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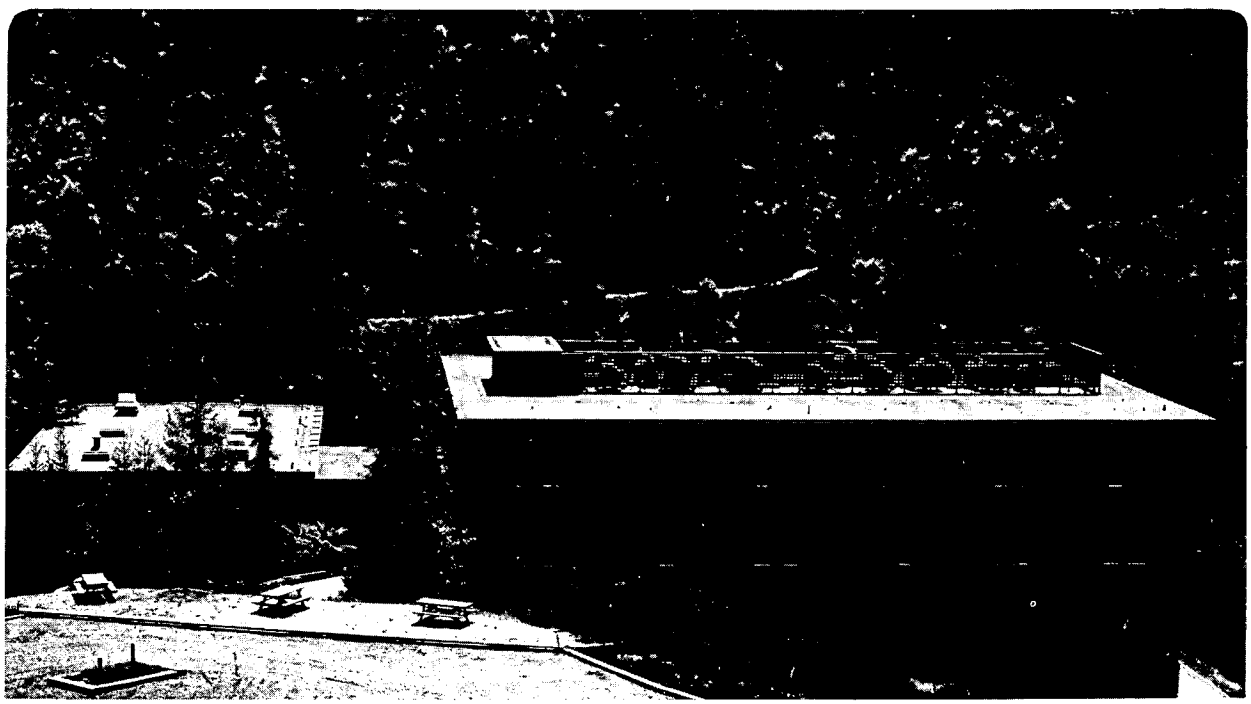

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OPTICAL CHARACTERIZATION OF SPUTTERED CARBON FILMS

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Abstract - **Sputtered carbon films are widely used as protective overcoats for thin film disk media. Raman spectroscopy is nondestructive and relatively rapid and is well suited for the characterization of carbon films. Specific features in the Raman spectra are empirically correlated with the rates of specific types of mechanical wear for both hydrogenated and unhydrogenated films. This observation is interpreted in terms of a random covalent network, in which the mechanical performance of the film is determined by the nature of the bonding that links sp^2-bonded domains.**

I. INTRODUCTION

The mechanical performance of sputtered carbon films as protective coatings for thin film media depends critically on the deposition conditions; small changes in the processing parameters (e.g., substrate temperature, sputtering gas composition, power density, etc.) can cause large changes in the composition of the films and in their performance. The structure of the film can vary from predominantly sp^2-bonded unhydrogenated (a-C) films to hydrogenated (a-C:H) films with substantial amounts of sp^3 bonding. There is a need for rapid, nondestructive characterization methods that are sensitive to these structural changes to monitor processing in production and to develop new films. As data densities increase, the thickness of the protective overcoat must decrease while retaining acceptable mechanical properties. The design of films and processing techniques to meet this challenge will benefit from a physical understanding of the relationship between the structure of the films and their mechanical performance.

