A SFF Approach Utilizing Condensed Gas Precursors and Pulsed Laser Deposition

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Abstract

Two techniques were studied in an effort to direct write diamond-like carbon (DLC) films. The first process employed a pulsed YAG laser to decompose a frozen precursor and deposit thin films directly on SiC and 304 stainless steel. After the initial film is deposited, additional layers may be subsequently condensed and deposited onto the substrate. A second approach is considered, whereby, the pulsed YAG is used to ablate the frozen precursor target and deposit a film on a nearby SiO_2 substrate that was locally heated by a CO_2 laser in an effort to augment the surface reaction rates.

Introduction

Diamond-like carbon (DLC) films synthesized by the decomposition of hydrocarbons by an energy source (electrical, thermal, or electromagnetic) have generated a lot of interest due to their wear resistance, hardness and chemical inertness. The diamond-like character of the film is controlled by the proportion of the sp_3 bonds relative to the sp_2 bonds. The Gibbs free energy difference between these two forms of carbon bonding is very small, on the order of 0.5 Kca/g-atom, so under most deposition conditions there is probability that some carbon atoms will bond in the sp_2 configuration and some in the sp_3 configuration. The role of atomic hydrogen can be critical in maximizing the sp_3/sp_2 ratio. Atomic hydrogen is considered to play an important role in diamond nucleation and growth through differential etching of sp_2 and sp_3 bond stabilization. [1] Although there has been a great deal of progress in the technological aspects of diamond CVD, the underlying gas/diamond interface chemistry is still not completely understood. The focus of this paper is to explore two methods of depositing DLC via variations of Selective Area Laser Deposition (SALD), which is a Solid Free Form Fabrication (SFF) technique.

SALD is a deposition process that uses localized chemical vapor deposition to deposit solid materials from precursor gases to create shapes in an additive manner. [2] The chemistry of the deposited material can be controlled through various process parameters like temperature, laser wavelength, and precursor pressure and composition. [3] The first approach used in this study involves condensing and solidifying the gaseous precursor onto the substrate and decomposing the precursor and directly depositing on the substrate. The solidification of the precursor allows for a high concentration of the precursor molecule in the SALD process zone, which can lead to increased deposition rates, and creates a highly uniform initial film. Acetylene is the precursor used for carbon deposition, owing to its relatively low melting and sublimation points (MP 191k SubT 193K) and the relatively weak C-H bond [0.36 eV]. [4] After the initial deposition, additional layers of the precursor may be subsequently condensed and decomposed. This technique is obviously suited for pulsed lasers, which don't require pyrolytic decomposition of the precursor and hence is ideal for low temperature processing. This methodology also allows for depositing on substrates that do not absorb the laser's

wavelength, however the problem of ablation of the substrates does arise. The second technique, pulsed laser deposition (PLD), relies on an increased laser energy density to ablate the condensed target precursor and essentially sputter the energetic dissociated precursor onto a locally heated substrate. PLD is widely used to produce DLC films by sputtering graphite. [5,6,7] The substrate is locally heated to augment the surface reaction rates and provide a method of controlling the deposition area. [8] Both 1064 and 266 nm wavelengths were used to sputter the acetylene, as it has been suggested that photon energy plays a role in the diamond-like properties of the film. [6,9]

Experiment

Film depositions were conducted in a stainless steel vacuum chamber evacuated by a rotary vane pump to a base pressure of 100 mTorr. Acetylene gas was than introduced into the reaction chamber, where it was condensed and solidified on a liquid nitrogen chilled substrate. A pulsed YAG laser (λ=1064 nm, 5-7ns pulse width) was operated at 10 Hz at approximately 45 degrees to normal at an energy density of 15 to 20 J/cm^2 . This laser was equipped with several harmonic generators capable of producing wavelengths at 266, 355, and 532 nm at decreased energy densities. For PLD, a secondary 25 W CO$_2$ laser was directed through a ZnSe window to heat a SiO2 substrate to 300 C as measured by an infrared pyrometer. To increase the ratio of sp$_3$ sites in the deposited material H$_2$ gas was added into the system and thermally cracked by a heated Tungsten filament to produce atomic hydrogen. The Raman measurements were collected by micro-Raman device utilizing a λ=514 nm green laser as an excitation source.

Results and Discussion

Several films were deposited under various conditions of substrate type , partial hydrogen pressure, laser wavelength, and laser energy density. The deposited films were characterized by Raman spectroscopy and determined to be either microcrystalline graphite or DLC depending upon the deposition conditions and technique. The films that could be deposited by PLD were observed to be very smooth except for an area of irregular crystal growth. Both the regular film surface and the larger crystallites displayed Raman spectra generally attributed to DLC. The direct deposition technique, by comparison, created depositions whose film density was highly irregular, due to ablation, and whose Raman spectra could be generally characterized as microcrystalline graphite.

