrystallization occurred under conditions of high dynamic pressure of CPF, high thermodynamic parameters gradients, and induced magnetic field.

5. CONCLUSION

Periodical wave-like patterns, as well as regular fracture features and exfoliations, are observed on silicon single crystal surface treated by CPF. Surface modification is performed by fast heating of the surface in the presence of high dynamic pressure, thermodynamic parameters gradients and induced magnetic field from the CPF. Periodical wave-like structures are induced by the plasma flow action on periphery part of the target and then quenched from the molten state during fast cooling and resolidification. Typical dimensions of parallel cylindrical structures are 2-3 μm in diameter and about 200 μm in length. The regular silicon surface structures can be obtained on the larger area, up to several square millimeters. These structures may be related to plasma induced capillary waves phenomena. The estimated frequency of the capillary waves is found to be in a good agreement as compared to the frequency of the observed CPF plasma structures. During surface treatment and fast cooling phase, differential stresses in surface layer occurred. As the results of all of these processes rectangular regular fracture features are obtained on the Si (100) surface. Some of these blocks are ejected from the surface.

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