The lack of long-range order and wide variety of possible structures make amorphous carbons difficult to characterize using traditional surface science techniques. For example, X-ray diffraction is weak due to the low atomic number of carbon and Auger spectroscopy is not sensitive to structural differences between films [1]. Electron energy loss spectroscopy (EELS) has been used in several studies [1-5] to gain qualitative information about carbon coordination in a-C and a-C:H films. Recently, careful modeling of the π and $\pi+\sigma$ plasmon peaks in the EELS spectrum has been used to determine the sp^3/sp^2 ratio quantitatively in CVD-grown a-C:H films [5]. Solid-state, magic-angle-spinning ^{13}C NMR has been used to determine the sp^3/sp^2 ratio quantitatively in a-C:H [6,7] and a-C [8] films. Recently, the radial distribution function (which was consistent with >90% sp^2 bonding) of an a-C film was measured with neutron diffraction [9]. However, these techniques have drawbacks that prevent them from being used routinely to characterize thin film disk media. All three techniques usually require removing the film from the substrate, and NMR and neutron diffraction require large amounts of material.

Optical characterization methods can yield comparable structural information, are non-destructive, and can be used on as-grown films. Raman spectroscopy, inelastic light scattering by phonons, is relatively rapid and is well suited for the characterization of carbon films. In an amorphous material, Raman spectroscopy measures a weighted phonon density of states, which indirectly reflects changes in bonding and ordering [10]. Since these same bonding and ordering issues influence the physical and mechanical properties of the film (hardness, fracture toughness, elastic modulus, stress, etc.), it is worthwhile to look for relationships between features in the Raman spectrum and these properties. Previous work on a wide variety of production and prototype carbon films will be summarized and an integrated model that relates the observed Raman spectrum to the structure of the film and to some of the mechanical properties will be presented. The application of other optical characterization methods including visible/near IR absorption, photoluminescence, and ellipsometry will also be proposed.

II. EXPERIMENTAL

Raman spectra at LBL were obtained with a custom-built, high sensitivity spectrometer that has been described in detail previously [11]; only a brief description will be given here. The laser light, typically 20 mW, was incident at 65° from surface normal and was focussed to a 15 μm spot on the sample. Laser power studies have shown that the films are not perturbed by laser heating. The scattered light was collected normal to the surface by 50 mm f/1 camera lens and imaged through a holographic interference notch filter and onto the entrance slit of a 0.3 m single spectrometer. The dispersed light was detected by a microchannel plate photomultiplier (1024×1024). All spectra presented here were obtained with the 488 nm line (2.54 eV) of an Ar ion laser. The Raman scattering in carbon films is resonance

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enhanced and the shape of the spectrum is known to change with laser frequency [12,13]; this should be noted when comparing Raman spectra between studies.

The penetration depth (1/e) of Raman spectroscopy using 2.54 eV radiation, measured by examining films of varying thickness made under identical conditions, is on the order of 400 - 500 Å [14]. Therefore, a Raman experiment will sample the entire thickness of the film for a typical thin-film coating (ca. 250 Å thick). Resonance enhancement of the Raman scattering leads to high sensitivity. We have obtained a spectrum from a 50 Å a-C film and estimate a detection limit of 10 Å [15]. Thus, Raman spectroscopy has more than adequate sensitivity to characterize the 100 Å (and below) films projected for the next generation of thin-film media.

Films studied include both unhydrogenated (a-C) and hydrogenated (a-C:H) magnetron-sputtered films obtained from a variety of commercial, government, and academic sources.

III. RESULTS

The Raman spectra of a-C and a-C:H films consists of two broad and overlapped features between 1000 and 1600 cm^{-1}. The Raman spectra of a typical a-C and a-C:H film are shown in Fig. 1. It has been observed that the Raman spectra of most a-C and a-C:H films are fit well by the sum of two Gaussian peaks, the G-band near 1570 cm^{-1} and the D-band near 1370 cm^{-1} [16]. Previous work by this group has shown that the position of the G-band and the ratio of the area of the D-band to the G-band (I_D/I_G ratio) are highly correlated with the mechanical properties of the film [17,18] and with the results of other characterization techniques [19]. The correlations with the mechanical properties are summarized in Fig. 2, which shows the relationship in a variety of prototype sputtered films between the G-band frequency and the tribochemical wear rate (measured in a low speed drag test on unlubricated media) and between the abrasive wear rate and the ratio of the area of the D- and G-bands (I_D/I_G ratio) [17,18].

