Buckling instability in amorphous carbon films

2007 J. Phys.: Condens. Matter 19 236227

(http://iopscience.iop.org/0953-8984/19/23/236227)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 236227 (6pp) doi:10.1088/0953-8984/19/23/236227

Buckling instability in amorphous carbon films

X D Zhu[1], K Narumi[2] and H Naramoto[2]

[1] CAS Key Laboratory of Basic Plasma Physics, Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
[2] Advanced Science Research Center, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

Received 16 October 2006, in final form 24 March 2007
Published 16 May 2007
Online at stacks.iop.org/JPhysCM/19/236227

Abstract

In this paper, we report the buckling instability in amorphous carbon films on mirror-polished sapphire (0001) wafers deposited by ion beam assisted deposition at various growth temperatures. For the films deposited at 150 °C, many interesting stress relief patterns are found, which include networks, blisters, sinusoidal patterns with π-shape, and highly ordered sinusoidal waves on a large scale. Starting at irregular buckling in the centre, the latter propagate towards the outer buckling region. The maximum length of these ordered patterns reaches 396 μm with a height of ∼500 nm and a wavelength of ∼8.2 μm. However, the length decreases dramatically to 70 μm as the deposition temperature is increased to 550 °C. The delamination of the film appears instead of sinusoidal waves with a further increase of the deposition temperature. This experimental observation is correlated with the theoretic work of Crosby (1999 *Phys. Rev.* E **59** R2542).

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

Spatial self-organization of matter is a common phenomenon in nature, presenting a rich gallery of engrossing self-made patterns such as sinusoids, snowflakes, and cloud structures. The complex patterns in nature have been a cause for wonder and fascination throughout human history. In recent years, increasing efforts have enabled us to grow in understanding pattern formation.

In the experiment of Yuse and Sano, they observed sinusoidal crack patterns propagating along a thermal stress gradient under well-controlled conditions [1]. Sinusoidal cracking has an intriguing analogue in compressive stress relief in thin films on solid substrates. As thin films are deposited on solid substrates, there is a build up of intrinsic internal stresses. The relief of the stress generally causes morphological changes. Bowden *et al* have recently developed complex ordered structures by the buckling of thin metal films due to compressive stress relief. They believe that this patterning process may find applications in optical devices [2].

Unfortunately, in most cases, the compressive stress is too large to be supported by the adhesive force binding the film and substrate, which gives rise to the buckling and delamination of films, even cracks. Buckling patterns, sinusoidal wrinkles, have been observed in many experiments [3–5]; however, the interpretation of the origin of this instability is still not satisfactory, though many mechanisms have been proposed to elucidate the formation of sinusoidal wrinkles, including anisotropy/isotropy stress, inertial effects, viscoelastic effects, and asymmetric surface energies [6–8].

The important challenge for this issue, we think, is that the experimental evidence is not sufficient to support the proposed theories. The formation of a self-organized pattern involves a nonequilibrium process; the system grown far away from thermodynamic equilibrium may reach a critical point, where a spontaneous pattern arises suddenly as an elegant solution of conflicting processes evolving in the systems. It is difficult to predict and control this critical point, since it is determined by many dynamic parameters. As a result, sinusoidal wrinkles often appear uncertainly in many cases. More recently, research on controllable buckling patterns has made progress. Moon *et al* fabricated patterned strips with Al_2O_3 layers on Si substrate to create areas of low interface adhesion surrounded by regions of high adhesion, and highly controlled buckle delamination patterns were successfully achieved [9]. Lee *et al* reported stress-induced delamination methods for the study of adhesion of Pt thin films to Si [10].

In this study, we directly deposited amorphous carbon films on mirror-polished sapphire (0001) wafers by ion beam assisted deposition. Many varieties of buckling patterns with large areas form, and also pattern evolution with deposition temperature is observed. It is expected that the research could supplement the universal understanding of buckling instability.

Ion beam assisted deposition (IBAD) was used in this study. The machine was equipped with an ion gun and a Knudsen cell. The ion beam incident angle was 60° from the substrate normal. C_{60} powder with a purity of 99.99% was placed in pyrolytic BN of the sublimator. The background pressure in the chamber was less than 1.2×10^{-6} Pa. The substrate temperature could be controlled from room temperature to 800 °C via resistive heating. C_{60} vapour was produced by heating the Knudsen cell resistively up to 400 °C, and simultaneously the growing film was bombarded with 2.0 keV Ne^+ ions. Due to the divergence and non-normal incidence, the spot shape forming on the substrate was ellipse-like, with a dimension of 10 mm. The ion current is about the magnitude of microamperes. Mirror-polished sapphire (0001) wafers were employed as the substrates during deposition. The working pressure was maintained around 6×10^{-4} Pa in the chamber. In this case, the deposition rate was around 8 Å min^{-1}. The thickness of the films was controlled by the deposition time, and all samples were deposited for 6 h.

