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LETTER TO THE EDITOR

Structural change of a hydrogenated carbon film upon heating

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Abstract

We report, in this letter, the thermal annealing behaviour of a metastable crystalline hydrogenated carbon film prepared by plasma-enhanced chemical vapour deposition. X-ray diffraction, micro-Raman and Fourier-transform infrared (FTIR) spectrometers were used to monitor the structural transition in the film upon heating in the air. The resultant change in the film properties, e.g., the mass density and optical band gap, was investigated by specular x-ray reflectivity measurement and by optical reflectivity measurement in the visible and ultraviolet range. It was found that the structural change as well as the resultant change, in the film properties, is closely related to the release process of the bonded hydrogen in the film at elevated temperatures.

For years the synthesis and properties of amorphous hydrogenated carbon films have attracted much research interest due to their potential applications, e.g., in surface coating [1, 2]. The research effort has recently been directed towards the thermal stability of these materials, as the applicability of amorphous hydrogenated carbon films is very much restricted by their structural instability [3–7]. It is known that heat treatment of amorphous hydrogenated carbon films will cause the release of hydrogen from the film as well as the transformation of their microstructure from diamond-like or polymer-like to graphite-like, and cause the relevant properties of the materials to deteriorate [3–7]. However, the relationships among the hydrogen release, the structural change and the film properties upon heating is still not clear and requires systematic study.

Radio-frequency plasma-enhanced chemical vapour deposition (rf-PECVD) was often used in previous studies to produce hydrogenated amorphous carbon films [8]. The advantage of this technique is that a homogeneous film can be deposited in a large area on any kind of substrate at a high deposition rate. In addition, the properties of the film can be controlled via adjusting the plasma power density and/or the negative bias between the substrate holder and the chamber wall. Recently, by means of this approach the authors have successfully grown

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films with a crystalline structure on silicon substrates [9]. This arouses research interest in determining the structure and properties of the crystalline hydrogenated film, as such films have not been reported on before. Also, making clear its thermal stability can be quite helpful as regards understanding the response of hydrogenated carbon films to thermal annealing.

In this letter, we report on the x-ray, FTIR and micro-Raman identification of the structural transition in a crystalline hydrogenated carbon film induced by thermal annealing as well as the resultant change in its properties. The changes in both the structure and properties of the film are caused by hydrogen release from the film at elevated temperatures.

A crystalline hydrogenated carbon film was deposited on a Si(001) substrate by rf-PECVD using a mixture of argon and methane (6.25%) as the gas source. Before deposition the chamber was evacuated to a high vacuum and then the working gas was introduced into the chamber to a pressure of about 8×10^{-2} Torr. The film was deposited with a plasma power density of about 0.13 W cm^{-2} . During deposition, the substrate temperature was kept at about $150 \text{ }^\circ\text{C}$ and no bias voltage was intentionally applied between the substrate and the chamber wall. After deposition the film was annealed in the air at temperatures from 100 to $400 \text{ }^\circ\text{C}$ for an hour. X-ray diffraction, FTIR and micro-Raman spectroscopy were used to characterize the structure of the film at each annealing stage. Specular x-ray reflectivity measurement and optical reflectivity measurement were also employed to determine the change of the film properties, e.g., the mass density and the optical band gap.

Figure 1 shows a typical x-ray diffraction pattern of an as-deposited film obtained by a Philips X'pert four-circle diffractometer with a 2θ resolution of 0.0005° . The Si(004) peak at about 69.1° was removed by tilting the sample at 15° when taking the diffraction pattern. The peaks shown in the pattern around 44.2° , 64.4° and 81.6° are from the hydrogenated carbon film and indicate that the film is of crystalline structure [9]. From the critical angle in the specular x-ray reflectivity curve of such a film, the mass density was determined as

