Dependence of the cathodoluminescence of diamond films on deposition temperature

Y. H. Shing, D. H. Rich, and F. S. Pool
Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109

(Received 12 August 1991; accepted for publication 28 February 1992)

The deposition temperature dependence of the cathodoluminescence (CL) of diamond thin films grown by microwave plasma-assisted chemical vapor deposition has been investigated. Depositions were made in the temperature range of 400 to 750 °C at a pressure of 10 Torr, with a gas mixture of 5% CH_4 and 5% O_2 in hydrogen. The intensity of the luminescent peak at 430 nm was used as a measure of diamond quality for the film. This peak was found to be a maximum above 600 °C. Examination of the intensities of CL emissions associated with nitrogen and silicon impurities at 530, 560, and 740 nm indicate incorporation of these impurities is more efficient at temperatures above 600 °C. Film quality was thus found to be an optimization of competing mechanisms, i.e., improvement of diamond quality as evidenced by the intensity of the 430 nm peak, with the apparent activation of impurities and vacancy defects at elevated temperatures.

I. INTRODUCTION

The advent of chemical vapor deposition (CVD) of diamond films has realized a useful form of diamond for technological applications. Diamond excels in chemical inertness, mechanical hardness, thermal conductivity, optical transparency, and electronic properties. These characteristics of diamond render CVD diamond films suitable for extreme environment applications.

Microwave plasma enhanced CVD of diamond films have been established as one of the standard methods for producing high-quality polycrystalline diamond films.[1-4] Microwave plasma depositions of diamond films are generally performed at high pressures of 50 to 100 Torr, high temperatures of 850 to 950 °C and low methane concentrations of less than 1% in H_2 plasmas. An increasing of the methane concentration in the plasma[5] and the addition of oxygen[6] can be employed to lower the deposition temperature of diamond films. Lower growth temperatures are necessary to allow for many applications of diamond thin films.

While achieving low temperatures is desirable, care must be taken to monitor the quality of the films at these lowered temperatures. The microstructure of the films may be effectively acquired by cathodoluminescence studies. By examining the luminescent centers in diamond identified with dislocations, vacancies, and impurity complexes, an understanding can be achieved as to how the microstructure is altered with deposition conditions. It is of particular importance to understand how defects and impurities are incorporated into the diamond structure as growth temperatures are lowered. In this study, we examined the temperature dependence of the cathodoluminescence for microwave plasma-assisted CVD of diamond films.

II. EXPERIMENT

The deposition system consists of a microwave source of frequency 2.45 GHz, plasma chamber, and a radio-frequency (rf) induction heated sample stage. The microwave power is transmitted in rectangular waveguide and coupled to the plasma chamber via a symmetric mode coupler and a quartz window. The substrate is independently heated by rf induction using a 3.75 kW, 60 kHz power supply. The temperature is monitored by a thermocouple embedded in the graphite susceptor of the rf induction heater. Silicon wafers ultrasonically treated with 10 μm diamond powder were employed as substrates for diamond film growth.

CL measurements were performed with a JEOL 840-F field emission scanning electron microscope (SEM). The CL optical collection system and cryogenic specimen stage were designed and constructed at the Jet Propulsion Laboratory.[7] An electron beam current of 600 pA (rastered over a 120×90 μm region for the CL spectra) at an accelerating voltage of 20 kV was used to probe the diamond film sample which was maintained at a temperature of about 77 K.

III. RESULTS

Figure 1 shows a set of CL spectra of diamond films deposited at temperatures of 400 to 750 °C. The microwave plasmas for the deposition of these films are generated from a gas mixture of 5% CH_4 and 5% O_2 in H_2 at a pressure of 10 Torr using a microwave power of 550 W. The CL spectra shown in Fig. 1 have a dominant emission at 430 nm and several weak emissions occurring at 480, 500, 560, and 740 nm. The main CL peak at 430 nm is a characteristic line of diamond which has been labeled as "band *A*" and is attributed to the nearest neighbor donor–acceptor recombination.[8,9] The group of weak CL peaks between 500 and 600 nm is associated with the nitrogen-

 0021-8979/92/126036-03$04.00

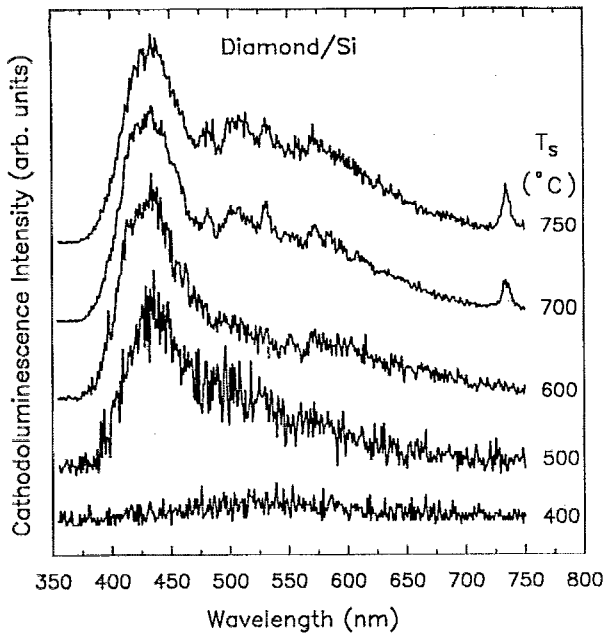

FIG. 1. Cathodoluminescence spectra of diamond films deposited at 10 Torr and substrate temperatures of 400 to 750 °C with 5% CH_4 and 5% O_2 in H_2 plasmas.

