Highly stressed carbon film coatings on silicon: Potential applications

T. Sharda,[a] T. Soga, T. Jimbo, and M. Umeno
Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466 8555, Japan

(Received 9 August 2001; accepted for publication 18 February 2002)

Highly stressed and strongly adhered nanocrystalline diamond films are grown on Si substrates by providing controlled and continuous bias current density (BCD) in microwave plasma chemical vapor deposition system. The stress and hence the curvature of the films on Si substrates can be varied and controlled by changing the BCD. We propose applications for such stressed films in the areas in which bent crystals are being used for various purposes, i.e., particle physics, x-ray optics, etc. These bent Si substrates can replace crystal benders, a cumbersome mechanical arrangement, used for bending Si in those areas.
[DOI: 10.1063/1.1471379]

There have been serious efforts in reducing high amount of stress in hard carbon thin films as it causes delamination of the films from the substrate[1–3] and also there have been efforts in engineering interfaces for adherent diamond coatings.[4] There are two aspects of looking at the advantages of strong adherence; first, it is a necessary condition for tribological applications of hard carbon films and, second, it allows one to obtain enormous amount of stress in the films. A high amount of stress in the films may cause bending of the substrates such as silicon.[5] The curved crystals find potential applications in the areas of x-ray optics and particle physics.[6–17] A bent Si wafer can be used in place of magnet to deflect a beam of charged particles and ions.[11,12] However, to date, a heavy mechanical mechanism (crystal bender) is being used to mechanically bend the crystal to the desired radius of curvature depending upon the application.[11,12,14] We propose to replace this cumbersome assembly for bending the Si wafer to the as-grown bent Si samples resulting from the thin stressed carbon films grown upon them. Highly bent samples can be obtained as a result of strong adhesion to the substrate and high internal stress in the films. In the present study, a processing method, based on the concept of implanting carbon below the Si substrate in the initial stages of the growth, is developed to obtain strong adhesion and, as a result, enormous amount of stress could be obtained leading to bent Si wafers. It is shown that a wide range of stress can be obtained by changing the growth parameters, which results in a wide range of curved Si wafers.

The key point in this method is introduction of a quartz shield to cover the conducting parts of the substrate holder assembly (other than the substrate), while applying negative bias to the substrate throughout the growth. The quartz shield enhances the bias current density (BCD) to the substrate at low microwave powers without affecting the microwave plasma and provides a tool, independent to microwave power, to control the BCD, making it possible to control the impingement carbon ion flux on the substrate in a better way. Implementing the above arrangement and the approach, films were grown on mirror polished Si substrates in a 2.45 GHz ASTeX, USA, microwave plasma chemical vapor deposition (MPCVD) system at various growth conditions, such as growth temperatures (600 °C), negative biasing voltage (200–320 V), methane concentration (2–6% in hydrogen), and deposition time (1–4 h), while keeping microwave power (1000 W) and pressure (30 Torr) constant. Substrates of various thickness, in the range of 325 to 700 μm, were used. Samples were characterized by high resolution scanning electron microscopy (SEM), UV Raman spectroscopy at 257 nm, and curvature of the samples was measured using Alpha-500 profilometer with a length of the scanned sample segment of 5 mm.

A wide range of the radius of curvature of the samples is obtained at different growth parameters. Plots of the radius of curvature as functions of biasing voltage and methane concentration are shown in Fig. 1. The methane concentration (5%) and biasing voltage (200 V) were kept constant, respectively, in the films grown at different biasing voltage [Fig. 1(a)] and methane concentration [Fig. 1(b)]. These two parameters in this study resulted in high amount of stress at particular conditions in the carbon films. Interestingly, the stress in the films shows reverse trends with the two parameters[18] and, as a result, the radius of curvature decreases and increases, respectively, as a function of biasing voltage and methane concentration. The films resulting in low radius of curvature had enormous amount of compressive stress and were bent visibly. For example, a few of the bent samples after the depositions are shown in Fig. 2. These samples account for an enormous stress in the films, which may be as high as 85 GPa. Moreover, in spite of having such a large stress, no cracks were observed in the films. As far as the size of the wafers is concerned, different sizes of Si wafers of different orientations have been used in this study.

No other group has obtained such a high amount of stress in the carbon films. It may be mainly because the films deposited by other groups delaminated soon after the deposition in the case of more than 2 GPa compressive stress due to weak adhesion. However, in our case, it may be due to strong adhesion of the films to the substrate that we could observe such an enormous stress. The strong adhesion in our films is a result of implantation of carbon ions, with suitable