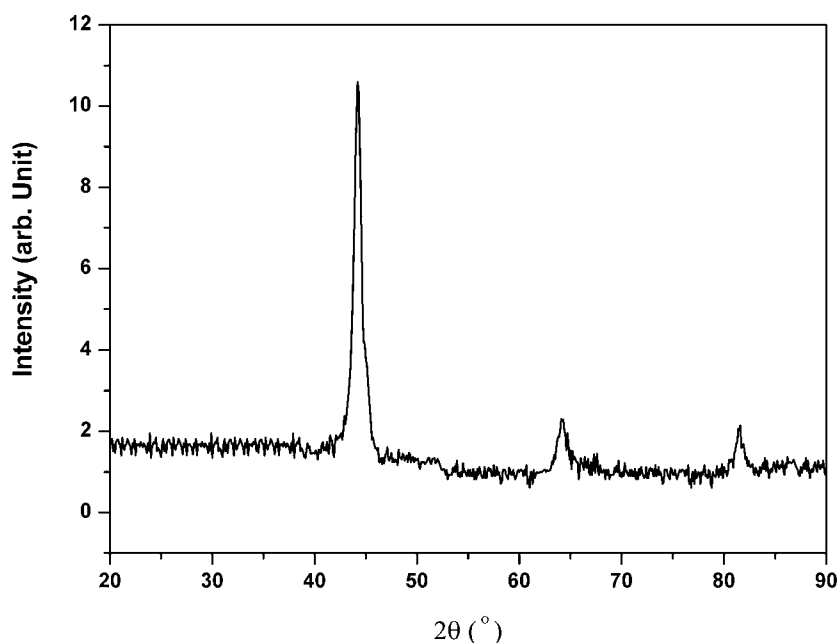


Figure 1. The x-ray diffraction pattern of as-deposited hydrogenated carbon film on Si(001). The silicon diffraction peaks were removed by tilting the sample at 15° .

1.25 g cm^{-3} [10]. Figure 2 shows a typical x-ray reflectivity curve of a film deposited on Si(001). The optical band gap of the film was deduced from its optical reflectivity measured in the visible and ultraviolet range using the Tauc relationship [11], and was about 2.75 eV [9].

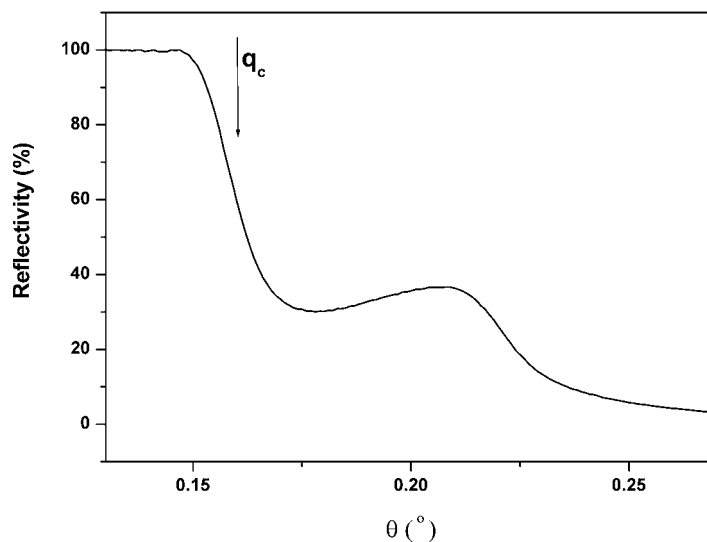


Figure 2. The specular x-ray reflectivity of a $5 \mu\text{m}$ thick as-deposited thick film on Si(001). Indicated by the arrow is the critical angle q_c below which x-rays are totally reflected by the film.

Figure 3 shows the x-ray diffraction patterns of the film after annealing at different temperatures. We see that the film can retain its structure at annealing temperatures up to $200 \text{ }^\circ\text{C}$, at which point a thermally induced lattice relaxation occurred. After an hour of annealing at $200 \text{ }^\circ\text{C}$, the diffraction peaks of the film shifted from 44.2° , 64.4° and 81.6° to 45.0° , 65.4° and 82.7° , respectively, suggesting a decrease of about 4.9% in the lattice volume which should in turn give rise to a decrease of its mass density by a same factor. A transition from metastable crystalline structure to graphite structure was triggered when the film was annealed at $250 \text{ }^\circ\text{C}$: the graphite (101) peak at about 44.3° emerged in the x-ray diffraction pattern. It is noted that the intensity of the graphite (101) peak increased at higher annealing temperatures and that when the film was heated to $400 \text{ }^\circ\text{C}$, the graphite (002) peak was also observed. This confirms the transition to graphite structure triggered at $250 \text{ }^\circ\text{C}$.