vacancy complexes.[10] The single, weak CL peak at 740 nm is identified with interstitial silicon impurities.[11]

Figure 2 shows the CL intensities of diamond films as a function of the substrate temperature. Systematic investigations of the CL spectra of diamond films have shown the intensity of band *A*, centered at about 430 nm, can be employed as a sensitive method for identifying the quality of the diamond film. The intensity of the main diamond CL line at 430 nm increases with the substrate temperature indicating a higher quality for diamond films deposited at temperatures of 600 to 750 °C. However, the weak CL lines at 530, 560, and 740 nm, which are identified with the nitrogen and silicon impurities and vacancy complexes in diamond films, also show an increase in the CL intensity with the substrate temperature. The increase of the impurity related CL intensities indicates impurity incorporation

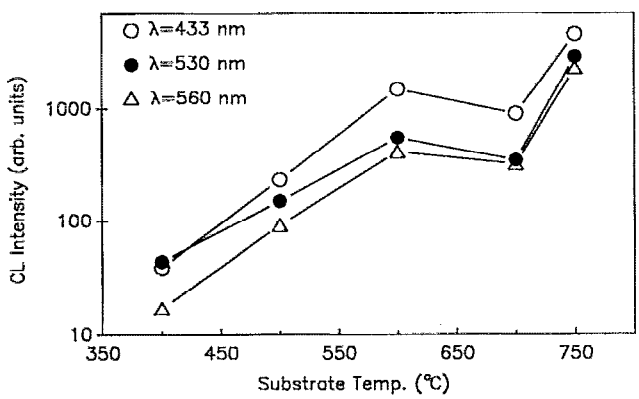

FIG. 2. Cathodoluminescence intensities of diamond films as a function of the substrate temperature.

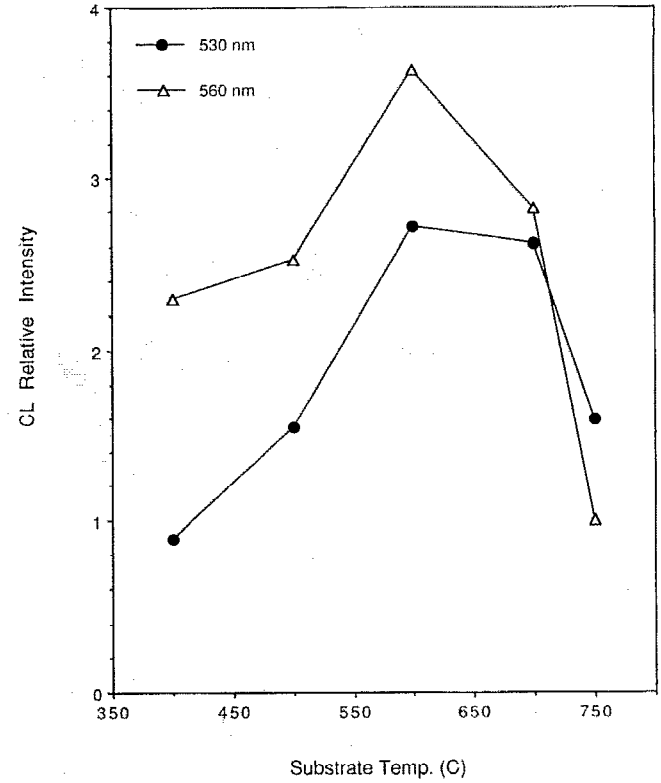

FIG. 3. Relative intensity of the band *A* peak to the impurity peaks at 530 and 560 nm.

into diamond films may be activated at temperatures above approximately 600 °C. Figure 3 shows that the quality of diamond films, as measured by the ratio of the intensity of the band *A* peak to the impurity peaks, is optimized at a substrate temperature of about 600 °C. The CL intensity measurements demonstrate that diamond films deposited at approximately 600 °C have very low nitrogen impurities and no detectable silicon impurities.

Figure 4 shows SEM micrographs of diamond films deposited at 10 Torr and temperatures of 500 and 600 °C, with 5% CH_4 and 5% O_2 in an H_2 plasma. The diamond crystallites in the film deposited at 600 °C are well faceted with dominant (100) faces and the size of the crystallites is about 1/2 μm. Diamond crystallites deposited at 500 °C are found to be less well defined than those at higher temperatures, with a much lower nucleation density.

