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# Laser and thermal induced micro-structural changes and decomposition of hydrogenated carbon films

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## Abstract

Micro-structural changes and decomposition of hydrogenated carbon films on magnetic disk substrates prepared by DC-magnetron sputtering were studied using Ar<sup>+</sup> laser irradiation and physical heating in air and nitrogen ambience, respectively. It was found that a weak Ar<sup>+</sup> laser of a fluence of 0.3 mW  $\mu\text{m}^{-2}$  could significantly decompose a-C:H films. The decomposition rate was fast initially and slowed down significantly after about 20 min. The decomposition rate of a-C:H increased with hydrogen concentration in the film. Raman light intensities of the irradiated sites reduced exponentially with irradiation time. Physical heating in air revealed that the oxidation-dominated decomposition took place between 320 and 350 °C within 15 min, and an increased hydrogen concentration made the a-C:H film more vulnerable to decomposition. At 150–300 °C, a phenomenon of nano-crystal graphite formation was observed from Raman spectra. XPS analysis indicated that there was no significant diffusion of carbon atoms into the substrate at 400 °C heating.

## 1. Introduction

Thin films of amorphous carbon (a-C) have been used as protective coatings in magnetic hard disks and heads for anti-corrosion and anti-wear purposes [1]. The films also show better tribology performance due to their high hardness, lower friction coefficient and higher electrical conductivity as compared to diamond [1, 2]. To adjust film properties, hydrogen is usually introduced in a-C films with the presence of H<sub>2</sub> or hydrocarbon gases during the sputtering or depositing process. The reported films were generally deposited on stable Si wafer substrate. Decomposition of a-C:H films has always been a concern in magnetic head and disk interface, of which thermal-induced decomposition is the dominant mechanism [3, 4]. Hydrogenated carbon (a-C:H) films were found to decompose into small hydrocarbon and hydrogen molecules at 400–1200 K and 700–1100 K [5, 6], respectively. In the tribochemistry

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condition, oxidation of carbon film was accompanied by the release of CO<sub>2</sub> [7]. Many post-treatment factors can change the film structures, of which heat and laser annealing were known to cause graphitization and crystallization [7–9]. Properties of a-C:H films are affected greatly by hydrogen concentration [9–13]. Practically, hydrogen concentration can be as high as 50 atm%. Generally, at low hydrogen level (<5%), most hydrogen atoms are bonded with carbon atoms due to sp<sup>3</sup> stabilization [11, 12]. At high hydrogen concentration, the fractions of unbonded hydrogen molecules and hydrocarbon species increase, which leads to poor mechanical properties of the film [11].

Raman scattering is one of the most important techniques to study the carbon structures [14, 15] although the fundamental interpretation is not completely clear. The application of conventional Raman systems using lasers of large beam sizes and powers has been restricted due to sample damages. In recent years, micro-Raman systems using various lasers of thin beam ( $\leq 3 \mu\text{m}$ ) and low incident power ( $\sim 5 \text{ mW}$ ) have been applied in many research institutes and manufacturing companies. They are suitable for microanalysis and much safer for sample chemistry. However, the damage of these lasers to amorphous carbon films and the relationship between the damage and film composition have not been reported.

In this work, it is found that an Ar<sup>+</sup> laser ( $\lambda = 514.5 \text{ nm}$ ) of  $\sim 3 \text{ mW}$  in a circular area of  $2.5 \mu\text{m}$  diameter can significantly induce decomposition of hydrogenated carbon films on commercial Co-alloy-based magnetic hard disks. The rate of decomposition depends on the hydrogen content in the films. Mechanisms of film damage due to the laser irradiation and physical heating are discussed.

## 2. Experiment

Hydrogenated amorphous carbon films of  $\sim 150 \text{ \AA}$  were prepared using DC-magnetron sputtering in H<sub>2</sub> and Ar ambient on magnetic hard disk alloys CoCrPtTa. A deposition pressure of  $5 \times 10^{-3}$  Torr and a graphite target of 99.999% were used. The films had three hydrogen concentrations of approximately 7 atm%, 22 atm% and 32 atm% as determined by time of flight secondary ion mass spectroscopy (ToF-SIMS) [16].