The structural transition in the film with thermal annealing was also observed by micro-Raman analysis. Figure 4 shows the Raman spectra of the film at different stages obtained using a 514 nm Ar^+ laser as the excitation source. The spectrum of the film after annealing at $200 \text{ }^\circ\text{C}$ has features similar to that of the as-deposited one, i.e. a broad peak around 1230 cm^{-1} and another one at 1600 cm^{-1} corresponding to the characteristic G line of carbon. This is in agreement with the x-ray diffraction analysis in indicating that no structural change occurred at this stage. Since the 1230 cm^{-1} peak has not been reported for *amorphous* hydrogenated carbon films, it is thus considered as a feature of *crystalline* hydrogenated carbon films. Significant change was observed when the film was annealed at $250 \text{ }^\circ\text{C}$: the peak at about 1230 cm^{-1} disappeared and, instead, a new peak at about 1360 cm^{-1} corresponding to the graphite D line, which is generally attributed to disordered or microcrystalline graphite, appeared [12]. The emergence of the D line suggests that a transition from metastable crystalline structure to graphite structure occurred. This transition is confirmed by the spectra taken after annealing at higher temperatures.

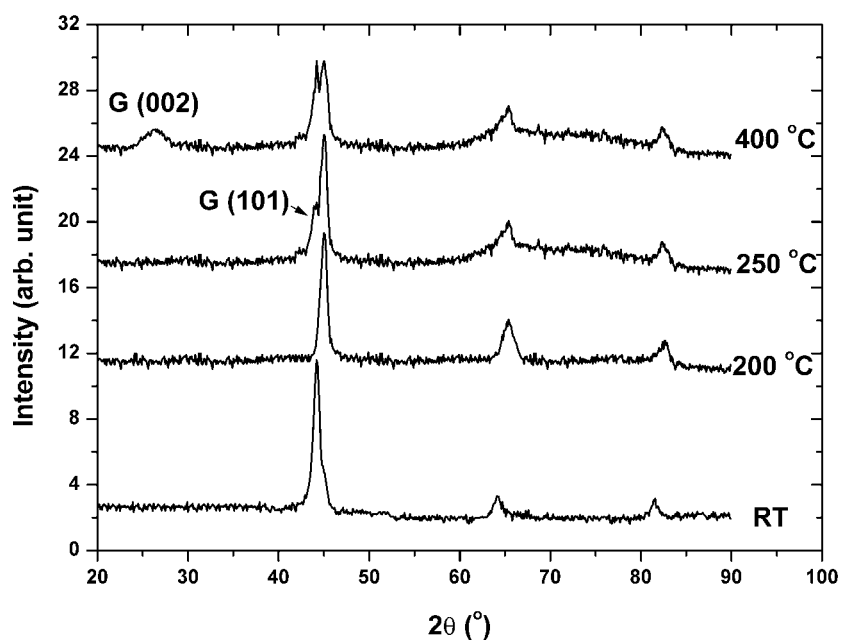


Figure 3. X-ray diffraction patterns of the hydrogenated carbon film at different annealing temperatures, showing a two-step change in the film structure.

