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## THERMAL STABILITY STUDIES OF DIAMOND-LIKE CARBON FILMS

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### ABSTRACT

Thin films of amorphous carbon/hydrogen, also known as diamond-like carbon or DLC, are of interest as an economical alternative to diamond in a variety of coatings applications. We have investigated the thermal stability of DLC films deposited onto tungsten and aluminum substrates via plasma CVD of methane. These films contain approximately 40 atom % hydrogen, and based on Auger spectra the carbon in the films is estimated to be 60 %  $sp^3$  hybridized and 40 %  $sp^2$  hybridized. Thermal desorption, Auger, and Raman measurements all indicate that the DLC films are stable to 250-300° C. Between 300 and 500° C, thermal evolution of hydrogen from the films is accompanied by the conversion of carbon from  $sp^3$  to  $sp^2$  hybridization, and Raman spectra indicate the conversion of the overall film structure from DLC to micro-crystalline graphite or so-called "glassy" carbon. These results suggest that DLC of this type is potentially useful for applications in which the temperature does not exceed 250° C.

### I. INTRODUCTION

There is much current interest in films of diamond-like carbon (DLC), since DLC is a potential cheap replacement for diamond that retains some of diamond's desirable physical properties. The term DLC is somewhat ill-defined and has been used to refer to carbon films with a variety of characteristics and properties, but for the purposes of this paper DLC is understood to be a form of carbon with a high hydrogen content (usually greater than 25 atom %) and a significant fraction (usually greater than 40 %) of the carbon in the  $sp^3$  hybridization state. These films are also denoted as a-C:H, meaning simply an amorphous carbon/hydrogen film. Depending on the method of preparation, these films can be prepared such that either their hardness or optical bandgap is sufficiently close to that of diamond to act as a substitute (1). While DLC films may be produced by several techniques, the films discussed in this study are produced by plasma-enhanced chemical vapor deposition (CVD) from methane. In previous studies, these films have been found to contain approximately 40 atom % hydrogen (2).

This paper focusses on the thermal stability of DLC. Thermal stability is of fundamental importance because it will determine the temperature range in which DLC is useful for any particular application. There have been some previous studies relating to the thermal stability of various types of DLC (3), but most of these are not very detailed and utilize only a single experimental technique to look at the issue of stability. Since the combination of several techniques will usually give a more complete picture of how a material changes as a function of temperature, we have undertaken the present study. The DLC films involved were deposited onto

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flat tungsten and aluminum substrates. These substrates were chosen more for experimental convenience than for their relationship to any particular application.

## II. RESULTS

The thermal stability of DLC films was investigated using thermal desorption analysis, Auger spectroscopy, and Raman spectroscopy. The experimental systems used to obtain the data have been described elsewhere (4). In this paper, we focus on the results. The different techniques were chosen to compliment one another, since each looks at a different aspect of DLC stability. Thermal desorption gives information about hydrogen retention by these films, Auger spectroscopy about carbon atom hybridization (i.e. carbon bonding on a local level), and Raman spectroscopy about long-range structure within the film. Additional studies of the hardness of these films after different annealing treatments are currently in progress.

### A. Thermal Evolution of Hydrogen

The thermal evolution of hydrogen from a DLC film on a tungsten substrate is shown in Figure 1. The film was grown using  $CD_4$  as the source gas instead of  $CH_4$ . This allows the hydrogen evolved from the film in the form of  $D_2$  to be distinguished from any  $H_2$  that might be desorbed

