Large area deposition of hydrogenated amorphous carbon films for optical storage disks

F. Piazza[a],*, D. Grambole[b], L. Zhou[c], F. Talke[c], C. Casiraghi[a], A.C. Ferrari[a], J. Robertson[a]

[a]*Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, UK*
[b]*Forschungszentrum Rossendorf, Institut für Ionenstrahlphysik und Materialforschung, Dresden, Germany*
[c]*Center for Magnetic Recording Research, University of California, San Diego, CA 92093, USA*

Abstract

Homogenous wear resistant carbon coatings with an optical gap of 3 eV but low stress are needed to increase the storage density in optical storage disks in order to reach 100 GB in 12-cm diameter disks. Here, hydrogenated amorphous carbon (a-C:H) films are deposited at room temperature using a large area electron cyclotron wave resonance plasma beam source of 14.2-inch diameter. Methane is used as the precursor. The ion flux and energy, plasma pressure, distance between the extraction grid and the substrate were varied. The films are characterized in terms of hydrogen content, stress, optical gap, refractive index, wear resistance, surface roughness and homogeneity by a variety of characterization techniques. Resonant Raman spectroscopy is used in order to non-destructively monitor the disk quality. We show how it is possible to produce homogenous, wear resistant a-C:H coatings with an optical gap of 3 eV and low stress (<500 MPa), without damaging the plastic disks.
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1. Introduction

Optical storage is the preferred technology when high-density storage on removable and exchangeable media is required. The advantages are its low cost, media exchangeability (standardization) and robustness. Over the past 20 years, the storage capacity in optical recording has been increased by increasing the numerical aperture of the focussing optics and decreasing the laser wavelength. The new generation of optical storage devices will have approximately 20-fold higher capacity than digital versatile disk, or approximately 100 GB per 12-cm diameter compact disk (CD). One approach to meet the demand for high data capacity of optical disks is the use of flying head technology, which is the method used in magnetic storage. The key feature to differentiate the new generation from the previous ones will be the very small free working separation (between 50 nm and 5 μm) between the objective lens or magnetic modulation device and the storage disk. The straightfor-

ward way to achieve such a small separation is to mount the lens or magnetic device on a slider, which flies above the spinning disk at a constant height on a hydrodynamic air bearing, without needing a complicated servo system [1]. In those conditions, a wear resistant layer is needed to protect the disk and slider from head crash. Magnetic disks use amorphous carbon as protective coatings [2–5]. They are used because they make extremely smooth, continuous and chemically inert films, with a surface roughness below 1 nm. They provide protection against corrosion and against mechanical wear and damage during head crashes. Their surfaces are compatible with the lubricant. However, carbon coatings for magnetic storage disks do not need to transmit light.

For optical storage, the carbon films must be transparent at the recording wavelength. The stress must be minimized as it can affect the magneto-optic response of the recording layers. This can be a significant problem for hydrogenated amorphous carbon (a-C:H) as its band gap is maximum and the stress is minimum for soft films [6]. It is possible to obtain harder films by increasing the C–C sp³ fraction. The hardness has been

*Corresponding author. Tel.: +44-1223-764138; fax: +44-1223-332662.

E-mail address: fp221@eng.cam.ac.uk (F. Piazza).

found to increase with the sp^3 fraction [7]. One problem is that a strong correlation between stress and sp^3 fraction in diamond-like carbon is usually observed [6–8]. Films with high sp^3 generally have also high stress [6–8], even though high stress is not necessary to have high sp^3 films [9]. Hence, it can be difficult to prepare a hard, stress-free film.

