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HIGH GROWTH RATE DIAMOND SYNTHESIS IN A LARGE
AREA ATMOSPHERIC PRESSURE INDUCTIVELY COUPLED
PLASMA

Submitted by

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HIGH GROWTH RATE DIAMOND SYNTHESIS IN A LARGE AREA ATMOSPHERIC PRESSURE INDUCTIVELY COUPLED PLASMA

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Abstract

Diamond synthesis is demonstrated in an atmospheric pressure inductively coupled argon-hydrogen-methane plasma. The plasma generated has a free stream active area of 20 cm^2 and has an equilibrium electron temperature T_e of approximately 4000 K. Growth rates are typically in the range of 25-50 $\mu\text{m}/\text{hour}$ and are found to depend on the processing conditions and position on the substrate. Individual crystallites are analyzed by micro-Raman spectroscopy. Large (50 μm) size well-faceted crystallites are found to be under a state of compression, displaying shifts in the principal phonon mode as great as 3 cm^{-1} from that of smaller polycrystalline diamond clusters or secondary nucleation sites. These shifts are shown to be expected within the framework of linear thermal expansion theory and the assumption of negligible stress relief at the crystallite-substrate interface.

High growth rate synthesis of polycrystalline diamond using atmospheric pressure plasmas and flames is a promising alternative to the more conventional synthesis techniques¹⁻³. It has already been demonstrated that growth rates as high as 200 $\mu\text{m}/\text{hour}$ can be achieved in direct current (DC) plasma arcs^{4,5}, with a noticeable improvement in quality when compared to microwave plasma deposited diamond film. In DC plasma arc deposition, diamond growth occurs primarily over the region where the arc is in contact with the substrate (usually the anode in the transferred arc mode) and the deposit is highly irregular and non-uniform⁴. High power transferred arcs suffer from additional disadvantages such as cathode material contamination, which suggests that applications of such synthesis strategies may be limited to production of industrial grade polycrystalline powder for abrasive applications. There has been some limited study of the use of inductively coupled thermal plasmas for diamond synthesis⁶. Such a plasma is electrodeless and is therefore preferred over the DC arc in the synthesis of diamond coatings with a minimum level of impurities. In addition, inductively coupled atmospheric plasmas can be generated over larger volumes than their DC counterparts. This makes it attractive for large area coating applications. Such plasmas however, have a number of disadvantages for laboratory investigation and some industrial applications

in that they are intrinsically noisy, generating RF interference at the operating frequency, and can establish relatively high (1-3 kV) plasma potentials⁷.

Perhaps most important to the understanding of the deposition chemistry is the fact that these plasmas are close to thermal equilibrium, and an analysis of the reacting stream is complicated solely by the presence of finite rate chemistry. In essence, the problem reduces to that of hot filament assisted chemical vapor deposition of diamond, and is free of the nonequilibrium features associated with low pressure (< 50 torr) microwave and DC discharge sources. A great deal of progress has been made in the modelling of reacting flows (with transport)⁸, and we may soon expect to see a one-dimensional transport code that incorporates surface chemistry⁹. In diamond synthesis at atmospheric pressure, supersaturation of hydrogen in the gas phase adjacent the substrate or growing surface is believed to be responsible for diamond synthesis. This supersaturation is established as a result of rapid diffusion and finite recombination rates through the thermal boundary layer adjacent the growth surface. Atomic hydrogen is known to preferentially "etch" or gasify non-diamond carbon^{10,11}, and is believed to play a role in producing an "active site" (through adsorbed hydrogen abstraction) in which a gas phase hydrocarbon monomer (of the type C_2H_x) can be inserted to propagate the crystal growth plane^{12,13}.

In this paper, we report on results of our investigation of diamond synthesis, in an atmospheric pressure inductively coupled plasma flow reactor. In the course of this investigation, we have studied nucleation and growth on a variety of substrates, and report here only our results of a set of experiments involving diamond growth on polycrystalline molybdenum. Our diamond films are grown under conditions similar to that of Matsumoto et al⁶ and Koshino et al⁴. No parametric study however, has been performed to investigate the range of optimum processing conditions, and we suspect that this range can be considerably different than that observed in low pressure PECVD of diamond¹⁴.

