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Irradiation of the amorphous carbon films by picosecond laser pulses

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ABSTRACT

The effect of a picosecond laser irradiation on structure modification of diamond-like carbon (DLC) and graphite-like carbon (GLC) films was analyzed in this work. The DLC films were irradiated by Nd:YVO_4 laser operating at the 532 nm wavelength with the picosecond (10 ps) pulse duration at the fluence in the range of (0.08–0.76) J/cm^2. The GLC films were irradiated only at the fluence of 0.76 J/cm^2. The different pulse number (1, 10, and 100) was used for irradiation the films. The micro-Raman spectroscopy measurements indicated that the laser irradiation led to rearrangement of the sp^3 C–C bonds to the sp^2 C═C bonds in the DLC films. The formation of silicon carbide (SiC) was found in the irradiated spot after 10 and 100 pulses. Modifications in the structure of the DLC film took place even in the areas with low intensity of the Gaussian beam wings (heat affected areas). The increase in the oxygen concentration up to ten times was detected in the heat affected areas after 100 pulses. Opposite to that, the laser irradiation decreased the oxygen concentration and smoothened the surface microrelief of the GLC films. The bonding type remained unchanged in the GLC films even after irradiation with 100 pulses per spot.

1. Introduction

Amorphous carbon films and nanostructures are used in many applications due to their unique optical, mechanical and electrical properties [1–3]. Microstructuring of the amorphous (diamond-like, glassy, graphite-like) carbon films by various techniques such as the photolithography, focused ion beam or plasma etching is widely applied [4–6]. Nowadays, the laser microstructuring of wide-bandgap dielectrics is required for their applications in UV photonics, photovoltaic and LED-based lighting applications [4–10]. The formation of micro or nano-pattern structures on various surfaces by laser pulses using the direct laser writing is a very promising technique. The main advantages of the pulsed laser processing method are: that it is non-contact, very fast, easily controllable technique, which allows patterning of large areas and getting various shapes [7–10]. It is well known that DLC films deposited on a Si substrate have the high internal stress leading to cracking and delamination of the coatings. The irradiation of DLC films with lasers anneals them and reduces the residual stresses at the interface with a substrate. It should be noted that the properties of various films can be modified not only inside the laser radius zone, but also in the periphery area of the laser beam during the irradiation process [7,11].

The laser irradiation can induce modifications in thickness and chemical composition of the carbon film due to different physical and thermal processes. The fraction of sp^2/sp^3 carbon sites reflects the structural modifications. The nature of the laser irradiation induced processes (ablation, spallation or delamination) and process behavior depend on the pulse duration. It was demonstrated that irradiation of the amorphous carbon films with dominant sp^3 C–C sites using nanosecond laser pulses resulted in structural transition to sp^2-carbon, formation of the graphite-like carbon (GLC) or nanocrystalline graphite (ncG) microdots or thin silicon carbide layer at the interface zone [10–19]. Picosecond and femtosecond lasers are attractive due to their extremely short pulse duration and possibility to achieve the high peak power. As a result, non-linear effects and the plasma-mediated ablation mechanism minimizing lateral thermal effects are favored [7,10]. It was demonstrated that application of ultra-short (picosecond or femtosecond) laser pulses could be promising technique for a fine structuring of the DLC films [10,20–22]. Irradiation of the graphite oxide films with picosecond lasers induced reduction of the material to graphene [23,24]. The sub-wavelength structures or nanostructures in DLC can be produced at the relatively low laser fluencies using fs-laser pulses [10,21]. N. Yasumaru et al. [25] demonstrated that surface hardness of glassy carbon increased after its irradiation with fs-laser pulses at low energy (up to 250 μJ). The influence of the pulse duration on the DLC films was investigated by T.V. Kononenko et at. [15]. It was found that thickness of the graphitized layer decreased with the shortening duration of a ns-pulse. Variation in pulse duration of the ultra-short (ps and fs) laser had no effect on the thickness of graphitized layer. Our previous studies indicated that the micropattering of the thick GLC films with nanosecond laser pulses even using high laser powers is complicated [18]. The main advantages in nanostructuring of amorphous carbon films by picosecond pulses are the high ablation rate and minimal thermal effect on remaining material. The irradiation with ps-laser