[a]Electronic mail: tarun_sharda@yahoo.com

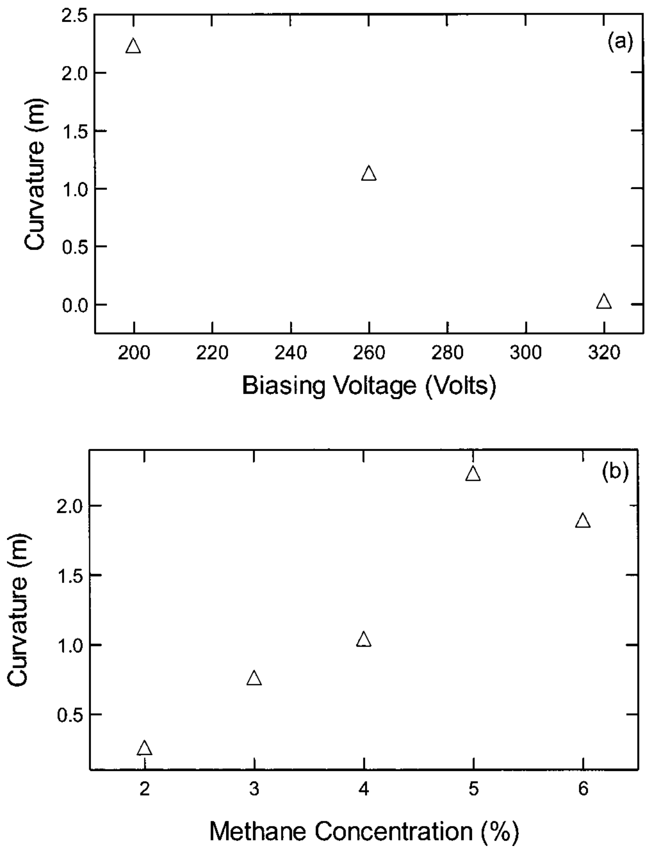

FIG. 1. Plots of radius of curvature as a function of (a) biasing voltage and (b) methane concentration.

energy, into the substrate in the initial stages of growth. In order to investigate how deep the carbon has diffused, an x-ray photoemission spectroscopy depth profile of a sample grown at -200 V was obtained as shown in Fig. 3. Stylus measurement of post-measurement (sputtered) sample showed a depth of ≈ 100 nm at the place where the sample was sputtered. This means that the carbon has diffused approximately to a depth of 100 nm into the Si substrate with a gradual change in the stochiometery of the interfacial SiC layer as seen in the Fig. 3. Such a kind of deep implantation of carbon with a gradual change in the stochimetery of SiC at the interface may be the key to the strong adhesion in our films.

Details of the structural and mechanical properties of the carbon films were reported elsewhere.[5,19,20] In brief, the visible Raman spectra of the films (not shown here) consist of a feature near 1150 cm^{-1} and well-known graphitic D and G bands. The former band is mostly associated to the presence of nanocrystalline diamond (NCD) in the films. In our films the relative intensity of this band to the graphitic G band is found to have a correlation to structural and mechanical properties of the films and is understood to represent concentration of NCD in the films. Surface morphology and UV Raman spectroscopy of one such film, which shows the high intensity of the NCD related feature (1150 cm^{-1}) in the visible Raman spectroscopy are shown in Fig. 4. Faceted grains of less than 30 nm are evident in the micrograph obtained by a high resolution SEM, and the cubic crystalline feature near 1333 cm^{-1} in the UV Raman spectroscopy is an unambiguous signature of those grains being crystalline diamond. The spectrum also shows a significant amount of the graphitic carbon in the films as evidenced by the G band at 1580 cm^{-1}.

As the films show characteristics of NCD, their large grain boundary area (GBA), accommodating nondiamond carbon impurities, and the hydrogen content of the films were hypothesized to be the origin of the large stress in the films. In order to further support this hypothesis, BCD together with the intensity ratio of the feature near 1150 cm^{-1} to the G band in visible Raman spectroscopy (I_n/I_g) are plotted as a function of the same parameters in Fig. 5. Interestingly, the BCD and the ratio I_n/I_g show inverse trends as a function of the growth parameters. This matches well with the hypothesis of origin of stress being the larger GBA. High BCD results in high nucleation density of diamond, which, in turn, results in high GBA in the films. High GBA contains higher amount of sp^2 carbon, resulting in higher stress and lower curvatures of the samples. It should also be mentioned that other parameters, such as growth temperature and deposition time also affect the radius of curvature. Nevertheless,

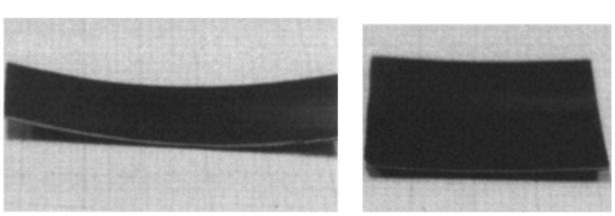

FIG. 2. Two visibly bent silicon samples after deposition because of high compressive stress in the carbon films deposited on them. The film is at the bottom side in the photographs.

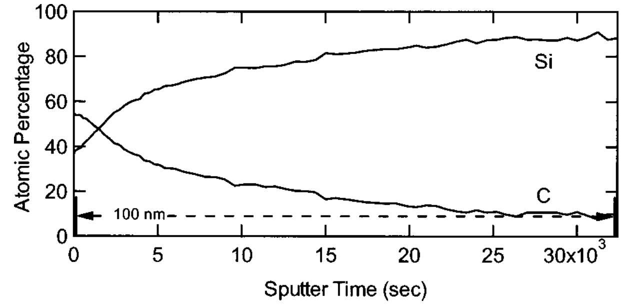

FIG. 3. XPS depth profile of a sample. The depth was estimated from stylus measurement on post-measured (sputtered) sample.