The plasma deposition facility includes a 50 kW RF generator operating at 4 MHz, and a commercially available inductive load coil torch head which acts as an antenna, coupling as much as 20 kW into the gas stream. For the results presented here, an energy balance on the system indicated that approximately 6 kW of power was coupled into a gas stream comprising a mixture of argon, hydrogen and methane with relative volumetric flow ratios of 210:32:1. The total volumetric flow was approximately 120 l/min. A specially designed water cooled quartz cylinder, 5 cm in diameter, surrounded the plasma flow and minimized air entrainment. A water cooled molybdenum substrate holder is mounted in stagnation point flow within this quartz envelope (see Fig.1). A molybdenum foil acts as the substrate, and is fastened by molybdenum clamps to achieve good thermal contact.

The plasma emission is monitored with a 3/4 meter scanning monochromator. Analysis of the relative intensity of hydrogen spectral lines permitted a measurement of the electron temperature which under these conditions is expected to be equal to the gas temperature. For the runs reported here, the line emission was well represented by a straight line on a Boltzmann plot and the free stream electron temperature was measured to be approximately 4000K, 2 cm below the substrate. A disappearing filament pyrometer is used to measure the surface brightness temperature. For the results presented here, the substrate surface is approximately 3x3 cm in dimension and is maintained at approximately 900 °C. The surface temperature did not appear to vary substantially across the substrate face (although this measurement was a difficult task) however, there may be a slight increase in the surface temperature (approximately 100 °C) from the center stagnation line to the substrate edge.

Results of numerous runs of 2 hours in duration indicate that the deposit is pattern is very reproducible and that the deposit varies substantially across the substrate surface. Nucleation and growth occurs primarily in the outer regions of the substrate surface. There is no nucleation in the central core ($r < 1$ cm). A low resolution scanning electron micrograph of the area near the interface between the region of no growth (center stagnation region) and the region where a continuous film is established, is depicted in Fig. 2. As one moves radially out from the centre, the nucleation density increases rapidly, with first a region of nicely faceted crystallites followed by a region of dense film. The crystallites appear to adhere very well to the substrate whereas the film can be physically detached from the substrate with some effort.

The larger well-faceted crystallites display a growth habit yet unreported in low pressure diamond CVD. Fig. 3a is a representative electron micrograph, showing that the (100) facets appear to form a "hollow" twinned structure with three fold rotational symmetry. Fig. 3b depicts a similar structure, again very typical for the deposit, only this crystallite may have reached a later stage in growth, having a more completed crystal habit. The twinned crystallites of the type illustrated in Fig. 3b usually show evidence of secondary nucleation on the completed (100) facets. The individual crystals and secondary nucleation sites were large enough for micro-Raman analysis. The Raman spectrum of the well-faceted crystallites (Fig. 4) contain the characteristic peak associated with the first order phonon mode of diamond although shifted somewhat to longer wavelengths (1335 cm^{-1}). This shift is significantly greater than the resolution and accuracy of the instrument (approximately 0.5 cm^{-1}) and is attributed to a compressive stress in the crystallite. This stress arises from the mismatch in thermal expansion between the diamond crystal and underlying interlayer (likely to be MoC or Mo₂C). Substantial shifts in the Raman peaks of CVD diamond grown on sapphire have been reported in the past¹⁵. The shifts observed here correspond to a compressive stress of approximately 1GPa, based on the pressure dependence of the first order Raman peak as

