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## Control of characteristic lengths for self-organized nanostructures of amorphous carbon

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### Abstract

We report the self-organized nanostructures of hydrogen-free amorphous carbon (a-C) with controllable characteristic length scales obtained by using ion beam assisted deposition. By selecting various temperature regimes, two kinds of nanostructure, mounds and ripples, are successfully formed. For the growth temperature of 200 °C, the fractal analysis of the surface shows that the lateral characteristic length for mounding structures increases with increasing ion energy. But for ripple structures formed in the relatively high temperature region, the ripple wavelengths are found to show a nonlinear dependence on the ion energy. Further, at certain temperatures there exist energy thresholds for stopping the formation of ripple structures. These results demonstrate that the characteristic scales of nanostructures for a-C can be significantly controlled through the tuning ion energy in a well-defined manner.

(Some figures in this article are in colour only in the electronic version)

Due to the continued drive for smaller device fabrication, surface patterning has recently become the subject of intensive research. The most often pursued way to pattern a surface on the nanometric scale is via the control of self-assembly in growth. Ideally, it is highly desirable to create surface patterns with controllable length scales.

Ion sputtering has been shown to be an effective approach for pattern surfaces, from self-affine surface roughness to regular waves or ripples [1, 2]. During ion sputtering, the evolution of solid surface topography is governed by the interplay and competition between the dynamics of surface roughening, on the one hand, and materials transport in surface diffusion, on the other [3]. Therefore, in principle, it should be possible to control the length scales of such patterns by manipulating the competition between ion erosion and surface diffusion.

Hydrogen-free amorphous carbon (a-C) has been extensively studied for decades owing to its excellent physical and chemical properties; it has great potential for coating and electronic applications [4]. Although the characteristic topography of an a-C film is essential for its applications very little is known about the self-assembling formation of a-C surfaces. This is due to the fact that most researchers had seen a-C as a diamondlike material, which exhibits the most 'diamondlike-ness' when grown at low temperature.

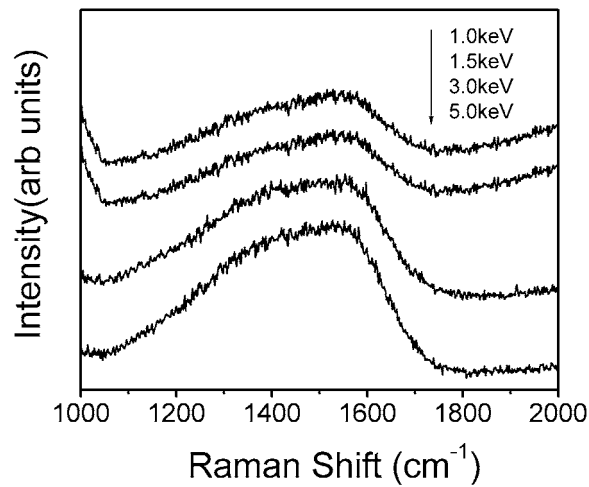
In the present study, a-C has been deposited by using ion beam assisted deposition (IBAD). By using simultaneous bombardment during deposition and extended temperature ranges, we investigate the possibility of creating certain surface patterns with controllable nanometre length scales in IBAD. In IBAD, an incident ion beam faces a solid surface that is also exposed to a flux of vapour atoms during deposition, and also the most decisive factors for influencing the film growth, ion energy, ion incidence, arrival ratio of ions to atoms, and growth temperature are independent. This provides us with a great chance to fabricate directly controllable surface patterns.

