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Diamond-like carbon films deposited at a temperature of 77 K by opposed target sputtering

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Diamond-like carbon films were deposited at liquid nitrogen temperature by an opposed target type dc sputtering system. Films deposited at 77 K have much higher resistivity, higher Vicker's hardness, larger refractive index, and larger optical band gap than those deposited at 300 K, so that these films are attractive protective coating material for high density magnetic recording media. These results seems to be derived from the fact that the films have a much larger density than theose deposited at room temperature. This increase in film density with decrease in substrate temperature is thought to be caused by the suppression of the formation of the graphite structure in the film. The suppression of the migration of carbon atoms on the film surface is effective in increasing sp^3 bonded carbon atoms in the film, which results in a higher density and larger hardness.

1.INTRODUCTION

Diamond-like carbon film is a well- known useful protective coating material[1-4] for high density magnetic recording media [5-7] because it has a very high hardness, low friction coefficient and excellent thermal conductivity. It is also attractive as a new semiconductor material with a wide band gap. J.J.Cuomo *et al.* reported that carbon films deposited at 77 K by ion beam sputtering have a density as high as 2.9 g/cc [8]. It can be expected that films with such a high density have excellent properties as protective coatings for the hard disk in magnetic recording. In this study, diamond-like carbon films were deposited at liquid nitrogen temperature by a opposed target dc sputtering system, and their structure and physical, electrical and optical properties were investigated.

Films deposited at 77 K have much higher resistivity, higher Vicker's hardness, larger refractive index, and larger optical band gap. The results suggest that these films are attractive protective coating material for high density magnetic recording media and that the suppression of the migration of carbon atoms on the film surface is necessary to increase the sp^3 bond in the films which will result in a higher density and larger hardness.

2.EXPERIMENTAL

An opposed target type dc sputtering system shown in Fig.1 was used for the film preparation. Graphite disks of 10 cm diameter were used as the targets. In this system, the substrate holder was directly cooled by liquid nitrogen as shown in the figure. Typical film preparation conditions are listed in Table 1. Films with thickness in the range from 500 Å to 3000 Å were deposited on glass slide and silicon wafer substrates. The substrate temperature was measured with a thermocouple contact with the substrate surface. The sputtering discharge current was fixed at a small value of 0.5 A in order to minimise the increase of substrate temperature during sputtering.

Film structure was investigated by both transmission electron microscope (TEM) and scanning electron microscope (SEM). Laser Raman spectra and the Vicker's hardness of the films were also measured. Optical properties of the film such as optical band gap and refractive index etc. were

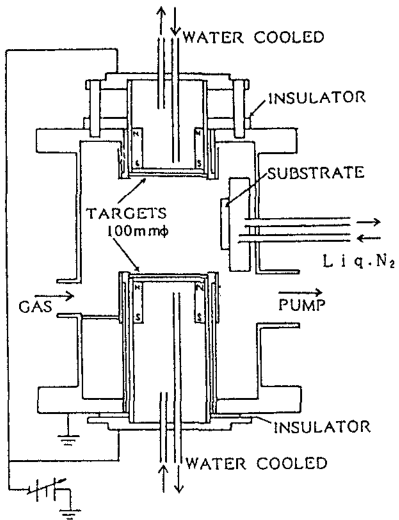

Fig.1 Schematic diagram of the sputtering system used in this work for the film preparation.

Table 1. Film preparation conditions.

Target	Graphite disk (100mm≈)
Sputtering gas pressure	Ar : 2 mTorr
Target voltage	900 V
Discharge current	0.5 A
Substrate temperature	77 K, 320 K
Deposition rate	77 K - - -110 Å/min
	320 K - - -140 Å/min
Film thickness	500 - 2800 Å

measured with both a spectrophotometer and an ellipsometer. Resistivity of the films was measured with a four point probe technique.

