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Research Article

Raman Spectroscopy of DLC/a-Si Bilayer Film Prepared by Pulsed Filtered Cathodic Arc

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DLC/a-Si bilayer film was deposited on germanium substrate. The a-Si layer, a seed layer, was firstly deposited on the substrate using DC magnetron sputtering and DLC layer was then deposited on the a-Si layer using pulsed filtered cathodic arc method. The bilayer films were deposited with different DLC/a-Si thickness ratios, including 2/2, 2/6, 4/4, 6/2, and 9/6. The effect of DLC/a-Si thickness ratios on the sp^3 content of DLC was analyzed by Raman spectroscopy. The results show that a-Si layer has no effect on the structure of DLC film. Furthermore, the upper shift in G wavenumber and the decrease in I_D/I_G inform that sp^3 content of the film is directly proportional to DLC thickness. The plot modified from the three-stage model informed that the structural characteristics of DLC/a-Si bilayer films are located close to the tetrahedral amorphous carbon. This information may be important for analyzing and developing bilayer protective films for future hard disk drive.

1. Introduction

In current hard disk drive technology, data are written and retrieved by a magnetic recording head, which consists of a magnetic transducer and a sensor, flying over the disk surface at a height of 10 nm or lower. At this tiny space, problems may occur if the recording head contacts with the disk surface during operation. Thus, coating recording head and disk surface with a protective film is highly required as it will minimize the contact force at the head/disk interface. At present, DLC film is becoming a preferred coating for the head and disk surface because of their unique properties of the sp^3 structure that is similar to the physical properties of diamond, such as high density, high wear resistance, low friction coefficient, chemical inertness, and optical transparency [1–6].

DLC film can be prepared by various methods, for example, ion beam assisted deposition [8], sputtering [9], filtered cathodic arc [10], plasma-assisted chemical vapor deposition [11], and pulsed laser deposition [12]. However, different preparation methods may offer DLC film of different forms, such as hydrogenated form of amorphous carbon (a-C:H) and nonhydrogenated form called tetrahedral amorphous carbon (ta-C). Most of the a-C:H form contains sp^3 fractions of less than 50%, while the ta-C can contain sp^3 fractions of up to 85% [13, 14]. Thus, the preferred structure of DLC for being a protective film is the tetrahedral amorphous carbon (ta-C). Liu and Wang [3], and Liu et al. [15] reported the coating of Si layer with a thickness of 1 nm on the substrate as seed layer before coating DLC film. However, the effects of Si layer on the sp^3 content of DLC film were not discussed.

In this work, amorphous silicon (a-Si) layer was initially deposited on germanium (Ge) substrate using direct current (DC) magnetron sputtering. Diamond-like carbon (DLC) layer was then deposited on the a-Si layer using pulsed filter cathodic arc (PFCA). The effects of a-Si layer thickness on the sp^3 content of DLC film were studied by varying the thicknesses of a-Si and DLC layers from 2 to 6 nm and 2 to 9 nm, respectively, depending on the DLC/a-Si thickness ratios, including 2/2, 2/6, 4/4, 6/2, and 9/6. Therefore, the total thicknesses of DLC/a-Si films are 4, 8, 8, 8, and 15 nm, respectively. The sp^3 content of DLC/a-Si films were characterized by Raman spectroscopy and transmission electron microscopy (TEM).

2. Experimental

DLC/a-Si bilayer films were deposited using the pulsed filtered cathodic arc (PFCA) system. The system consists of four vacuum chambers, including (i) load lock chamber, (ii) transfer chamber, (iii) preclean chamber, and (iv) pulsed filtered cathodic arc (PFCA) chamber. Crystalline n-type germanium wafers with (100) orientation, and a dimension of $1 \times 1\,cm^2$ with a thickness of 0.05 cm were used as a substrate. The DLC/a-Si deposition process consists of three steps: (i) the substrate was cleaned with low energy Ar^+ ion plasma etching at an incident angle of 60° with respect to substrate, for 60 sec, (ii) a-Si seed layer was deposited on the Ge substrate at an incident angle of 44° with respect to the substrate, using DC magnetron with a power of 150 W and an argon gas flow rate of 40 sccm, and (iii) DLC layer was deposited at the normal incident angle with respect to the substrate using pulsed filtered cathodic arc (PFCA) with a pulse frequency of 1 Hz, arc voltage of 950 V, and coil voltage of 900 V. The first two steps were carried out in preclean chamber, while the third step was prepared in the PFCA chamber. The film thickness was monitored using *in situ* ellipsometry. Table 1 shows the details of the DLC/a-Si thickness ratios for all DLC/a-Si films.