Raman spectra is ideally suited for examining DLC deposits, as both crystalline diamond and to a greater extent graphitic carbon are strong Raman scatters. Raman spectra of amorphous carbon films are generally composed of 2 peaks: the G line centered at 1550 cm^{-1}; and the D line which is centered around 1350 cm^{-1}. The D peak becomes active in the presence of small graphite crystallites. Normally a sharp peak at 1332cm^{-1} is to be expected for diamond, but the sensitivity of the Raman line is approximately 50 times lower than graphite. The G peak is due to C=C stretching vibrations of graphite. The positions, widths and relative intensities of these G and D peaks have been found to vary systematically with film properties. [10, 11] It was observed by Tamer et al [11 that an increase in G line width corresponds with increased density and hardness. The ratio of the intensities of the D to G peaks is also used as an indicator of the nature of the films, as a high I$_D$/I$_G$ ratio indicates very small graphite crystals which may be indicative of DLC films. [10] DLC Raman spectra generally consists of a broadband from 1540 to 1600 overlapped by a component lying between the two graphite bands. [10, 12]

The direct deposition method utilized 304 stainless steel, SiC and amorphous SiO_2 as substrates. The majority of deposits on stainless steel displayed Raman spectra with relatively narrow G and D lines of roughly the same intensities as seen in fig 1. In particular, for steel lower energy densities ($15 J/cm^2$) were conducive to greater film densities as ablation of films was often a problem. A combination of the 1st, 2nd and 4th harmonics of the YAG did yield a DLC Raman spectra for distinct parts of the deposit as shown in figure 2. Figure 3 depicts the silicon carbide substrate which was coated with a thin deposit of polycrystalline graphite. We have been unable to deposit on the SiO_2, which is transparent to the YAG wavelength, thus far. It was noted that a very low concentration of hydrogen, less than 10 torr, often leads to a slight decrease in the intensity of the D peak, but for higher hydrogen partial pressures no noticeable difference was detected.

The PLD technique was able to consistently deposit DLC on a quartz substrate. Raman characterization yielded a distinct DLC spectra as shown in figure 4. The ability to direct write with PLD by attempting to control the process zone via localized heating of the quartz, however, is admittedly more technically difficult than the direct deposit method. The partial pressure of hydrogen was varied but it was determined that any benefit a higher density of atomic hydrogen might produce was negated by the decrease in the mean free path of the sputtered hydrocarbons. Various combinations of wavelengths were also explored, but only the primary beam had a sufficient energy density to ablate the target.

Conclusion

While much still remains to be optimized in the process both methods have been shown to be able to deposit DLC. Future work will focus on attempting to create rudimentary DLC structures and more extensive characterization of the films.