There are a number of conclusions to be drawn from Fig. 2, both within and between the two groups of films. In both groups of films, low G-band frequencies are correlated with low tribochemical wear rates. The a-C:H films have, as a group, lower tribochemical abrasive wear rates compared to the a-C. Interesting, there is a slight negative correlation of the I_D/I_G ratio with hardness (low abrasive wear rate) in a-C:H films, which contrasts with the much larger positive correlation of the I_D/I_G ratio with hardness in a-C films.

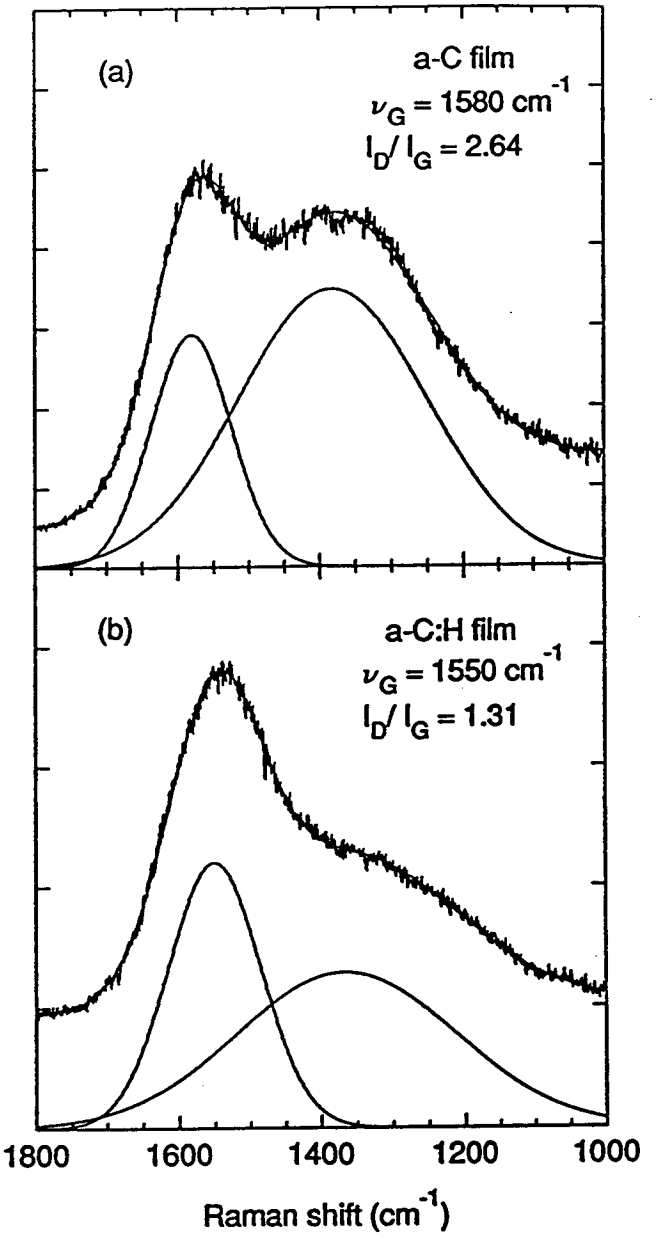

Fig. 1 Raman spectra and fit to two Gaussians and a linear background term of (a) an a-C film and (b) an a-C:H film. The individual contributions to the fit of the G-band near 1570 cm^{-1} and the D-band near 1390 cm^{-1} are also shown.

