PREPARATION OF POLYCRYSTALLINE DIAMOND FILMS IN A PARALLEL-PLATE RF DEPOSITION SYSTEM

P. WOOD,[1] T. WYDEVEN,[1] and O. TSUJI[2]

[1]*Opto Films, Sunnyvale, CA 94089, U.S.A.*
[2]*SAMCO International, Inc., 33 Tanakamiya-cho, Takeda, Fushimi-ku, Kyoto 612, Japan*

A commercially available parallel-plate, plasma-enhanced chemical vapor deposition (PECVD) system was modified to conduct research on the deposition of diamond films from dilute methane/hydrogen (CH_4/H_2) mixtures. Preliminary experiments to determine the feasibility of depositing polycrystalline diamond on untreated and treated silicon or molybdenum substrates over the temperature range of 500–650°C suggested that significant diamond deposition does not occur at these mid-range temperatures, at least using the apparatus described here. Subsequent experiments with substrate temperatures of 750–850°C resulted in up to a ten-fold increase in the film deposition rate on silicon substrates and a hundred-fold increase in the deposition rate on molybdenum substrates.

1. Introduction

There have been a number of reports that suggest it is feasible to deposit crystalline diamond films by activated chemical vapor deposition (CVD) over a wide substrate temperature range of 500–1000°C.[1)–3)] Deposition of diamond films over the lower end of this temperature range would enable deposition on materials which cannot withstand the 800–1000°C substrate temperatures for which well-characterized polycrystalline diamond depositions have been reported.[3)–5)] In this paper we describe preliminary results which indicate that deposition of polycrystalline diamond over the temperature range of 500–650°C is not routine in a parallel-plate, radio frequency (rf) plasma-enhanced CVD (PECVD) system. Significant film deposition rates were not achieved until substrate temperatures of 750–850°C were employed.

2. Experimental

A modified SAMCO Model PD-10 PECVD system with parallel-plate electrodes driven by a 13.56 MHz rf power supply was used to study the deposition of polycrystalline diamond thin films. Modifications to the standard PECVD system with metallic electrodes were necessary because it was found by X-ray photoelectron spectroscopy (ESCA) that carbon films deposited on 1 cm^2 silicon substrates contained up to 26 at.% aluminum. Aluminum incorporation into the films occurred when depositions were accomplished on the lower rf anode using a 2% methane (CH_4) in hydrogen (H_2) gas mixture, a substrate temperature of 400°C, rf powers of 100–300 watts and pressures of 0.1–0.4 Torr. Figure 1 shows the ESCA spectrum of a contaminated carbon film deposited at 400°C, 200 watts and 0.1 Torr. Aluminum appears in the spectrum as peaks centered near 74 eV (Al 2p) and 136 eV (Al 2s). There was also 47 at.% oxygen (O1s, 531 eV) in the film which was incorporated upon exposure of the film to air following deposition. The high percentage of oxygen probably resulted from the formation of hydrated aluminum oxide. The aluminum contamination was apparently due to sputtering of the aluminum rf cathode by the reactant gases.[6)] Metal incorporation into the carbon films was also observed when the cathode was constructed of stainless steel. When the aluminum cathode was clad with graphite, no deposition was observed and the silicon substrates were slightly etched. It is postulated that the sputtered metal atoms acted as nucleation sites for a hydrocarbon polymer, since the metal-contaminated films were quite soft and

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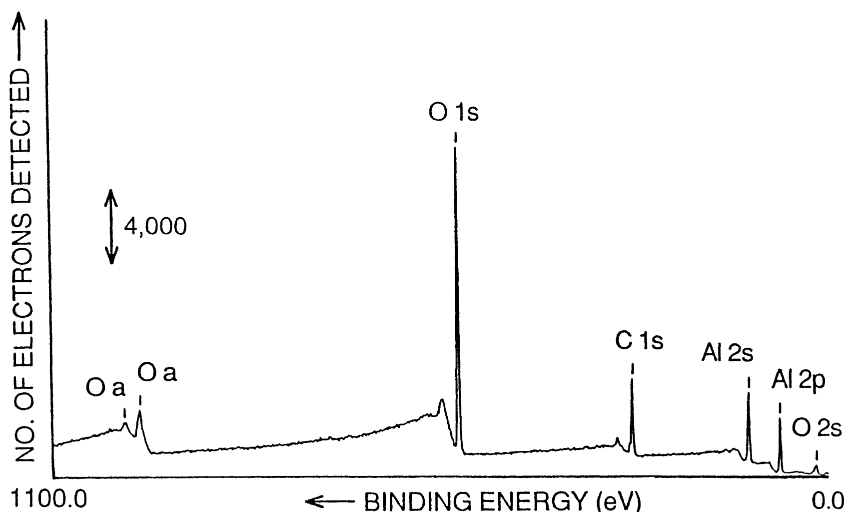

Fig. 1. ESCA spectrum for aluminum-contaminated carbon film.

since no deposition occurred using a non-metallic cathode.

