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Self-organized subwavelength ripple by nanosecond laser induced chemical vapor deposition

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ABSTRACT

Polymeric hydrogenated amorphous carbon (α-C:H) thin films were prepared by laser induced chemical vapor deposited method using a KrF excimer laser (λ = 248 nm, fwhm = 25 ns) with different laser intensities. Field emission scanning electron microscopy and atomic force microscopy were used to investigate the surface morphology of the films. It was found that the surface morphologies were affected by the laser intensity significantly. Self-organized subwavelength fine ripples perpendicular to the laser beam polarization with periodicities of about 200 nm were observed and a reasonable explanation was proposed for the formation of the ripples. Raman spectroscopy and Fourier transform infrared spectroscopy were used to study the structure of the α-C:H films. The results suggested that there was oxygen in the films, which came from the ambient contamination and the incomposited impurities during and after deposition. The relationships between the composition and chemical bond types were discussed in detail.

1. Introduction

For the application in different fields of modern technology due to a wide variety of promising properties, hydrogenated amorphous carbon (α-C:H) thin films attracted growing scientific interest in the last decade. There are two kinds of α-C:H, which are the well-known diamond-like coating of hardness and chemical inertness and the polymeric α-C:H prepared at low energy [1,2]. The polymeric α-C:H thin films with high H content are important for the study of proton emission from the target irradiated by an ultrashort and ultraintense laser [3,4]. For preparing the polymeric α-C:H thin films with high H content, low intense laser induced chemical vapor deposition (CVD) method is a preferred technology. In this method, a low intense laser was perpendicular to the substrates, the styrene molecules in the flowing H_2 were polymerized on the substrates, and the polymeric α-C:H thin films were synthesized. On the other hand, in this process, the interaction of laser and the growing polymeric α-C:H thin films happened.

Laser-induced periodic surface structures (LIPSSs) are one of the most interesting phenomena of the interaction of laser and the material, which has attracted extensive attention during the past decades, focusing both on their potential applications and formation mechanism [4–9]. Laser-direct writing using front-side and rear-side ablation has been applied in photomask production [8]. There are several kinds of LIPSSs, which show different spatial periods in contrast with the irradiated laser wavelength. Some LIPSS period is larger than the laser wavelength; some are equal to the laser wavelength and some are less than the laser wavelength. Several explanations have been proposed to explain their formation mechanism. For the period of the LIPSS, lager or equal to the laser wavelength, the formative mechanism is thought to be the interference of incident light with reflected (scattered) light. The interspacing of the periodic grating structures is given by $\lambda/n(1 \pm \sin\theta)$, where λ, θ and n are the laser wavelength, the laser beam incidence angle, and the refractive index of the material, respectively. This kind of LIPSSs can be produced by nanosecond laser and other type of laser [10,11]. The LIPSS, whose period is shorter than the laser wavelength (<0.85 λ) and the gratings are perpendicular to the laser polarization plane, was always observed for metals irradiated with a femtosecond-pulse laser [6]. Some reasonable explanations were proposed for the formative mechanism, such as the interaction of laser pulses with laser-produced surface plasma, and the nanoscale Coulomb explosion [5,6]. None of the LIPSSs with a period shorter than the laser wavelength was reported to be produced by nanosecond-pulse laser. But the LIPSS with a period shorter than the laser wavelength was observed in our experiment by nanosecond laser irradiated. The aim of our experiment is to produce polymeric α-C:H thin films through a nanosecond-pulse induced CVD technique.

In this paper, polymeric α-C:H thin films were prepared by nanosecond-pulse induced CVD with laser energy density varying from 23 to 46 mJ/cm^2. The effect of laser energy density on the surface

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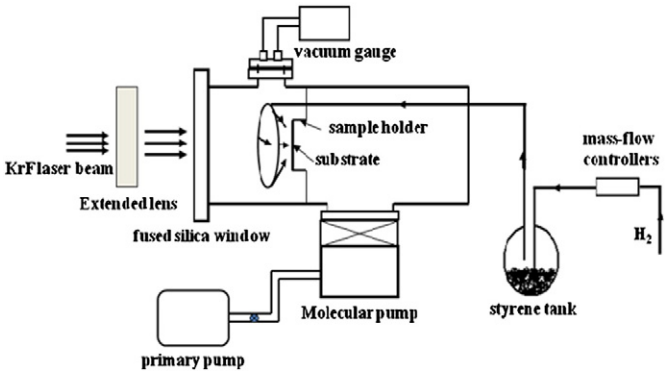

Fig. 1. Schematic diagram of the laser induced CVD system.

morphologies and the composition of the polymeric α-C:H thin films was discussed in detail.

1.1. Experimental details

The polymeric α-C:H thin films were prepared by nanosecond laser induced CVD method and the experimental set-up is schematically drawn in Fig. 1. The KrF excimer laser ($\lambda = 248$ nm, fwhm = 25 ns) beam that is 5×2.5 mm in size was expanded to 25×25 mm by an expanded beam system, which entered the stainless steel flow reactor through a fused silica window. Styrene (analytically pure) was carried into the vacuum chamber by high-purity H_2 (6 N purity). The H_2 flow was fixed at 5 sccm using a mass flow controller. The base pressure of deposition chamber was about 8×10^{-4} Pa before introducing H_2 and kept at 8 Pa during deposition. The Si (100) was used as substrate, which was ultrasonically cleaned in acetone, absolute alcohol bath, then etched by HF acid for 20 s to stripe for the oxide, then rinsed with distilled water, and finally dried in flowing N_2. Laser energy density ranged from 23 to 46 mJ/cm^2, with the frequency of 2 Hz, and the deposition last 3 h for all the films. The α-C:H thin films prepared under the laser energy density of 23, 30, 38 and 46 mJ/cm^2 were characterized as S1, S2, S3 and S4, respectively.