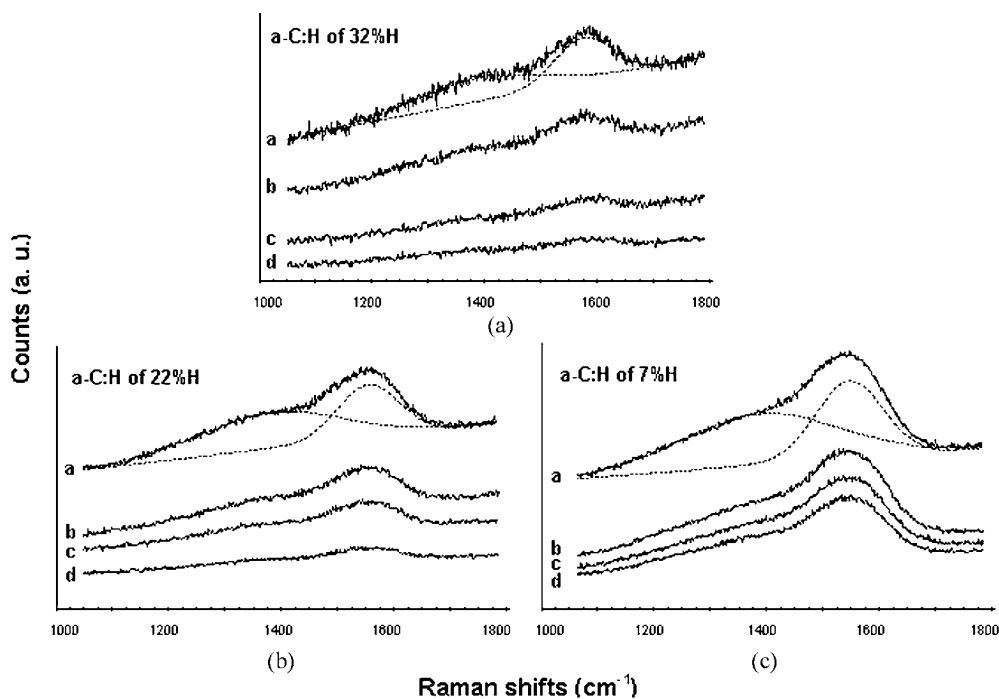
A Renishaw Raman microscope 1000 equipped with an Ar<sup>+</sup> laser ( $\lambda = 514.5 \text{ nm}$ ) was used to monitor carbon decomposition and structural changes. The system had an adjustable laser power from 0 to 23 mW, corresponding to the incident power of 0 to 6 mW on a circular sample area of  $2.5 \mu\text{m}$  diameter, or a fluence rate of 0 to  $0.3 \text{ mW } \mu\text{m}^{-2}$ . 3 mW is the incident power for laser-irradiation and spectrum capturing, unless otherwise stated. For laser-irradiation study, the same sample spot was consistently irradiated while the Raman spectra were captured *in situ* at intervals. Each Raman spectrum was captured for 30 s. Curve-fitting of the spectra was done using a Gaussian distribution function and a linear baseline. DI NanoscopeIII atomic force microscopy (AFM) was used to study the topography of the laser-irradiated carbon films.

The films were heated in air (muffle furnace) and N<sub>2</sub> (tube furnace), respectively, at designated temperatures for 15 min. The temperature of the furnace was set at 150, 250, 300, 320, and 350 °C for air, and 350 °C for N<sub>2</sub>, respectively. Samples were analysed using Raman microscopy and x-ray photon spectroscopy (XPS).

## 3. Results and discussion

### 3.1. Laser-induced carbon film decomposition

In the experiment, it was found that the irradiation of the Ar<sup>+</sup> laser of  $\sim 3 \text{ mW}$  on an area of  $2.5 \mu\text{m}$  diameter of a-C:H films caused a significant and consistent reduction of Raman