measured by Boppart et al¹⁶. A compressive stress of such magnitude is expected if one assumes that the interlayer is Mo₂C with a linear expansion coefficient of approximately $7 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ¹⁷ over the temperature range of interest. Upon cooling, $\Delta T \sim 1000 \text{ K}$, and assuming negligible stress relief at the interface, this translates to a linear compression in diamond of about $a/a_0 = 0.9993$ (here a is the bond length and a_0 the bond length at atmospheric pressure). Theoretical shifts calculated by Sherman¹⁸ for this compression are in the $2\text{-}3 \text{ cm}^{-1}$ and hence in agreement with our observations. It should be pointed out that Raman analysis of secondary nucleation sites present on (100) facets show a substantial non-diamond component usually attributed to disordered sp^2 structure¹⁵ and an unshifted Raman peak (Fig. 5). The unshifted Raman peak of diamond is frequently observed when a substantial non-diamond contribution is evident in the Raman spectra, and may be indicative of stress relief by the amorphous matrix.

Growth rates on the order of $25\text{-}50 \text{ }\mu\text{m/hour}$ have been observed for well faceted crystallites and are more than an order of magnitude greater than that observed in low pressure microwave plasma deposition strategies¹⁴. This difference is attributed to the higher carbon and atomic hydrogen flux associated with such thermal plasmas at these temperatures. This growth rate is based on an estimate of the crystallite size and the run duration, and may be substantially higher if one takes into account the "induction" time necessary for nucleation¹⁹. The absence of diamond growth in the region near the stagnation point of the flow is attributed to too high an atomic hydrogen flux, and is the subject of a future publication.