The thickness of the α-C:H samples was measured by a Dektak150 step-measurer (Vecco Instrument Inc.). The surface morphology of the films was characterized by field emission scanning electron microscopy (FESEM) (Oxford, Nova400) operating at 3 kV. Before the SEM measurement, an Au layer of 10 nm was deposited on the surface to enhance the conductivity. The 2D surface morphology and the root mean square (RMS) roughness were obtained using atomic force microscopy (AFM, Digital Instruments, Nano-scope III) in non-contact mode. The Raman measurements were carried out at low laser power (10%) with 10 s acquisition time, and the laser wavelength was 532 nm. The Fourier transform infrared spectroscopy (FTIR) absorption was measured using MAGNA750 over the wave number ranging from 400 to 4000 cm^{-1}.

2. Results and discussion

The thickness of the polymeric α-C:H samples was measured by a Dektak150 step-measurer, and the thickness of the films was about 98, 148, 216 and 243 nm for S1, S2, S3 and S4, respectively. It suggests that the deposition rate of the films increases with the laser energy density, which can be explained that high energy density can cause more styrene to polymerize, and more polymeric α-C:H was synthesized on the substrates.

Typical surface morphology and RMS roughness of the polymeric α-C:H thin films were characterized by AFM. The RMS of the films surface is about 2.42, 1.96, 1.30 and 0.95 nm for S1, S2, S3 and S4, respectively. Such a result indicates that the surface of the films is generally smooth. Larger laser energy density will result a smoother surface. Fig. 2 shows the 2D surface morphology of the films deposited under different laser energy densities, which indicates that the surface morphology was affected by the laser energy density significantly. It can be seen that the surface of S1 is characterized with self-organized sphere structure, and the diameter of the sphere is about 220 nm. With an increase in laser energy density, the surface of the polymeric α-C:H is characterized with self-organized spheres and ripples structures for S2, with the periodicity of about 205 nm. The surface of the film is characterized with uniform self-organized ripple structure with increasing laser energy density for S3, and the periodicity of the ripples is about 190 nm. Further investigation indicates that the ripple is perpendicular to the laser beam polarization. The uniform ripples disappear with further increasing laser energy density for S4. All the measured spacing, which is less than the wavelength of the used laser, cannot be explained with an inclination of the beam, because the laser is incidence perpendicular to the surface. Similar laser induced subwavelength self-organized ripple structures were observed by other teams. Huang et al. observed deep-subwavelength ripples with periodicities of 170, 120, and 70 nm on the surface of pyrolytic graphite irradiated by femtosecond laser of 800 nm. They also found that the ripples are perpendicular to the laser beam polarization. They suggested that the nanoscale Coulomb explosion was responsible for the formation of this phenomenon [5]. S. Sakabe et al. found 400 and 680 nm subwavelength self-organized ripple structures on metal surface under the irradiation of femtosecond laser at 800 nm. They thought that these self-organized ripples result from the interaction of laser pulses and laser-produced surface plasma [6]. Costache et al. investigated the surface of CaF_2/BaF_2 ablated by femtosecond laser beam. They proposed that self-organizing relaxation of a non-equilibrium surface

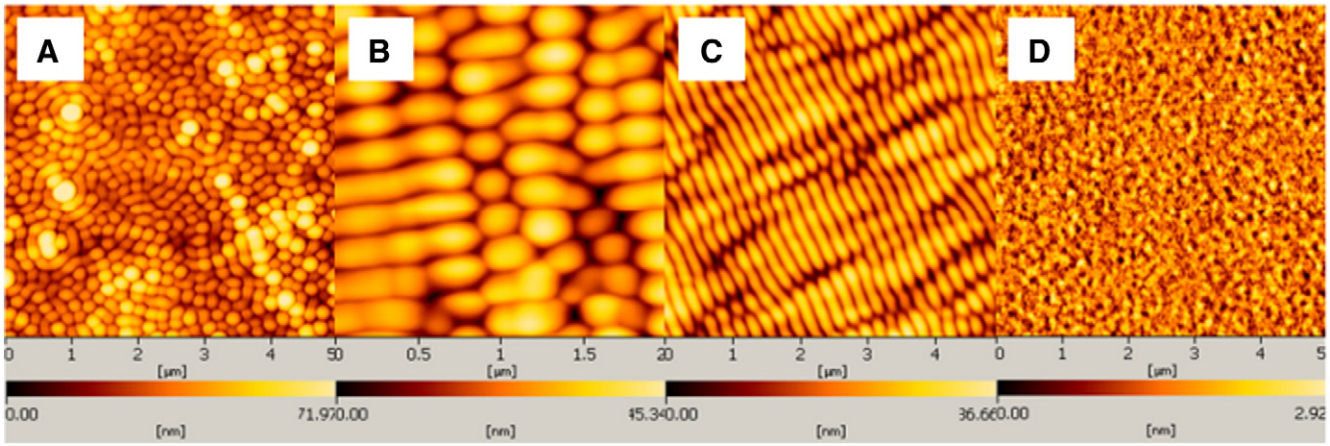

Fig. 2. AFM images of 2D surface morphologies of the polymeric α-C:H films prepared at different laser intensities. (A) 23, (B) 30, (C) 38, (D) 46 mJ/cm^2.