Large-area homogeneous periodic surface structures generated on the surface of sputtered boron carbide thin films by femtosecond laser processing

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Abstract

Amorphous and crystalline sputtered boron carbide thin films have a very high hardness even surpassing that of bulk crystalline boron carbide (≈ 41 GPa). However, magnetron sputtered B-C films have high friction coefficients (C.o.F) which limit their industrial application. Nanopatterning of materials surfaces has been proposed as a solution to decrease the C.o.F. The contact area of the nanopatterned surfaces is decreased due to the nanometre size of the asperities which results in a significant reduction of adhesion and friction. In the present work, the surface of amorphous and polycrystalline B-C thin films deposited by magnetron sputtering was nanopatterned using infrared femtosecond laser radiation. Successive parallel laser tracks 10 μm apart were overlapped in order to obtain a processed area of about 3 mm².

Sinusoidal-like undulations with the same spatial period as the laser tracks were formed on the surface of the amorphous boron carbide films after laser processing. The undulations amplitude increases with increasing laser fluence. The formation of undulations with a 10 μm period was also observed on the surface of the crystalline boron carbide film processed with a pulse energy of 72 μJ . The amplitude of the undulations is about 10 times higher than in the amorphous films processed at the same pulse energy due to the higher roughness of the films and consequent increase in laser radiation absorption.

LIPSS formation on the surface of the films was achieved for the three B-C films under study. However, LIPSS are formed under different circumstances. Processing of the amorphous films at low fluence (72 μJ) results in LIPSS formation only on localized spots on the film surface. LIPSS formation on the top of the undulations formed after laser processing

with 78 μJ of the amorphous film deposited at 800 °C. Finally, large-area homogeneous LIPSS coverage of the boron carbide crystalline films surface was achieved within a large range of laser fluences although holes are also formed at higher laser fluences.

Keywords: Surface nanostructuring, boron carbide, Sputtering, Femtosecond laser, LIPSS

1. Introduction

Boron carbide is among the hardest (≈ 41 GPa) and most abrasion-resistant materials at ambient temperature and is even harder than diamond at high temperature [1,2]. Besides light weight armour and thermoelectric energy conversion, boron carbide is also an excellent material for hard and wear-resistant tribological coatings [3]. Polycrystalline B_4C is only obtained when highly energetic deposition techniques are used [4]. Most of the work on the deposition of boron carbide by sputtering resulted in the deposition of amorphous B-C films. As a result, annealing of the as-deposited films at high temperature is necessary to crystallize the boron carbide structure [5,6]. Nevertheless, the as-deposited amorphous B-C films were shown to have very interesting mechanical properties with reported hardness even surpassing that of bulk crystalline boron carbide [7,8]. However, magnetron sputtered B-C films have high friction coefficients (C.o.F) which limit their industrial application [3,9]. Several authors attempt to decrease the C.o.F of amorphous boron carbide films by using hydrocarbons in the sputtering discharge [5,6]. Although the C.o.F of the deposited films was substantially decreased by incorporating higher amounts of carbon in the films, the results were obtained at the expenses of film hardness which undermine the industrial application of the films.

Nanopatterning of materials surfaces has been proposed as a solution to decrease the C.o.F [10-12]. The contact area of the nanopatterned surfaces is decreased due to the nanometre size of the asperities which results in a significant reduction of adhesion and friction. On the other hand, nanometre-sized asperities may be much harder than its corresponding bulk material due to their large surface area-to volume ratio, which will considerably enhance the wear resistance of a surface. In addition, the presence of nanopatterned asperities increases the surface hydrophobicity, which also leads to the reduction of adhesion and friction forces in a humid environment [9]. Several approaches have been proposed in the literature to achieve surface nanopatterning, such as UV, X-ray and scanning probe lithography, electron beam writing and focused ion beam milling, among others [13]. However these technologies are costly and have low flexibility and long processing times. In contrast, surface patterning using pulsed lasers beams is a powerful and versatile process for micro-machining and patterning of materials surfaces [14,15]. In particular, femtosecond lasers are promising tools for this purpose [16] since their extremely short pulse duration and very high peak power generate intense non-linear effects. As a result, almost any type of material can be processed, including transparent dielectrics, polymers and metals, without undesirable collateral thermal effects [17-20].

