On the Plasma Chemistry of the C/H System Relevant to Diamond Deposition Processes

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The chemistry of hydrogen-rich hydrocarbon-hydrogen mixtures is of primary interest for the understanding of the low-pressure synthesis of diamond. We performed experiments under well-defined conditions like temperature, pressure, initial gas composition, etc. The gas composition at the end of a flow reactor was analyzed by a calibrated mass spectrometer and compared to results obtained from the Chemkin computer code. Residence time in the reactor as well as other process parameters were similar to those of diamond-growing PACVD processes performed earlier with the same experimental set-up. Modeling and experiment under isothermal conditions show quantitative agreement. We realized time-resolved mass spectrometry by means of a helium-flushed gas sampling probe. There is evidence that the commonly used reaction kinetic data for the dissociation \( \text{C}_2\text{H}_6 (+M) \leftrightarrow 2\text{CH}_3 (+M) \) gives too small \( \text{C}_2\text{H}_4 \) concentrations for hydrogen-rich conditions. This could be attributed to the poorly known third-body efficiencies of the \( \text{H}_2 \) molecules compared to \( \text{Ar} \) or \( \text{C}_2\text{H}_6 \) from which kinetic data are commonly derived.

KEY WORDS: Diamond synthesis; atomic hydrogen; modeling; mass spectrometry; pulsed rf discharge.

1. INTRODUCTION

Low-pressure synthesis of diamond normally takes place in hydrogen-rich hydrogen-hydrocarbon mixtures. Different gas discharge techniques using microwaves, dc and rf activation, or just thermal activation by a hot filament are common for obtaining the nonequilibrium state of the gas phase necessary for low-pressure/low-temperature deposition of diamond thin films.\(^{(1-3)}\) Atomic hydrogen plays the major role in driving the gas phase during the nonequilibrium state.\(^{(4)}\) We investigated chemical processes induced by activation of the gas producing a supersaturation of atomic H. As the concentration of H is a crucial factor in driving the C/H system a

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direct and absolute determination of the H concentration would be extremely valuable.\(^{(5)}\)

Laser-diagnostic methods\(^{(6)}\) are rather expensive and were not available to us. Optical emission spectroscopy, on the other hand, using argon as an actinometer gives only relative H concentrations. As the time constant for the production of atomic H is something like a few milliseconds,\(^{(7)}\) the reaction processes typically lead to significant changes in species concentrations during the very first time after the beginning of the plasma discharge. We developed a fast probe system which allows us insights into the formation of different stable species on a time scale down to 10 ms. One important aim of this study is to improve and verify numeric modeling on the basis of the chemical reaction mechanism that is based upon C\(_1\) and C\(_2\) species and which has already been published.\(^{(8)}\) With respect to the evidence of C\(_2\) shown in emission spectrometric data, we now also included C\(_2\) in our model.\(^{(9)}\) Modeling of the gas-phase reactions takes place on the basis of the CHEMKIN computer code.\(^{(10)}\)

2. EXPERIMENTAL DETAILS

An electrodeless rf plasma (discharge length 24 cm) in a quartz tube of 2.5 cm inner diameter is the centerpiece of the experimental set-up (Fig. 1). The discharge is operated with rf power from a solid-state generator with a peak power output of 1.1 kW at a frequency of 13.56 MHz through an automatic matching network. Before this reactor was slightly modified, it was used for diamond deposition on silicon carbide substrates.\(^{(11)}\)

Pressure inside the tube is adjusted by a throttle valve. Over a length of 80 cm the tube is positioned inside a well-insulated electric furnace to provide a homogeneous temperature changeable from room temperature up to 1200\(^\circ\)C. Temperature tolerance is \(\pm 5\) K over the central 40 cm including the plasma zone. Absolute temperature and homogeneity were verified with a Chromel–Alumel thermocouple and confirmed by two-wavelength pyrometry. The initial gas composition at the upstream end of the tubular reactor is chosen by means of mass flow controllers. More details of the experimental set-up are given elsewhere.\(^{(12)}\)

At the downstream end of the reactor the gas composition is analyzed by a quadrupole mass spectrometer. Time-resolved analysis is performed with a specially designed probe with helium flushing which is inserted into the quartz tube. The tip of the probe reaches right into the plasma zone. Figure 2 shows the principle of the probe system. The probe itself is made of two small-diameter quartz glass tubes which are melted together in a U-shaped form. A 0.3-mm-diameter hole was melted in the head through which the gas mixture from the plasma is extracted. High purity (99.9999%)