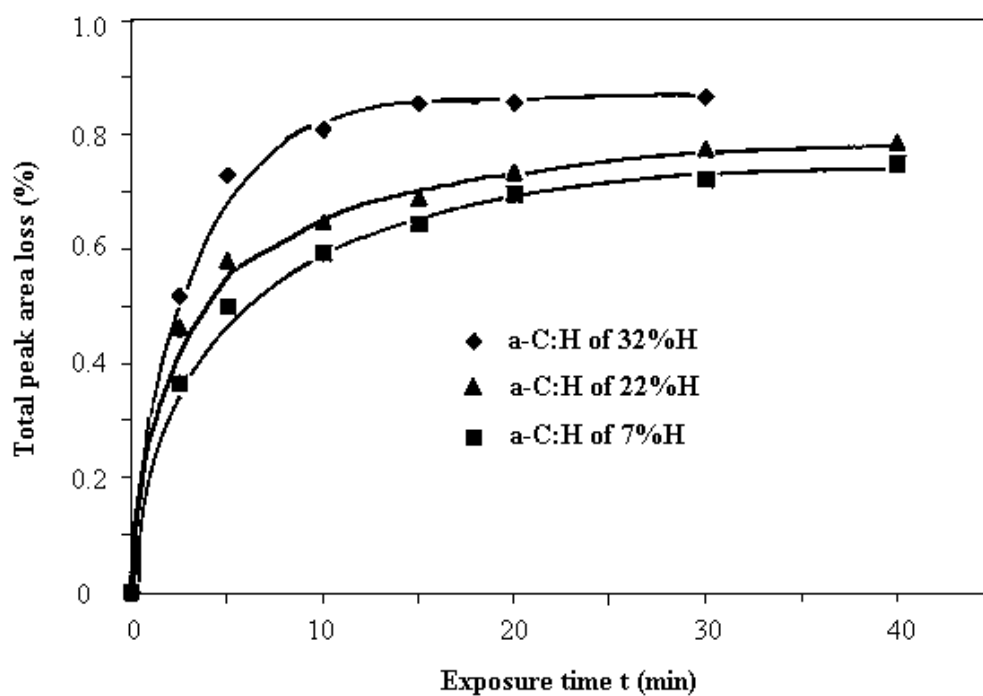


**Figure 1.** Raman spectra of a-C:H films with elapse of laser-irradiation time at  $0.3 \text{ mW } \mu\text{m}^{-2}$ . Curve a pre-irradiated film; b irradiated for 5 min; c irradiated for 15 min; d irradiated for 30 min.

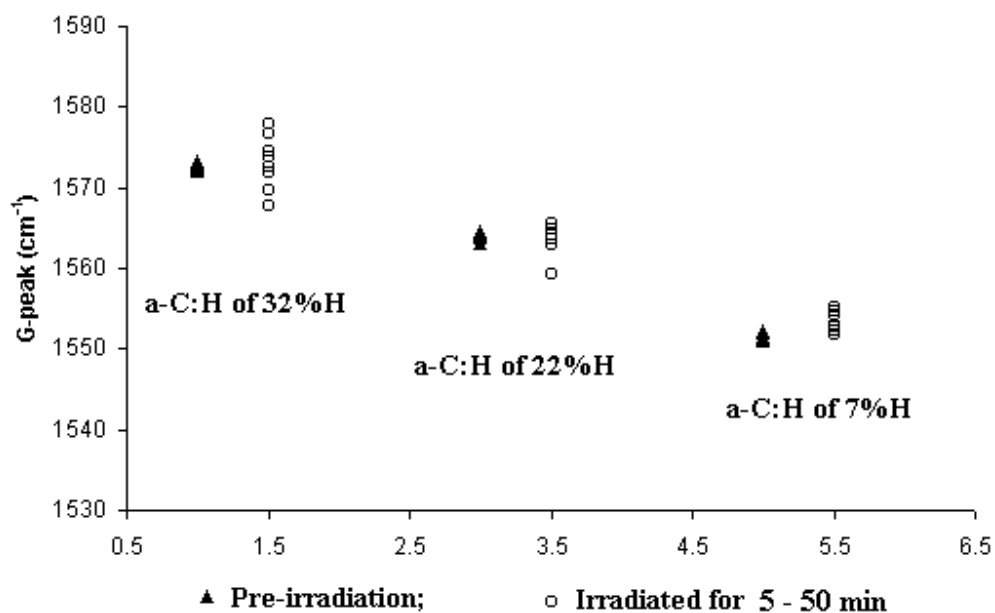
light intensities (figure 1). From literature, a-C structure composed of graphitic nano-crystals embedded in an amorphous matrix, and the thickness of carbon films with uniform properties is proportional to Raman light intensities although the relationship may not be linear [17]. Two characteristic peaks in a Raman spectrum, the G-peak and D-peak, were caused by atomic displacements of the  $E_{2g2}$  mode and the disorder mode of a graphitic structure which belongs to the  $D_{6h}^4$  space group [14]. The decrease of the two peak signals indicates a gradual disappearance of amorphous carbon structure at the laser-irradiating site. This process is further elaborated below. It is noted that in visible Raman measurements, the excitation energy (2.4 eV for 514 nm) corresponds to the vibrational  $\pi-\pi^*$  transition modes of  $sp^2$  sites in the a-C structure.