Irradiation of solid surfaces by femtosecond laser pulses produces regular surface structures with sub-micrometre spatial periodicity, frequently called laser-induced periodic surface

structures (LIPSS). LIPSS are observed in a wide range of laser treated materials and their periodicity and orientation depend on the radiation wavelength, angle of incidence, and polarisation of the laser beam. Low spatial frequency LIPSS (LSFL) have a period of the same order of magnitude of the radiation wavelength (or slightly lower), while high spatial frequency LIPSS (HSFL) have periods of a few hundred nanometres. It has been shown in the literature that LSFL can be used to improve the tribological performance of thin solid films [21]. However, from an application point of view, large -area processing of the boron carbide films surface is mandatory. Processing of extended areas using femtosecond lasers has already been reported for other materials [22-24]. The aim of the present work is to produce large-area uniform femtosecond LIPSS on the surface of boron carbide thin films. For this purpose the influence of laser processing parameters on the formation of LIPSS on both polycrystalline and amorphous boron carbide thin films surface was studied.

2. Experimental

Boron carbide films (B-C) were deposited by magnetron sputtering from a hot-pressed polycrystalline B_4C target with 99.95 % purity in a pure argon atmosphere. The thickness of the as-deposited films was 600 nm, as measured by scanning electron microscopy (SEM), regardless of the substrate deposition temperature. The ultimate vacuum pressure before deposition was lower than 5×10^{-4} Pa. Silicon substrates placed at 60 mm from the target were used in all depositions. The Si substrates were heated during the deposition process up to 200, 800 and 1000 °C. All experiments were carried out with a 450 W power applied to the B_4C target and a deposition pressure close to 0.5 Pa.

Femtosecond laser surface treatments of the boron carbide thin films were performed with a Yb:KYW chirped-pulse regenerative amplification laser system (Amplitude Systèmes s-Pulse HP) with a central wavelength of 1030 nm and a laser pulse duration of about 500 fs. The laser beam was focused by a 100 mm focal length lens and incident perpendicularly to the sample surface. The direction of its polarisation vector in relation to the beam scanning direction was controlled by a half-wave plate. The mean pulse energy was varied in the range 50 to 100 μJ by means of an attenuator in order to achieve average fluences at the surface of the sample ranging from 0.65 to 1.3 J/cm² at a pulse repetition rate of 10 kHz. Adjacent linear laser tracks approximately 100 μm wide are produced by moving the B-C film substrates under the stationary laser beam using a computer-controlled XYZ stage with a scanning speed of 5 mm/s. In order to achieve complete surface coverage with 3 mm² of treated area a lateral displacement of 10 μm is applied between adjacent tracks by moving the stage in a direction perpendicular to the scanning direction.

The surface morphological details of the coatings were examined in a Philips XL30 scanning electron microscope (SEM) operated at 20 kV. Micro Raman spectroscopy was performed in HORIBA Jobin-Yvon Raman device with visible light source of 532 nm wavelength. The spectrum was measured in the range 240 to 2000 cm⁻¹ with laser power of 20 to 25 mW for 30 seconds acquisition time. All measurements were performed at room temperature. White light interferometry was also used to characterize the surface topography in the thin films. The technique is able to image large sample areas with very high z resolution.

3. Results

3.1 As deposited films

The surface of the as-deposited boron carbide films deposited at 200 and 800 °C is smooth and featureless (Figure 1a and b, respectively), much like the surface of the silicon substrates used in this work. In contrast, the surface of the film deposited at 1000 °C is heterogeneous and has a much higher roughness (Figure 1c). As can be observed from the higher magnification SEM image shown in Figure 1d, heating at 1000 °C resulted in the formation of well define grains with sharp edges and sizes up to about 100 nm.

