X-RAY REFLECTIVITY OF ULTRA-THIN DIAMOND-LIKE CARBON FILMS

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ABSTRACT

Grazing incidence x-ray reflectivity has been employed to investigate ultra-thin films of tetrahedral amorphous carbon (ta-C) grown with an S-bend filtered cathodic vacuum arc. The results indicate that x-ray reflectivity can be used as a metrological tool for thickness measurements on films as thin as 0.5 nm, which is lower than the range required for carbon overcoats for magnetic hard disks and sliders if they are to reach storage densities of 100 Gbits/in^2. The density of the films was derived from the best-fit to simulated reflectivity profiles from models for the structural parameters. In such thin films, the x-rays are reflected mainly at the film substrate interface, rather than the outer surface, so that the film density is derived from analysis of the oscillations of the post-critical angle reflectivity.

INTRODUCTION

Hard amorphous diamond-like carbon (DLC) coatings exhibit mechanical, thermal and optical properties close to those of diamond. They can be deposited over a wide range of thickness by different deposition processes, on a variety of substrates at or near room temperature. This versatility, combined with high hardness, good wear and corrosion resistance properties has resulted in their extensive use as ultra-thin overcoats for magnetic media.

In the past, electron energy loss spectroscopy (EELS) has been used to obtain the sp^3 content (from the size of the π^* peak in the carbon K edge absorption spectrum), and the mass density (deduced from the valence plasmon energy in the low energy loss spectrum). However, this analysis is dependent on choice of an electron effective mass and there has been extensive argument in the literature as to the correct value [1-3]. Grazing incidence x-ray reflectivity measurements permit the near surface mass density to be determined independently of the plasmon energy [4]. We have recently shown that the combination of electron energy loss spectroscopy and grazing incidence reflectivity resulted in the identification of a unique effective mass for all amorphous carbons and diamond to be used to convert the plasmon energy in mass density [5]. The correct general relation between density and coordination for carbons could then be determined [5].

In Ref. [5] we also showed, from the grazing incidence x-ray reflectivity data, that layering was not intrinsic to DLC films, but a function of deposition conditions. Most of the data were from films typically 20-100nm thick. As the thickness of films for application in magnetic recording media is typically only a few nanometers, we have examined the limits to the sensitivity of the x-ray technique for thickness and density measurement. In this paper we show that the technique is capable of being used as a metrological tool for nanometer thick DLC films. In such thin films, the x-rays are reflected mainly at the film substrate interface, rather than the

outer surface, so that the film density is derived from analysis of the oscillations of the post-critical angle reflectivity.

SAMPLE PREPARATION

The ta-C films were deposited using a Filtered Cathodic Vacuum Arc (FCVA) with an integrated off plane double bend (S-Bend) magnetic filter. The deposition chamber was evacuated to 1×10^{-8} Torr using a turbo molecular pump. Ta-C films with particle area coverage of less than 0.01% and uniform cross section are consistently deposited using this system [5,6]. A series of films was grown for increasing deposition times of 6,10 and 20 seconds defocusing the beam in order to achieve a small deposition rate and so to produce ultra-thin samples in a more controlled way. Another sample was grown for 15 seconds, but in this case the plasma was not stable and thus the effective deposition time was lower.

EXPERIMENTAL TECHNIQUE

Specular x-ray reflectivity measurements were made with a Bede GXR1 reflectometer using CuK$_\beta$ radiation (λ=1.3926 Å). In all cases, the forward diffuse scatter was measured by recording a coupled θ-2θ (specimen-detector) scan with the specimen offset by -0.1° from the specular condition. The intensity in this scan was subtracted form the measured specular scatter to obtain the true specular scatter. These data were automatically fitted, with little constraint on the available parameters, to the scatter simulated from model structures using the Bede REFS-MERCURY code [7]. The program uses a genetic algorithm to avoid trapping in local minima in searching for the least absolute logarithm of the difference between experiment and the simulation. The simulation is based on the fractal model developed by Sinha et al. [8] and extended by Wormington et al. [9].