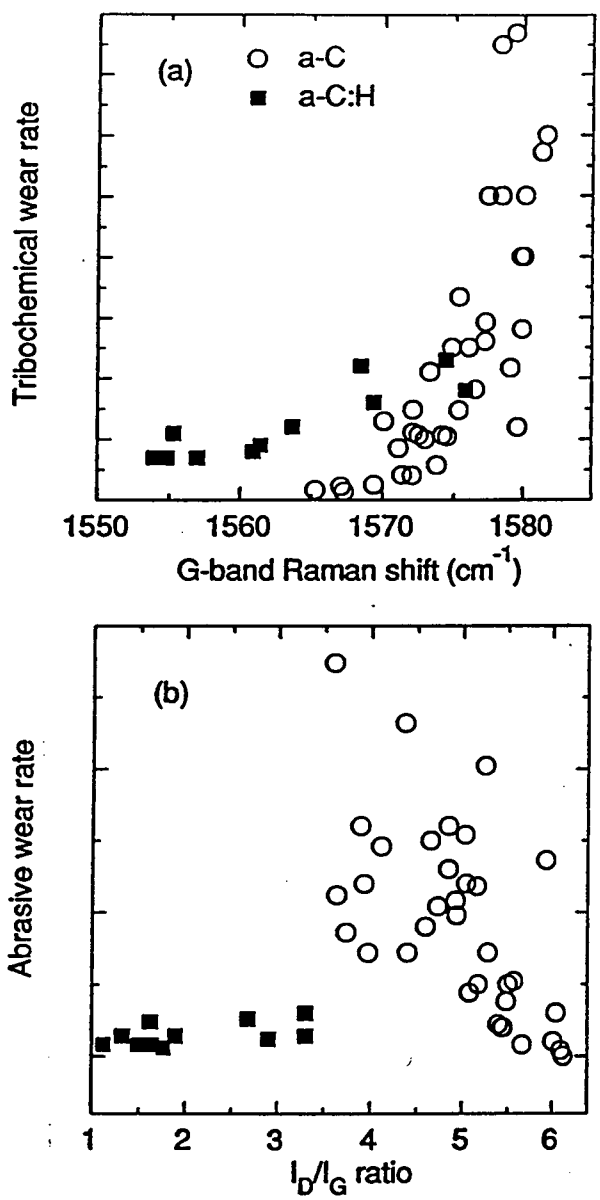

Fig. 2 Relationship between (a) the rate of tribochemical wear and the G-band frequencies and (b) the rate of abrasive wear and the I_D/I_G ratio for a large number of a-C (open circles) and a-C:H (filled squares) films. A low I_D/I_G ratio is associated with superior abrasion resistance (hardness) in a-C:H films; the opposite is true in unhydrogenated (a-C) films.

IV. Discussion

Previous work [17] explained the correlation between the abrasion resistance and the G-band position in a-C films by invoking the theoretical results of Beeman *et al.* [20]. In that work, it was found that increasing the sp^3 content in all-carbon amorphous networks produced a Raman spectra that was shifted as a whole to lower frequency. Hence, the G-band position can be used as a measure of the sp^3 content of a-C films. The superior wear resistance of films with lower G-band frequencies was then attributed to the oxidation resistance of an sp^3-terminated surface compared to an sp^2 surface.

Recently, the random covalent network model developed by Phillips [21] and Thorpe [22] has been used to develop a structural model for a-C:H films that is consistent with hardness, strain, sp^3/sp^2 ratio, and optical gap measurements [5,23-25]. The random covalent model considers the number of constraints on the lattice imposed by the bond-stretching and bending forces of the possible bonding coordinations. For example, a carbon atom sp^3-bonded to 4 other carbons has a coordination number of 4 and contributes 7.5 constraints to the lattice [24]. Dangling bonds, such as a C-H bonds or pendant CH_3 groups do not contribute constraints. Modifications to the theory were made to account for the ability of carbon to form both sp^3 and sp^2 bonds [24] and to form sp^2-bonded domains [25]. A random network is ideally constrained when the average number of constraints is equal to three, the number of translational degrees of freedom of an atom. Imposing this condition allows an critical average coordination number to be calculated, which is 2.4. Lattices with coordination numbers greater than this value are rigid but strained (both rigidity and strain increase with coordination number); lattices with an average coordination number less than 2.4 are floppy and lack rigidity.

The model that emerges from this analysis is that a-C:H consists of sp^2-bonded domains connected by sp^3-bonded, slightly overconstrained, crosslink regions. The sp^2-bonded domains, which form to partially relax strain caused by overconstraint in the crosslink regions, control the optical properties. The position of the optical gap has been modeled function of sp^2 domain size using Hückel theory [21]; smaller domain sizes shift the gap to higher energy. The bonding in the crosslink regions determines the mechanical properties. Crosslinking carbon atoms that are sp^3-bonded with 0 or 1 bonds to H provide strong, three-dimensional crosslinks, while $-CH_2-$, $-CH_3$, and sp^2 bonds lead to weaker films. The size of the sp^2 domains and the nature of the crosslinking can be controlled by adding H to the film. Hydrogen incorporation saturates double bonds, forming smaller sp^2 domains and encouraging sp^3 crosslinking, thus moving the optical gap to higher energy and increasing the film hardness. However, at H contents of >60%, the average coordination

number falls below the critical value and $-CH_2-$ crosslinks are produced. These lack three dimensional strength, and the films become soft [5].