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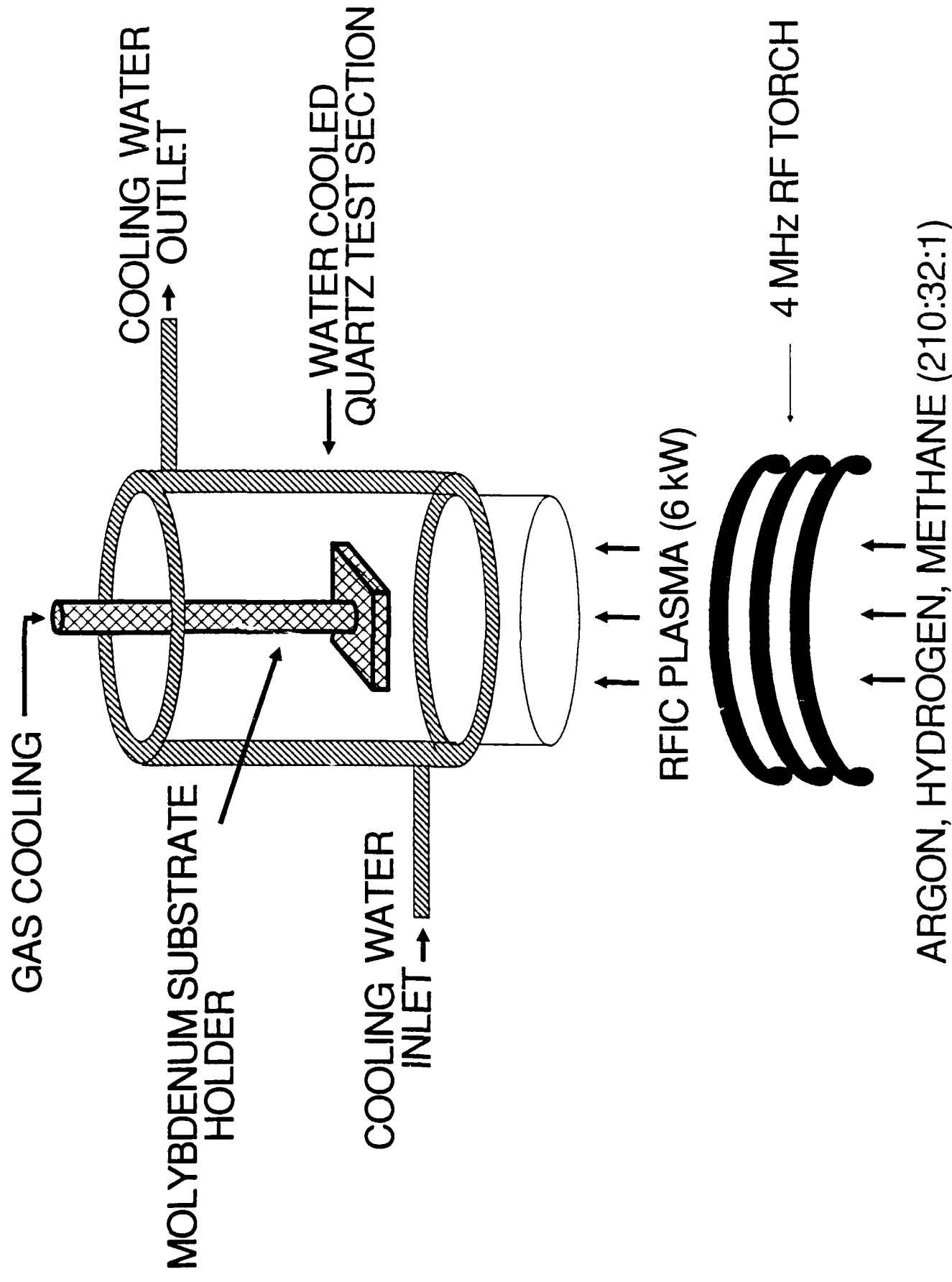
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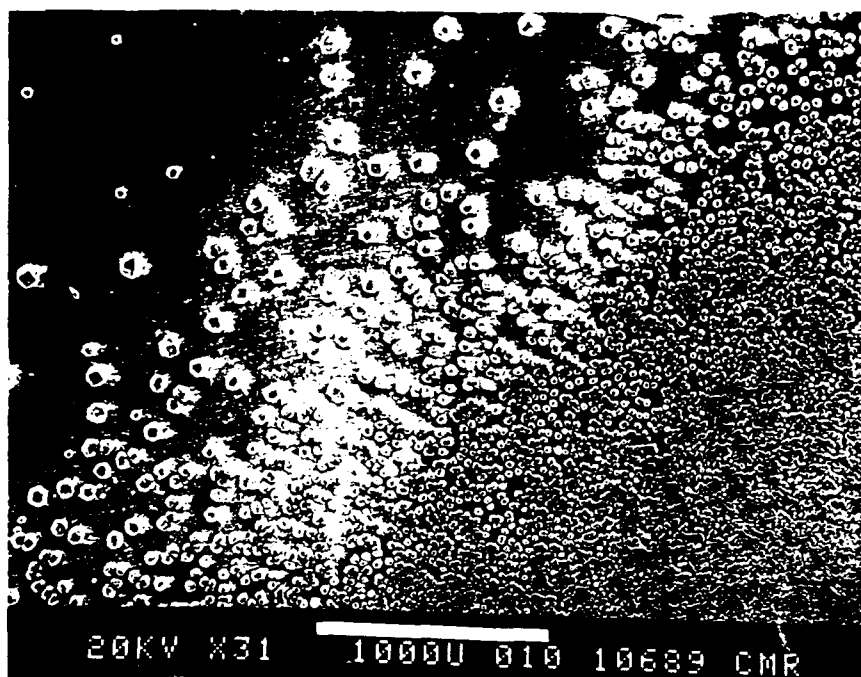
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Figure Captions