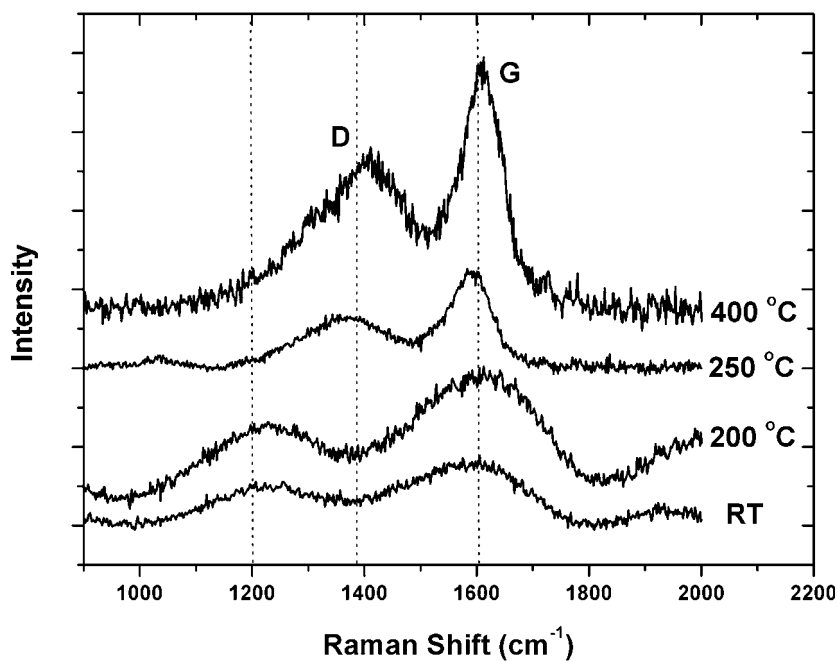


Figure 4. The Raman spectra of the hydrogenated carbon film at different annealing stages. The dashed lines show the positions of the characteristic peaks of the film upon heating.

The structural change behaviour of the film is closely related to the release process of the bonded hydrogen in the film upon heating. Figure 5 plots the area of C–H stretching bands integrated from the Fourier-transform infrared (FTIR) absorption spectra of the film as a function of the heating temperature. A similar tendency in the release process of the bonded hydrogen is observed: at temperatures up to 200 °C, the film only slightly released its bonded hydrogen; at temperatures above 250 °C, the release of bonded hydrogen was drastically accelerated. This indicates that 250 °C is a critical point, above which a structural transition occurs accompanied with drastic release of the bonded hydrogen from the film. Below that point the film retains its structure with a slight release of the bonded hydrogen.

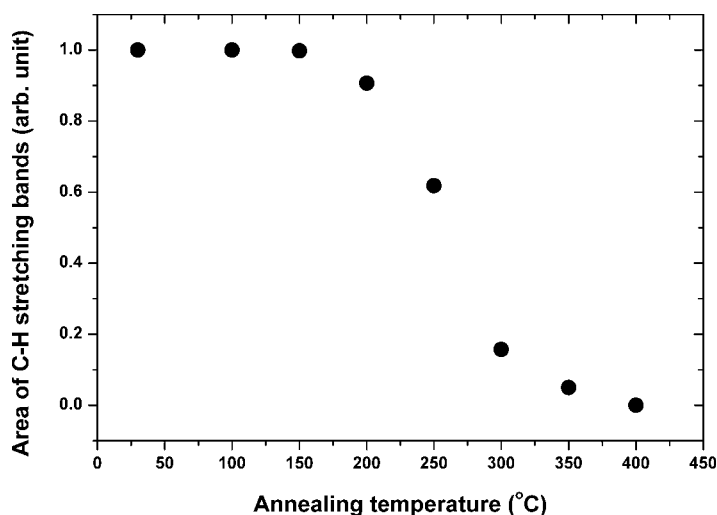


Figure 5. The normalized area of the C–H stretching bands integrated from FTIR absorption spectra of the film, showing a two-step release of the bonded hydrogen in the film at elevated temperatures.

Since the film properties, e.g., the mass density and the optical band gap, are related to the content of bonded hydrogen and the structure of the film, there should also be a similar tendency in the change of the film properties. Figure 6 shows the optical reflectivity of the film at various annealing temperatures. With the release of bonded hydrogen, we notice that the absorption edge of the reflectivity curve shifted towards the long-wavelength (low-photon-energy) side, indicating a decrease in the optical band gap of the film. Corresponding to the accelerated release of the bonded hydrogen at temperatures above 250 °C, there is also an accelerated shift of the absorption edge. At temperatures below 250 °C, however, the shift is quite small.