3. RESULTS AND DISCUSSIONS

The deposition rate of the film changes significantly with substrate temperature and decreases about 30 % as the substrate temperature decreases from 320 K to 77 K. This decrease suggests that the film deposited at 77 K will have much higher density than the film deposited at 320 K, since a decrease of substrate temperature should not lead to a decrease in sticking probability of the sputtered particles. This result agrees with the results reported by Cuomo et al. [4]. Structure and physical properties of the film also change with substrate temperature, although all of the films obtained in this work have an amorphous crystal structure. Figure 2 shows typical TEM micrographs and electron diffraction patterns of the carbon films deposited at 77 K and 320 K. The film deposited at 77 K has a more uniform and dense structure than the film deposited at 320 K. The SEM micrographs of a cleaved cross section of these films are shown in Fig.3. Differences in the morphology of the cross section is not clearly observed between the films deposited at 77 K and 320 K.

Figure 4 shows the changes in resistivity of films deposited at 77 K and 320 K with film thickness. The resistivity of the film deposited at 77 K is higher by two orders than that of the film deposited at 320 K. This result suggests that the film deposited at 77 K contains much larger amounts of sp^3 bonded atoms than the film deposited at 320 K. In order to confirm this fact, Raman spectra of these films were measured.

Figure 5 shows typical Raman spectra of the films deposited at 77 K and 320 K. Beeman et al. reported that the increase of fourfold coordinated atom

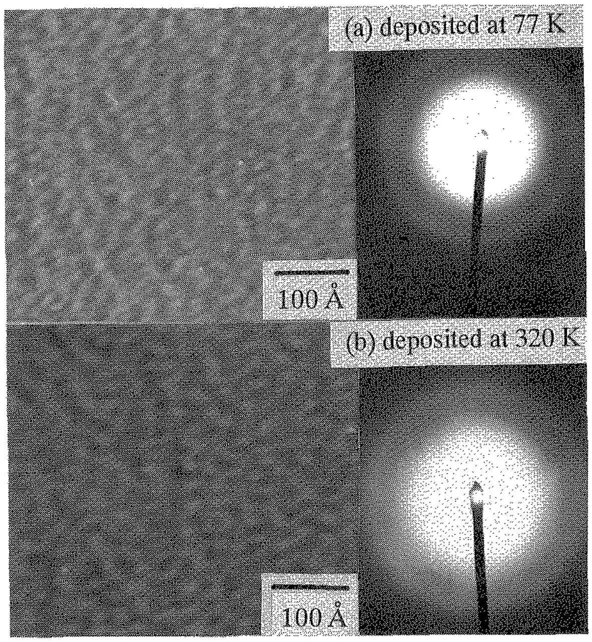

Fig.2 TEM micrographs and electron diffraction patterns of the films deposited at 77 K and 320 K.

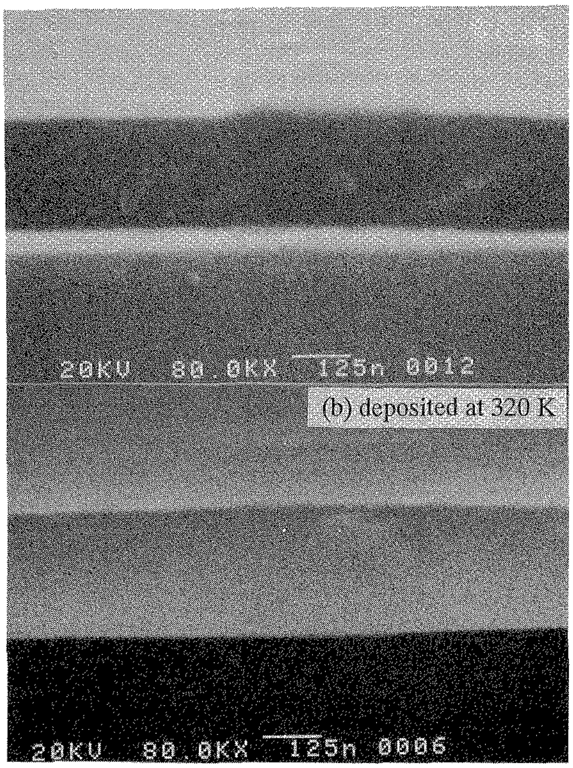

Fig.3 SEM micrographs of the cleaved cross section of the films deposited at 77 K and 320 K.

