Bonding and mechanical properties of ultrathin diamond-like carbon films

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Ultrathin 2-nm-thick carbon coatings are needed to increase the storage density in magnetic hard disks. We show how x-ray reflectivity, surface Brillouin scattering, resonant Raman scattering, and electron energy loss spectroscopy can measure consistently the structural and mechanical properties of these thin films. 2 nm films retain a Young’s modulus of 100 GPa. © 2002 American Institute of Physics. [DOI: 10.1063/1.1510179]

Diamond-like carbon (DLC) films form a critical protective layer on magnetic hard disks, sliders, and their reading heads. Storage densities are presently doubling every year. This requires the read head to approach the magnetic layer, and ever thinner carbon layers. Film thicknesses < 2 nm are needed for storage densities > 100 Gbit/in². To be protective, the films must be continuous and pin-hole free. This correlates to smoothness, atomic density, and sp³ bonding. As film thickness reaches the nm range, it is unclear if carbon retains the bulk properties, and it is critical to have accurate methods of characterization. The sp³ bonding is metastable and may not be stable at the surface. The integrity may be lost as the thickness approaches the roughness value. Electron energy loss spectroscopy (EELS) is a destructive technique. Nondestructive techniques are preferable. This letter shows how Raman, surface Brillouin scattering (SBS), and x-ray reflectivity (XRR) can successfully measure such thin films. In particular, by means of SBS, we can measure the elastic constants of a ~2 nm film. No other technique has to date been able to derive elastic constants for such thin films.

The DLC films used are hydrogen-free tetrahedral amorphous carbon (ta-C) deposited by filtered cathodic vacuum arc (FCVA) at floating potential with an S-bend filter. Sets of films were grown for different times in the same run on bare Si and on Si covered by evaporated Al. Two bare substrates and four ta-C ultrathin films of different thickness h were analyzed, plus another two thicker films of ~15 and ~27 nm.

SBS requires accurate values of film thickness and density. XRR is the method of choice for this. Figure 1 shows the reflectivity of bare Si (covered with some native oxide) and two ultrathin films. A typical reflectivity curve consists of a critical angle peak, followed by a decay with oscillations due to interference of waves reflected from the surface and the substrate interface. The thickness is derived from the oscillation period with good accuracy even on very thin films. On relatively thick films, the density is derived from the critical angle for external reflection. On films thinner than 20 nm, the x-ray evanescent wave reaches the substrate. The critical angle is now due to the substrate. The film density must be derived by fitting the whole reflectivity curve.

Thicker ta-C films (h > 15 nm) have a mean density of ~3.2 g/cm³, while the surface and substrate layers have lower densities. We use a three-layer model for the to fit the reflectivity. We find that the surface and interface layers are as in thicker films: 0.5–1.5 nm and 2.0–2.5 g/cm³ density. The central layer is denser, and its thickness increases with total thickness. This gives a mean density of ~2.8 g/cm³ for the 2.2 nm film due to these surface and interface layers. For SBS analysis we used the average film properties.

SBS measures the elastic moduli. SBS a 514 nm laser in backscattering with a Sandercock interferometer. The incident angle, to enhance the visibility of low contrast fringes, for Si substrate (b) and 2.2 nm (c) and 3.5 nm (d) films, see Table I.

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FIG. 1. Specular intensity multiplied by fourth power of the incidence angle, to enhance the visibility of low contrast fringes, for Si substrate (b) and 2.2 nm (c) and 3.5 nm (d) films, see Table I.
the surface acoustic wave (SAW) velocity \( v(q_i) \) is measured. SBS is time consuming, but probes wavelengths up to 100 times shorter than laser-induced SAW. This gives SBS unique potential for ultrathin films.

The scattered waves consist of a Rayleigh wave modified by the film [modified Rayleigh wave (MRW)]. Figure 2 shows its velocity as function of \( q_i h \), where \( h \) is the film thickness. For thin films \((q_i h < 1)\) the MRW lies mostly in the substrate. However, its maximum amplitude is at the surface, and this senses the film’s properties. The MRW is more confined in the film at large \( q_i h \). Hence, MRW velocity increases with \( q_i h \) for films faster than the substrate, and decreases with \( q_i h \) for slower films. The elastic constants are found by fitting computed velocities to measured ones. Amorphous films are assumed to be isotropic. Their elastic constants are defined by the Young’s modulus \( E \) and shear modulus \( G \). Our analysis assumes that a positive Poisson’s ratio and a bulk modulus less than diamond.

