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Growth Dynamics of Carbon Nano-Particles and Their Incorporation in DLC films

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Abstract

The in-situ investigation of the dust particle growth in a capacitively coupled RF plasma in Ar/CH_4 indicates that precursors might be negatively charged $C_2H_x^-$ molecules. The 7th harmonic signal of the RF driving voltage is a useful indicator for the presence of dust particles and their growth. We have incorporated nano-meter size carbon particles of pre-selected size into DLC films yielding substantial relaxation of the compressive stress of the film.

Introduction

It is pointed out that thin films incorporating nano-meter size particles could have useful new material properties [1,2]. To modify thin film properties using incorporated dust particles, it is necessary to understand the growth dynamics of the dust particles in reactive plasmas and to have an external parameter as an indicator to monitor their size.

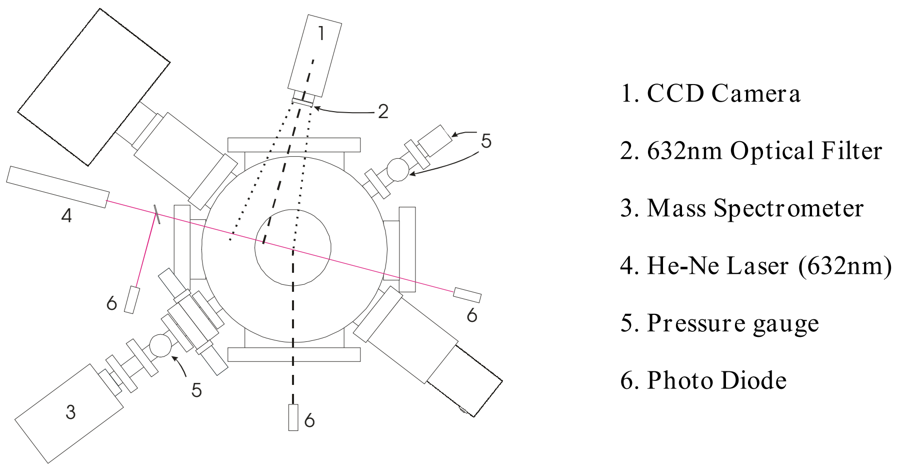


Fig.1 Experimental Setup

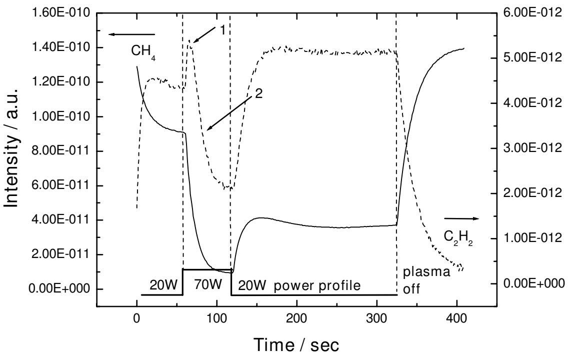
Experimental Setup

Figure 1 shows the experimental setup. We have used a capacitively coupled parallel plate reactor (GEC Cell) at 13.56MHz with a coupled net input power of 20W except for the ignition phase of the Ar/CH_4 discharge (>60Watt for 30 seconds). Typical pressures in the reaction chamber are about $1.3x10^{-1}$ mbar ($Ar:CH_4$=8:2 sccm). Laser light scattering (LLS) and absorption by dust particles, spectrum analysis for the change of plasma impedance by the presence of dust particles, and mass spectroscopic measurements are performed in-situ.

Experimental Results

To initiate particle formation in a Ar/CH_4 discharge, a transient high power (>60W, 15-30sec) is needed. The particles continue to grow to large size (~µm) and weight until they are lost from the discharge. No further particle growth occurs unless the power is increased again to high values. On the other hand, particles are formed spontaneously in Ar/C_2H_2 discharges. They also grow to large size and are lost from the discharge, but a new growth cycle starts spontaneously leading to a periodic behavior of the discharge and particles. Similar periodic behavior is also observed for the IR-absorption in an optical multi-path cell (Whyte-Cell). To analyze the initiation of growth in Ar/CH_4 we have coupled in a first experiment a single square pulse superimposed on a constant low RF power level. The input power is 20W for 60 seconds at ignition time, then 70W for next 60 seconds, and then 20W for the rest of the experiment. The response of the residual gas components is shown in figure 2. When the Ar/CH_4 discharge is ignited, the CH_4 concentration decreases whereas the C_2H_2 concentration increases (confirmed by FTIR measurements [3]). As soon as the input power is higher than 60W, the discharge is changed to a new mode. In this mode, CH_4 consumption increases dramatically, whereas C_2H_2 concentration increases rapidly until well-defined maximum is reached and decreases thereafter. Note that although the input power is lowered to 20W after 60 seconds, the discharge mode is not changed to its initial mode again: CH_4 consumption and C_2H_2 production rates remain higher than in its initial mode. CH_4 and C_2H_2 concentrations show opposite behavior as soon as the discharge is turned off. We assume that once the C_2H_2 concentration is large enough, the precursor concentration reaches its critical density to initiate particle formation (label 1 at Fig. 2). C_2H_2 decrease indicates the gas consumption during particle growth (label 2 at Fig 2).