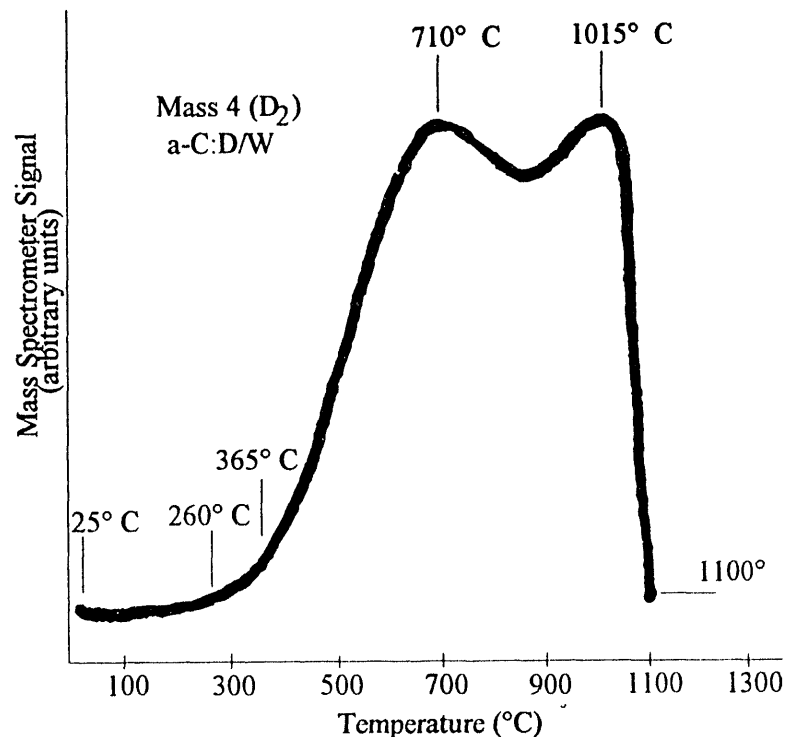


Figure (1): Thermal evolution of  $D_2$  from DLC on tungsten grown using  $CD_4$ .

due to contamination of the film surface or desorption from elsewhere in the ultrahigh vacuum (UHV) chamber. A very high heating rate of approximately 70 C/second was used for the spectrum shown in order to attain the highest temperature (approximately 1100° C) that can be attained with our sample mounting arrangement. The leading edge of the desorption spectrum was similar in cases where lower heating rates were used.

Hydrogen desorption from the film begins near 260° C. Above about 350° C the desorption rate rises sharply, and two desorption maxima are observed near 710 and 1015° C. It is quite possible that more maxima could be resolved if

substantially lower heating rates were used. The steep trailing edge of the spectrum above 1000° C is at least partially an artifact, resulting from the fact that the heating rate drops gradually to zero above this temperature. However, the observation that hydrogen desorbs in the range between approximately 260 and 1100° C is still expected to be reasonably accurate. This agrees well with a previous study of H<sub>2</sub> evolution from a DLC film on stainless steel by Winter et al., where desorption was observed between approximately 300 and 1100° C with a heating rate that was an order of magnitude lower (3a).

The thermal desorption results suggest that the fundamental structure of the DLC film is stable to at least 250-300° C. This observation is supported by Auger and Raman spectroscopy results presented below. The very broad desorption range observed is probably related to the fact that the D atoms in the film must diffuse to the film surface prior to recombination and desorption as D<sub>2</sub>. This seems especially likely in view of the Raman results discussed below, which indicate essentially complete conversion of the film structure to micro-crystalline graphite by about 500° C.

### B. Auger Spectroscopy

Auger spectra were obtained from a number of DLC films on both tungsten and aluminum substrates. Carbon was the only element detected in survey spectra of these films. (Hydrogen cannot be detected using Auger spectroscopy). Analysis of the carbon peak fine structure in first derivative Auger spectra yields information on the average degree of hybridization of the carbon atoms in these films. In particular, the sp<sup>3</sup>/sp<sup>2</sup> ratio may be estimated from the energy separation,  $\Delta$ , of the positive and negative maxima in the first derivative spectra (5). Figure 2 shows some representative spectra. An unannealed DLC film, which attained a maximum temperature of 100° C during chamber bakeout, exhibits a  $\Delta$  value of 17.9 eV. The average value for several such films was  $17.6 \pm 0.8$  eV. Annealing the films for 15-30 minutes at temperatures in the range of 530-580° C resulted in a marked increase in  $\Delta$ , to  $20.8 \pm 0.3$  eV (Figure 2(b)). These values compare to values of 14 eV for diamond and 23 eV for graphite (5). Taking these values as typical for films composed entirely of sp<sup>3</sup> and sp<sup>2</sup> carbon, respectively, approximate estimates of