Another problem is that, although it is known that the π states introduced by the sp^2-carbon determine the gap, the relationship between the structure, gap and stress is quite complicated. On one hand, the optical gap generally decreases linearly with the increase of the sp^2 fraction in as-deposited plasma enhanced chemical vapor deposition a-C:H films [6,7]. On the other hand, the gap actually depends on the precise arrangements of the sp^2 sites, such as their clustering and orientation, not just the sp^2 fraction [10–12]. In practice, most of these features tend to reduce the band gap rather than increase it. This is what happens when films are annealed at high temperature or subjected to high ion bombardment during the growth [10]. In some a-C:H films the gap has been shown to shrink with the increase of the stress and sp^3 fraction [13]. This was attributed to the distortions of sp^2 rings and chains induced by the stress and disorder [13]. One of the few methods to increase the band gap is to introduce more hydrogen during deposition, for example, by using a hydrogen-rich gas such as methane [8], but this may soften the films [8]. The challenge is thus to produce relatively hard films with low stress and wide band gap (of at least 3 eV, corresponding to the recording laser wavelength of 400 nm).

In addition, the energy flux during the growth onto plastic substrates of low thermal conductivity must be controlled in order to prevent over-heating and preserve the substrate integrity. This is another significant problem since it has been shown that, for a given ion energy, the diamond-like character increases with the ion flux [14,15] and is optimized when the ion energy is close to 100 eV [6].

In this work, electron cyclotron wave resonance (ECWR) plasma beam source is used to produce large area homogenous, wear resistant a-C:H coatings with an optical gap of 3 eV and low stress (<500 MPa), without damaging the plastic disks.

2. Experimental

a-C:H films were grown on ⟨1 0 0⟩ silicon, quartz and poly-carbonate CD substrates using a ECWR plasma beam source of 14.2-inch diameter. This is much bigger than the 6.6-inch source used in previous studies [7,16–19]. The source comprises a single-turn inductively coupled RF (13.56 MHz) discharge with a superimposed static transverse magnetic field. A grounded tungsten extraction grid is included [16,17]. The principle of the

ECWR has been previously described in detail [16,17]. At resonance there is a strong absorption of energy by the electrons in the plasma as the rotation of the electric field vector of the right-hand polarised wave coincides with the gyration direction of the plasma electrons [16]. Hence, the plasma is heated very efficiently. Combined with a reduction in electron losses to the walls through electron cyclotron motion around the magnetic field lines, this resonance energy transfer enables high plasma densities to be achieved even for excitation frequencies of 13.56 MHz (plasma density $n_e \sim 10^{11}$–10^{12} cm^{-3} compared with 10^9 cm^{-3} for conventional RF based plasma processing discharges). Consequently, highly ionised plasmas may be produced at both low operating powers and pressures. The source provides a high dissociation degree (up to 80% for N_2 plasma) and ion current density between 0.05 and 3 mA cm^{-2}. At low working pressure (<0.05 Pa) the ion energy distribution is near Gaussian in shape with a width $\Delta E/E \leqslant 5\%$. The source enables an independent control of the ion current and ion energy. The presence of the grounded extraction grid allows some capacitive as well as inductive coupling of the plasma. Consequently, the ion energy could be controlled by varying the extent of capacitive coupling within the source as this determines the RF induced DC bias of the electrode relative to the ground [17].

Methane was used as precursor. Previous studies using smaller sources found that when C_2H_2 is used as feed gas, the stress σ is relatively high: σ > 5 GPa [17]. In addition, the optical gap E_T (Tauc gap) is relatively low: $E_T < 2.1$ eV. However, when CH_4 is used as precursor, the stress varies from 2.2 to 5 GPa depending of the ion energy [18,19]. The lower stress films have higher hydrogen content (between 50 and 32 at.% compared to 30 at.% using C_2H_2) and smaller sp^3-carbon fraction (0.58 compared to 0.75). In the case of the films deposited using CH_4 as precursor, the optical gap was not reported [18,19].

