Photoluminescence And Raman Spectroscopy In Hydrogenated Carbon Films

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Abstract—a-C:H films prepared by DC-magnetron sputtering in an H_2:Ar mixture exhibit strong photoluminescence (PL) peaks superimposed upon the Raman scattering spectrum. PL becomes observable at a hydrogen content of ca. 34%, and increases exponentially thereafter, driven by the progressive saturation of carbon dangling bonds. In this %H range, hardness and elastic modulus decrease and CSS durability reaches an optimum. The Raman G peak position is very sensitive to deposition temperature (shift of 0.1 $cm^{-1}/^0C$) and was found to correlate with the sp^3/sp^2 bonding ratio as measured by EELS, and therefore can also be used as a predictor of carbon tribological performance.

I. INTRODUCTION

In the last decade, a number of papers have discussed the role of hydrogen incorporation into DC-magnetron sputtered hydrogenated carbon films (a-C:H), and its relationship with head/disc interface tribology [1-6]. Some of these papers emphasized the importance of Raman spectroscopy in the structural characterization of the films, in an attempt to use this technique as a predictive tool to assess the durability of a given carbon process [2-6]. In the case of pure a-C (non-hydrogenated), the position of the G-band of the Raman spectrum has been correlated to the rate of frictional increase during constant-speed drag testing of untextured, unlubricated films [2]. More recently, some authors have reported on the photoluminescence of carbon films, prepared in a methane-enriched Argon plasma [6]. This paper is an attempt to describe more fully some of the process/structure/property relationships of a-C:H films.

II. EXPERIMENTAL

Carbon films were prepared on Al/NiP disc substrates, using conventional DC-magnetron sputtering. Film thickness was 25nm, except for nano-indentation work which was performed using 100nm thick films. Raman spectra were obtained on a Dilor XY, triple monochromator system, using an ionized Argon (514.5nm, 200mW) Laser. Photoluminescence data were obtained by excitation at 488.0 nm (50 mW). The disk was spun at 3600 rpm to avoid heating and PL saturation effects. Electron energy loss spectra were obtained by a Phillips CM30 TEM with a parallel Gatan 666 electron spectrometer. Bonding fractions were calculated from the carbon K-edge by the ratio of the π^*(285 eV) to σ^* (290 eV) peak areas. Diamond and polycrystalline graphite were used as standards. It was necessary to fit the π^* peak with an asymmetric Gaussian to obtain accurate bonding ratios. Hardness measurements were performed on a nano-indenter from Nano-instruments, using 20nm indentation depth. Contact-Start-Stop (CSS) testing was performed on 65mm discs, with standard mechanical texture and lubricant system, using 70%, thin-film heads. Crash was defined as a complete, 1x visible wear through of the overcoat in the first 5000 cycles. Abrasivity data were obtained using a SiC abrasive tape loaded at 6 psi, against a rotating disc, for two minutes. Resistance to abrasion was estimated by counting the number of scratches on the film, in the field of view of a x200 micrograph.
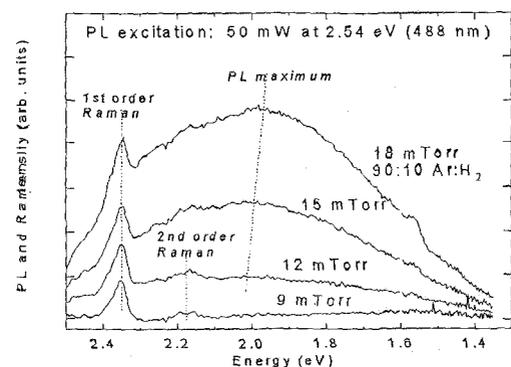
III. RESULTS AND DISCUSSION

a) Photoluminescence

Figure 1: Raman and photoluminescence spectra of a-C:H

Fig. 1 shows the Photoluminescence (PL) spectra for carbon films sputtered at various Ar:H_2 (85:15) pressures. Increasing sputtering pressure leads to an increase in the hydrogen content of the film, and this leads to a strong PL background that superimposed on the first order Raman lines. This PL emission has been reported before for glow-

discharge a-C:H films [7], as well as DC magnetron carbon overcoat [6]. The PL is due to recombination of electron hole pairs within sp^2 bonded clusters in an sp^3 bonded amorphous matrix. The PL intensity tends to increase with increasing H concentration due primarily to the saturation of non-radiative recombination sites (e.g., dangling bonds).