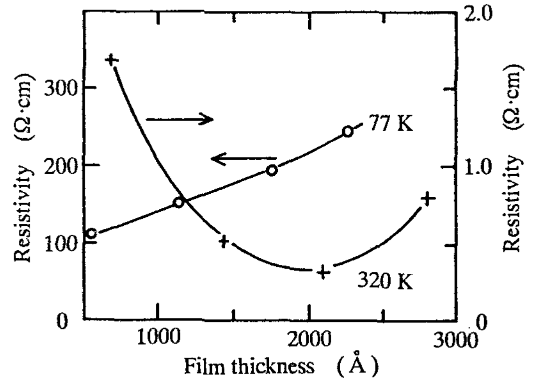

Fig.4 Change in resistivity of films deposited at 77 K and 320 K with film thickness.

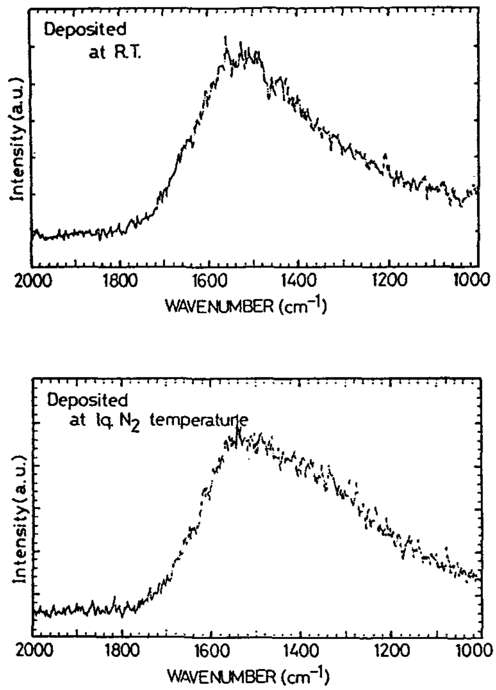

Fig.5 Raman spectra of films deposited at 77 K and 320 K.

leads to a shift of the G peak around 1540 cm^{-1} to a lower frequency [9]. However, the peak shift of the G peak is not observed in the film deposited at 77 K, although the film has a much larger D peak around 1360 cm^{-1} than the film deposited at 320 K, as shown in Fig. 5. We reported that the increase in the intensity of the D peak and a shift of the G peak to a higher wave length is observed in the film

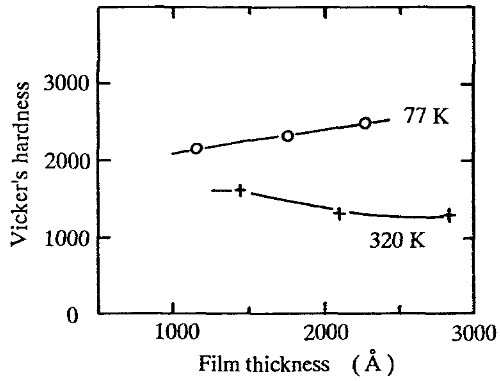

Fig.6 Change in Vicker's hardness of films deposited at 77 K and 320 K with film thickness.

deposited at a higher sputtering gas pressure, which may be caused by the increase of graphitic structure in the film[10]. The increase in gas pressure causes an increase in the amount of sputtered atoms which arrive at the substrate with large incident angles and with decreased kinetic energy. As a result, the increase in gas pressure leads to a formation of films with a lower density which contain larger amounts of threefold atoms.