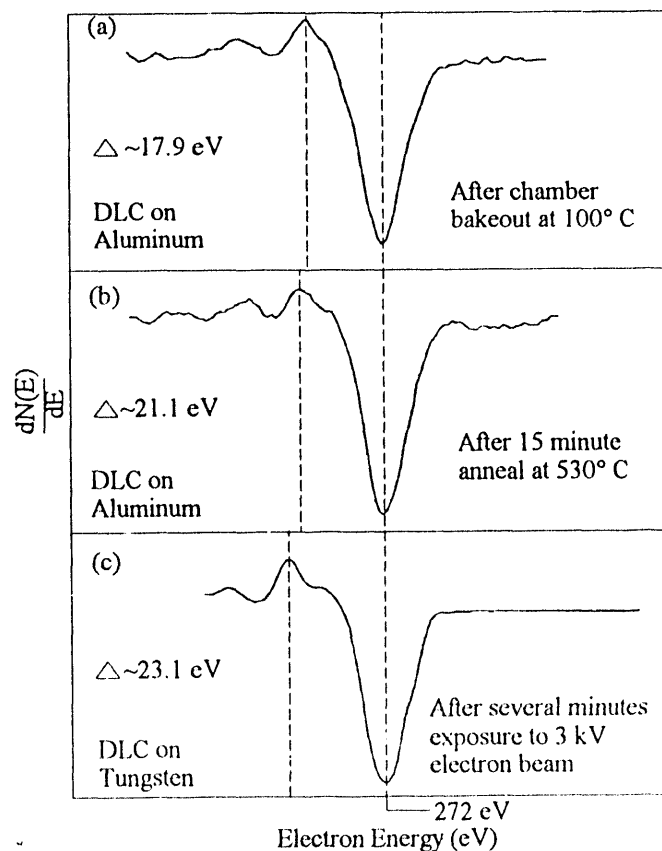


Figure (2): Typical Auger spectra of (a) an unannealed DLC film, (b) a DLC film annealed at 530° C and (c) a DLC film exposed to a 3 kV electron beam.

the  $sp^3/sp^2$  ratio in our films are 60 %/40 % prior to annealing and 25 %/75 % after annealing. Additional Auger studies for intermediate annealing temperatures suggest that the bulk of the observed changes in the Auger spectra occur between 300 and 500° C, with little change for annealing temperatures below 300° C. The estimate of 60 %  $sp^3$  carbon for the unannealed film is in good agreement with estimates from previous studies of DLC films deposited via RF plasma CVD of organic gasses. Various studies have utilized EXAFS (3b), infrared spectroscopy (3d), and NMR (1) to estimate the  $sp^3/sp^2$  ratio and have reported  $sp^3$  contents of 40-86 %. Our results were obtained using a 1 kV beam energy and very brief exposure times to minimize beam damage effects. Exposing a DLC film to a 3 kV electron beam for several minutes caused extensive surface damage, producing an Auger spectrum [Figure 2(c)] identical to that of graphite (5,6).

### C. Raman Spectroscopy

Raman spectra of a DLC film on tungsten obtained before and after annealing in ambient air are shown in Figure 3. Thirty minute anneals were performed at 50° C and subsequently at 50° C intervals up to a maximum temperature of 450° C. The room temperature spectrum, showing a broad peak centered at 1522  $cm^{-1}$ , is characteristic of this kind of DLC (4b).