Experiments were carried out on an ion beam assisted deposition device. This machine was equipped with an ion gun and a sublimator. C<sub>60</sub> powder with the purity of 99.99% was placed in a pyrolytic BN crucible of the sublimator. The background pressure in the chamber was less than  $2 \times 10^{-6}$  Pa. The Si(111) wafers used as substrates were rinsed ultrasonically with de-ionized water, acetone, and ethanol, respectively, before they were placed on the substrate holder. C<sub>60</sub> vapour was produced by heating electrically the sublimator up to 400 °C, and the growing film was simultaneously bombarded with Ne<sup>+</sup> ions with the ion incidence angle of 60° from the substrate normal. The emission of the filament in the ion gun is fixed at 20 mA. The working pressure was maintained at around  $6 \times 10^{-4}$  Pa in the chamber. After the deposition, the carbon films were analysed by micro-Raman spectroscopy and atomic force microscopy (AFM). Micro-Raman spectra were recorded at room temperature using the 514 nm line of the Ar<sup>+</sup> ion laser.

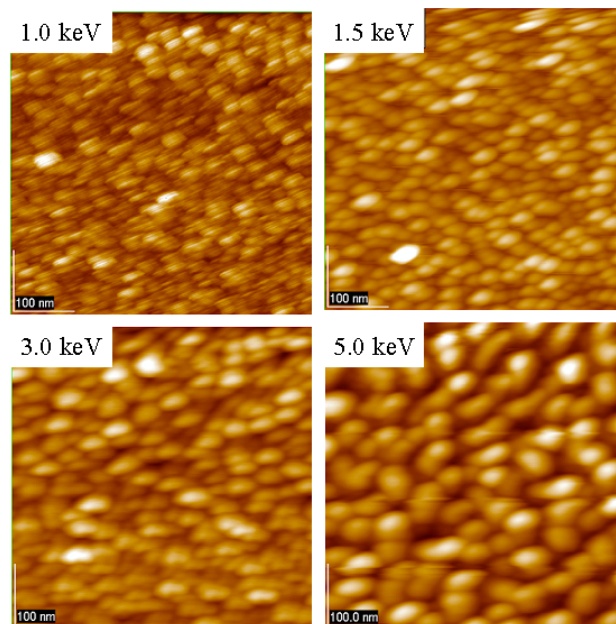
Figure 1 shows the Raman spectra of films deposited at different ion energies, where the substrate temperature is set at 200 °C. The Raman spectra obtained consist of a broad peak centred at energies  $\sim 1547$  cm<sup>-1</sup> (symmetric G peak) with a small shoulder at  $\sim 1353$  cm<sup>-1</sup> (asymmetric D peak), manifesting the characteristics of amorphous diamondlike carbon films [5–7].

The topographies of the samples were examined by AFM, as shown in figure 2. The surfaces of the a-C films appear to be series of continuous mounds with different lateral lengths.

Further dimensional analyses were carried out to extract correlation lengths based on AFM data. Critical parameters from the surface roughness evolution include the roughness and the dynamic scaling exponents,  $\alpha$  and  $\beta$ , and the lateral correlation length,  $L_c$ . As shown in figure 3, the root mean square (rms) roughness is plotted versus length scale for the films in figure 1. In each case, the roughness increases with measurement length, then saturates at a value. The lateral correlation length,  $L_c$ , is the distance at which the surface roughness first reaches its saturation value. With increasing ion energy,  $L_c$  increases on nanometre scales. The increase in  $L_c$  with ion energy can be attributed to the enhancement of adatom surface mobilities. Part of the adatom surface mobility comes from thermal energy gained from the substrate and part from the kinetic energy of the ion beam. At low substrate temperature, the latter may play a more important role. As the ion energy rises, the surface mobility of the adatom becomes high, and thus they can move further along the surface before they bond with the underlayer. This could give rise to the formation of islands with bigger lateral dimensions. On the basis of figure 3, the roughness exponent  $\alpha$  is also determined from the fit to the linear part of the log–log plot of rms versus  $L$ . The roughness exponents are determined to be about