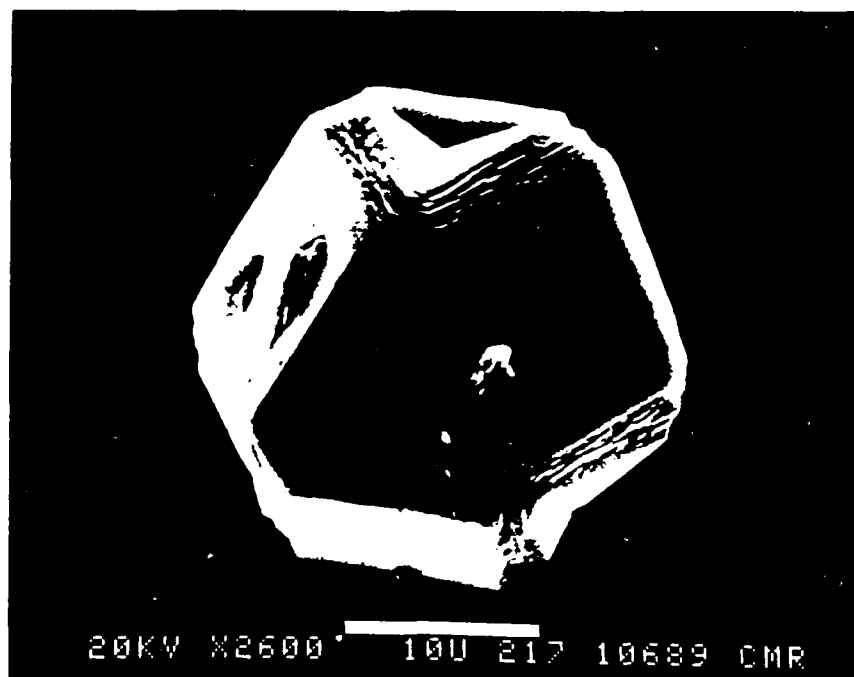
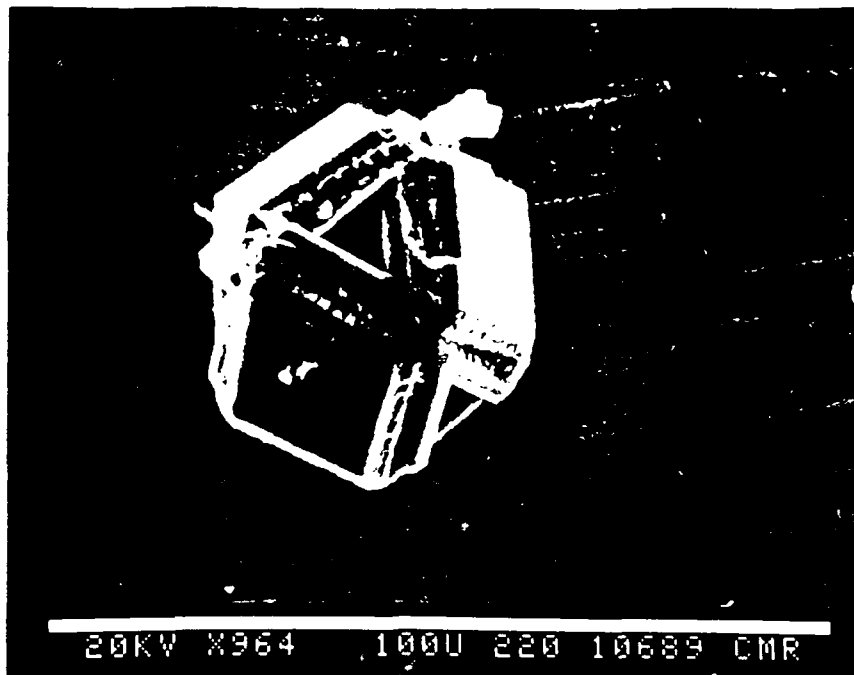
- Fig. 1. Experimental Schematic of the thermal atmospheric pressure induction plasma deposition facility.
- Fig. 2. Low resolution scanning electron micrograph of region between discrete particle growth and growth of a continuous film.
- Fig. 3. Electron micrographs of a) twinned "hollow" structure and b) similar structure believed to be in a more complete stage of growth.
- Fig. 4. Raman spectrum of a typical well faceted crystallite. The Raman peak associated with the principal phonon mode (normally at 1332 cm^{-1}) is shifted by approximately 3 cm^{-1} .
- Fig. 5. Typical micro-Raman analysis of secondary nucleation sites on well faceted crystallites. The Raman peak associated with diamond is evident above a background amorphous signature, and is unshifted, centered at approximately 1332 cm^{-1} .