Fig. 2 shows a close-up of the 900-1900 cm^{-1} Raman region, showing the PL intensity as a linear scattering background, and the G (ca. 1560 cm^{-1}) and D (ca. 1380 cm^{-1}) peaks. A convenient way to estimate the PL intensity is to ratio the slope of the PL background to the fitted Gaussian intensity of the G peak. This slope parameter S has a dimension of length, and is best described in micrometer (μm) units.
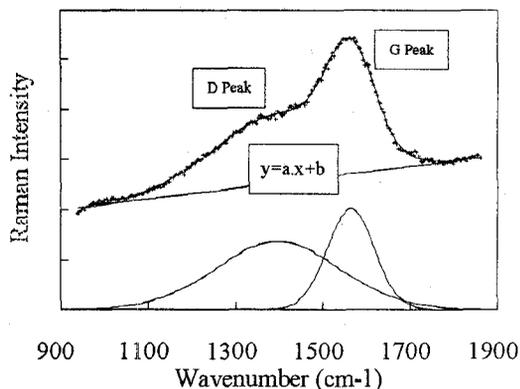

Figure 2: Raman spectrum with PL background. Spectrum is fitted with two Gaussian peaks over a linear background.

The PL intensity, as estimated by S, is an extremely sensitive function of the hydrogen content in the film, measured by Hydrogen Forward Scattering (HFS), as seen in Figure 3. According to these data, PL activity starts with about 34% hydrogen, and rapidly grows to a point where hardly any Raman scattering can be observed (over ca. 42% hydrogen).
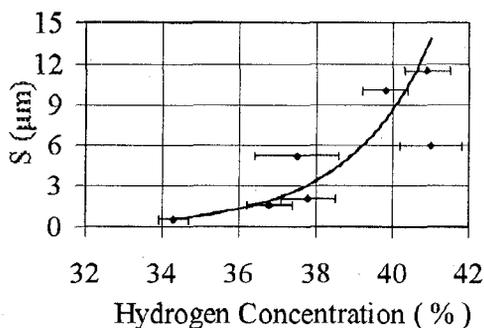
In this hydrogen content range were PL intensity starts to rise, both film elastic modulus and hardness decrease (Figure 4), as recently reported by Taki [9] et al., and White et al. [10]. This behavior is consistent with a loss of tri-dimensional network bonding, caused by C-H bond termination, and polymeric -CH_2- bond formation.
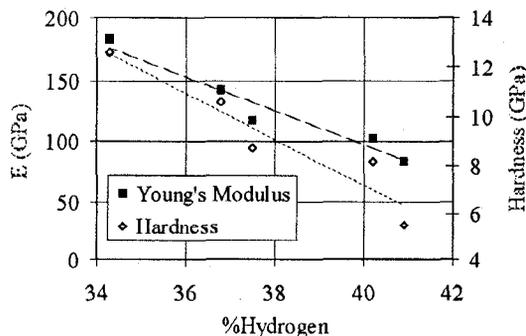

Figure 4: Young's modulus and hardness vs. film hydrogen content. Dashed lines are linear fit.

Contact-Start-Stop (CSS) data, however, suggest that, in this particular hydrogen content range, durability increases. As seen in Figure 5, CSS crash rate decreases monotonically at the onset of photoluminescence, to reach zero at a value of about S=2.0μm. This result is in apparent contradiction with conventional wisdom that harder films should be more durable. However, given the multitude of other mechanical (adhesion, fracture toughness), tribochemical [11], and physico-chemical properties [12] that are likely to play a role in the performance of a lubricant/overcoat combination of a head/disc interface, these seemingly surprising data are not totally unexpected. Increasing the amount of hydrogen in the film further eventually degrades the mechanical properties, as the film becomes mostly polymeric (data not shown here).
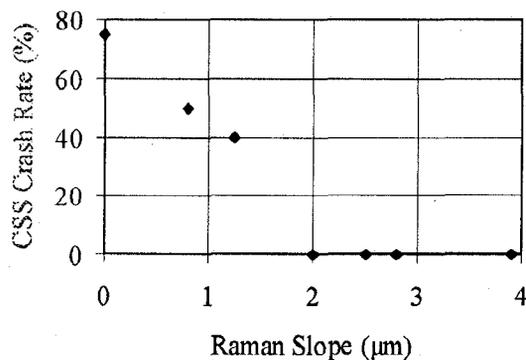

Figure 3: Slope parameter S vs %hydrogen. The solid line is an exponential fit to the data.