The ion flux (ϕ_+) and energy (E), plasma pressure (P), gas flow (F), distance between the extraction grid and substrate (d) were varied. The ion flux and energy were monitored using a Faraday cup mounted in the substrate plane. The films were deposited at ion energies between 20 and 75 eV and at ion flux between 0.72×10^{15} and 2×10^{15} ions cm^{-2} s^{-1}. The distance between the extraction grid and substrate was varied between 7 and 30 cm. The gas flow and plasma pressure were varied from 30 to 100 sccm and from 1.8×10^{-3} to 8.4×10^{-3} mbar, respectively. The RF power was fixed at 300 W. The coil voltage and current were 16 V and 1.1 A, respectively. The magnetic field strength B was of 13 G.

The films were characterized in terms of their structural, mechanical and optical properties. The film thickness and index of refraction were determined by
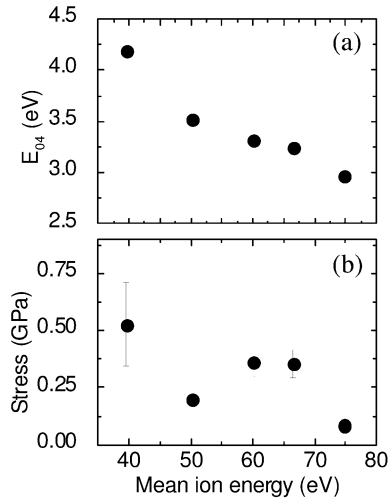
Fig. 1. Optical gap E_{04} (A) and stress (B) as a function of the mean ion energy ($P=1.8\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $d=20$ cm).

ellipsometry using a Gaertner Scientific L117 ellipsometer. The optical properties were investigated by optical absorption spectroscopy using an ATI Unicam UV2-200 UV–Vis spectrophotometer over the 200–1100 nm wavelength range. For these measurements films were deposited on quartz, and both transmittance and reflectance spectra were recorded. The absorption coefficient was calculated and the optical gap E_{04} determined.

The stress was estimated from the Si substrate radius of curvature measured both before and after deposition using a Tencor Alpha-step 200 profilometer. A series of six measurements along two perpendicular directions in the middle of the sample were performed. The stress was then estimated using the Stoney's equation [20].

The hydrogen content was determined from nuclear reaction analysis using the resonance at 6.385 MeV of the reaction: $^{15}N + ^1H \rightarrow ^{12}C + ^4He + \gamma$. The effect of the hydrogen out-diffusion occurring during the bombardment with nitrogen ions was taken into account.

Unpolarised Raman spectra were acquired at 244 and 514.5 nm using two different spectrometers. They were collected using two Renishaw micro-Raman 1000 systems optimized for visible and UV excitation measurements. UV Raman measurements are prone to damage hydrogenated samples. In order to avoid damage the power on the sample was kept well below 1 mW. The spectra were collected by varying acquisition times (between 15 and 60 s) spinning the samples at a high speed (>3000 rpm). This ensured no visible damage and no change of the spectral shape during the measurements.

Contact start/stop tests (CSS) were performed on carbon-coated CDs. Pico-sliders with a flying height of 15 nm (at 4200 rpm) were used. The nominal load of

these sliders was of 25 mN. The maximum disk velocity during the CSS tests was of 1000 rpm, i.e. the slider was not flying, but dragging on the disk surface. Ten CSS cycles were performed in each test.

The surface topography was investigated using a Nanoscope III, Digital Instrument atomic force microscope operated in air in tapping mode. The AFM tips are made from etched silicon with resonance frequency of 254–390 kHz and cantilever length of 160 μm.

3. Results and discussion

3.1. Optical gap and stress

Fig. 1a and b show the evolution of the optical gap E_{04} and stress as a function of the mean ion energy using the ECWR source in standard conditions: $P=1.8\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $d=20$ cm. The ion flux decreases gradually from 1.85×10^{-15} to 0.72×10^{-15} ions cm^{-2} s^{-1} when the ion energy is varied from 40 to 75 eV. The thickness of the films was constant at ~70 nm. Fig. 1a shows that E_{04} decreases from 4.18 to 2.96 eV when the ion energy varies from 40 to 75 eV. The stress (~250 MPa, Fig. 1b) is much lower compared to previously reported values and shows no increase for increasing ion energy. No buckling, cracks or blur effects were observed on the coatings deposited onto disks.