Thickness of DLC/a-Si film on Ge substrate was investigated using TEM (Tecnai G2 20). It should be noted that before carrying out TEM cross-sectional image, the DLC/a-Si film was coated with Cr layer. This additional layer acts as a protective layer to prevent passivation from ion bombardment during cross-sectional preparation using a focused ion beam (FIB). Raman measurements were performed with a Renishaw inVia Reflex Raman Spectrometer at 514 nm of Ar^+ ion gas laser. The laser output power of 20 mW and 50x objective lens were used, which resulted in an incident power at the sample of approximately 4 mW. The scan range was from 1180 to 1800 cm^{-1}. The raw spectra were fitted using Gaussian profile to obtain smooth curve. Then, the smooth curve was fitted with two Gaussian-Lorentzian functions corresponding to the *G* and *D* band wavenumbers. *G* band is originated from the stretching vibration of any pair of sp^2 sites, whether in C=C chains or in hexagonal rings, while *D* band is the breathing mode of those sp^2 sites only in rings, not in chains [7, 14].

3. Results and Discussion

Cross-sectional morphologies of DLC/a-Si films prepared from different DLC/a-Si thickness ratios (2/2, 2/6, 4/4, 6/2, and 9/6) are similar, but they are different in the thickness of a-Si and DLC layers. Figure 1(a) shows a typical cross-sectional TEM image of the bilayer film prepared from the DLC/a-Si thickness ratio of 9/6 on Ge substrate. There are four regions presented in the image, including Ge substrate, a-Si layer, DLC layer, and Cr layer (a protective layer for preventing passivation from ion bombardment during preparation of cross-sectional film). Two regions according to a-Si and DLC layers are of our interest. The morphology and density of a-Si and DLC layers are slightly different as shown in white and gray and are also seen in Figure 1(b) which is the cropped image of Figure 1(a) after brightness and contrast adjustment.

Table 1: Thickness of DLC and a-Si layers, DLC/a-Si thickness ratio, and total thickness of DLC/a-Si film.

Thickness		DLC/a-Si	Total thickness (nm)
DLC layer (nm)	a-Si layer (nm)	Thickness ratio	
2	2	2/2	4
2	6	2/6	8
4	4	4/4	8
6	2	6/2	8
9	6	9/6	15

Table 2: Information extracted from Raman spectra of DLC/a-Si films prepared from different DLC/a-Si thickness ratios.

DLC/a-Si thickness ratio	Total thickness (nm)	*G* Wavenumber (cm^{-1})	I_D/I_G
2/2	4	1552	1.528
2/6	8	1552	1.507
4/4	8	1557	0.744
6/2	8	1561	0.568
9/6	15	1565	0.453

The structural characteristics of DLC layer prepared from different DLC/a-Si thickness ratios were investigated by Raman spectroscopy. Figure 2 shows Raman spectra of DLC/a-Si films prepared from the DLC/a-Si thickness ratios of 2/2, 2/6, 4/4, 6/2, and 9/6. The spectra exhibit a broad wavenumber ranging from 1200 to 1800 cm^{-1}. This informs the formation of sp^2 and sp^3 contents, which can be used for indicating the structural characteristics of DLC layer [16].

To have further understanding on the structural characteristics of the bilayer film, Raman spectrum of DLC/a-Si film from each thickness ratio was fitted to obtain *G*-band wavenumber and D/G intensity ratio (I_D/I_G) using Gaussian function. The typical fitted spectrum of DLC/a-Si film is shown in Figure 3 which includes graphite (*G*) band, disorder (*D*) band, and fitted spectrum. *G*-band wavenumber and I_D/I_G ratio from the fitted spectra are given in Table 2. For DLC/a-Si ratios of 2/2 and 2/6, where DLC film thickness is 2 nm and a-Si layer thicknesses are 2 and 6 nm, respectively. The *G* band positions for these two ratios are the same with a *G* wavenumber of 1552 cm^{-1}. This result indicates that a-Si layer has no effect on the structure of ta-C film. For DLC/a-Si ratios of 4/4, 6/2, and 9/6, that is the thicknesses of DLC film are 4, 6, and 9 nm, respectively. It is seen from Table 2 that the *G* band position shifts to the higher wavenumber when the thickness of DLC film increases. This result implies that the structure of ta-C film depends only on the thickness of DLC film. The thicker DLC layer in the bilayer film offers higher vibrational energy which comes