Figure 5: CSS crash rate vs. Raman slope

b) G peak position and sp³ content

Figure 6 shows how sensitive the G peak position of a-C:H films is to the sputtering temperature. In these data, films containing about 38% hydrogen show a nearly linear relationship of the resulting G peak position, with deposition temperature. A linear regression yields variations of ca. 0.1 $cm^{-1}/^{\circ}C$.
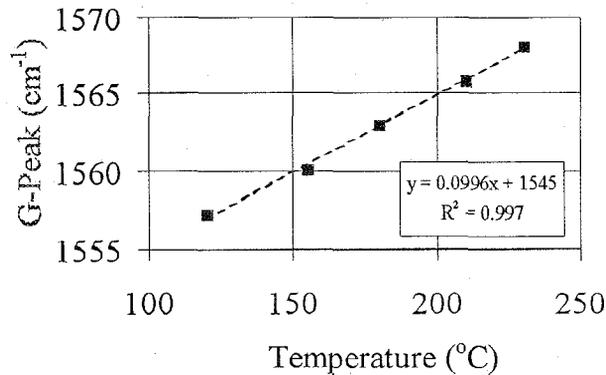

Figure 6: G peak position vs. sputter temperature. The dashed line is a linear fit to the data.

Furthermore, Electron Energy Loss Spectroscopy (EELS) data indicates that films sputtered at higher temperature (higher G peak position) have lower sp^3 carbon content (Figure 7). This result is similar to earlier studies on unhydrogenated a-C films, that have shown increase in sp^2 content at higher deposition temperatures, by both STM imaging and Raman I(D)/I(G) intensity ratio [13]. Both CSS (data not shown here) and film abrasivity data indicate that higher sputtering temperatures yield films with decreasing mechanical performance (Figure 8), consistent with a higher, softer sp^2 content. In this figure, both G peak position and number of scratches were averaged over four surfaces.

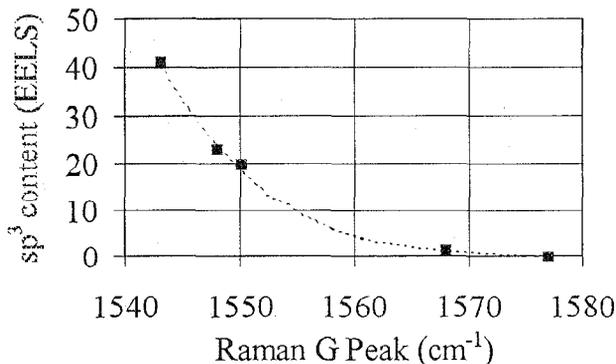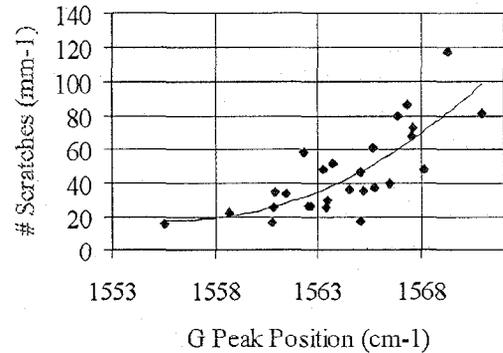Figure 7: EELS sp³ content vs. G peak position. The dashed line is to guide the eye.

Figure 8: Abrasivity vs. G peak position. The dashed line is to guide the eye.

IV. CONCLUSION

We have shown that DC-magnetron sputtered hydrogenated carbon films exhibit strong photoluminescence activity in a very narrow range of hydrogen content, with an onset of emission at a concentration of ca. 34%. PL emission eventually overwhelms Raman scattering for values above ca. 42%. Similar to a-C:H films prepared by other deposition techniques, we believe that the PL comes from isolated sp^2 clusters and that its intensity increases with H content due to progressive saturation of carbon dangling bonds. In this range of hydrogen content where network terminator CH and polymeric CH_2 bonds are formed, hardness and elastic modulus decrease. At the same time, CSS durability is enhanced and reaches a optimum. Besides hydrogen content, sputter temperature also plays a critical role in the carbon durability. Raman G peak position and EELS data show that films prepared at higher temperature have an increased sp^2/sp^3 bonding ratio, detrimental to the head/disc interface tribology.

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