Acknowledgements

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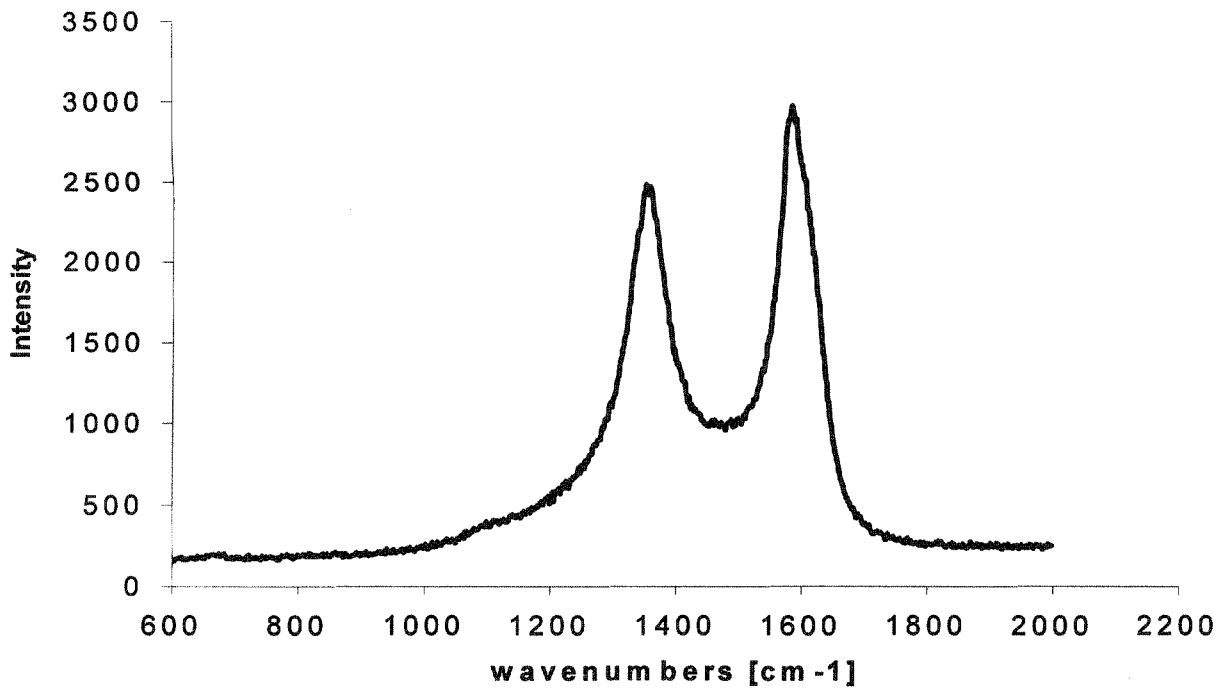
FIG 1 Raman spectra of microcrystalline graphite on 304 stainless steel by direct deposition
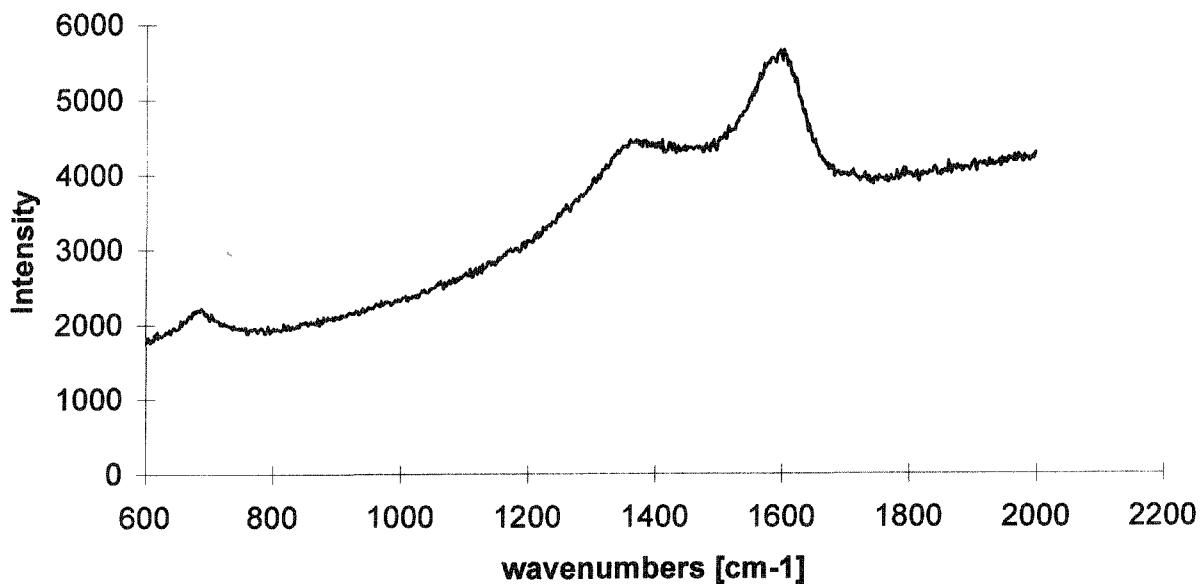

