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# Structural modification of polymeric amorphous hydrogenated carbon films induced by high energetic $He^+$ irradiation and thermal annealing

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**Abstract**

Structural modifications of polymeric amorphous hydrogenated carbon (a-C:H) films by 2 MeV $He^+$ irradiation and by thermal annealing up to 400°C have been made. After irradiation with a dose of $1.2 \times 10^{15}$ $cm^{-2}$, the film hardness was increased by a factor of 3. Correspondingly, the optical band gap shrank from 3.0 to 2.5 eV and the refractive index was increased from 1.5 to 1.6. In contrast, although the optical band gap was found to be decreased to a similar small value of 2.0 eV after the films were thermally annealed in a vacuum of $10^{-6}$ torr at 400°C for 30 min, the variations in the refractive index and film hardness were not detectable. The structural modifications of the carbon network in the a-C:H films by the ion irradiation and thermal anneal are discussed. © 2000 Published by Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The effects of high energetic ion implantation to amorphous hydrogenated carbon (a-C:H) and diamond-like a-C:H films have been intensively investigated. It has been reported that the optical bandgap of a-C:H films is decreased with increasing $He^+$, $C^+$, $N^+$ and $F^+$ ion dose [1–4]. Other complementary findings, based on infrared (IR) absorption and Raman scattering measurements, for the a-C:H films irradiated by high energetic $H^+$, $He^+$ and $N^+$ ions, suggest that this phenomenon is related to hydrogen removal induced by ion-implantation, which may directly cause a transformation from $C(sp^3)-H_n$ to $C(sp^2)$ clusters [5–8]. The dehydrogenation process in a-C:H films also occurs when the films are heated at elevated temperatures. As a result, the optical bandgap has been found to shrink [9–13]. Similarly, it has been proposed that removal of hydrogen from hydrogen bonded $C(sp^3)-H_n$ ($n = 1$, 2 and 3) structures is followed by formation of a new double bond $C(sp^2)=C(sp^2)$ structure.

In this report, we address the different effects of 2 MeV $He^+$ ion irradiation and thermal anneal on the structural modification of a-C:H films.

## 2. Experimental conditions

The a-C:H films used in this study were prepared using the ECR-CVD technique. Upon introducing a mixture of 10 sccm pure methane and 100 sccm hydrogen to the chamber, the plasma was excited in the ECR zone by feeding microwave at 2.45 GHz [14]. The

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substrate was only heated by the plasma during film growth and the substrate temperature was found not to exceed 60°C. Prior to deposition the chamber was pumped down below $5\times10^{-6}$ torr using a turbo molecular pump. The film was prepared under a constant microwave power of 600 W, pressure of 23 mtorr on ⟨100⟩-oriented single crystal silicon. The thickness of the as-deposited film was approximately 1.3 μm.

$He^+$ ion irradiation (2 MeV) and elastic recoil detection analysis (ERDA) measurements were performed using a nuclear microscope which was based around a HVEC AN2500 single ended Van de Graaf accelerator [15]. The operation pressure was approximately $10^{-6}$ torr. The irradiation was performed under two doses of $1.2\times10^{15}$ and $1.0\times10^{16}$ $cm^{-2}$ at an incidence angle of 12°. To prevent excessive sample temperature rise during irradiation, the ion current intensity was controlled at $9\times10^{-8}$ A $cm^{-2}$. The temperature of the irradiated area was estimated to be below 200°C. For ERDA measurement, both the incidence angle of the 2-MeV $He^+$ ion beam and the emission angle with respect to the sample surface were 12°. Thermal anneal was performed at each annealing temperature for 30 min in a vacuum of $10^{-6}$ torr.

Raman scattering measurements, excited by an $Ar^+$ laser (514.5 nm), was carried out using the Ranishaw micro-Raman spectrometer. The ellipsometer (Uvisel) was employed to evaluate the optical properties of the films. The film thickness and its variation were measured using the Dektak surface profiler. It was found that the thickness measured using the profiler was consistent with that deduced using the ellipsometer.