After the deposition, the carbon films were analysed by micro-Raman spectroscopy recorded at room temperature using the 514 nm line of an Ar^+ ion laser, laser microscopy (LM), and atomic force microscopy (AFM).

The buckling process may begin some time after exposure to air at atmospheric pressure. Two different regions on the surfaces of samples can be found: the buckling patterns appear at the centre region of sample, whereas no buckling can be observed in other parts of the film. In this work, only the buckling area is investigated.

Figure 1 illustrates the observed micrographs of the buckling area for the surface of the film deposited at 150 °C by LM and AFM, respectively. The deposited films present an amorphous carbon (a-C) characteristic, demonstrated later by Raman spectroscopy. Figures 1(a) and (b) correspond to the centre buckling region. Buckling patterns, such as networks and blisters, can be observed. In the outer regime, a blister with branches and sinusoidal patterns with π-shape appear, as shown in figures 1(c) and (d). Besides, we observed large-scale, and highly ordered sinusoidal waves, as displayed in figure 1(e). These wavy patterns start at the irregular buckling in the centre region, and propagate towards the outside. The maximum length

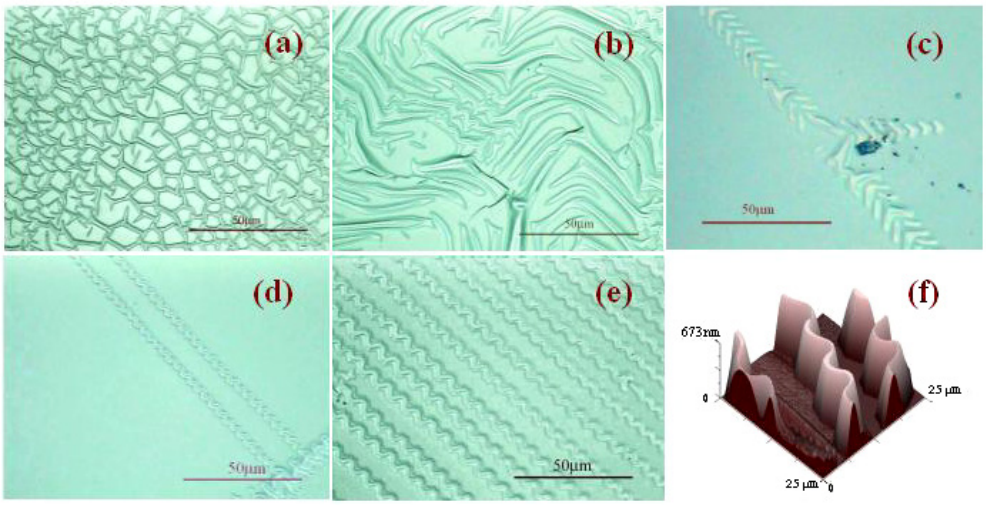

Figure 1. The observed micrographs of buckling area for the surface of an a-C film deposited at 150 °C. (a)–(e) and (f) are LM and AFM images, respectively. (a) and (b) correspond to the centre buckling region. (c)–(f) refer to the outer buckling regime, and the AFM image shown in (f) is taken from the centre part of (e).

reaches 396 μm. These sinusoidal patterns were further checked by three-dimensional AFM for detailed analysis: figure 1(f) depicts an AFM image taken at the centre region in figure 1(e), where the scanning size is 25 × 25 μm^2. One can find that the height for sinusoidal patterns is 500 nm, with a wavelength of ∼8.2 μm.

It is acknowledged that the shapes and configurations of buckled areas are caused by very specific loading conditions (internal stresses), adhesion energy and layer geometry. The former depends on the film's deposition condition. With a-C films, many buckling patterns have been observed in plasma chemical vapour depositions and ion beam depositions [3–5]. Only for a small range of internal stresses does the film buckle out with interesting patterns. However, lesser stresses are well accommodated in the film, and for higher stresses the film cracks or totally peels out.

In this work, the surface of the deposited film presents two different regimes, with and without buckling patterns. We think that this phenomenon is related to the high relative stress at the centre region. The Ne^+ ion beam spot was not scanned in order to obtain the higher Ne^+ ion current and the higher Ne^+ ion to thermal C_{60} flux ratio at the centre region of substrate, which may induce the uneven thickness. It is generally agreed that the intrinsic compressive stress is also related to the energetic bombardment during the growth of films. In the centre region, the higher ion flux may induce an increased compressive stress [5, 6]. Because of the nonuniformity of internal stresses, different and complex buckling patterns form, as shown in figures 1(a)–(e).