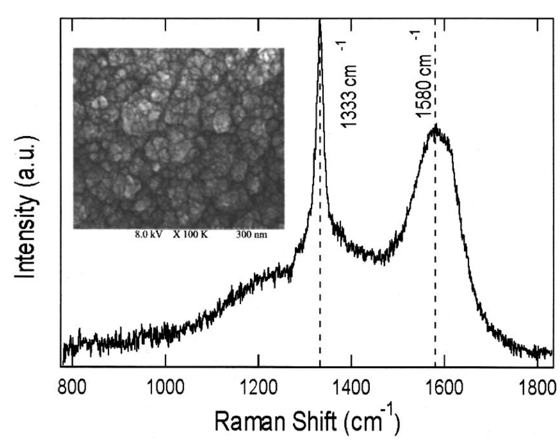

FIG. 4. UV Raman spectrum taken at 257 nm of an NCD sample. Inset is a high resolution SEM micrograph of the sample.

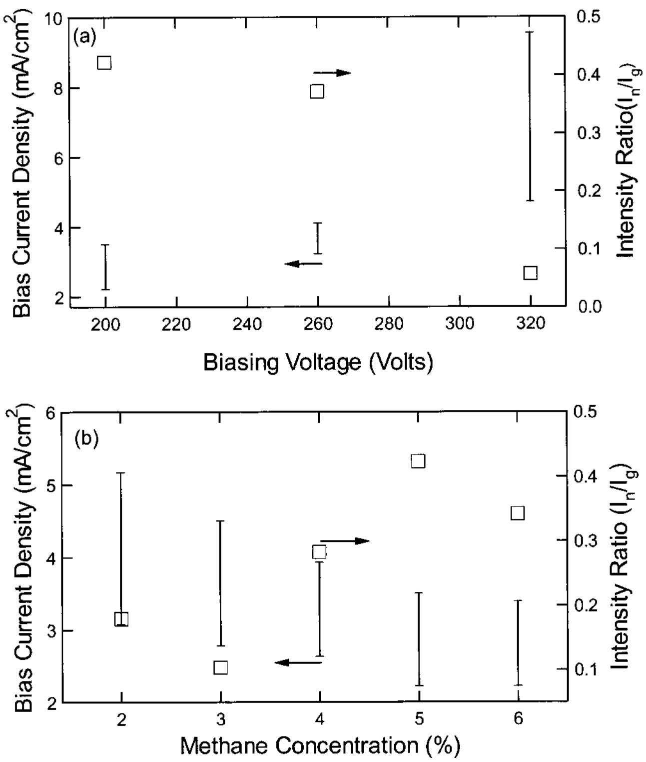

FIG. 5. Plots of BCD and the ratio of intensities of the Raman feature at $1150\ cm^{-1}$ (in visible Raman spectra) to graphitic G band (I_n/I_g) as a function of (a) biasing voltage and (b) methane concentration. The bars indicate the range of variation of the BCD from start to end.

different growth conditions result in films with a wide range of radius of curvature (0.02 to 3.5 m).

We propose applications for such stressed films in the areas where bent crystals are being used for various purposes, i.e., particle physics, x-ray optics, etc. These bent Si substrates may replace crystal benders, a cumbersome mechanical arrangement, used for bending Si in those areas. To compare the range of the radius of curvature used in x-ray optics and particle physics, a few data in the related literature were collected and presented together in Table I. Interestingly, the range of the radius of curvature of the NCD coated Si wafers obtained in this work fall in the range of radius of curvature of bent crystals used in x-ray optics and particle physics experiments. Therefore, these free-standing bent wafers in the area of x-ray optics and particle physics experiments may be used to replace the cumbersome mechanism of crystal benders.

TABLE I. A comparison of the radius of curvature obtained in this study with the one mostly being used in x-ray optics and particle physics experiments.

Reference	Application related to	Wafer thickness (μm)	Radius of curvature (m)
6	X-ray optics	100	0.2
7	X-ray optics	50	0.1
8	X-ray optics	600	2.0
9	X-ray optics	380	2.0
10	X-ray physics	50	0.01
11	Particle Physics	1500	3.0
This study	⋯	325–700	0.02–3.5

In conclusion, highly stressed and strongly adhered NCD films are grown on Si substrates by providing controlled and continuous BCD in a MPCVD system. The advantage of strong adhesion is used to obtain large stress in the films, which bent the Si samples with different radius of curvatures depending upon the growth conditions. A wide range of the Si samples with different radius of curvatures were prepared that may find potential applications in the areas of x-ray optics and particle physics.

This work was supported by the Japan Society for Promotion of Science (JSPS) under the program ''Research for the Future'' and by Nagoya Institute of Technology research promotion program. The authors thank Prof. H. Takeuchi from Tohoku University for the uv-Raman spectroscopy measurements. One author (T. Sharda) gratefully acknowledges JSPS for awarding him a post-doctoral fellowship to conduct the present work.

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