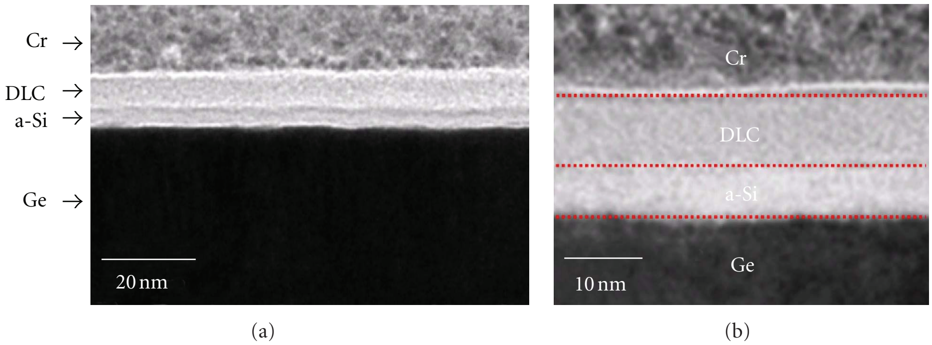

FIGURE 1: (a) Cross-sectional TEM image of the bilayer film prepared from the DLC/a-Si thickness ratio of 9/6. (b) Cropped image from (a) with a brightness and contrast adjustment to provide a clear vision on the cross-sectional morphology of the films.

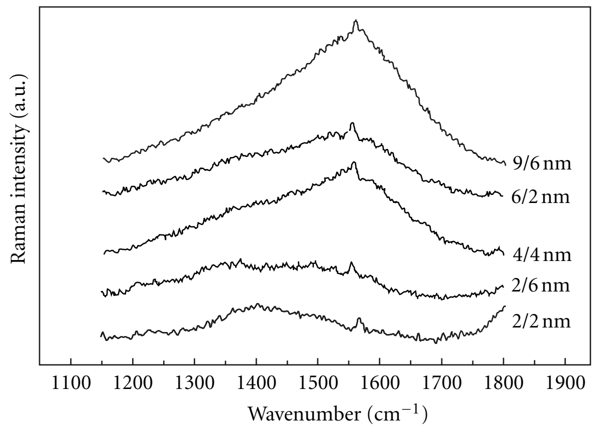

FIGURE 2: Raman spectra of the bilayer films prepared from different DLC/a-Si thickness ratios: 2/2, 2/6, 4/4, 6/2, and 9/6.

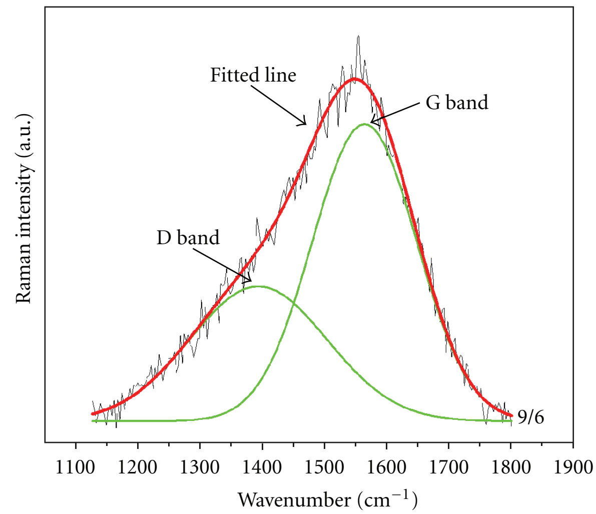

FIGURE 3: Raman spectrum of the bilayer film was fitted into *G* and *D* bands. The film was prepared from the DLC/a-Si thickness ratio of 9/6.

from the change in bond stretching mechanism of any pair of sp^2 sites due to the increase in short C=C chain contents [7, 17] and result in the higher sp^3 contents of ta-C structure [14, 18, 19].

This result is also in agreement with the three-stage model reported by Ferrari and Robertson [7] to analyze Raman spectra of ta-C film. As shown in Figure 4, the relationship between *G*-band wavenumber of DLC/a-Si film and its thickness ratios was plotted. The data analyzed according to the three-stage model inform that *G*-band wavenumber can be used for indicating sp^2 configuration of the material. For example, the *G*-band wavenumbers at 1580, 1600, 1510, and 1570 cm^{-1} indicate the sp^2 site from graphite, nanocrystalline-graphite (NC-graphite), amorphous carbon (a-C), and tetrahedral amorphous carbon (ta-C), respectively. Thus, Figure 4 confirms that the structural characteristics of DLC layers prepared from all types of DLC/a-Si thickness ratio are very close to the tetrahedral amorphous carbon (ta-C) structure since they are located close to the ta-C structure.