By using the laser of 3 mW incident power, the Raman light intensities of pre-exposed a-C:H of 32 atm% H (figure 1(c), curve 'a') was much weaker than that of the film with 7 atm% H (figure 1(a), curve 'a'). However, when the incident power was switched to 0.8 mW, the intensity difference of the respective Raman spectra was significantly reduced. This indicates that the 32 atm% H film was much more damaged during the first 30 s of 3 mW laser-irradiation. Hence, in practical usage of Raman technique for hydrogenated carbon, one should adjust the laser power to lower levels. The large luminescence background of the spectra increased with H% in a-C:H, indicating an increased softness of structure [13, 14].

The spectra of figure 1 were curve-fitted and the results are summarized in figures 2 and 3. The loss of Raman light intensities (figure 2) is the result of carbon-film thinning because the intensities are proportional to film thickness in a wide thickness range (0–1000 Å) [17]. Decomposition was considered as the major cause of film thinning under the laser irradiation. The other possibilities may be transient displacement of the film surface in response to optical

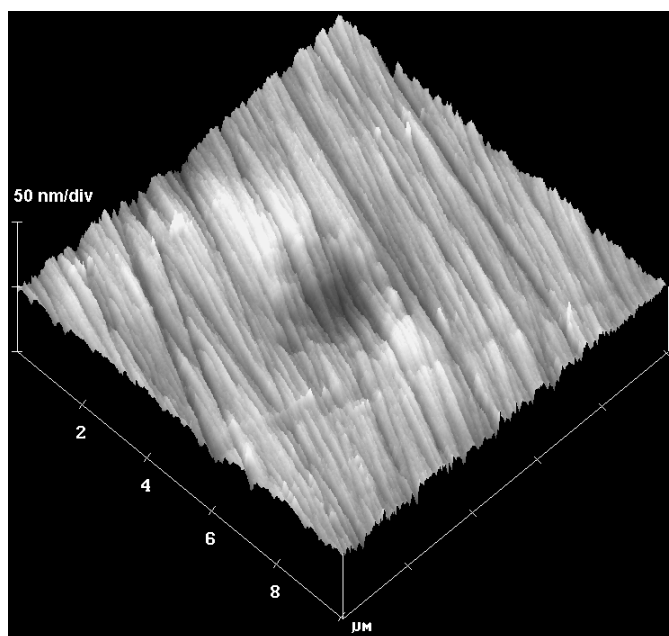


**Figure 2.** Percentage losses of Raman D-peak and G-peak signals for carbon films with elapse of laser-irradiation at a fluence of  $0.3 \text{ mW } \mu\text{m}^{-2}$ .



**Figure 3.** G-peak frequencies of a-C:H films without and with laser-irradiation at  $0.3 \text{ mW } \mu\text{m}^{-2}$ .

heating and the formation of metal carbides by carbon diffusing into Co-alloy substrate. Laser-induced displacement of material surface would result in a permanent buckling and deformation



**Figure 4.** AFM micrograph of a-C:H film with 32%H after Raman-laser irradiation at  $0.3 \text{ mW } \mu\text{m}^{-2}$  for 5 min.

of the sample surface [18]. However, AFM data (figure 4) showed no indication of film displacement. XPS analysis for physically heated a-C:H films excluded the existence of metal carbides. Therefore, the loss of Raman peak intensities was a result of film decomposition. Material decomposition due to laser irradiation is caused by photon–surface interaction which generally produces defects by altering the electronic status of atoms [19]. From figure 2, the loss rate of Raman peak intensities (slope of the tangential line at a particular point) increases in the order of samples containing 7 atm%H, 22 atm%H and 32 atm%H. After  $\sim 30$  min exposure the percentages of G-peak loss were approximately 73, 78 and 87 for a-C:H of 7 atm%H, 22 atm%H, and 32 atm%H, respectively. This indicates that the rate of decomposition is hydrogen sensitive, and the film with lower hydrogen content is more resistant to the laser-induced structural decomposition. From figure 2, the initial rate of decomposition for all the films was high and became much lower after  $\sim 20$  min exposure.