Figure 2 shows micro-Raman spectra of the as-deposited B-C thin films. Boron carbide has a complex structure consisting of icosahedral arrangements of twelve atoms at the vertices of a rhombohedral unit cell connected with three-atom chains along the main diagonal [25]. According to literature [26,27] the micro-Raman spectra of crystalline B₄C has two narrow bands near 500 cm⁻¹, associated to vibrations of the inter-icosahedral chains, and much wider peaks in the range from 600 to 1200 cm⁻¹, associated to vibrations of the icosahedra. The micro-Raman spectrum of the B-C film deposited at 1000 °C clearly shows these intense icosahedra related peaks with relative intensities corresponding to crystalline B₄C. The narrow bands associated with the inter-icosahedral chains may be masked by the intense Si substrate peak although a small intensity peak is detected near 480 cm⁻¹. The micro-Raman spectra of the films deposited at 200 and 800 °C only show a very low intensity broad band in the range corresponding to the icosahedra vibrations (600 to 1200 cm⁻¹) which is overlapped by background features. Both spectra are characteristic of amorphous boron carbide which consists of a disordered network of icosahedra.

3.2 Laser processing of thin-films deposited at 200°C

Figure 3 shows SEM micrographs of the surface of films deposited at 200 °C after femtosecond laser irradiation with pulse energies between 65 and 78 μJ. The surface of the film processed with 65 μJ is smooth and featureless much like the as-deposited surface (Figure 3a). A mostly smooth and featureless surface is also observed after processing with 72 μJ although with features dispersed on the film surface (Figure 3b). Observation of these features at higher magnification shows that they actually consist LIPSS perpendicular to the scanning direction with a spatial period of about 180 nm (Figure 3c). A further increase of the pulse energy up to 78 μJ (Figure 3d) leads to the complete removal of the film and to the formation of worm-like structures characteristic of silicon processed with femtosecond laser radiation [28].

The laser processed surfaces were also analysed by white light interferometry. Although the lateral resolution of this characterization method is too low to detect the formation of LIPSS, the vertical resolution allows observation of features with heights down to the nanometre. Figure 4 depict 3D images and 2D topographical profiles of the surface of the films processed with 65 and 72 μJ. The presence of undulations parallel to the scanning direction

with a period of about 10 μm is clearly seen on both 3D images. The undulations amplitude is about 1.5 nm for the film processed with 72 μJ , as can be readily concluded from the corresponding 2D topographical profile. Although the undulations are not clearly discernible in the 2D profile of the film processed with 65 μJ , an amplitude of about 0.2 nm was found after mathematical processing to extract a sinusoidal signal.

Figure 5 displays micro-Raman spectra of the films treated with 65 and 72 μJ . The micro-Raman spectra obtained over the treated surfaces show broad bands in the range from 600 to 1200 cm^{-1} with low intensity and resolution, similar to those detected for the as-deposited amorphous film. As a result, the films remain amorphous even after laser processing and no structural transformation were detected. A micro-Raman spectrum was also acquired on the film treated with 78 μJ (not shown in Figure 5). In this case only Si and SiO_2 were detected by spectroscopy confirming the complete film removal already observed by SEM.

3.3 Laser processing of thin-films deposited at 800°C

Figure 6 depicts SEM micrographs of the surface of the B-C films deposited at 800 °C after irradiation with pulses energies between 65 and 85 μJ . Once again the surface of the film laser processed at 65 μJ is smooth and featureless (Figure 6a), similar to the as-deposited surface. Increasing the pulse energy up to 72 μJ does not significantly change the film surface, although the formation of a few holes randomly dispersed on the surface film can be observed (Figure 6b). Note that LIPSS with a period of about 185 nm are formed on the border of the holes. At 78 μJ parallel stripes of LIPSS along the scanning direction are formed, separated by regions of unaltered film (Figure 6c). The distance between the stripes centre is about 10 μm which corresponds to the overlapping distance between adjacent laser tracks. A close inspection shows that the LIPSS are perpendicular to the scanning direction with a period of 228 nm. Finally, at 85 μJ the film is completely removed and the worm like structures characteristic of silicon processed with femtosecond laser radiation are formed (Figure 6d).