Figure 6 shows the changes in Vicker's hardness of films deposited on glass slide substrates with film thickness. It is clear from the figure that the film deposited at 77 K has a much larger hardness than the film deposited at 320 K. This may be due to the increase of the amount of sp^3 bonded atoms in the film.

Table 2 shows the typical optical properties of the films deposited at 77 K and 320 K. The refractive index and extinction coefficient is measured by ellipsometric measurement at a wave length of 633 nm. It should be noted that the refractive index n increases remarkably from 2.4 to 2.9 as the substrate temperature decreases from 320 K to 77 K, although the extinction coefficient k depends little on the substrate temperature and has a value about 0.93.

Table 2. Optical properties of the films.

temp.	film thickness	optical band gap	refractive index	extinction coefficient
320 K	1450 Å	0.3 eV	2.4	0.92
	2090 Å	0.3 eV	2.4	0.93
77 K	1150 Å	0.4 eV	2.9	0.93
	1750 Å	0.5 eV	2.9	0.92

This increase in refractive index is thought to be caused by the remarkable increase in the density of the films. Taking the fact that graphite and cubic diamond have a density of about 2.25 g/cc and 3.5 g/cc, respectively, the increase of the fourfold carbon atoms in the film will lead to an increase of its density.

The optical band gap was estimated from the $(h\nu\,\alpha)^{1/2}$ vs. $h\nu$ plot as shown in Fig.7, where, α is the absorption coefficient and $h\nu$ is the photon energy. The optical band gap of the film increases from 0.3 to 0.5 eV as the substrate temperature decreases from 320 K to 77K. This may also be caused by the increase of sp^3 bonded atoms in the film, which is coincident with the results shown for the resistivity and hardness of the film.

The above film properties are summarized as follows; by comparison with the properties of the films deposited at 320 K, the film deposited at 77 K has higher density, higher resistivity, higher hardness, larger refractive index and larger optical band gap.

The increase in film density on decreasing the substrate temperature is thought to be caused by the suppression of the migration of sputtered atoms on the film surface, which leads to the formation of less graphitic carbon films. Therefore, the suppression of the migration of carbon atoms on the film surface by decreasing the substrate temperature is necessary to obtain carbon films with higher density and larger hardness. These carbon films with a large hardness deposited at a low temperature are an attractive protective coating material for high density magnetic recording media.

4.CONCLUSIONS

Diamond-like carbon films were deposited at liquid nitrogen temperature by an opposed target type dc sputtering system. The films deposited at 77 K have much higher resistivity, higher Vicker's hardness, larger refractive index, and larger optical band gap than those deposited at 300 K. These results seems to be derived from the fact that the film has a much larger density and contains much larger amount of sp^3 bonded carbon atoms than the film deposited at room temperature.

These results indicate that the suppression of the migration of sputtered atoms on the film surface is very important to suppress the formation of the sp^2 bond in the films which leads to a graphitic structure.

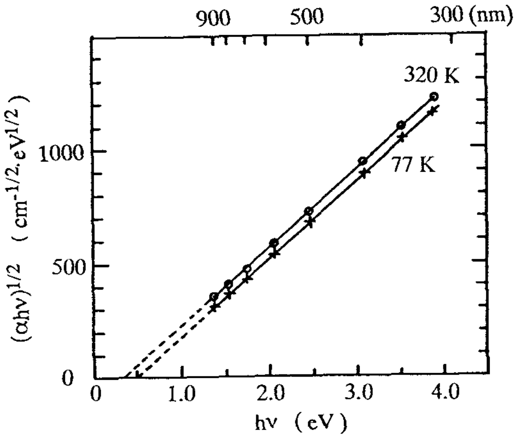

Fig.7 $(h\nu\,\alpha)^{1/2}$ vs. $h\nu$ plot, where, α is absorption coefficient and $h\nu$ is photon energy.

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