RESULTS

Even for the shortest deposition time, a distinct difference could be detected between the reflectivity profiles from the bare silicon substrate and those wafers on which carbon films had been deposited. Fig. 1 shows the reflectivity curves multiplied by the fourth power of the incidence angle. This method of data presentation enhances the visibility of low contrast fringes. For a perfectly smooth surface and in the absence of noise, beyond about twice the critical angle, such a plot is parallel to the x axis. As the deposition time increases, there is a displacement of the broad fringe towards smaller angle, consistent with increasing thickness of the ta-C film. For the longest deposition time, a second fringe becomes visible as the period decreases. There is no doubt that a film is present following only 6 seconds deposition.

The critical angle is defined by the spike in the plot (at about 700 arc seconds) and from its position the near surface density can be determined. Within the accuracy of this measurement, there is no significant variation in the critical angle between the samples.

Fits between the simulation from a model structure consisting of a single carbon layer and the observed specular reflectivity are shown for samples deposited in 6, 10 and 20 seconds in Figs 2(A,B,C). Fig 2(D) shows the silicon substrate. Best-fit parameters are listed in Table 1. Figure 3 shows the carbon thickness as a function of deposition time. We note that the intercept at t=0 is 1.7nm, suggesting that this corresponds to the thickness of native oxide film. The