Figure 7 shows 3D images and 2D topographical profiles of the surface of the films laser processed with 72 and 78 μJ . The presence of periodic undulations parallel to the direction of the laser tracks is clearly detected on both images. The period of the undulations is again the same as the laser tracks spacing (10 μm). The 2D profile of the film processed with 72 μJ shows sinusoidal-like undulations with an amplitude of about 1 nm. The undulations formed after laser processing at 78 μJ are no longer sinusoidal-like, presenting a plateau-like shape on the top, and have a significantly higher amplitude (about 30 nm) than in the previous case.

The micro-Raman spectrum of the surface of the B-C film processed with 72 μJ (Figure 8) is similar to the one obtain for the as-deposited film, showing that the amorphous as-deposited structure is not significantly changed. Although a mostly amorphous structure is still detected on the surface of the film processed at 78 μJ , the intensity of the broad Raman bands between 600 and 1200 cm^{-1} is higher than in the as-deposited film (Figure 2 for 800 °C). In this case, the characteristic shape of crystalline boron carbide Raman bands starts to emerge. At higher laser energies only Si and SiO_2 are detected by micro-Raman

spectroscopy, confirming the complete film removal already observed by SEM (not shown in Figure 8).

3.4 Laser processing of thin-films deposited at 1000°C

SEM micrographs of the surface of the crystalline boron carbide film after laser processing are shown in Figure 9. Processing with laser fluences of 50 and 65 μJ resulted in complete homogeneous coverage of the film surface with LIPSS (Figure 9a and b). Complete coverage of the film surface with LIPSS is also achieved at 72 μJ although the formation of a few holes randomly dispersed on the film surface is also observed (Figure 9c). Increasing the laser fluence to 80 μJ significantly increases both the number and the size of the holes while the remaining film surface is still fully covered with LIPSS (Figure 9d). A further increase of the pulse energy up to 90 μJ leads to the complete film removal and formation of worm like structures (not shown). The spatial period of the LIPSS increases with the laser pulse energy, between 125 and 200 nm, while their orientation is always perpendicular to the laser beam polarization.

Figure 10 shows 3D images and 2D topographical profiles of the surface of the crystalline boron carbide film processed with 65 and 72 μJ . Both surfaces have a much higher roughness than the surface of the amorphous films processed with the same laser fluences. In both cases the film surface was laser ablated resulting in the formation of LIPSS which cannot be resolved by white light interferometry although originating a higher roughness. The formation of undulations, similar to the ones previously reported for the amorphous films, is also observed on the surface of the film processed at 72 μJ . As LIPSS were simultaneously formed the undulations are much less defined than in the amorphous films. Nevertheless, an amplitude of 15 nm was estimated from the topographical graph (figure 10b). Although undulations may have been formed on the surface of the film processed at 65 μJ , their presence is completely masked by the LIPSS covering the entire film surface.

The micro-Raman spectra of films deposited at 1000°C and processed with 65 and 72 mJ pulse energy are shown in Figure 11. Well resolved and intense bands are present between 600 and 1200 cm^{-1} in both spectra showing that boron carbide remains crystalline after the laser processing. Two large bands centred near 1350 and 1600 cm^{-1} which are characteristic of an amorphous carbon phase also appear after laser processing. The intensity of these bands increases with increasing pulse energy showing that the quantity of amorphous carbon formed due to the laser treatment increases with the laser energy. For even higher laser energies (not shown) only Si and SiO₂ are detected by micro Raman spectroscopy, showing that the film was stripped off the substrate.