Some explanation for laser-induced solid material decomposition is that the initial interaction of the laser and the solid surface induces electronic transitions that depend on the electronic energy and electronic state of the solid material. When the excited energy is converted into the driving energy for nuclear motion, atoms, ions and molecules can be ejected from the surface. Although the exact mechanism is still in vigorous dispute, heating is generally the primary concern [19]. In this experiment, the wavelength of the laser was 514.5 nm, corresponding to a photo-energy of  $230 \text{ kJ mol}^{-1}$ . For comparison, dissociation energies of some bonds normally seen in a-C:H films are listed in table 1 [20]. Although the exact mechanism of laser-induced a-C film decomposition is still not completely clear, especially for a-C films with different hydrogen concentration, the following points may help us understand the observed phenomena. Higher hydrogen content in the film generally yields softer structure and higher porous fractions entrapping gaseous molecules like  $\text{H}_2$ ,  $\text{CH}_4$  etc in the matrix [1, 11, 13, 14]. The gaseous molecules can easily be released after absorbing

**Table 1.** Bond energies of diatomic structure<sup>a</sup> [20].

Bond	kJ/mol
C–C	607
C–H	338
C–O	1076
C=C <sup>b</sup>	733
C=O	1500

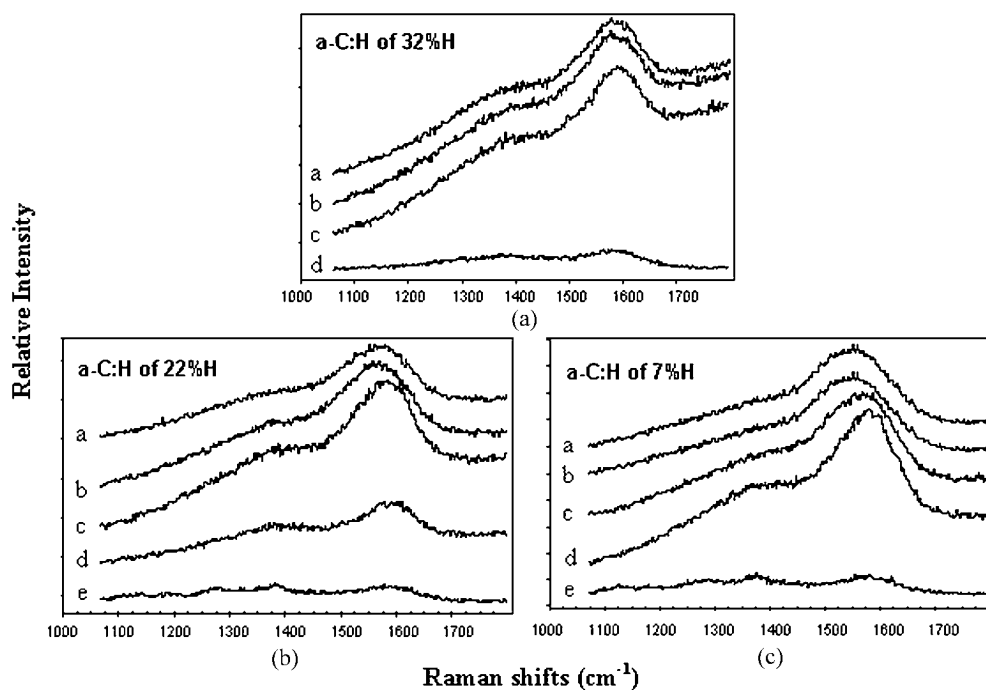
<sup>a</sup> At 298 K.<sup>b</sup> H<sub>2</sub>C=CH<sub>2</sub>.

enough energy during laser-irradiation. This can destabilize film integrity and facilitate film decomposition. Most of the hydrogen loss in a-C:H films under heat could be due to the unbound small gaseous molecules rather than bound hydrogen atoms. However, C–H bonds are generally weaker in a-C films against oxidation as compared to C–C bonds due to their higher dipole moment. They are also more easily dissociated as compared to C=C bonds [1, 20, 21]. All these factors may be the reasons for the increase of decomposition rate with hydrogen concentration in a-C:H films.

Thermal annealing of amorphous carbon films generally causes the film to graphitize. In a Raman spectrum, the graphitization can be seen from the G-peak shifting to a higher frequency, while most likely, the D-peak to a lower one [4, 5, 22]. In this experiment, no clear directional shifting of the Raman peaks was seen for the a-C:H films (figure 3) although the film of 7 atm%H showed a very slight high frequency shifting of the Raman G-peak, which was very small and had a large variation. After the a-C:H film was significantly thinned after laser irradiation, curve-fitting of the Raman spectra could result in large errors. Therefore, the peak parameters should be viewed with suspicious after the films were significantly thinned. This may be the reason for large variations of G-peak frequencies after laser exposure as shown in figure 3. The slight and general upward shifting of the G-peak for a-C:H of 7 atm%H after exposure might indicate a small graphitic transformation from the amorphous structure of the film during laser-irradiation. This G-peak shifting phenomenon was not observed for the other two films.