thickness of the film deposited for 15 seconds is low due to instability of the plasma during a significant part of the deposition time.
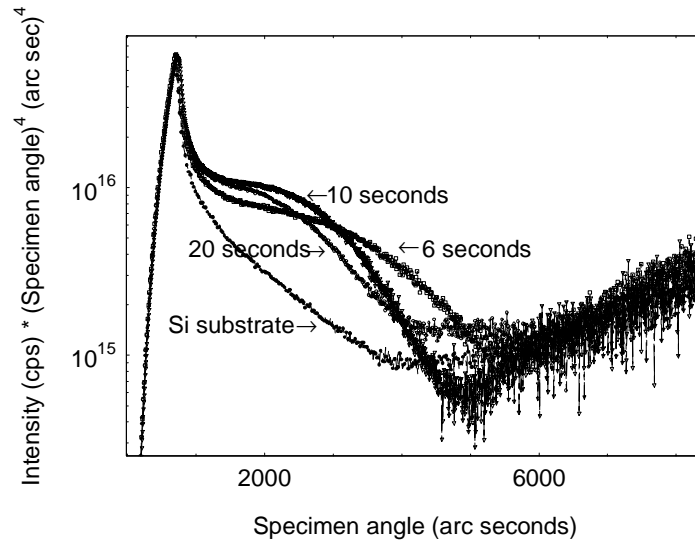
Fig 1: Specular intensity multiplied by the fourth power of the incidence angle for films with various deposition times
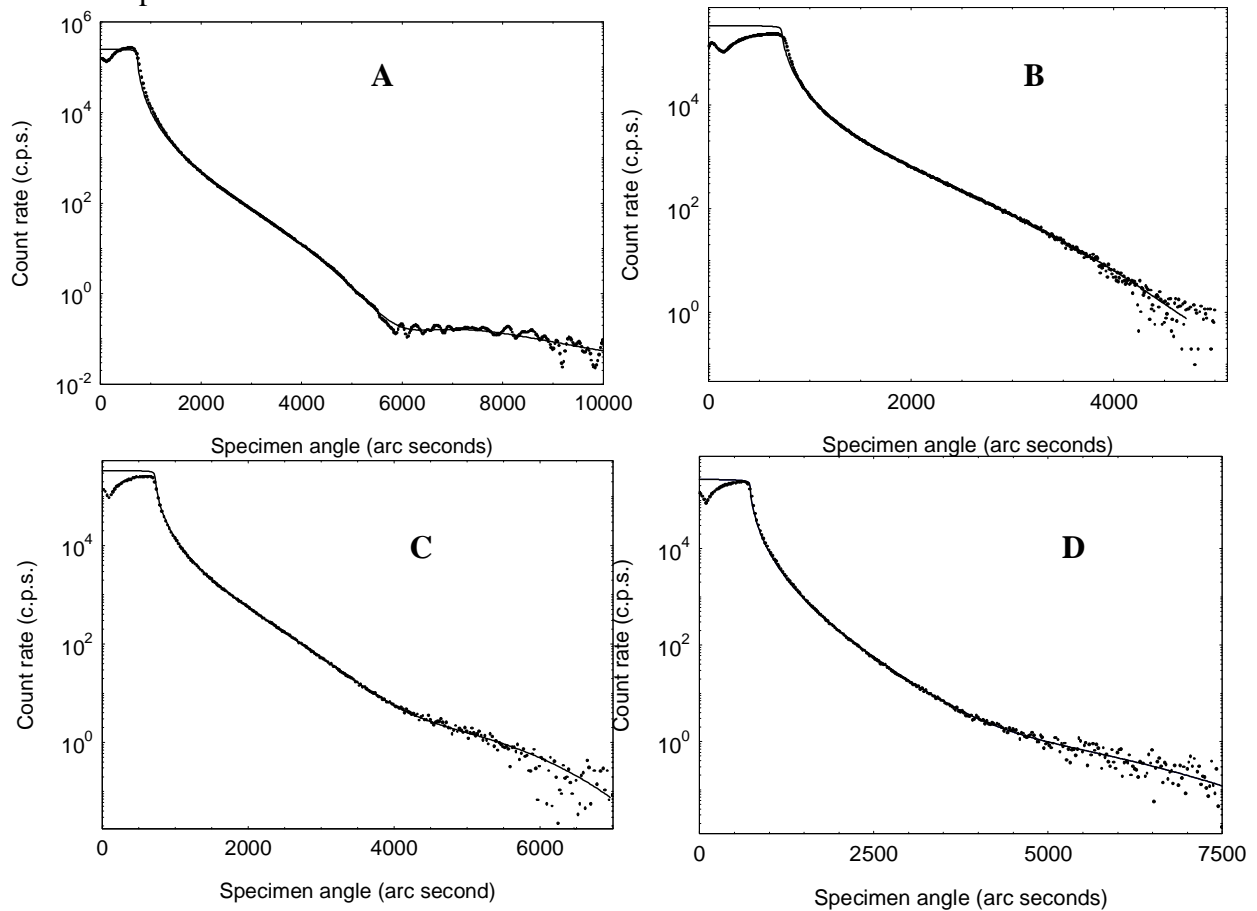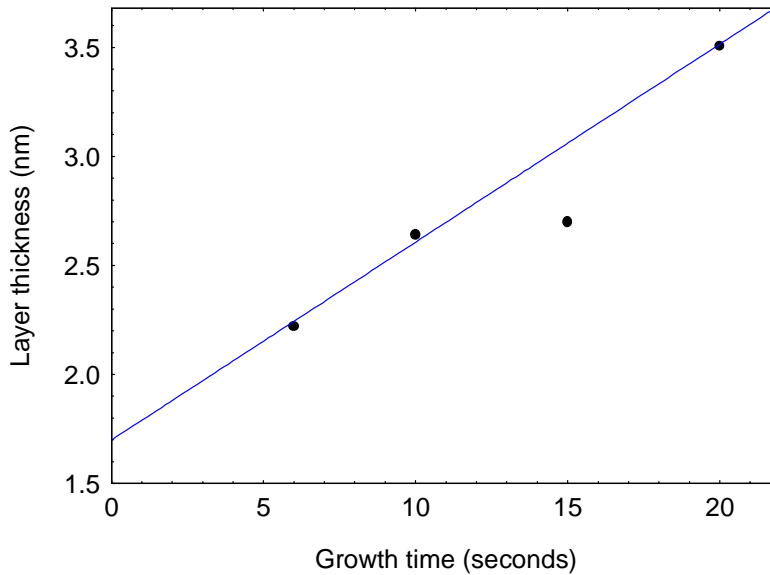

Fig 2: Experimental (points) and best-fit simulations (lines) to ta-C films deposited for (A) 6 seconds, (B) 10 seconds, (C) 20 seconds and (D) Si substrate.