## 3. Results and discussion

It is well known that many properties of a-C:H films are strongly influenced by their hydrogen content. The concentration of hydrogen in our as-deposited film was monitored using ERDA and was approximately 42 at.% [16]. In such hydrogen-rich carbon films, up to 80% of $sp^3$-bonded carbon atoms are expected to be hydrogenated and the number of $C(sp^3)$–H could be factors of 1.6 and 5.7 larger than the numbers of $C(sp^3)-H_2$ and $C(sp^3)-H_3$, respectively [17].

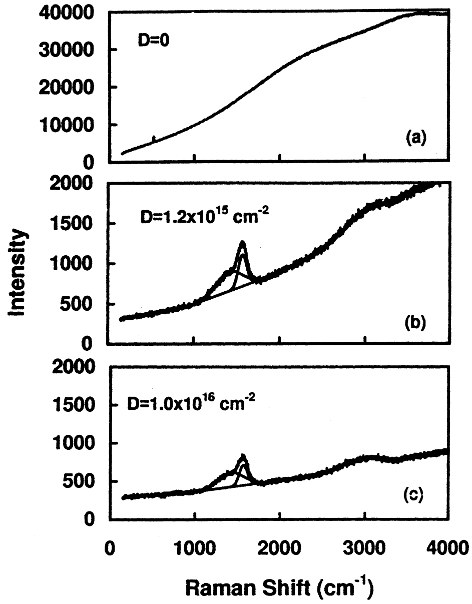

Fig. 1. Raman spectra of the a-C:H film before $He^+$ ion irradiation (a). The Raman scattering band at 1400–1600 $cm^{-1}$ appears after the irradiation with doses of $1.2\times10^{-15}$ $cm^{-2}$ (b) and $1.0\times10^{-16}$ $cm^{-2}$ (c), respectively.

Due to the small incidence angle of the ion beam, a few hydrogen atoms are kicked out of the films. Besides this, it has been suggested that under the impact of high energetic ions, if two C–H bonds are broken within a short characteristic distance from each other within a short time compared with the lifetime of free hydrogen atoms in the irradiated a-C:H films, the two hydrogen atoms may recombine to form hydrogen molecules and then diffuse out of the films [18]. Based on this model, more than two-thirds of the hydrogen atoms were released from the films after the ion irradiation with a dose of $1.0\times10^{16}$ $cm^{-2}$. A significant loss of hydrogen could create a number of carbon dangling bonds which in turn could bond together under the impact of deposited energy of the ions, resulting in a structural change. The structural change was monitored using Raman scattering, as shown in Fig. 1. Before the ion irradiation, a strong and smooth background increasing with wavenumber indicates that the photoluminescence signal excited by the $Ar^+$ laser (514 nm) dominates the measurement range, see Fig. 1a. This result suggests that the a-C:H film possessed a polymer-like carbon structure [14]. However, after $He^+$ irradiation, the background was decreased dramatically and a Raman scattering band at 1400–1600 $cm^{-1}$ and its second order scattering peak at approximately 3000 $cm^{-1}$ was detected, see Fig. 1b,c. This scattering band can be deconvoluted into two Gaussian peaks, i.e. 'D' peak at 1442 $cm^{-1}$ and 'G' peak at 1572 $cm^{-1}$, as shown in solid curves in the figures. It is seen that the G peak at full-width half maximum (FWHM) of approximately 113 $cm^{-1}$ is larger than those for normal hydrogenated diamond-like carbon (DLC), but comparable with those for hard hydrogen-free DLC [19]. For the irradiated area with a dose of $1.2\times10^{15}$ $cm^{-2}$, the intensity ratio of the D peak to G peak $I_D/I_G$ was approximately 1.8, comparable with those of typical hard DLC films. Correspondingly, the film hardness was increased by a factor of 3, while the film thickness was decreased by approximately 20%. These results suggest that the carbon network had transformed from loose polymer-like to dense diamond-like structure.