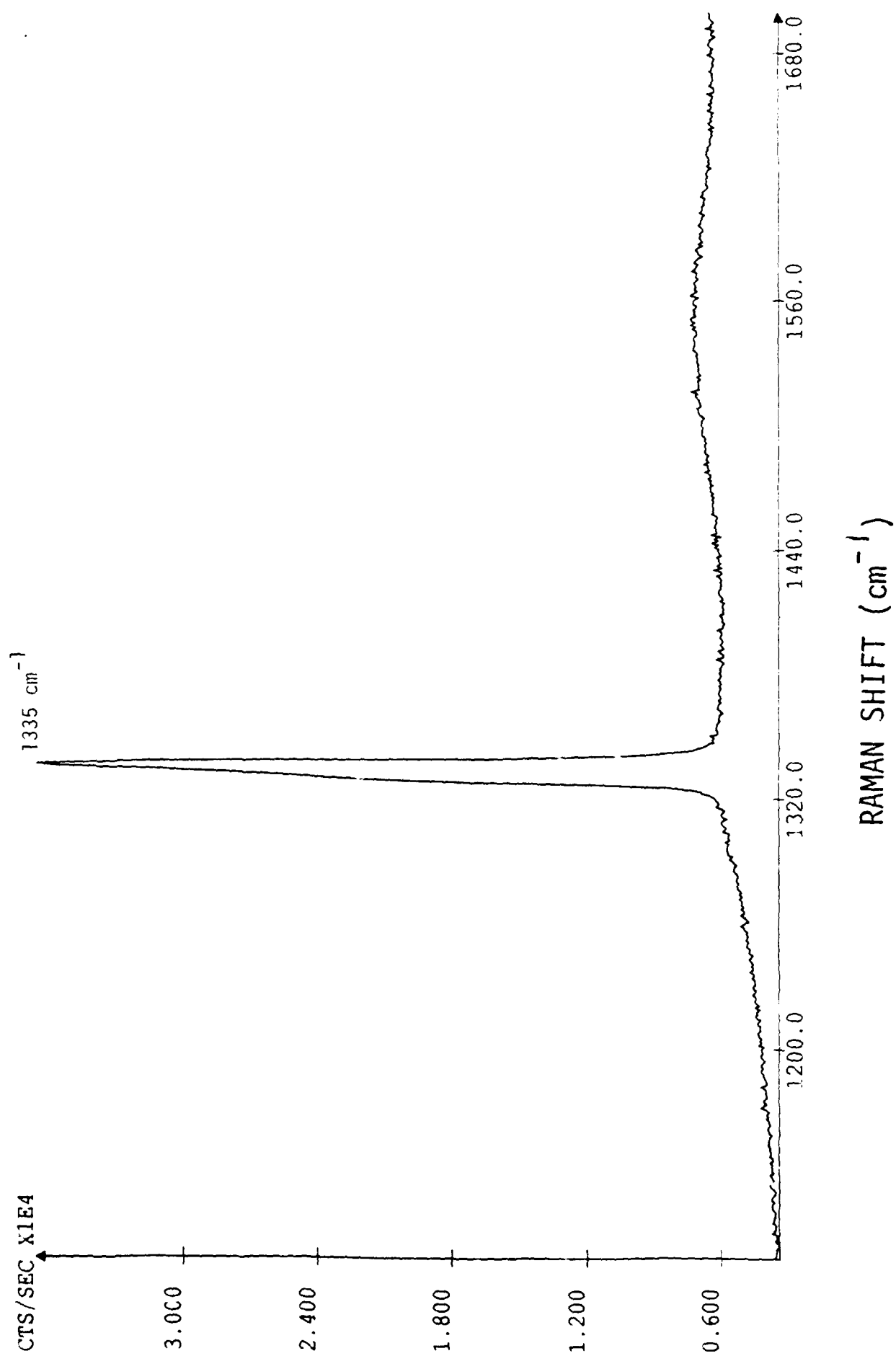
THERMAL PLASMA DEPOSITION OF DIAMOND