In order to fit the specular reflectivity of the bare substrate, it proved essential to include the presence of a native oxide film within the simulation model. Figure 2(D) shows the best fit between experiment and simulation and here the silicon oxide thickness was determined to be 1.75nm, with 0.48nm effective roughness. The effective roughness arises principally from the density gradient through the oxide layer; specular reflectivity measurements cannot distinguish between compositional grading and true roughness, as there is no component of the scattering vector in the plane of the sample. However, an equally good statistical fit could be found for a number of oxide thickness and densities. Within the dynamic range of the laboratory experiments, it is impossible to define the oxide properties more tightly.

Table 1
Layer parameters (thickness, t, interface width, σ, and density, ρ) derived from best-fit simulations. (Silicon substrate density 2.33 g/cm^3)

Dep. time (s)	σ(Si) nm	t(ta-C) nm	σ(ta-C) nm	ρ(ta-C) g/cm^3
6	0.05	2.22	0.8	3.2
10	0.05	2.64	0.94	3.12
15	0.05	2.70	0.72	2.74
20	0.05	3.51	0.66	2.72

Fig. 3: Film thickness versus carbon deposition time.

The fit shown in Fig 2(D) corresponds to a film of thickness consistent, within the measurement precision, with the extrapolated value from Fig 3. The success of fitting a single layer to the data for the ta-C films suggests that the density of the silicon oxide is increased during the initial deposition stages of the ta-C film, probably by intermixing of C ions. Indeed, given the initial HF cleaning of the substrate, even if the deposition were not performed

immediately afterwards, we do not expect a pure SiO_2 interface, but a mixture of Si, C and oxygen, as shown by cross sectional EELS measurements of the interface [10].

DISCUSSION

As is evident from Fig. 3, measurement of a film of 2 nm thickness is quite within the capability of the technique. Measurement of the thickness of films, typically 2-4nm, used for magnetic recording coatings is thus feasible. While the statistical precision on the best-fit parameter is sub-Ångstrom, it is difficult to be confident in the thickness measurement to better than 0.1nm. At this level, errors in alignment, resulting in slipping off the specular ridge, and incomplete subtraction of the forward diffuse scatter can result in different best-fits being returned.

Unlike the case of thicker films [5], for the ultra-thin carbon films the critical angle is not strongly influenced by the film density. This is because the evanescent wave reaches the silicon substrate below the critical angle and the substrate density determines the critical angle. Forward simulations of thin films of differing density confirm the insensitivity. Only for ta-C films on silicon over about 20nm thickness can the critical angle be used reliably to measure the near-surface density. Although the density influences the fringe contrast, the film interface width also influences the contrast. On the other hand, the film density does affect the position of the fringe maximum. Despite the ability to measure quantitatively the precision of the fit as the two parameters vary, a degree of uncertainty remains in the determination of the film density for these ultra-thin layers. X-ray reflectivity is not composition-specific and we have already noted that success of fitting a single layer to the data for the ta-C films suggests that the density of the silicon oxide is increased during the initial deposition stages of the ta-C film, probably by intermixing of C ions. In any case our data show that a density of ~3 g/cm^3 can be attained even for such ultra-thin ta-C films, which suggests that the high corrosion resistance can be maintained down to the nm scale, together with a sufficiently high Young's Modulus of at least 300 GPa [12]. Note as well that the structure of the ultra-thin S-bend FCVA films resembles that of the thicker S-bend films, with a scaling of the bulk layer thickness, but not of the surface ond interface layers (which are in the sub-nanometer range both in thick and thin films).

CONCLUSION

Grazing incidence reflectivity does provide a non-destructive metrological tool for the measurement of the thickness of nanometer thick diamond-like carbon films The X-ray reflectivity technique for film thickness measurement is directly traceable to international standards of length [11]. Measurement of the density, on the other hand is more difficult and less reliable for these ultra-thin carbon films. It can only be deduced by careful fitting of a number of interacting parameters in model structures of the films and the density values derived should be interpreted cautiously.

ACKNOWLEDGEMENTS

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