3.2. Structure

Fig. 2 shows the evolution of the hydrogen content and deposition rate with mean ion energy for films deposited under standard conditions. The hydrogen content in the films is relatively high, >40 at.%. This can be explained by the relatively low ion energy and flux values of the 14.2-inch source [16–19]. The hydrogen content slightly decreases from ~46 to 41 at.% when the ion energy increases from 40 to 75 eV. This parallels the decrease in the gap reported in Fig. 1. Fig. 2 shows
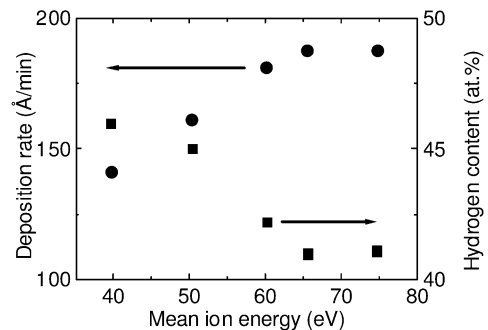

Fig. 2. Deposition rate (circles) and hydrogen content (squares) as a function of the mean ion energy ($P=1.8\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $d=20$ cm).
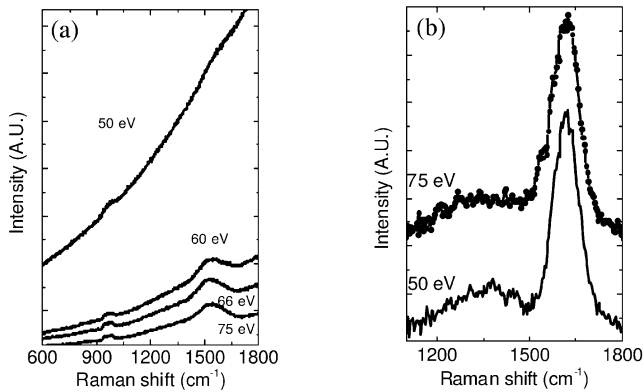
Fig. 3. Evolution of the visible (a) and UV (b) Raman spectra as a function of the mean ion energy ($P = 1.8 \times 10^{-3}$ mbar, $F = 30$ sccm, $P_{RF} = 300$ W, $d = 20$ cm).

Fig. 4. Evolution of the stiction as a function of the CSS cycle for films deposited on CDs ($P_{RF} = 300$ W, $d = 20$ cm).

that the deposition rate increases from ∼14 to 19 nm min^{-1} with increasing ion energy. This is consistent with the relatively high values of the hydrogen content and its slight decrease, since hydrogen incorporation and the deposition rate were found to be inversely correlated [21].

Fig. 3a and b show the evolution of the visible and UV Raman spectra with ion energy. The visible Raman peaks are masked by the luminescence background when the ion energy $E \leqslant 50$ eV. This is typical of polymeric films [10,22] and is consistent with the high hydrogen content and optical gap values. Fig. 3a shows that when the ion energy is further increased, the relative intensity of the luminescence background decreases. This agrees with the simultaneous decrease of the hydrogen content and optical gap and the observation that the luminescence background generally increases exponentially with hydrogen content [6,23].

The UV Raman spectra show that a clear dip at approximately 1500 cm^{-1} between the D and G peaks is visible for films deposited at low ion energy and this tends to disappear when the ion energy is increased, Fig. 3b. It has been shown that a dip at ∼1500 cm^{-1} is a typical fingerprint of polymeric a-C:H. It does not appear in ta-C:H or diamond-like a-C:H [22,24]. The Raman data thus show that polymeric films grown at low ion energy tend to become more diamond-like when the ion energy is increased. This is consistent with the decrease of the hydrogen content and optical gap.