Figure 2 shows that SBS can distinguish the ~2 nm film from the bare Si. E, G values are given in Table I. The data from the two native oxide films fall on the same line; the MRW velocity decreases with \( q_i h \), as the oxide is slower than the substrate. The velocity for the 2.2 nm film also decreases, implying a film slower than Si, but stiffer than the oxide. The velocities for 3.5 and 4.5 nm films are increasing functions of \( q_i h \). The elastic constants of these films are similar, and larger than the 2.2 nm film. Data for the 8 nm film fall on a higher curve, indicating a significantly higher stiffness: the elastic moduli are comparable to thicker ta-C.

As both SBS and XRR are pushed to their sensitivity limits, the robustness of the elastic constants was checked. A 5% change in film density or thickness results in overlapping confidence regions, with mean values shifted by ~5%, but much less than the confidence regions. Thus, our procedure is robust against inaccuracies. For very thin films, the results are very sensitive to errors in substrate properties. If we assume Si elastic constants to be ~1% lower, this gives 30% higher elastic constants for thinner films. However, we can test our accuracy of the substrate properties as we have measurements on both slow and fast films. The relations in Fig. 2 were fitted by linear or quadratic functions, with the velocity at \( q_i h = 0 \) as a common fitting parameter for all films. This showed that the elastic constants of the substrate could be overestimated by only a fraction of a percent. Thus the values of Table I are underestimated at most by a few percent.

Figure 3(a) shows \( E \) vs. \( E \) ta-C film thickness for the ultrathin films and also for two films of intermediate thickness (15 and 27 nm produced by single bend FCVA) and data on other thicker ta-C films produced by single and S-bend FCVA from Ref. 11. Data from LISAW measurements on ultrathin films produced by high current arc are also included. Note how LISAW data lie above our SBS values for the thinnest films: this reflects the lower film sensitivity of this higher wavelength technique. Figure 3(a) shows that films >10 nm behave mechanically like bulk ta-C.

Now, in bulk ta-C, the density and \( E \) depend solely on \( sp^3 \) fraction. For bulk ta-C films, a general \( E-sp^3 \) relation and density-\( sp^3 \) relation were derived. Assuming these relations to hold for thin films, working backwards we can derive \( sp^3 \) fractions from \( E \) [Fig. 3(c)], and then the densities [Fig. 3(b)]. Figure 3(b) also plots the density directly measured by XRR and Fig. 3(c) plots the \( sp^3 \) fraction derived from the density versus \( sp^3 \) relation applied to our XRR density. Figure 3(c) also shows the \( sp^3 \) content directly measured by cross-sectional EELS.

Figure 3 allows some significant conclusions. The density of ta-C thin films increases with increasing thickness, and is larger than that of bulk materials. This is because the decrease in film density results in overlapping confidence intervals from XRR and density measurements. The elastic moduli of these films are similar to the bulk ta-C. However, its maximum amplitude is at the surface, indicating a significantly higher stiffness: the elastic moduli are comparable to thicker ta-C.
peak, around 1060 cm\(^{-1}\), is detected only with UV excitation and is due to C–C \(sp^3\) modes.\(^{14}\) For a given substrate, the \(G\) peak frequency at 514 nm excitation decreases from 1565 to 1510 cm\(^{-1}\) from bulk to 2.2 nm films. The \(I(T)/I(G)\) ratio in UV Raman decreases from 0.5 to 0. These trends are consistent with a lower \(sp^3\) fraction and lower density in ultrathin films. Hence, there is a general consistency between the Raman, XRR, and EELS data.

In the 4.5 nm film, the \(G\) peak frequency dispersion with excitation energy (0.21 cm\(^{-1}\)/nm) is less than in the 8 nm sample (0.45 cm\(^{-1}\)/nm, the same as bulk films).\(^{17}\) The UV Raman spectrum of the 8 nm film approaches that of thicker films and has a significant \(I(T)/I(G)\) ratio, consistent with a high \(sp^3\) content (>60%–70%) and with the \(sp^3\) fraction derived from the XRR density.

However, does SERS provide a representative spectrum? We compared the Raman spectra of a thick ta-C film grown on Al to a thick film on Si. They are similar for both visible and UV excitation, showing that Al does not affect the ta-C properties in this case. However, we could expect some differences for ultrathin films. Comparing spectra of ta-C films of the same thickness on Si or Si+Al shows that the latter have a slightly higher \(I(D)/I(G)\) ratio (0.1–0.2), lower \(G\) peak dispersion (max. 0.35 cm\(^{-1}\)/nm), and a lower \(I(T)/I(G)\) ratio (max. 0.35). This is consistent with an enhancement of the interface layer with a lower density and lower \(sp^3\) content. This change could also be due the Al modifying the films. Nevertheless, a comparison of surface enhanced and normal Raman spectra shows that it is possible to probe interface layers, achieving a nanometer vertical resolution.

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