In the research by Lamberton *et al* [8] using He–Ne and Ar<sup>+</sup> lasers to irradiate a-C:H thin films sputtered on Si, a very similar observation to thermal annealing was seen, i.e., growth of graphitic nano-crystals with irradiation, which resulted in the Raman G-peak shifting to higher frequencies and peak intensity enhancement. These phenomena were not observed in our research. The reason may be the substrate effect. The Co-alloy/NiP that we used can dissipate heat more quickly than Si, and therefore, heat might not accumulate to cause a thermal annealing effect. Moreover, the Co-alloy may have a catalyzing effect on a-C decomposition.

As has been discussed, the intensity reduction of Raman light in laser-irradiation is a result of film decomposition. Since Raman light intensity (peak height or area) was directly related to film thickness, it is possible to correlate Raman light intensities with decomposition mechanism. Two conditions must be satisfied for this consideration, which are: (1) Raman light intensity is linearly proportional to film thickness; (2) the carbon film maintained uniform during laser-irradiation. The first condition is no problem in our study because good linear relationships for a-C:H films within 30 to 200 Å thickness were found in our laboratory. The second condition could also be satisfied. From the above discussion that there was no significant Raman peak shift and a change of their relative intensity ratios during laser-irradiation, the film was generally uniform in the irradiation process. With both conditions met, exponential decrease of Raman light intensities with time may indicate that the decomposition is first order or diffusion controlled. Table 2 lists the most frequently used equations for solid material



**Figure 5.** Raman spectra of a-C:H films heated in air at different temperatures: curve a pre-heat; b 150 °C; c 300 °C; d 320 °C; e 350 °C.

**Table 2.** Kinetic equations for solid-state decomposition [23].

Reaction model	$g(\alpha) = kt^a$
First-order kinetics	$-\ln(1 - \alpha)$
One-dimensional diffusion	$\alpha^2$
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
Two-dimensional phase boundary reaction	$[1 - (1 - \alpha)^{1/2}]$
Random nucleation (Avrami equation)	$[-\ln(1 - \alpha)]^{1/2}$
Random nucleation (Erfeev equation)	$[-\ln(1 - \alpha)]^{1/3}$

<sup>a</sup>  $\alpha$  is the fraction of solid decomposed at time  $t$ , which is represented by the total peak area loss in the Raman spectrum.

decomposition [23]. These equations were applied for the a-C:H decomposition in laser irradiation study. In the calculation,  $\alpha$  was replaced with the total peak (D+G) area loss in Raman spectra. After trying all the equations in table 2, no straight lines could be obtained between  $g(\alpha) \sim t$ , although the first-order equation gives the best match. This indicates that the a-C:H decomposition under laser-irradiation is a complicated process which may be controlled by multiple factors.

The AFM image on the laser-irradiated site in figure 4 revealed ablation of surface material by the laser, which was seen as a circular pit. There is no rising-up edge, indicating that no transient displacement occurred during laser irradiation. The diameter of the exposed area was about 2.5  $\mu\text{m}$ . Grooves and ridges in the picture are due to the texturing lines of the commercial magnetic hard disc.