3.3. Wear resistance

Fig. 4 shows the evolution of the stiction coefficient as a function of the CSS cycle for films deposited on CDs ($P_{RF} = 300$ W, $d = 20$ cm). The stiction coefficient or static friction is the maximum friction force just before the relative movement of the two surfaces. It is usually much higher than kinetic friction. It is the force
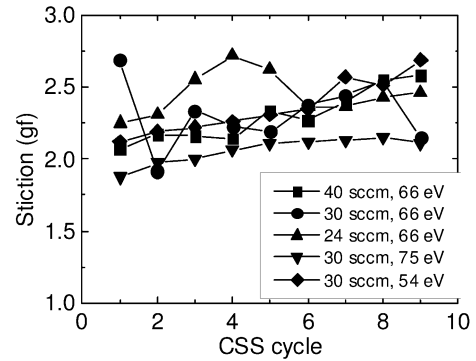
that needs to be overcome to start the movement. In Fig. 4 the stiction is expressed in gram force (gf). No wear track was observed after tests. Fig. 4 shows that the stiction value are low. The best wear resistance is obtained for films grown using the highest ion energy of 75 eV. This is consistent with previous studies since it has been shown that the diamond-like character increases with the ion energy [7]. The diamond-like character is thus expected to increase further if the ion energy is further increased. However, contrary to previous studies, we do not observe any stress increase with ion energy, Fig. 1b. A further ion energy increase might thus lead to better mechanical properties without a further stress increase but, according to Fig. 1a this may lead to an optical gap decrease below the minim threshold of 3 eV required for next generation optical storage disks. However, since our target is to let the blue laser line go through the carbon coating, what really matters is the film transmittance rather than its optical gap. One way to increase the transmittance for a lower gap is to decrease the film thickness. Fig. 5 shows the evolution of the transmittance at 400 nm as a function of the thickness for the films grown at high ion energy. It shows that the transmittance increases significantly when
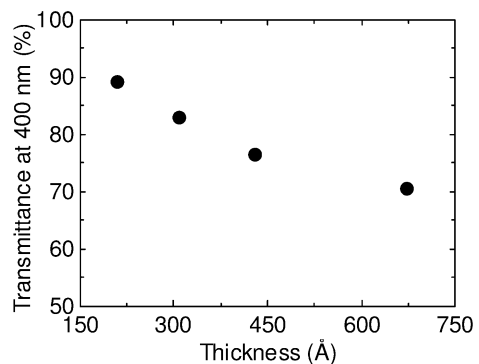

Fig. 5. Transmittance at 400 nm as a function of the thickness ($P = 1.8 \times 10^{-3}$ mbar, $F = 30$ sccm, $P_{RF} = 300$ W, $E = 75$ eV, $d = 21$ cm).
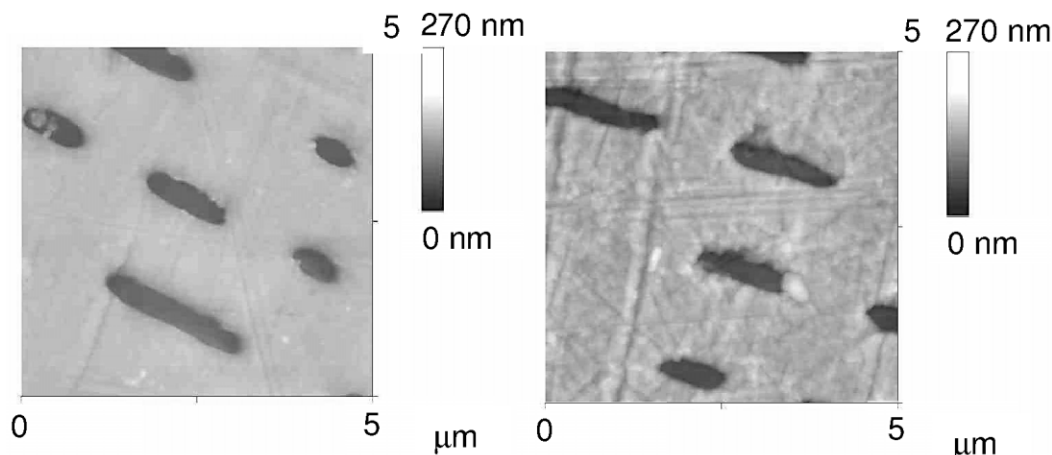
Fig. 6. AFM pictures of the surface of a CD before (A) and after (B) deposition of a carbon overcoat ($P=2\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $E=75$ eV, $d=7.4$ cm). The darker regions are the data storage grooves.