In a second experiment we have injected a small pulse of C_2H_2 into a pure Ar discharge at constant low power level of 20W. Several minutes after the injection of the C_2H_2 pulse, we have added CH_4 continuously. Figure 3 shows that the background emission intensity is slight increased due to the small change of gas mixtures, but no indication of particle formation is observed by LLS after the C_2H_2 pulse. As soon as CH_4 is injected, however, the scattered light intensity increases, indicating particle formation in the discharge. Consequently, a single cycle of the particle formation occurs as for Ar/CH_4 discharge with the transiently increased power. Particle formation was observed even 20 minutes after the C_2H_2 pulse, showing that the precursors are well confined and are probably *negatively* charged. Care must be taken that the amount of C_2H_2 injected into the Ar discharge is low enough that no dust particles are formed spontaneously in that "Ar/C_2H_2" discharge.



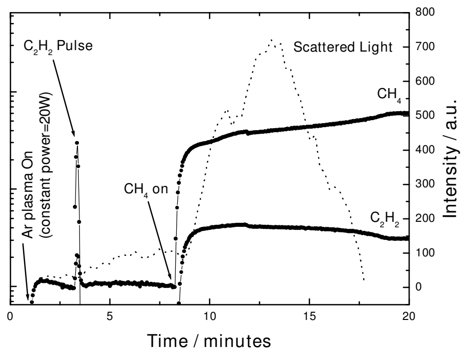


Fig.2 Mass spectrum of Ar/CH_4 discharge with transient high power (solid: CH_4, dashed: C_2H_2)

Fig. 3 Mass spectrums of CH_4 and stable C_2H_2 (dot-dashed) and scattered light (dashed) in the Ar/C_2H_2/CH_4 discharge with respect to time

Boufendi et al. have reported that harmonics of the RF driving voltage or current are sensitive to particle formation [4]. We have confirmed the finding. The 7^{th} harmonic of the voltage signal is very sensitive to the particle formation in both Ar/CH_4 and Ar/C_2H_2 discharges [5]. We have used the amplitude of the 7^{th} harmonic frequency as real-time monitor for the growth process. In order to determine the particle diameter, the growth process is interrupted at specific values of the 7^{th} harmonic and particles are collected, and their diameter is determined by SEM ex-situ. Measured particle sizes were about

100nm to 700nm depending on processing time, and their size distribution is essentially mono-disperse. Figure 4 shows the particle size and 7th harmonic of voltage signal versus time respectively. Since the 7th harmonic is highly reproducible, we could monitor the dust particle size in-situ during the growth process. Figure 5 shows a deposited 2-dimensional structure of "dust dots" onto a silicon wafer. The particle size is controlled by the 7th harmonic signal to be 150nm in diameter. We have deposited successively a DLC film of about 250nm thickness using pure C_2H_2 under conditions where no dust formation occurs. Figure 5 shows that the internal stress of the DLC film leads to delimitation areas without dust incorporation. A well-adhered high quality film is remaining in the areas with incorporated dust, indication of a substantially relaxed compressive stress. This incorporation of nano-particle may be used to produce stress-free thick dispersion coatings.

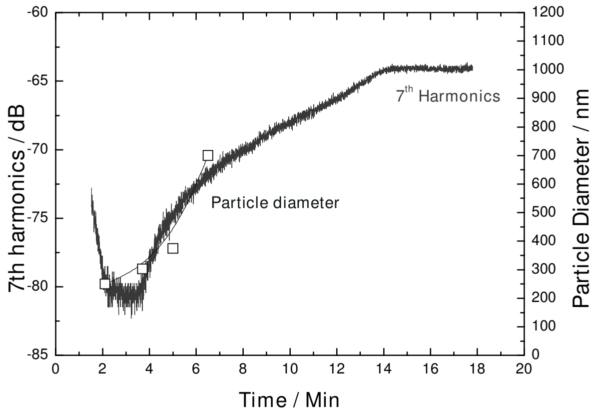


Fig.4 particle diameter (SEM measured) and 7th harmonic signal.

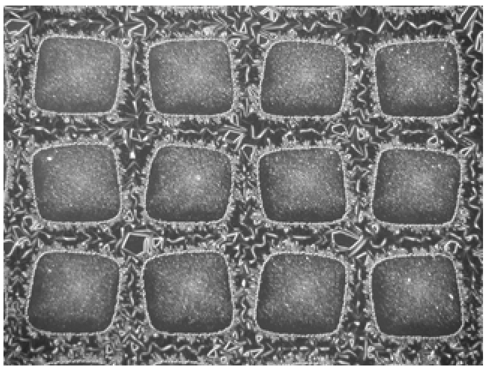


Fig. 5 incorporated "dust dots" in DLC film. Internal stress is highly reduced.

Acknowledgement

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