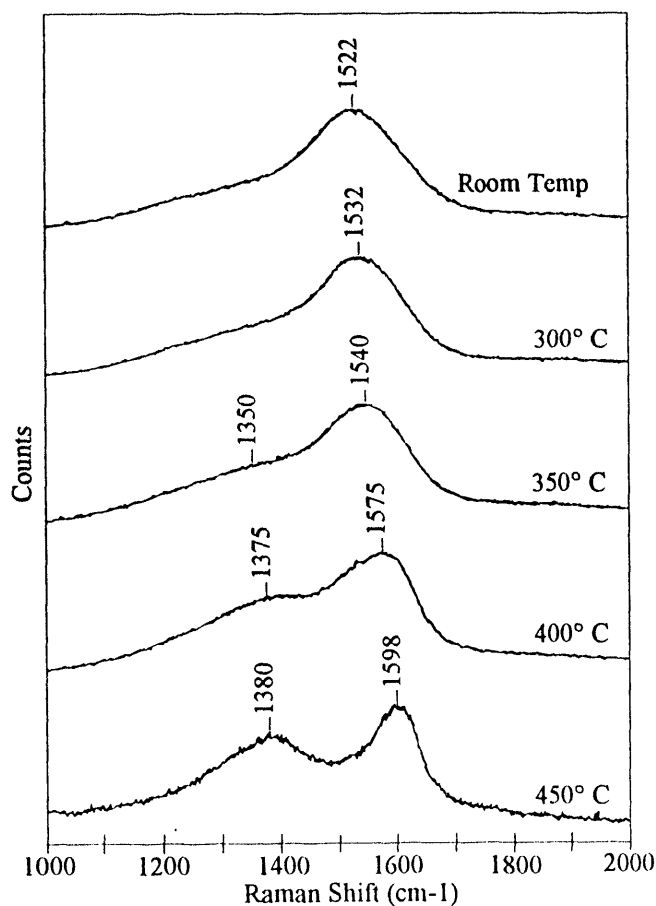


Figure (3): Changes in the Raman spectrum of a DLC film on tungsten as a function of annealing temperature in ambient air.

The spectrum is virtually unchanged after annealing at 300° C. Further annealing causes distinct changes in the Raman spectrum, including an upshift in the frequency of the original peak and the appearance of a second broad peak at 1350-1380  $cm^{-1}$ . After annealing at 450° C, these changes are complete, and the Raman spectrum is characteristic of micro-crystalline graphite or "glassy" carbon. These changes suggest a substantial conversion of  $sp^3$  to  $sp^2$  carbon between 300 and 450° C, consistent with the Auger data. The Raman data are discussed in considerably more detail elsewhere (4b).

Raman studies were also conducted to test the stability of DLC in certain severe environments, and these results have also been discussed in detail elsewhere (4b). No changes were observed in the Raman spectra of DLC films deposited onto aluminum and tungsten substrates after the films were

immersed in boiling (95° C) deionized water for periods of up to 88 hours. There was also no observed change in the Raman spectrum of a DLC film on tungsten that was exposed to a high humidity environment for two hours by placing it in a furnace at 225° C along with a beaker of boiling water.

### III. DISCUSSION and CONCLUSIONS

The thermal desorption, Auger, and Raman results are all consistent in pointing to 250-300° C as the maximum temperature range in which DLC is sufficiently stable to serve as a potential substitute for diamond in coatings applications. It is thus clearly suitable for any applications where only ambient temperatures will be encountered. These results apply to the DLC in this study, which is deposited via plasma CVD from methane and is estimated to have an  $sp^3/sp^2$  carbon ratio of 60%/40% and a hydrogen content of approximately 40 atom %. Given that the type of hydrocarbon used in plasma CVD of carbon films seems to be of relatively little importance in determining film properties, we would expect similar results for films grown via plasma CVD using other hydrocarbon starting materials. The results could well differ significantly for other types of carbon films. In particular, films with less hydrogen and a higher  $sp^3/sp^2$  ratio would be expected to be more similar to true diamond, and thus could be stable to significantly higher temperatures.

As discussed above, the experimental techniques employed in this study all examine different microscopic properties of the DLC films. While these microscopic properties should control the macroscopic physical properties of the films, it is desirable to examine key macroscopic properties directly in order to confirm that transitions do in fact occur in the temperature range that our results suggest. Towards this end, hardness measurements on these films as a function of annealing temperature are planned for the near future.

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