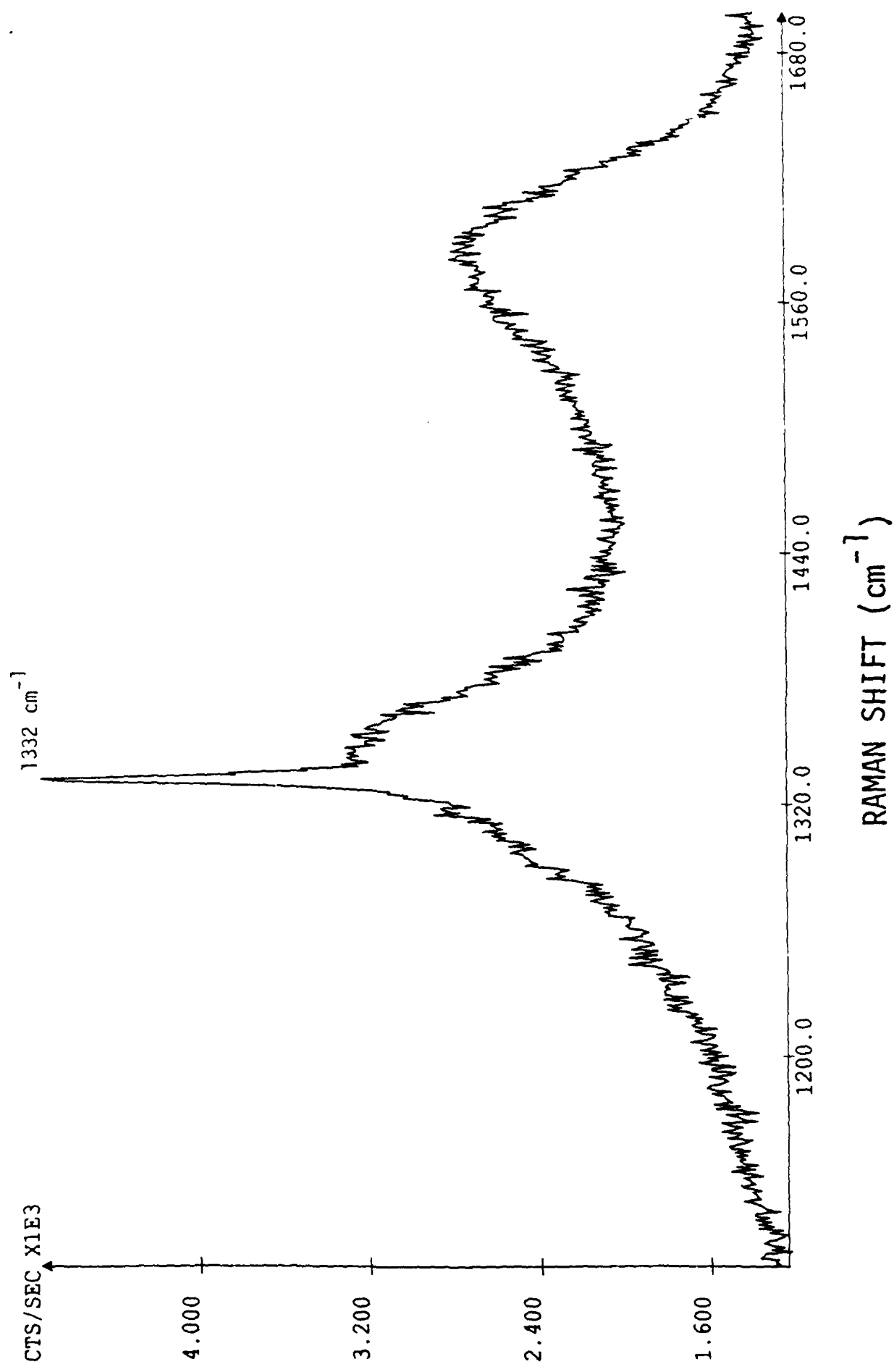




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