Figure 2 is a diagram of the modified PECVD system. The modifications consisted of the installation of a water-cooled, graphite shower-head cathode which was equipped with a graphite sheath shield to confine the plasma between the cathode and anode. This confinement increased the plasma power density in the sample region when compared to the non-shielded cathode at the same input power level. Rather than heating the entire lower electrode, only a central 7.6 cm diameter disc was heated, while a grounded graphite annulus completed the rf anode surface. For experiments in which midrange (500–650°C) substrate temperatures were investigated, heat was supplied by a 600 W, spiral-wound, stainless steel sheathed resistance heater. In order to achieve substrate temperatures as high as 650°C using this heater, it was necessary to place the substrates directly on the stainless steel heater coils, which were at 800°C. Substrate temperatures were estimated by a sheathed thermocouple in direct contact with the top surface of a chip of silicon. In subsequent experiments employing higher substrate temperatures, the stainless-steel heater was replaced by a 5 cm diameter, pyrolytic boron nitride-encapsulated, pyrolytic-graphite heater (Union Carbide, Advance Ceramics, Cleveland Ohio).

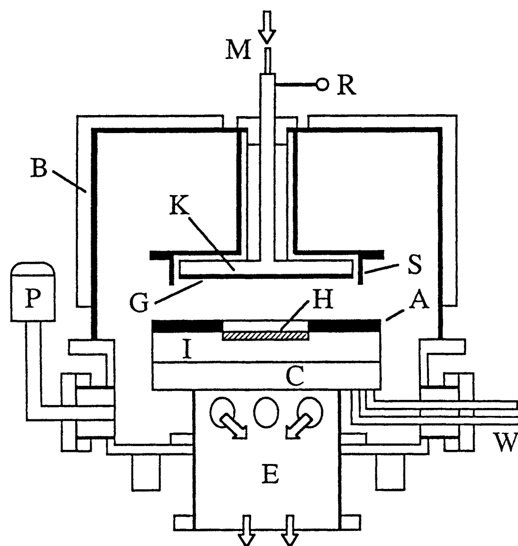

Fig. 2. Parallel-plate, diamond film deposition system. A, reactor; B, water-cooled bell jar; C, water-cooled platform; E, evacuation port; G, graphite shower head; H, heater; I, ceramic insulation; K, cathode; M, gas inlet; P, capacitance manometer; R, rf connection; S, graphite sheath shield; W, cooling water port.

To enhance nucleation of diamond on the 1 cm^2 silicon and molybdenum substrates, the surfaces were abraded with diamond powder and copper wire in a manner similar to that described by Chang *et al.*[4] Some of the substrates were scratched with diamond powder and then cleaned, and others had residual diamond powder embedded in

the surface, while others were marred by copper wire. Film growth or etching was indicated by the weight change of the substrates as measured on a microbalance.

Various gas mixtures of H_2, CH_4, and oxygen (O_2) were employed in the experiments. Chang *et al.*[4] suggested the addition of O_2 to the CH_4/H_2 mixtures to enhance diamond nucleation. Methane concentration was varied from 1–10%, O_2 from 0–0.5% and H_2 from 90–99% to make up the difference. The total gas flow rate was maintained at 50–100 sccm and the pressure was varied over the range of 0.5–2.0 Torr.

Typical protocol for an experiment was as follows. After the substrates had been heated to temperature in flowing H_2, a H_2 glow discharge was initiated at 200–300 watts to clean the surfaces. No significant substrate weight loss was observed during this period. With the plasma still on, CH_4 and sometimes O_2 were metered into the manifold in which H_2 was flowing. At the end of the 2–4 h deposition period, the CH_4 and O_2 flows were stopped prior to turning off the plasma.

3. Results

Within the range of experimental conditions described above, no detectable weight gain was observed for any of the silicon substrates over the temperature range of 500–650°C except when the CH_4 concentration was 5–10% of the total gas mixture. However, with this higher CH_4 concentration, weight gain over a 4 hour deposition was only 2–4 micrograms on a 1 cm^2 substrate. Assuming a density for diamond of 3.5 g/cm^3, the calculated growth rates were 0.2–0.5 Å/min. This rate on silicon is in marked contrast to the deposition rates of 160 Å/min reported by others at 800–1000°C and a total pressure of 2 Torr.[4] Weight gains on the molybdenum substrates were approximately three-fold higher (1.5 Å/min). However, the higher deposition rate on molybdenum may have been due to carbide formation on the surface. It seemed apparent from these preliminary experiments that growth of diamond does not occur to any significant extent when the substrate temperature is between 500–650°C and under the experimental conditions employed here. When higher substrate temperatures (750–850°C) were tested, it was found that the film deposition rate on silicon increased to 5–7 Å/min and on molybdenum to 25–50 Åmin.

4. Discussion

Many other researchers have reported on the importance of diamond-scratched or polished substrates to enhance nucleation.[2)–5),7),8)] However, in this study the nucleation of diamond on substrates heated to 500–650°C was apparently not enhanced significantly by surface pretreatment. Attempts to employ the "oxygen effect" reported by Chang *et al.*[4] also did not appear to enhance nucleation of diamond at these mid-range temperatures.

Although the possibility of obtaining crystalline diamond at substrate temperatures of 500–650°C has been encouraged by the range of temperatures reported in the literature,[1)–3)] we question whether the true substrate surface temperatures were this low during deposition. This disparity in the substrate temperature would be even more likely in experiments where temperature probes were in contact with susceptors, not samples,[1] or where pyrometry was done with the discharge-on.[4),5)] It is a distinct possibility that the contributions of heat energy from microwave discharges, rf discharges, or heated filaments significantly raised the substrate surface temperature above the measured temperature under these conditions.

When substrate temperatures were increased to the 750–850°C range, significant film growth occurred on both silicon and molybdenum substrates. We are currently further exploring this temperature range and characterizing the films obtained at these higher temperatures. Based on our initial experiments, it appears that the film growth rate is much higher on molybdenum than on silicon. Further study will be required to determine the mechanism for this apparently higher deposition rate.

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