IV. CONCLUSIONS

A systematic study has been performed on the deposition temperature dependence of the CL for diamond thin films deposited by microwave plasma-assisted CVD. Examination of the peak intensities of the impurity related luminescent centers and the band *A* intensity indicate

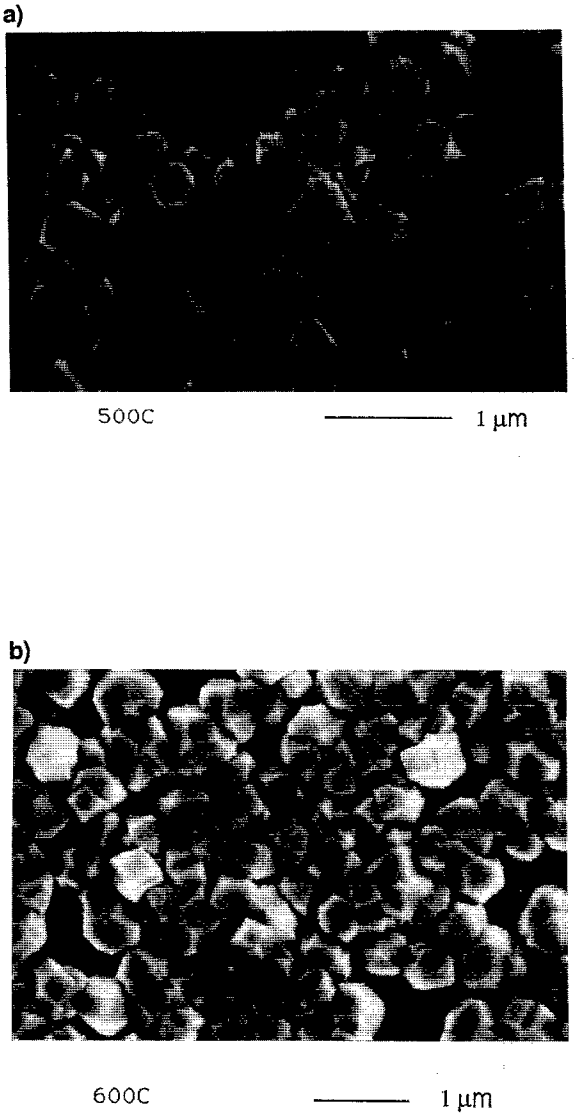

FIG. 4. SEM micrographs of diamond films deposited at 10 Torr and deposition temperatures of (a) 500 °C and (b) 600 °C, with 5% CH_4 and 5% O_2 in H_2 plasmas.

600 °C to be an optimum temperature for diamond growth under the conditions of this study. Below 600 °C diamond-film quality decays, as indicated by the reduction in intensity of the band *A* luminescence, while above 600 °C impurity incorporation appears more readily activated. Competing mechanisms must be balanced for growth optimization of diamond thin films, that of improved diamond quality at elevated temperatures with the more efficient incorporation of impurities.

ACKNOWLEDGMENTS

This work was performed at the Center for Space Microelectronics Technology of the Jet Propulsion Laboratory, California Institute of Technology and was sponsored by the Strategic Defense Initiative Organization/ Innovative Science and Technology Office through an agreement with the National Aeronautics and Space Administration. The authors would like to thank Dr. Carol Lewis of JPL for her technical discussion.

[1] V. P. Varnin, I. G. Termetskya, D. V. Fedosev, and V. B. Deryagio, Sov. Phys. Pokl. **29**, 419 (1984).
[2] M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, J. Cryst. Growth **62**, 642 (1983).
[3] A. R. Badzian and R. C. DeVries, Mater. Res. Bull. **23**, 385 (1988).
[4] S. Matsumoto, M. Hino, and T. Kobayashi, Appl. Phys. Lett. **51**, 737 (1987).
[5] J. Wei, H. Kawarada, J. Suzuki, and H. Hiraki, J. Cryst. Growth **99**, 1201 (1990).
[6] L. Liou, R. Weimer, D. Knight, and R. Messier, Appl. Phys. Lett. **56**, 437 (1990).
[7] D. H. Rich, A. Ksendzov, R. W. Terhune, B. A. Wilson, H. Shen, M. Dutta, S. M. Vernon, and T. M. Dixon, Phys. Rev. B **43**, 6836 (1991).
[8] L. H. Robins, L. P. Cook, E. N. Farabaugh, and A. Feldman, Phys. Rev. B **39**, 13367 (1989).
[9] H. Kawarada, Y. Yokota, Y. Mori, K. Nishimura, and A. Hiraki, J. Appl. Phys. **67**, 983 (1990).
[10] A. T. Collins, M. Kamo, and Y. Sato, J. Phys. D: Appl. Phys. **22**, 1402 (1989).
[11] B. G. Yacobi, A. R. Badzian, and T. Badzian, J. Appl. Phys. **69**, 1643 (1991).