4. Discussion

Sinusoidal-like undulations were formed on the surface of all the amorphous B-C films as a result of femtosecond laser processing. In all cases the period of the undulations corresponds to the spacing of the laser tracks (10 μm). At low pulse energies the surface of the films is not significantly changed after laser processing, showing that the undulations do not result from laser ablation of the film surface. On the other hand, the structure of the surface after laser processing remains amorphous, as in the as-deposited state, which rules

out phase transformations as a possible cause for the formation of the undulations. It is well known that amorphous boron carbide films deposited by magnetron sputtering have high residual compressive stresses dependent on the deposition conditions [29]. The residual stresses can be relaxed by annealing of the films [30]. In this work a Gaussian laser beam was used. The spatial fluence profile $F(r)$ is given by

$$F(r) = \frac{2E}{\pi w_0^2} e^{-\frac{r^2}{w_0^2}}$$

where E is the pulse energy, w_0 is the beam radius defined as the distance from the beam axis where the fluence drops to $1/e^2$ of the peak value, and r is the distance from the beam axis. The most probable explanation for the formation of undulations is that the laser radiation is thermalized within the B-C films resulting in relaxation of the intrinsic compressive stresses. Since the laser intensity distribution is Gaussian, the temperature profile at the film surface is also Gaussian-like, resulting in more effective relaxation of the intrinsic compressive stresses near the centre of the laser beam. As a result, the stress relaxed regions will be under compression by the adjacent unaffected regions and local increase of the volume will occur.

The amplitude of the undulations formed after processing the amorphous B-C films at 72 μJ is lower for the film deposited with a higher substrate temperature (1 and 1.5 nm, respectively). This results agrees well with the previous argument as heating of the B-C films during deposition decreases the compressive stresses which then results in lower volume increase after laser processing. On the other hand, the undulations amplitude increases with the laser fluence as should be expected from the compressive stresses relaxation mechanism due to the higher temperatures reached on the film surface.

The formation of undulations with a 10 μm period was also observed on the surface of the crystalline boron carbide film processed with a pulse energy of 72 μJ . Although lower residual stresses are to be expected in this film, as a result of the higher deposition temperature, the amplitude of the undulations is about 10 times higher than in the amorphous films processed at the same pulse energy. The surface of the crystalline boron carbide film has a much higher roughness than the surface of both amorphous films (see Figure 1). Since surface roughness enhances laser radiation absorption, the higher undulations amplitude results from the higher temperatures reached with the same laser fluence on the surface of the crystalline film.

The formation of LIPSS on the surface of the films was achieved for the three B-C films under study. However, LIPSS formation occurs under different circumstances. Processing of the amorphous films at low fluence (72 μJ) results in LIPSS formation only on localized spots on the film surface as shown in figure 3c. It is well known from the literature that LIPSS form at radiation fluences close to the material ablation threshold [16]. Since most of the B-C film surface is not ablated for this pulse energy, the generation of LIPSS is most probably due to the presence of surface defects which enhances laser radiation absorption and locally increases the effective radiation fluence above the films ablation threshold. This conclusion is supported by the evolution of the spots into holes with LIPSS on the border at higher fluences, as shown in Figure 6c. LIPSS formation was also obtained on the top of the

undulations formed after laser processing with 78 μJ of the amorphous film deposited at 800 $^{\circ}\text{C}$ (Figures 6d and e). The top of the undulations correspond to the higher radiation fluences where the ablation threshold of the material is exceeded. Assuming that the beam radius w_0 is equal to half the width of the laser track (50 μm), the fluence threshold for LIPSS formation can be estimated to be about 2.0 J/cm^2 . Complete removal of the film was observed after treatment at 85 μJ which correspond to a maximum radiation fluence of 2.2 J/cm^2 . Finally, homogeneous LIPSS covering the entire processed surface were obtained after processing the crystalline boron carbide film with pulses energies above 50 μJ . In this case the fluence threshold for LIPSS formation was estimated to be about 1.3 J/cm^2 .

The spatial period of the LIPSS formed in this work ranges from 140 to 200 nm depending on the laser pulse energy, as shown in table 1. Upon irradiation of solids with linearly polarized femtosecond laser pulses in air under normal incidence, two distinct types of LIPSS are observed: LSFL and HSFL. LSFL have spatial periods close to the irradiation wavelength λ while HSFL have spatial periods significantly smaller than the irradiation wavelength [31]. Since the wavelength of the laser radiation used in this work is $\lambda = 1030$ nm, the spatial period of the LIPSS generated in the B-C thin films surface is about 5 times smaller than the irradiation wavelength and all the observed LIPSS can be classified as HSFL.