This model can be used to understand the correlations of the mechanical performance and the Raman spectrum in a-C:H films. The lower tribochemical wear rate of the a-C:H films compared to most of the a-C films is attributed to the increased proportion of sp^3-bonding. The surface of the film also sp^3-terminated, which leads to a reduced oxidation rate [18]. The same effect can be used to explain the correlation of the tribochemical wear rate with G-band frequency in the a-C:H films, assuming the Beeman model [20] can be used in a-C:H films to associate G-band position with sp^3 content [18].

The lower abrasive wear (increased hardness) of the a-C:H films compared to the a-C films is attributed to greater proportion of sp^3 bonding between the sp^2 domains. The correlation of the film hardness with the I_D/I_G ratio for a-C:H films can be explained in terms of resonance Raman effects. Ramsteiner and Wagner [12] and Yoshikawa *et al.* [13] have found that the G-band is resonance-enhanced in a-C:H films and that in a given film, the I_D/I_G ratio decreases with increasing laser energy from 1.9 to 3.1 eV. This effect is attributed to an enhancement of the G-band as the laser energy approaches a π - π^* resonance whose maximum occurs around 4-6.5 eV. A similar effect can be used to explain the current results in Fig. 2(b). Films with smaller sp^2 domains will have optical gaps closer to the laser energy, 2.54 eV. Resonance enhancement of the G-band by the optical band edge will decrease the I_D/I_G ratio (both the valence and conduction states of the optical gap are associated with the sp^2 domains). In the films studied here, increasing amounts of H incorporation both shift the optical gap to higher energy (lowering the I_D/I_G ratio) and increase the sp^3 crosslinking, leading to harder films. This trend is expected to reverse in films with very large optical gaps (large H content), as soft, films with polymeric $-CH_2-$ bonds in the crosslink region are produced.

The present model gives an adequate explanation of the correlation of the I_D/I_G ratio with hardness in a-C:H films. However, the correlation in a-C films, which has the opposite sign, is more difficult to explain. Resonance effects are unlikely, because of the low value of the optical gap, ca. 0.5 eV. Previous STM work by this group has suggested that large I_D/I_G ratios in a-C films are correlated with increases in the number, but not the size, of sp^2-bonded domains [26]. It is possible that the higher density of sp^2 domains in a a-C film encourages strong crosslinking, which would lead to harder films and lower abrasive wear rates.

V. Conclusions

Raman spectroscopy, when interpreted with the random covalent model, can be used to understand the structural foundation of the mechanical properties of a-C:H films. The correlation of Raman measurements with mechanical properties of thin film media support a picture in which hardness is maximized for films that have small sp^2-bonded domains interlinked with predominantly sp^3 bonds with 0 or 1 bonds to H. This information should be useful in designing processing methods for high-performance carbon overcoats. There have been recent reports on producing ultrahard pure carbon films with high sp^3/sp^2 ratios, using plasma arc deposition [27]. The large proportion of sp^3 bonding is attributed to high deposition energies leading to non-equilibrium growth. Maximizing film hardness is only one part of film design for disk media applications. Factors such as film adhesion to the substrate (partially related to stress), friction (related to lubricant retention and surface morphology), and corrosion resistance, as well as compatibility with other process steps, must also be considered.

In a-C:H films, film hardness is related to the optical properties of the film. Thus, other optical techniques can also be used for film characterization. Optical absorption measures the optical gap directly but must be performed on films deposited on a transparent substrate. Ellipsometry performed as a function of wavelength can measure the refractive index and absorption coefficient, provided the optical constants of the substrate are known. Photoluminescence (PL) spectroscopy, which can also measure the optical gap, can, in principle, be performed with a Raman spectrometer. However, the long wavelength cutoffs of the standard Raman detectors - 900 nm or 1.38 eV for a red-extended PMT, 1000 nm or 1.24 eV for a CCD, and 1100 nm or 1.12 eV for a Si photodiode array - may not allow the entire PL peak to be observed. The development of improved coatings for the low-flying, thin-film, disk media will likely benefit from optical characterization methods incorporating Raman spectroscopy and some measure of the optical gap.

Acknowledgments

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