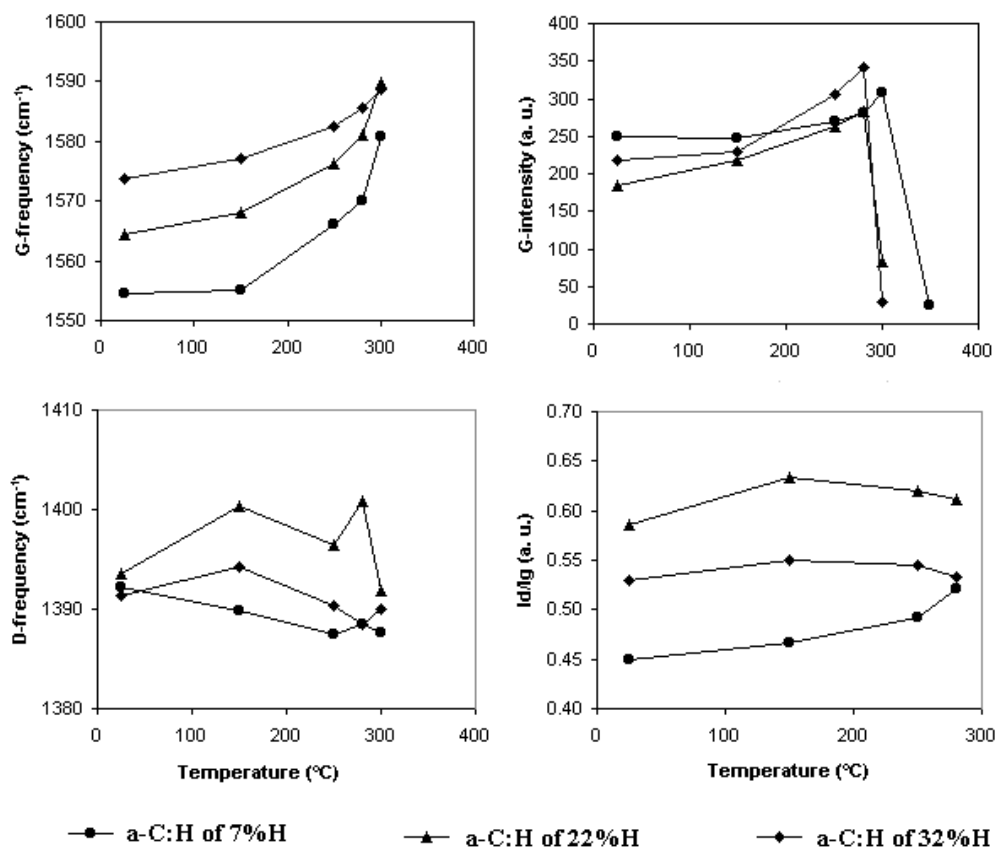
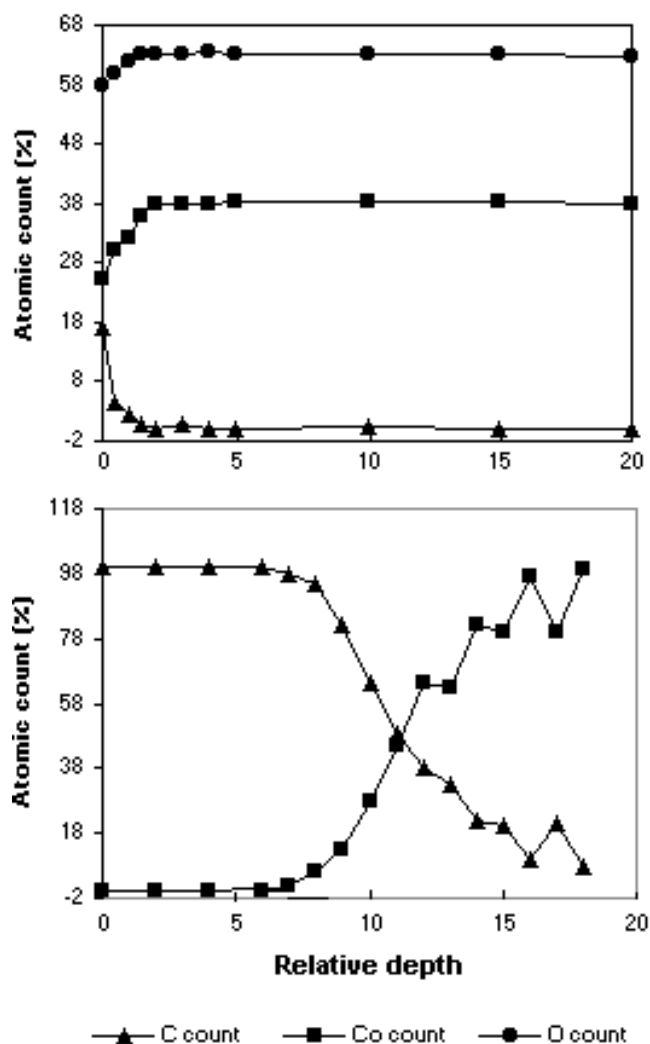


Figure 6. Changes of Raman D-peak and G-peak frequencies and intensities for a-C:H films heated at different temperatures in air.

### 3.2. Decomposition of carbon films due to physical heating

Because heating is the primary concern in the laser-irradiation experiment, it is highly possible that the films show some commonalities between the laser-irradiation effect and the physical heating effect. From the following results, both physical heating and laser-irradiation caused a-C:H decomposition, and the process was hydrogen sensitive, i.e., a-C:H of higher H% was more vulnerable to decomposition. However, different from the observations in laser-irradiation, the films heated in air significantly showed graphitization and crystallization trends. Also, the violent decomposition of the structures took place between 320 °C and 350 °C.