To confirm the previous explanation on the sp^3 content, the I_D/I_G ratio which is normally correlated to the sp^3/sp^2 fraction was evaluated. Ideally, the I_D/I_G value for ta-C should be close to zero since the *D* band is the breathing mode of sp^2 sites only in rings, not in chains [7]. The I_D/I_G ratios of DLC/a-Si films are 1.528, 0.568, and 0.453 for the DLC/a-Si thickness ratios of 2/2, 6/2, and 9/6, respectively, as shown in Figure 5. This result indicates that when DLC layer becomes thicker, there are more sp^3 contents. Moreover, from the plot in Figures 4, and 5, it was found that the thickness of a-Si layer has no effect on the DLC formation and the sp^3/sp^2 fraction. However, it may has an important role in the mechanical properties of the DLC film such as adhesion, hardness, and wear resistance which will be necessary for future investigation.

4. Conclusions

DLC/a-Si bilayer films of different DLC/a-Si thickness ratios were deposited on Ge substrates. *G*-band wavenumber shifts to higher value when the thickness of DLC layer increases due to higher sp^3 contents. This is also confirmed by the decrease in I_D/I_G ratio. The plot modified from the three-stage model points out that the structural characteristics of DLC layers

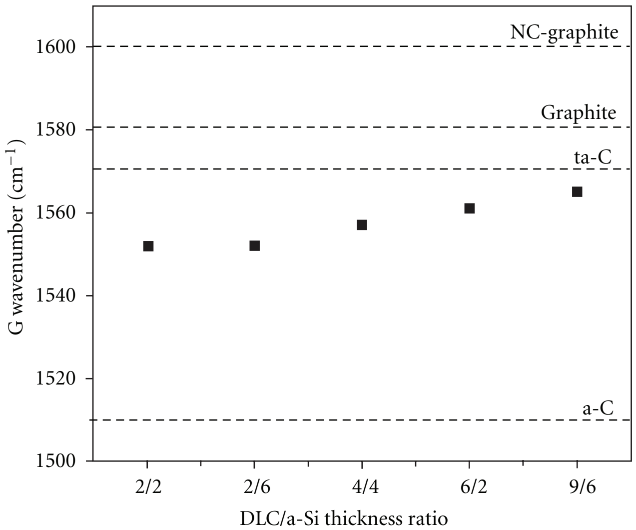

Figure 4: The plot modified from the three-stage model [7] to obtain structural characteristics of DLC in the bilayer film. Four structures are presented: nanocrystalline-graphite (NC-graphite), graphite, amorphous carbon (a-C), and tetrahedral amorphous carbon (ta-C).

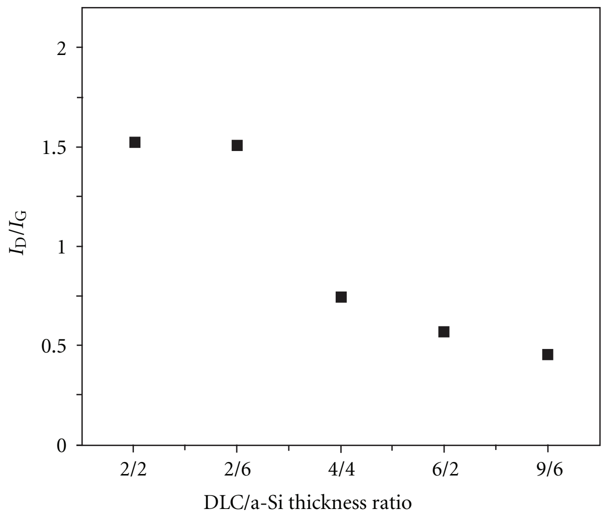

Figure 5: Plot of I_D/I_G ratio of the bilayer film as a function of DLC/a-Si thickness ratio. Decrease in the I_D/I_G ratio represents the increase in sp^3 contents of the films.

prepared from all types of DLC/a-Si thickness ratio are very close to the tetrahedral amorphous carbon (ta-C). Thickness of a-Si layer, a seed layer to improve the adhesion between DLC and substrate, barely affects the DLC formation and the sp^3 bonded. This information can be applied for developing DLC for bi- and multilayer protective coatings in which structural characteristics such as sp^3 content can be analyzed easily from the modified plot.

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