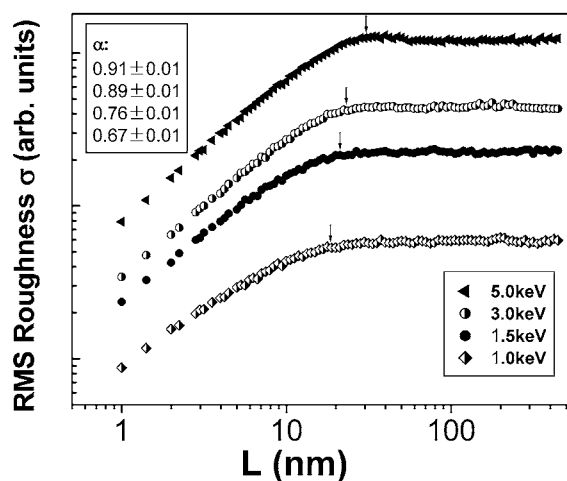
**Figure 1.** Raman spectra of samples deposited at different ion energies. The growth temperature is controlled at 200 °C.



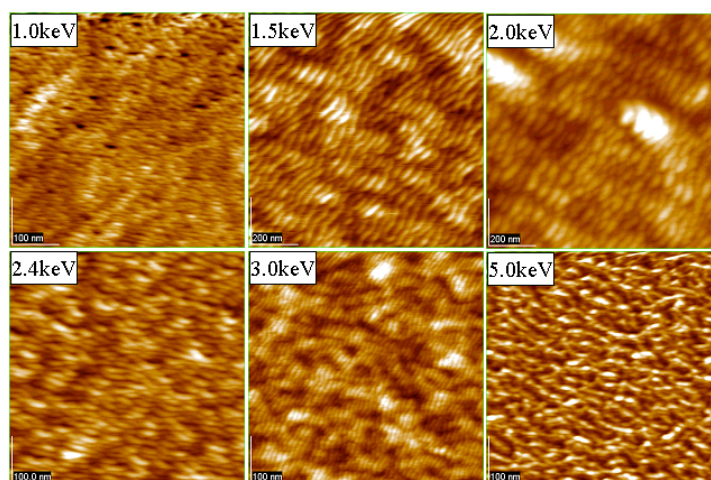
**Figure 2.** AFM images for the a-C films in figure 1, showing mound roughening for the films. The scanning size is 500 nm × 500 nm.

0.67, 0.76, 0.89, and 0.91, suggesting that the film surfaces become rougher with increasing ion energy. It is very likely that enhanced sputtering effect is responsible for this increase.

At high growth temperatures, we found the morphological transition of the a-C surface from mound roughening to ripple structure. Figure 4 shows the a-C surfaces deposited at various ion energies as the temperature is increased to 700 °C. The film surfaces present periodic ripples from 1.0 to 3.0 keV. The wavevectors are parallel to the component of the ion



**Figure 3.** Fractal analysis of the deposited films based on the AFM data in figure 2. The correlation length,  $L_c$ , where the rms roughness saturates with length, increases with increasing ion energy.  $L_c$  takes the values 18, 21, 23, and 31 nm, respectively, with increasing energy, from 1.0 to 5.0 keV. This shows that the surfaces were adjusted on nanometre scales. Arrows are guides for the eye.



**Figure 4.** AFM images of the films deposited at 700 °C, showing periodic ripples. However, at 5.0 keV ion energy, the surface of a-C becomes cratered. The scanning sizes are 1000 nm × 1000 nm for images at 1.5 and 2.0 keV, and 500 nm × 500 nm for other cases.

beam in the surface plane. At 5 keV ion energy, the surface of a-C becomes cratered due to enhanced sputtering.