the thickness decreases, as we expect from the Lambert's law. For the film in Fig. 5 it increases from ~76.6 to 89.3% when the thickness is decreased from 43 to 21 nm.

3.4. Homogeneity

The evolution of the ion current density as a function of the distance from the center of the source has been studied for a N_2 plasma. N_2 was selected to avoid the deposition of a carbon coating on the Faraday cup. The ion current density varies by $\pm9\%$ across a 50-mm diameter for $d=20$ cm. This could lead to slight film in-homogeneity. The distance d was changed to reduce this variation.

Faraday cup measurements showed that the ion flux increases significantly from 0.60×10^{15} to 2.06×10^{15} ions cm^{-2} s^{-1} when d is decreased from 30 to 4 cm in a N_2 plasma ($P=7.3\times10^{-4}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $25<E<30$ eV). For a given ion energy, a change in the ion flux could cause a variation in structure [14,15,21].

The evolution of the film thickness over 12 cm as a function of d ($P=1.8\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $E=65$ eV) was studied. The thickness variation is found to be between ±9 and $\pm16\%$ over 12 cm. The corresponding refractive index change is 1.7–5.5%. This shows that radial thickness in-homogeneity does not correspond to a significant structural in-homogeneity.

The evolution of the optical gap E_{04} and index of refraction n as a function of d ($P=1.8\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $E=65$ eV) and the corresponding evolution of the stress show that the reduction of d to 13 cm does not cause a drastic change in optical gap, n and stress. The optical gap stays at 3.2 eV and the stress at ~250 MPa. n shows a $\sim5\%$ change. Visible and UV Raman spectra do not point to any

significant structural change. The hydrogen content remains nearly constant.

The root mean square surface roughness of films deposited on silicon does not vary significantly with d in the present experimental conditions, being ~0.14 nm.

The decrease of d leads to an increase in the deposition rate. The deposition rate increases from 15 to 24 nm min^{-1} when the distance d is reduced from 30 to 7 cm.

3.5. Effect of the ion bombardment on the disk morphology

The morphology of the CD was observed before and after deposition to detect any possible damages induced by the ion bombardment. No melting of the disk and no blur effects were observed. AFM was used to study the variation of the CD roughness (as opposite to the pure carbon overcoat roughness, which was measured on Si substrates to decouple the influence of the rougher plastic substrate, see Section 3.4). The AFM pictures and roughness analysis (Fig. 6) show that the CD roughness in the data storage grooves remains constant. The RMS surface roughness variation is <0.2 nm ($P=2\times10^{-3}$ mbar, $F=30$ sccm, $P_{RF}=300$ W, $E=75$ eV, $d=7.4$ cm). Outside the grooves the RMS surface roughness varies from ~4.21 to 7 nm, but this is within the range of roughness measured in bare plastic CD substrates in different positions. We can thus safely assert that the ion bombardment does not induce a dramatic increase in the roughness in the experimental conditions used.

4. Conclusions

We reported the deposition of a-C:H films for next

generation high storage density optical disks. The films show a suitable wear resistance, low stiction, an optical gap of 3 eV, very low stress values ($\ll 500$ MPa). The films can be deposited at a deposition rate of up to ~ 24 nm min^{-1} with $<9\%$ thickness variation over 12 cm and negligible structural variations. The ion bombardment during the growth does not damage the plastic disk.

Acknowledgments

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