In a recent study Chrakravarty and co-workers [32] compared the spatial period of LIPSS formed in semiconductors with different bandgaps. The authors showed that, under the same laser processing conditions, LSFL are observed in narrow bandgap semiconductors while HSFL are observed in wide bandgap semiconductors. These results were explained considering that LIPSS are formed due to the excitation of a surface plasmon wave at the semiconductor surface which interferes with the incident laser radiation. According to the authors, the critical factor in deciding the LIPSS spatial period is the electron density of the surface plasmon wave. LSFL are obtained for high plasma electron densities while HSFL are observed when the electron density approaches a minimum critical value for which the formation of LIPSS is no longer observed. Since the absorption of ultra-short laser pulses in materials with a narrow bandgap occurs through a combination of linear and non-linear absorption processes, a larger availability of free electrons in the conduction band is expected in these materials when compared with wide bandgap materials, where only non-linear absorption processes can take place. As a result, a much lower surface plasma electron density is expected for wide bandgap semiconductors and, accordingly, the formation of HSFL is observed in these materials. In addition, the authors reported that the spatial period of the HSFL increases with increasing laser radiation fluence, an effect they explained by the dependence of the plasma electron density on the incident laser radiation intensity. The results reported in this work for the boron carbide films are consistent with this interpretation of LIPSS formation: i) as the estimated bandgap of boron carbide (1.64 eV [33]) is higher than the energy of the incident laser radiation used in this work (1.2 eV) boron carbide can be considered a wide bandgap semiconductor; ii) the spatial period of the HSFL observed in the boron carbide films increases with increasing pulse energies. Finally, it should be noted that the formation of LSFL was not observed in neither crystalline nor amorphous B-C films. It is well known from the literature that LSFL form at laser radiation fluences slightly higher than those required for HSFL [32]. In this work the films were

completely removed from the substrate before reaching the radiation fluences for LSFL formation.

The fluence threshold for HSFL formation in the crystalline films (1.3 J/cm^2) is significantly lower than for the amorphous films (2.0 J/cm^2). Once again, this result is due to the higher surface roughness of the crystalline film which enhances laser radiation absorption. The crystalline film presents a lower threshold for HSFL formation because it absorbs more laser radiation than the amorphous films. This is consistent with the observation that for similar pulse energies, the spatial period of the LIPSS is smaller for the amorphous films. In addition, it is also well known from the literature that roughened surfaces lead to a more efficient excitation of surface plasmons [34] which in turn may contribute to facilitate the formation of LIPSS in the crystalline film at lower radiation fluences.

From the application point of view, laser processing of the crystalline boron carbide films seems to be more promising than processing of the amorphous films. Large-area homogeneous LIPSS coverage of the boron carbide crystalline films surface was achieved within a large range of laser fluences although holes are also formed at higher laser fluences. Furthermore, the spatial period of the LIPSS can be tune by changing the laser fluence. Although LIPSS formation was also observed on the surface of the amorphous films within a narrow window of laser fluences, complete homogeneous coverage was not achieved. However, the undulations formed on the surface of the amorphous boron carbide films may have a beneficial effect on the films coefficient of friction. Note that the amplitude of the undulations can be tune at the nanometre scale trough the laser fluence. Processing of the amorphous film deposited at 800°C with a laser fluence of $78 \mu\text{J}$ promoted simultaneous formation of LIPSS (over most of the film surface) and undulations, resulting in a heterogeneous nanopatterned surface which may also reduce the friction coefficient.

5. Conclusions

Amorphous and polycrystalline boron carbide thin films deposited by magnetron sputtering were processed using infrared femtosecond laser radiation. Successive parallel laser tracks $10 \mu\text{m}$ apart were overlapped in order to obtain a processed area of about 3 mm^2 .