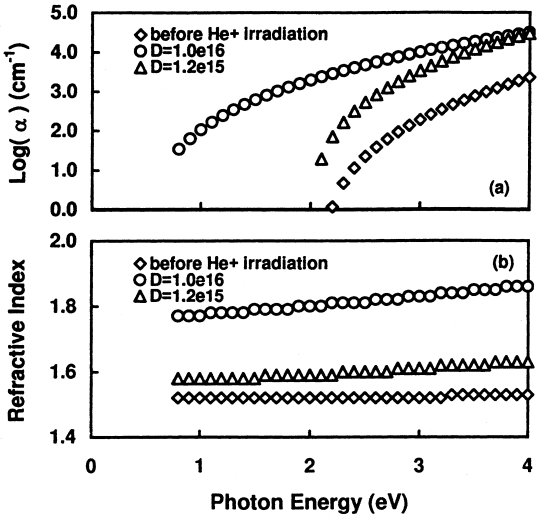

Fig. 2. The $He^+$ ion irradiation induced changes in optical coefficient (a) and refractive index (b) of the a-C:H films. The doses of the $He^+$ ion irradiation are indicated.

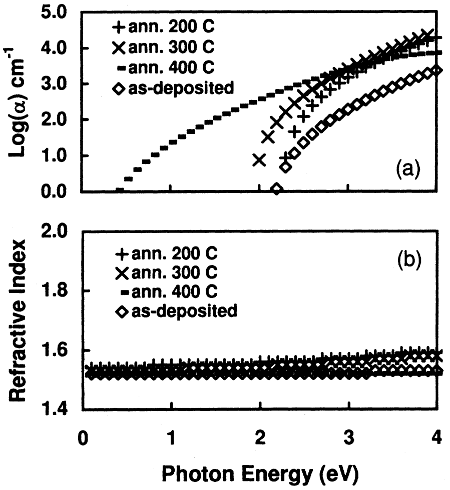

Fig. 3. Thermal anneal-induced changes in optical coefficient (a) and refractive index (b) of the a-C:H films. The anneal temperature is indicated.

Interestingly, in company with an increase in the optical absorption coefficient α, the refractive index was increased by 5%, as shown in Fig. 2. The optical bandgap deduced from the Tauc plot was reduced from 3.0 eV for as-deposited film to 2.5 eV. Upon a high irradiation dosage of $1.0 \times 10^{16}$ $cm^{-2}$, it was observed that the $I_D/I_G$ was increased up to 2.1, while the film hardness was decreased by 30% in comparison with the irradiation of $1.2 \times 10^{15}$ $cm^{-2}$. The α was increased by more than one order of magnitude at the photon energy of 4.0 eV and the optical bandgap was reduced to 2.0 eV. However, the refractive index was increased by approximately 15%. These results indicate that graphitization had happened in the film under such high dosage irradiation.

Hydrogen release from a-C:H films also happens when the films are annealed at elevated temperatures, leading to a decrease in optical band gap [9–13]. Up to an annealing temperature of 400°C, the optical bandgap was reduced to 2.0 eV. Correspondingly, the absorption coefficient was greatly increased, as shown in Fig. 3a. The variations in the optical bandgap and absorption coefficient induced by thermal anneal are comparable with those induced by $He^+$ ion irradiation with a dose of $1.0 \times 10^{16}$ $cm^{-2}$. In contrast, the thermal anneal led to little changes in the refractive index (see Fig. 3b), film hardness and thickness. Fig. 4 shows the Raman spectra for as-deposited and annealed states. Although the photoluminescence signal was largely decreased after the anneal with respect to the as-deposited state, the signal was still strong enough to mask the Raman scattering signals. These results indicate that the annealed films still hold the loose polymer-like structure. This could be the reason why the film thickness and hardness did not change detectably. It should be mentioned that a significant reduction in the film thickness was observed after the a-C:H films were thermally annealed in a poor vacuum of $10^{-2}$ torr at 400°C for 90 min [20].