A very interesting finding is the evolution of these sinusoidal patterns with the deposition temperature. As the deposition temperature is raised to 550 °C, the surface feature varies largely, as shown in figure 2(a). The dimension of the network increases, the sinusoidal length deceases dramatically to 70 μm, and the wavelength becomes 10.8 μm. However, on elevating the deposition temperature further, the buckling modes disappear. Figure 2(b) shows the surface of a film deposited at 700 °C: one only can find delamination and wrinkling of the film. Ssinusoidal buckling waves have been widely reported in the literature; however, most reports

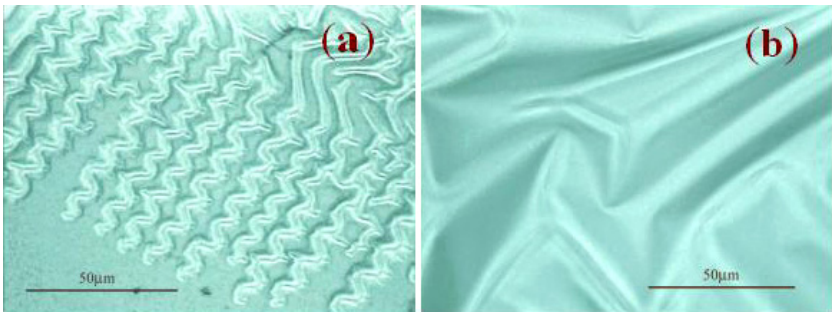

Figure 2. Two LM images for the surface features of the deposited films at increased deposition temperatures. (a) and (b) refer to 550 °C and 700 °C, respectively.

about this kind of pattern are deficient due to complex and rich processes for compressive stress relief, and it is difficult to observe the evolution of these regular patterns with deposition parameters. To the best of our knowledge, this is the first experimental observation that a regular sinusoidal wave at such a large scale forms and evolves with the deposition conditions.

Though more than four decades have passed since the discovery of sinusoidal wrinkles, the phenomenon remains incompletely understood. The work of Moon *et al* clearly demonstrated that the formation of the buckling mode, the smooth Euler mode or the telephone cord mode depends on the compressive biaxial stress [9]. Crosby *et al* proposed a model to investigate pattern formation during delamination and buckling of thin elastic films on a rigid substrate [7]. In their work, it is demonstrated that a variety of remarkable stress-relief forms emerge from the simulation: the most striking of the stress-relief patterns is the sinusoidal wrinkle as $\varepsilon_1 \leqslant \varepsilon \leqslant \varepsilon_2$, where ε is strain, ε_1, ε_2 are two critical strain values. However, a sinusoidal wrinkle may bifurcate, and further evolve to a complex, lobed buckling front, as the internal stresses are too large to support the propagation of a sinusoidal wrinkle. We think our experimental observation that large-scale and highly ordered sinusoidal waves appear and evolve with the growth temperature is consistent with the model of Crosby *et al*. Raman spectroscopy has been used to probe the stress/strain conditions of materials with quite consistent results [11]. This is because the stress/strain-dependent property is the frequency of the atomic vibrations in a material that can be characterized with the laser Raman spectroscopic technique. Figures 3(a)–(c) depict Raman spectra of the films deposited at different substrate temperatures, demonstrating the characteristic of a-C. Graphite has two significant Raman lines: the so-called G peak and D peak. The major features of Raman spectra of amorphous carbon films can be derived from corresponding features in the spectrum of graphite. In figures 3(a)–(c), these Raman spectra were fitted to two components, the D peak and G peak, by using Gaussian fitting. The G-peak position is observed to locate at 1558 cm^{-1}, 1581 cm^{-1}, and 1584 cm^{-1} respectively, with the different growth temperatures. The magnitude of the Raman shift can be related to the variation of the residual stress $\Delta\sigma$ by the following equation [12]: $\Delta\sigma = 2G\frac{1+\nu}{1-\nu}\frac{\Delta\omega}{\omega_0}$, where $\Delta\omega$, ω_o, G, and ν are the shift in the Raman wavenumber, the wavenumber of the reference state, the shear modulus of the material, and the Possion's ratio of the materials, respectively. It can be seen that the G peak of the samples shifts significantly towards to higher wavenumber, indicating that the internal compressive stress of the films increases as the deposition temperature increases. It is likely that at 150 °C, the stress is suitable to form the sinusoidal patterns.