Figure 5 shows Raman spectra of the films captured at different heating temperatures. Figure 6 shows the Raman peak frequencies, G-peak intensities and intensity ratios of the D-peak to the G-peak ( $I_d/I_g$ ) from the spectra in figure 5. From figures 5 and 6, enhancement of the Raman peaks was seen for the films heated between 150 and 250 °C. At 320 °C, the intensities for films of 22 atm%H and 32 atm%H reduced by 70–80%, while the film of 7 atm%H kept almost unchanged.  $I_d/I_g$  generally increased with the heating temperature, which agrees with observations from other authors [22]. At 350 °C in air, the carbon signals of all the films disappeared. From these two figures, it is found that the Raman G-peaks for all the three films are shifted to higher frequencies with heating temperature. On the other hand, the D-peak of the film with 7 atm%H shifted to lower frequencies, but a non-directional



**Figure 7.** XPS depth profile of a-C:H of 7%H. Upper graph: heated at 350 °C for 15 min; Lower graph: virgin.

shifting of the D-peak was seen for the films with 22 atm%H and 32 atm%H. The D-peak usually yielded larger variations as compared to the G-peak. The Raman light enhancement plus the shift of the peak indicate that the carbon films became more graphitic and graphite nano-crystals were formed [22]. The graphitization of carbon films is much more obvious in physical heating in air than that in the laser-irradiation.

The disappearance of the films with 22 atm%H and 32 atm%H at 320 °C and that with 7 atm%H at 350 °C indicates that the structure was decomposed at these temperatures. The decomposition may also cause carbon atoms to diffuse into the magnetic alloy and form carbides. However, XPS depth analysis for a-C:H heated at 350 °C in air does not support the diffusion mechanism. The XPS results are shown in figure 7. The upper graph is the film heated at 350 °C in air while the lower one is the original film. The decomposed products may be small hydrocarbon molecules and/or CO<sub>2</sub> since the operation was in air. The high oxygen count in the heated film was due to oxidized metal components in the substrate.

In a heating process, release of unbonded gaseous molecules may be involved in the initial process; oxidation of the a-C:H films would also occur since the experiment was carried out in air. The disappearance of carbon films of 22 atm%H and 32 atm%H at 320 °C, and of 7 atm%H at 350 °C in air must be due to carbon oxidation because all the structures still showed strong Raman peaks at 350 °C in an N<sub>2</sub> environment. Films of higher hydrogen concentration are vulnerable to oxidation because of the relatively higher amount of C–H bonds.

#### 4. Conclusions

Using an Ar<sup>+</sup> ( $\lambda = 514.5$  nm) laser of  $\sim 3$  mW focusing on a 2.5  $\mu\text{m}$  diameter circular area or a fluence rate of 0.3 mW  $\mu\text{m}^{-2}$ , significant damage of hydrogenated carbon films of 7 atm%H, 22 atm%H and 32 atm%H sputtered on magnetic hard disks by DC-magnetron was observed. Decomposition of the films was seen with consistent reduction of Raman light intensities. The decomposition rate was faster in the early exposure period (about the first 20 min) and became much slower after that. The process could not be explained with frequently used decomposition equations for solid materials, indicating a complicated mechanism associated with the process. The decomposition rate due to laser-irradiation increased obviously with hydrogen concentration in the films. During the laser-irradiation, in general, no structural graphitization was observed although a slight upward shifting of the G-peak was seen for the film of 7 atm%H. In the laser-irradiation study, release of entrapped gaseous species of hydrogen and hydrocarbon as well as decomposition of a-C:H structure were considered to be the dominant processes. Decomposed areas due to laser-irradiation appeared as circular pits in the AFM image.

On physical heating, all the hydrogenated carbon films showed obvious trends of graphitization and crystallization. In air atmosphere, the graphitization was seen from 150 to 300 °C for all the films. At 320 °C and 350 °C for films of 22–32 atm%H and 7 atm%H, respectively, significant and sharp reduction of carbon signals was seen. XPS analysis indicated that the disappearance of carbon signals was due to film decomposition rather than inter-atomic diffusion. The decomposition temperature of films decreased with increasing hydrogen concentration in the structure. In the temperature range where graphitization was observed, film restructuring was predominantly caused by the release of entrapped hydrogen or hydrocarbon molecules, as well as dissociation of chemical bonds. At 320 °C and 350 °C for films of 22–32 atm%H and 7 atm%H, respectively, violent oxidation caused the total decomposition of the films.

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