Diamond Synthesis by DC Thermal Plasma CVD at 1 atm

Z. P. Lu, L. Stachowicz, P. Kong, J. Heberlein, and E. Pfender

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Diamond crystals and films have been successfully synthesized by DC thermal plasma jet CVD at a pressure of 1 atm. A novel triple torch plasma reactor has been used to generate a convergent plasma volume to entrain the participating gases. Three coalescing plasma jets produced by this reactor direct the dissociated and ionized gaseous species onto (100) silicon wafer substrates where the diamond grows. In a typical 10-min run, depending on the method of substrate preparation, either microcrystals with sizes up to 8 μm or continuous films with thicknesses of 1–2 μm have been obtained. X-ray diffraction, scanning electron microscopy, and Raman spectroscopy have been used for the characterization of the crystals and of the films.

KEY WORDS: Diamond; plasma synthesis; atmospheric pressure; triple-torch plasma reactor.

1. INTRODUCTION

There have been increasing research efforts to produce diamond under thermodynamic metastable conditions. Numerous processes have been reported over the past decade including hot filament CVD, microwave plasma-assisted CVD, RF plasma-assisted CVD, arc discharge-assisted CVD, hollow-cathode CVD, and oxygen-acetylene flame CVD. Among the various plasma-assisted chemical vapor deposition processes, the majority of the research has been conducted under reduced pressures, i.e., 1–100 torr. Attempts have been made to synthesize diamond at 1 atm and, recently, there have been reports on the thermal plasma synthesis of diamond films. For example, Matsumoto et al. briefly reported...
diamond deposition with an inductively coupled atmospheric-pressure thermal plasma and Cappelli et al.\textsuperscript{(14)} published a more detailed paper on the subject recently.

Thermal plasmas are by definition in a state of equilibrium or, more precisely, in local thermodynamic equilibrium (LTE). The high number densities of species associated with LTE plasmas give rise to high collision frequencies and, as a result, the heavy particles (atoms and ions) have essentially the same temperature as the electrons. If such a plasma is rapidly quenched, as for example at the surface of a cooled substrate, chemical reactions will be "frozen," i.e., strong deviation from chemical equilibrium will occur. As a consequence, the hydrogen ions, atoms,\textsuperscript{(15-17)} and other radicals, such as CH\textsubscript{3},\textsuperscript{(18,19)} which are believed to be responsible for the successful synthesis of diamond, will have a much higher concentration than if they would have in a corresponding equilibrium state.

2. EXPERIMENTS

Figure 1a shows the experimental apparatus. The heart of the system consists of three identical DC plasma arc torches (only two of them are shown in the schematic). The plasma torches are mounted on the top flange of the reactor chamber in such a way that the plasma jets of the torches coalesce, forming a converging plasma volume. A water-cooled gas feeding probe is located above the temperature valley formed by the three plasma jets. Details of the equipment can be found in a previous publication.\textsuperscript{(20)} These jets impinge on (100) silicon substrates which are glued onto a pressurized water-cooled copper substrate holder with a ceramic-base high-temperature adhesive. In some of the experiments, substrates are scratched with a 1 μm grit diamond paste for several minutes and cleaned with acetone in an ultrasonic bath for about 30 min.

The reactor chamber is evacuated to 0.01 torr and flushed with argon. The plasma torches are started in a pure argon environment at 1.0 atm. Hydrogen is then gradually added into the plasma torches. Additional hydrogen and methane are fed through the center feeding probe. The temperature valley between the plasma jet helps to direct the participating gases onto substrates. The substrate temperature was roughly monitored by a small strip of copper glued to the side of the silicon substrates. The substrates are raised until the copper strip starts melting, indicating a temperature of 1083°C, which is the melting point of copper. This is, of course, not a temperature measurement but rather a rough indication. Usually three silicon wafers are attached to the substrate holder for each run. The arrangement is shown schematically in Fig. 1b, and typical experimental conditions are summarized in Table I.