As the deposition temperature increases to 550 °C, the average stress becomes larger based on the above equation, and the surface region with the suitable stress range for forming

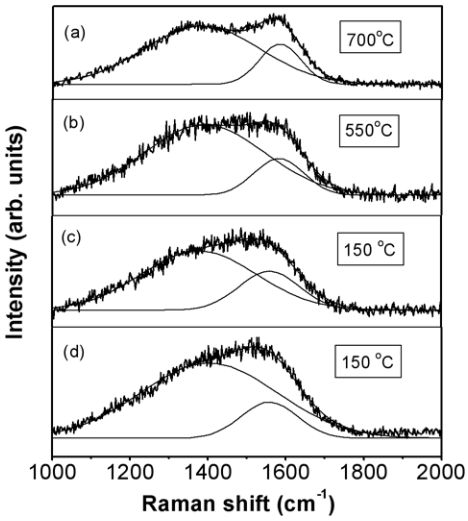

Figure 3. Raman spectra of the amorphous carbon films. (a), (b), and (c) refer to the buckling regions for the samples deposited at different growth temperatures, 700, 550, and 150 °C, respectively. (d) corresponds to the outside region without the buckling observation for the sample deposited at 150 °C. These Raman spectra were fitted to two components, the D peak and G peak, by using Gaussian fitting. The G-peak position is observed to locate at 1558 cm^{-1}, 1581 cm^{-1}, and 1584 cm^{-1} in the buckling regions for the different deposition temperatures, respectively. The G-peak position in (d) is located at 1557 cm^{-1}, but no significant change is observed compared to that in (c).

sinusoidal patterns becomes smaller; thus the length of sinusoidal wave decreases. At the higher temperature, the average stress is too large to form interesting patterns, and delamination of the films is observed.

For the sample deposited at 150 °C, the outside region without any observation of buckling was also checked by Raman spectroscopy, as shown in figure 3(d). No significant change is observed compared with that in figure 3(c), and the G-peak position in figure 3(d) is located at 1557 cm^{-1}. As discussed before, it is suggested that the buckling phenomenon in the centre region is induced by the high relative stress. Unfortunately, we did not observe the stress difference in the various regions by Raman measurement in this case. It is very likely that the small variations of stress are not detected significantly based on Raman measurement.

In summary, several stress relief patterns in amorphous carbon films deposited on sapphire (0001) wafers by ion beam assisted deposition have been presented. At low relatively deposition temperature, many interesting patterns, such as network, blisters, sinusoidal patterns with π-shape, and highly ordered sinusoidal waves, form on a large scale. The maximum length for the sinusoidal patterns reaches 396 μm with a height of $\sim$500 nm and a wavelength of $\sim$8.2 μm. As the temperature is increased, the length of these sinusoidal structures deceases dramatically to 70 μm. The buckling patterns disappear; instead, delamination of the film is observed with a further increase of the deposition temperature. The experimental observation is correlated with the existing theoretical model.

Acknowledgment

One of the authors (Zhu) appreciates the project being sponsored by the National Natural Science Foundation (Grant Nos 50472010 and 10635010) of the People's Republic of China.

References

[1] Yuse A and Sano M 1993 *Nature* **362** 329
[2] Bowden N, Brittain S, Evans A G, Hutchinson J W and Whitesides G M 1998 *Nature* **393** 146
[3] Seth J, Paghunath R and Babu S V 1992 *J. Vac. Sci. Technol.* A **10** 284
[4] Gille G and Rau B 1984 *Thin Solid Films* **120** 109
[5] McKenzie D R 1993 *J. Vac. Sci. Technol.* B **11** 1928
[6] Lee D H, Walter K C and Nastasi M 1999 *J. Vac. Sci. Technol.* B **17** 818
[7] Crosby K M and Bradley R M 1999 *Phys. Rev.* E **59** R2542
[8] Wang M, Li D, Shu D, Bennema P, Mao Y, Pan W and Ming N 2005 *Phys. Rev. Lett.* **94** 125505
[9] Moon M W, Lee K R, Oh K H and Hutchinson J W 2004 *Acta Mater.* **52** 3151
[10] Lee A, Clemens B M and Nix W D 2004 *Acta Mater.* **52** 2081
[11] Schadler L S and Galiotis C 1995 *Int. Mater. Rev.* **40** 116
[12] Wei Q, Narayan R J, Sharma A K, Sankar J and Narayan J 1999 *J. Vac. Sci. Technol.* A **17** 3406