To clearly show the relationship between the film properties and the structural change, we plot the mass density, the optical band gap and the hydrogen release versus the annealing temperature in figure 7. One sees that, like the release process of the bonded hydrogen, there is a similar tendency in the change of the film properties upon heating. After annealing at 200 °C for an hour, the optical band gap of the film shrank by about 10% and its mass density increased by 4.2%. The small increase in the mass density at this stage was attributed to the thermally induced relaxation, i.e. a $\sim 4.9\%$ decrease in the lattice volume. Significant change in both properties was observed at a temperature of 250 °C, i.e. a $\sim 25.5\%$ decrease in the optical band gap and a $\sim 16.7\%$ increase in the mass density together with a $\sim 38\%$ release of the bonded hydrogen, which was caused by the transition to graphite structure.

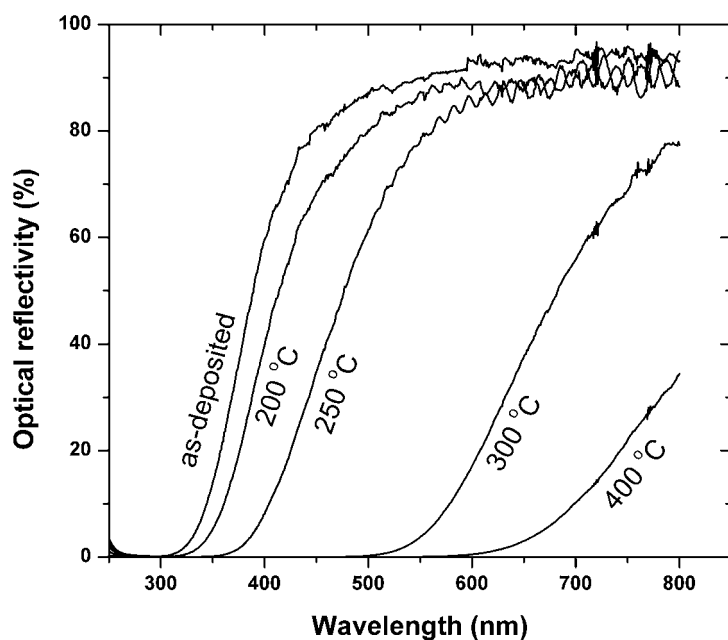


Figure 6. The optical reflectivity curves of the hydrogenated carbon film at various annealing stages in the visible and ultraviolet range.

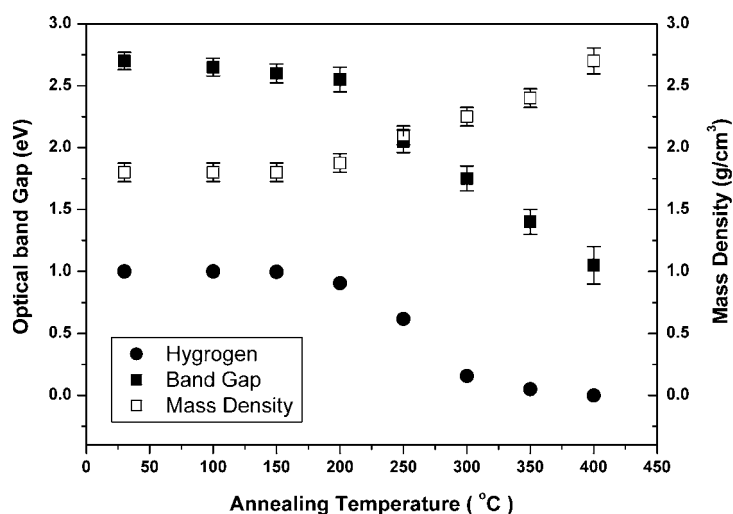


Figure 7. The optical band gap, the mass density and the release of bonded hydrogen in the film versus the annealing temperature. The error bars are also shown for the optical band gap and the mass density.

In summary, the structural and property changes of a crystalline hydrogenated carbon film produced by rf-PECVD were investigated by annealing the film at elevated temperatures in the air. The structural change of the film is closely related to the thermally induced release behaviour of the bonded hydrogen in the film, which resulted in a similar change in behaviour of the film properties.

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