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pulses led to the modification of the a-C:H or a-C films even near the irradiated spot and causes damage (melting, amorphization) of the substrate [7,11,15]. The correct process parameters should be obtained at which the lateral and depth impact effect would be minimized in order to micro-structuring the amorphous carbon films. So far no reliable experiments have been made investigating effects of the picosecond laser pulses and pulse energy on DLC and GLC films. To pattern different kinds of carbon films, a detailed study on the influence of laser parameters (pulse duration, pulse energy, wavelength, pulse number, etc.) should be performed. The main purpose of this work was to investigate the influence of laser fluence and the number of pulses of a picosecond laser on the surface morphology and structure of the DLC (composed mainly from the sp^3 carbon sites) and GLC (with dominating sp^2 C = C sites) films.

2. Experimental setup

2.1. Film deposition

The DLC film was deposited on the Si substrate by the radio frequency plasma-enhanced chemical vapor deposition technique using acetylene gas. The thickness of the DLC film was ~300 nm, the refractive index was 2.03, and its hardness was 30 GPa. The porous GLC film was grown on the stainless steel (1X18H9T) substrate by the direct current plasma torch at atmospheric pressure [26]. The composition of the stainless steel was: Fe, Cr (17–20%), Ni (8–11%), Ti (0.8%), Mn (≤2%), C (≤0.12%), Si (0.8%), S (0.03%), and P (0.035%). The argon-acetylene gas flow ratio was 150:1 (Ar—6.6 l/min, C_2H_2—0.044 l/min), the torch power was 870 W, and the deposition time was 30 s. The thickness of the GLC film was ~10 μm. The micro-hardness of the GLC films was ~10 GPa.

2.2. Irradiation of the films

The DLC and GLC films were irradiated with a picosecond Nd:YVO_4 laser (Ekspla, PL10100) at the second ($\lambda = 532$ nm) harmonic. The laser beam with the Gaussian transverse spatial intensity profile was used in the irradiation experiments. The average laser fluence (F) in the central part of the beam was evaluated by:

$$F \approx \frac{4E_p}{\pi d^2} \tag{1}$$

where E_p is the laser pulse energy, $d \approx 40$ μm is the spot diameter on the sample at $1/e^2$ level. The laser pulse energy was set to 1 μJ, 3.7 μJ and 9.5 μJ producing the average laser fluence of ~0.08 J/cm^2, ~0.3 J/cm^2 and ~0.76 J/cm^2. The repetition rate was 100 kHz, and the pulse duration was 10 ps. The Gaussian beam wings with area of low intensity affected the material as well in the area within $3d \geq x \geq d$. This area is called “the heat affected area”. To vary the irradiation dose, the pulse number was selected at 1, 10 and 100 per spot.

2.3. Characterization of the irradiated films

The bond type in the laser irradiated samples was analyzed by μRaman spectroscopy (Renishaw inVia spectrometer, using 1 mW excitation at the wavelenght of 633 nm, focused to 2 μm spot, the accumulation time was 100 s) in the spectral range of 100–4000 cm^{-1}. The surface morphology was analyzed by the scanning electron microscope (SEM) JEOL JSM6490LV. The elemental composition of the films was investigated by the energy dispersive X-ray spectroscopy (EDS) (Bruker Quad 5040 spectrometer). The EDS measurements indicated that the DLC film (including the silicon substrate) was composed of: carbon (55.1 at.%), oxygen (2.0 at.%) and silicon (42.9 at.%). It should be noted that the EDS was measured in the depth exceeding DLC film thickness. The GLC film (including the steel substrate) consisted of the following elemental composition: carbon (74.0 at.%), oxygen (16.8 at.%) and S_t (9.2 at.%). S_t means the total atomic mass of chemical elements attributed to steel substrate.