Sinusoidal-like undulations with the same spatial period as the laser tracks were formed on the surface of the amorphous boron carbide films after laser processing. The most probable explanation for their formation is that the laser radiation is thermalized within the B-C films resulting in local relaxation of the intrinsic compressive stresses and consequent local volume increase. The undulations amplitude increases with increasing laser fluence. The formation of undulations with a $10 \mu\text{m}$ period was also observed on the surface of the crystalline boron carbide film processed with a pulse energy of $72 \mu\text{J}$. The amplitude of the undulations is about 10 times higher than in the amorphous films processed at the same pulse energy due to the higher roughness of the films and consequent increase in laser radiation absorption.

The formation of LIPSS on the surface of the films was achieved for the three B-C films under study. However, LIPSS formation occurs under different circumstances. Processing of the amorphous films at low fluence ($72 \mu\text{J}$) results in LIPSS formation only on localized spots on the film surface. LIPSS formation on the top of the undulations formed after laser

processing with 78 μJ of the amorphous film deposited at 800 °C. The fluence threshold for LIPSS formation can be estimated to be about 2.0 J/cm². Finally, homogeneous LIPSS covering the entire processed surface were obtained after processing the crystalline boron carbide film with pulses energies above 50 μJ . In this case the fluence threshold for LIPSS formation was estimated to be about 1.3 J/cm². The significant lower fluence threshold for LIPSS formation as compared to the amorphous films was also explained by the increased radiation absorption due to much higher surface roughness. The spatial period of the LIPSS increases with laser fluence from 140 to 200 nm. In all cases the LIPSS spatial period is much lower than the laser wavelength showing that HSFL were formed.

From the application point of view, laser processing of the crystalline boron carbide films seems to be more promising than processing of the amorphous films. Large-area homogeneous LIPSS coverage of the boron carbide crystalline films surface was achieved within a large range of laser fluences although holes are also formed at higher laser fluences.

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Figure Captions

Fig. 1: SEM micrographs of the as-deposited B-C thin films obtained at different substrate temperatures: (a) 200°C; (b) 800°C; (c) and (d) 1000 °C.

Fig. 2: Micro-Raman spectra of the as-deposited B-C thin films.

Fig. 3: SEM micrographs of the surface morphology of B-C films deposited at 200 °C after irradiation with pulse energies of (a) 65, (b) and (c) 72, and (d) 78 μJ .

Fig. 4: 3D topographical images and 2D profiles of the surface of B-C films deposited at 200 °C treated with pulses energy of (a) 65; and (b) 72 μJ .

Fig. 5: Raman spectra of the films deposited at 200 °C, before and after femtosecond laser processing with pulse energies of (a) 65 and (b) 72 μJ .

Fig. 6: SEM micrographs of the surface morphology of B-C films deposited at 800 °C after irradiation with pulse energies of (a) 65, (b) 72, (c) 78, and (d) 85 μJ .

Fig. 7: 3D topographical images, 2D profiles and amplitude spectrum of the surface of B-C films deposited at 800 °C treated with pulses energies of (a) 72 and (b) 78 μJ .

Fig. 8: Raman spectra of the films deposited at 800 °C after femtosecond laser surface processing with pulses energies of (a) 72 and (b) 78 μJ .

Fig. 9: SEM micrographs of the surface morphology of B-C films deposited at 1000 °C after irradiation with pulse energies of (a) 50, (b) 65, (c) 72 μJ , (d) 80 μJ .

Fig. 10: 3D topographical images and 2D profiles of the surface of B-C films deposited at 1000 °C treated with pulse energies of (a) 65 and (b) 72 μJ .

Fig. 11: Micro Raman spectra for B-C films deposited at 1000 °C and processed using different femtosecond laser pulses energy.

Table Captions

Table 1: Spatial period of the LIPSS

Film deposition temperature (°C)	Laser pulse energy (μJ)	LIPSS spatial period (nm)
200	72	180
300	72	185
	78	225
1000	50	140
	65	150
	72	200

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11