According to the TRIM simulation, electronic stopping consumes more than 90% of energy of the MeV $He^+$ ions, while nuclear stopping only takes strong effect at the end of the trajectories (approx. 7 μm in this type of a-C:H film). The interaction of the $He^+$ ions and a-C:H film results in an ionization volume in which the target atoms are excited or ionized so as to break some of C–H and C–C bonds. Similarly, C–H and C–C bonds would be broken when they receive enough thermal energy during the anneals. The released hydrogen atoms and some small hydrocarbon units could either re-combine together to form hydrogen and methane molecules and diffuse out of the films or diffuse in the small units and then form molecular complexes near the surface, leaving a hydrogen-less $C(sp^2)$–$C(sp^3)$ network behind. The following bond re-

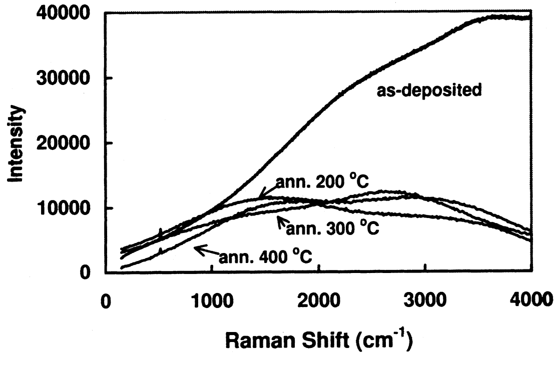

Fig. 4. Raman spectra of the a-C:H film for as-deposited state and annealed states. The anneal temperature is indicated.

actions might happen [21]; e.g. formation of C=C bonds from C–C bonds {Reaction (a): $6C(sp^3)–C(sp^3) \rightarrow C(sp^2)=C(sp^2) + 4C(sp^3)–C(sp^2)$}, formation of $H_2$ from $sp^3–H_n$ {Reaction (b): $2C(sp^3)–H \rightarrow C(sp^3)–C(sp^3) + H_2$} and formation of methane {Reaction (c): $4C(sp^3)–H + 6C(sp^3)–C(sp^3) \rightarrow CH_4 + C(sp^2)=C(sp^2) + 4C(sp^3)–C(sp^2)$}. Reactions (a–c) are endothermic with energies of approximately 0.11, 0.49 and 0.14 eV, respectively. With hydrogen release and formation of hydrogen-free $C(sp^3)–C(sp^2)$ bonding clusters, the photoluminescence efficiency was reduced and the Raman scattering band at 1400–1600 $cm^{-1}$ is activated, as shown in Fig. 1b. When the processes proceed, more and more $C(sp^2)=C(sp^2)$ bonds are simultaneously produced so that they could rearrange into bigger size of $C(sp^2)$ atom rings. This is believed to be the reason for the optical bandgap shrinking [22]. However, optical bandgap may not entirely reflect the structure modification. Though the optical bandgap was narrowed down to 2 eV by both the ion irradiation and thermal anneal narrowed, many other properties remained different as presented above.

It is worth pointing out that the microprocesses in the films induced by ion irradiation and thermal anneal show differences in some aspects. Once the high energetic $He^+$ ions penetrate into the films, a cascade of secondary collisions are excited in the vicinity of the primary collision event, causing energy deposition on the carbon network around the ion track in a short time of $\sim 10^{-13}$ s [5]. Therefore, the bonding rearrangement could only happen very locally and then quench in a very short time if the irradiated ion flux is so small that the interaction among the incident $He^+$ ions can be neglected. In contrast, thermal annealing provides a uniform thermal energy distribution and the rearrangement of carbon bonds happens in the entire bulk of the films. In spite of these, thermal annealing is a slow process in which bonding rearrangement proceeds in quasi-thermal equilibrium. Thus, amorphous C:H network would receive much more energy in the ion irradiation due to a very large energy deposition than in the thermal anneal so as to overcome a larger endothermic reaction, such as Reaction (b), forming a $C(sp^3)$ network. As a result, the newly reformed carbon structure under the ion irradiation is denser than that formed under the thermal anneals. The former structure has a higher hardness, higher refractive index and larger film contraction than the latter.