3. Results and discussion

The EDS measurements of the DLC film after the ps-laser irradiation are presented in the Fig. 1. The irradiation of the DLC films with a single pulse at a fluence of 0.08 J/cm^2 had no effect on its surface morphology. The increase of the fluence to 0.3 J/cm^2 led to partial removal of DLC in the irradiated spot. The carbon content in the center was 43.7 at.%, while amount of oxygen increased up to 5.1 at.% (Fig. 1a). The irradiation of the DLC film with a single pulse at the fluence of 0.76 J/cm^2 increased ablation of the DLC film in the center. The carbon content in the center of the irradiated spot decreased down to 36.5 at.%, while the oxygen content increased up to 7.2 at.%. The C–H (4.28 eV) and C–C (3.47 eV) bonds were broken during the irradiation due to the lowest binding energy. Some of them were transformed into C═C bonds (6.29 eV), while carbon atoms (near the surface) were bond to oxygen atoms arriving from the air and created C–O (3.38 eV) bonds. The terrace-like relief was observed at the periphery of irradiated spot for the both (0.3 J/cm^2 and 0.76 J/cm^2) fluencies. The terrace-like layers width was in the range of 1–2 μm (Fig. 1a–b). The appearance of such structure indicates the multilayer delamination [12]. This delamination is related to the Gaussian shape of the laser beam, and results from the energy (heat) distribution which was uneven through the irradiated spot. Differences in the temperatures led to stress formation inside the film and its delamination. The appearance of the hydrogen diffusion due to temperature gradient in the irradiated area also could stimulate the delamination of the film. The heating of the films with variable elemental composition induced the additional internal stresses. The elemental compositions in the areas outside the laser spot (1 pulse 2 zone) were similar as that of the non-radiated DLC film (Table 1 and Fig. 1 a,b). The melted Si substrate-film zone (diameter of ~35 μm) appeared with the increase of the pulse number up to 10 at 0.76 J/cm^2 (Fig. 1c). The particles of 100–200 nm size were chaotically distributed on the melted Si substrate zone. The carbon content was 3.4 at.% and oxygen ~3 at.%. The narrow (~2 μm) zone at the periphery of the irradiated spot indicates the existence of the delamination. The increase of the oxygen concentration was observed also within the $d \geq 40$ μm area. Very similar elemental composition and surface morphology were found when the irradiation was done by 3.7 μJ energy and 10 pulses. Melted area of the Si with the diameter of ~10 μm was observed after irradiation with 100 pulses at 0.76 J/cm^2. The melted silicon area was surrounded by a zone where irregular micro-ripples were formed (Fig. 1d). The ripples were large near the melted zone and decreased in size at the spot periphery with decreasing ripple period (Fig. 1d). The clear boundary between the Si substrate and the film is visible and this indicates the full ablation of the film in the spot center. It should be noted that during the laser irradiation of the DLC film, ablation of the film and melting of the substrate was observed only within areas limited by the laser beam diameter (measured at $1/e^2$ level). The sample surface outside this area was covered by irregular fragments with the size of 500 nm. Concentration of the oxygen considerably increased up to 19.5 at.% (100 pulses 3 zone). It should be noted that even ~30 μm away from the ablated area, the oxygen fraction (100 pulses 4 zone) was higher compared to the non-affected DLC film (Table 1). The decrease of the fluence down to 0.3 J/cm^2, resulted to the formation of the irregular micro-ripples zone in the spot center (Fig. 1e). The ablated area narrowed, however clear boundary between the Si substrate and the film was observed. The surface at $d > 40$ μm was covered by irregular fragments and the high fraction (10.5 at.%) of the oxygen was obtained (see zone 2). The increase of oxygen and decrease of the carbon content outside the laser beam spot area is a result of the ablation or spallation. The film and substrate splashing create carbon and silicon particles with a high fraction of unbounded sites where the atmospheric oxygen binds.