Figure 5 shows the Raman spectra of a-C obtained at 700 °C under various ion energies; they consist of well-separated D and G peaks, suggesting that severe graphitization in deposited films happens at high temperatures. In our previous work, we have contributed the ripple formation to the linear theory described by Bradley and Harper (BH model), which arises because of the curvature-dependent sputtering effect [8]. The translation from mound morphology to ripple structures is due to the change of surface diffusion. Because the bounding

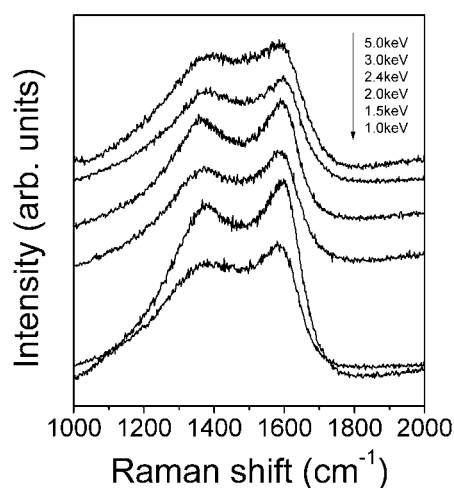
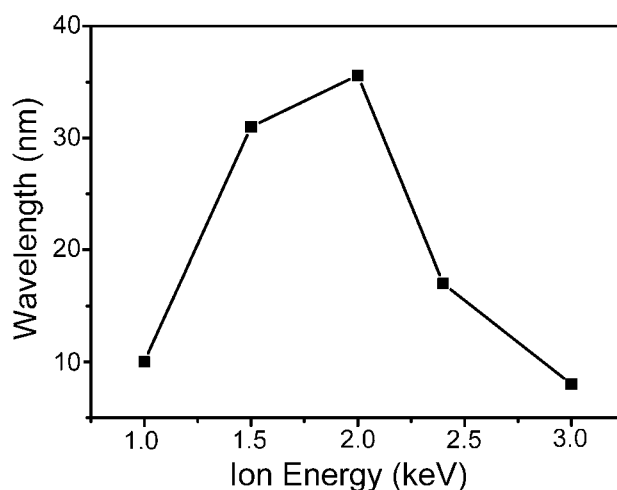


Figure 5. Raman spectra of the samples deposited at 700°C under different ion energies.

structures of a-C strongly depend on the temperatures, the D and G peaks will separate with increasing temperature. The separation will become more pronounced as the temperature is increased further, as can be seen in the comparison between figures 1 and 5. These results demonstrate the distinct graphitization in the deposited films at high temperatures. But at low temperatures, the films present amorphous features. There exist differences in surface features for the films deposited at high and low temperature. In these two cases, ion-induced relaxation levels should be different, in response to the observed different surfaces. The large values of ion-induced viscous flow relaxation hinder ripple formation at relatively high temperature [9], but the surface diffusion induced by ion irradiation would be suppressed due to the graphitization process at high temperature.

Here we focus on the ion energy dependence of ripples. One can identify different characteristic lengths with ion energies for these periodic ripples from the images in figure 4. The wavelengths are determined by Fourier translation of the AFM images, and are plotted with ion energies in figure 6. Recent Monte Carlo simulation of ion beam deposition for carbon films does indeed predict surface ripple morphologies and also the wavelengths are of 15–40 nm [10], which is in good agreement with our experimental observations. The wavelengths in figure 6 do not show a linear relation with ion energies, but first rise and then begin to decrease around 2.0 keV with increasing ion energy.

Beam-induced surface roughening has been studied extensively now, but the understanding of the mechanism of roughening is still lacking, especially when it involves the change of bonding structures induced by ion bombardment. According to the BH theory, the ripple wavelength should decrease with increasing ion energy, where the thermal diffusion process dominates at high temperature. However, this prediction has rarely been confirmed experimentally. Recently, Chini *et al* [11] have investigated the energy-dependent wavelength of ion-induced nanoscale ripples. They reported that the ripple wavelength decreases with increasing energy for irradiation in ion beam scanning. They suggested that the ion-beam-induced surface temperature profile initiates the thermally activated diffusion process, which is responsible for this observation. In most of the works reported in the literature on the ion energy dependence of ripple structures, ripple wavelength has been shown to increase with ion energy [3, 12]. A nonlinear continuum theory was developed to explain these experiments, in