## 4. Summary

Both 2 MeV $He^+$ ion irradiation and thermal annealing result in dehydrogenation microprocesses in a-C:H films. Although the optical bandgap is reduced from 3 eV to 2 eV under the influence of the ion irradiation with a dose of $1 \times 10^{16}$ $cm^{-2}$ and the 400°C thermal anneal, the ion irradiation leads to a denser carbon network structure, a higher film hardness, higher refractive index and a larger film contraction than with thermal annealing.

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## References

[1] S. Prawer, R. Kalish, M.E. Adel, V. Richter, J. Appl. Phys. 61 (1987) 4492.
[2] S.P. Wong, S. Peng, N. Ke, P. Li, Diamond Relat. Mater. 2 (1993) 580.
[3] G.L. Doll, J.P. Heremans, T.A. Perry, J.V. Mantese, J. Mater. Res. 9 (1994) 85.
[4] G. Compagnini, U. Zammit, K.N. Madhusoodanan, G. Foti, Phys. Rev. B. 51 (1995) 11168.
[5] M.S. Dresselhaus, R. Kalish, Ion Implantation in Diamond, Graphite and Related Materials, Springer, Berlin, 1992, p. 159.
[6] T. Wang, W. Wang, B. Chen, Nucl. Instrum. Methods Phys. Res. B 71 (1992) 186.
[7] W.J. Wang, T.M. Wang, C. Jing, Thin Solid Films 280 (1996) 90.
[8] M.J. Paterson, K.G. Orrman-Rossiter, S. Bhargava, A. Hoffman, J. Appl. Phys. 75 (1994) 792.
[9] N.H. Cho, D.K. Veirs, J.W. Ager III, M.D. Rubin, C.B. Hopper, D.B. Bogy, J Appl. Phys. 71 (1992) 2243.
[10] B. Oral, R. Hauert, U. Müller, K.-H. Ernst, Diamond Relat. Mater. 4 (1995) 482.
[11] S.A. Alterovitz, J.J. Pouch, J.D. Warner, Mater. Res. Soc. Symp. Proc. 92 (1987) 311.
[12] A. Grill, V. Patel, B.S. Meyerson, J. Mater. Res. 5 (1990) 2531.
[13] Y. Bounouh, M.L. Theye, A. Dehbi-Alaoui, A. Matthews, J.P. Stoquert, Phys. Rev. B. 51 (1995) 9597.
[14] S.F. Yoon, H. Yang, Rusli, J. Ahn, Q. Zhang, T.L. Poo, Diamond Relat. Mater. 6 (1997) 1683.
[15] F. Watt, I. Oelic, K.K. Loh et al., Nucl. Instrum. Methods Phys. Res. B 85 (1994) 708.
[16] Q. Zhang, S.F. Yoon, J. Ahn, et al. Microelectron. J. (in press).
[17] H. Efstthiadis, Z.L. Akkerman, F.W. Smith, J. Appl. Phys. 79 (1996) 2954.
[18] M.E. Adel, O. Amir, R. Kalish, L.C. Feldman, J. Appl. Phys. 66 (1989) 3248.
[19] M.A. Tamor, W.C. Vassell, J. Appl. Phys. 76 (1994) 3823.
[20] Q. Zhang, S.F.Yoon Rusli, H. Yang, J. Ahn, J. Appl. Phys. 83 (1998) 1349.
[21] Z.L. Akkerman, H. Efstthiadis, F.W. Smith, J. Appl. Phys. 80 (1996) 3068.
[22] J. Robertson, Structure and electronic properties of diamond-like carbon, in: R.E. Clausing, L.L. Horton, J.C. Angus, P. Koidl (Eds.), Diamond and Diamond-like Films and Coatings, Plenum Press, New York, 1990, p. 331.