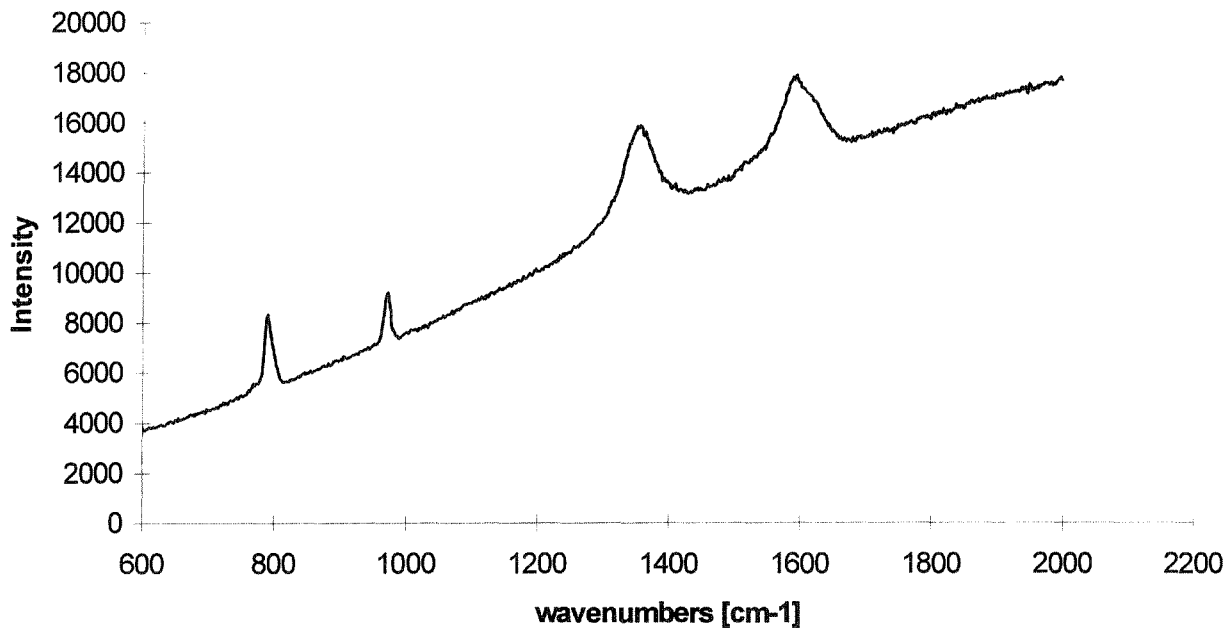FIG 2 Raman spectra of DLC on 304 stainless steel by direct deposition

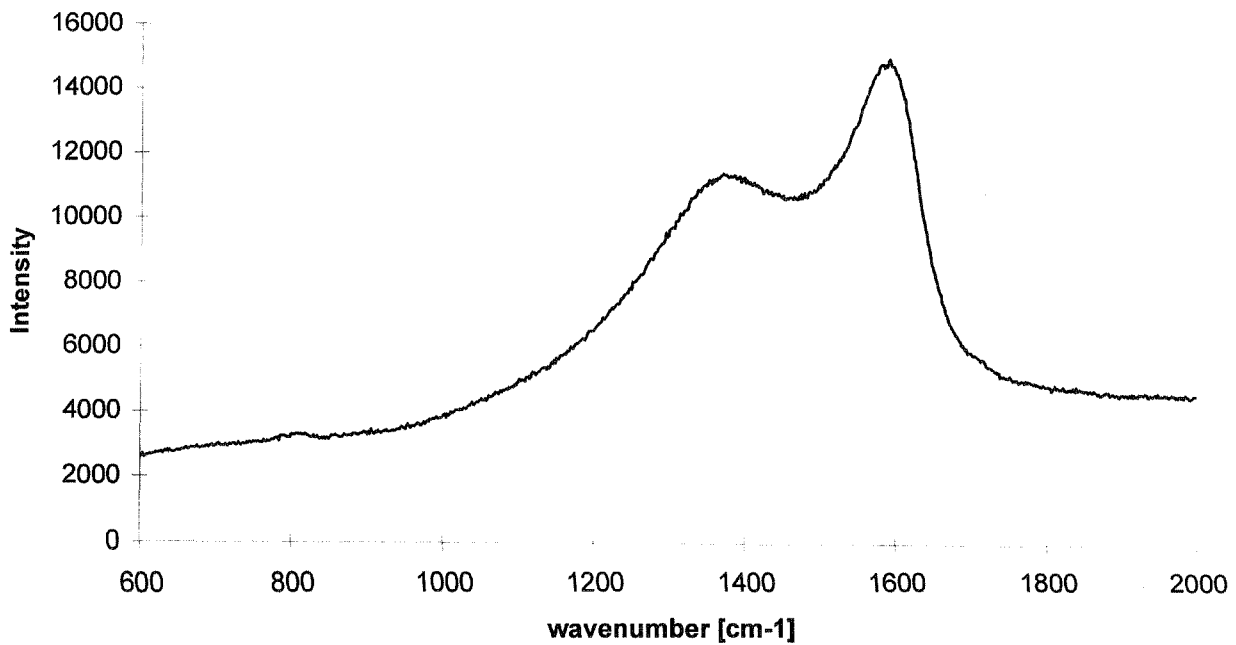FIG 3   Raman spectra of microcrystalline graphite on SiC by direct deposition

FIG 4   Raman spectra of DLC on SiO_2 by PLD technique