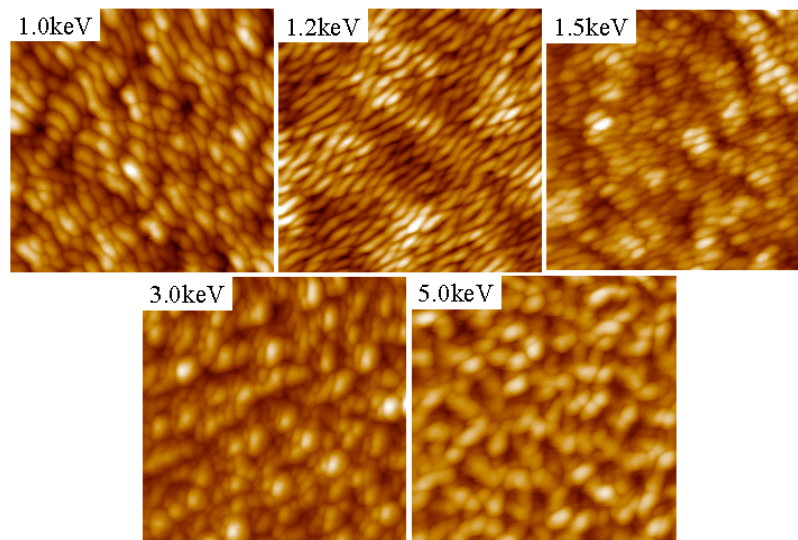
**Figure 6.** The dependence of the ripple wavelength on the ion energy for the samples deposited at 700 °C. The wavelengths present first an increase and then a decrease around 2.0 keV with increasing ion energy.

which the ion-induced effective surface diffusion process was recognized besides the thermally activated surface diffusion [13, 14].

In this work, we found a complex ion energy dependence of wavelengths, which cannot be explained by using current models. Even though we can attribute the reduction of wavelengths with increasing ion energy after 2.0 keV to BH theory, it is still difficult to understand the first increase of wavelength with increasing ion energy, because we believe that the thermal diffusion process should be dominant at this temperature, especially at relatively low ion energy. One fact should be noted: most ripple structures have been reported during the post-sputtering process of samples. In our case, the ripples are formed directly in the deposition processes for a-C. Furthermore, the variation of the ion energy affects the bonding structure of a-C. Thus, it is very likely that more complicated mechanisms may be involved in ripple morphologies produced in IBAD.

In figure 4, one can see that the ripple structures vanish with further increasing ion energy, to 5.0 keV. Similar phenomena can also be found at 550 °C as displayed in figure 7. At relatively low ion energies, the surfaces present ripple structures. However, at 3.0 keV or higher ion energies, the ripples disappear. In this case, the ion energy responsible for this ripple stopping is lower than that at 700 °C. We believe that this difference is due to the change of surface diffusion process. Because more graphitization takes place at 700 °C, ion-induced diffusion would then be weaker. In this case, the a-C films can stand higher ion energies to form ripples as compared to the case at 550 °C.

In summary, we have investigated the formation and control of self-organized nanostructures for amorphous carbon obtained by using ion beam assisted deposition. Mound roughening appears commonly in low temperature regimes. The lateral length for mounding structures can be significantly tuned by controlling the ion energy. As the deposits are made in high temperature regimes, periodic ripples are formed. The ripple wavelength is found to display a nonlinear dependence on the ion energy, which is difficult to explain with existing models. At a certain temperature, there exists an energy threshold for stopping the formation of ripple structures. This study demonstrates that the ion beam assisted deposition technique is a simple and versatile method for fabricating and controlling nanostructures for a-C.



**Figure 7.** AFM images of the a-C films deposited at 550°C, showing periodic ripples at low ion energies. At 3.0 keV, or higher ion energies, the ripples disappear. The scanning sizes are 300 nm × 300 nm for all images.

### Acknowledgments

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