

The synthesis and characterization of phosphorus-doped diamond films using trimethyl-phosphite as a doping source

Chia-Fu Chen, Shiow-Fang Lo, Sheng-Hsiung Chen

Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan

Abstract

Producing impurity-doped diamond films is a critical task for modern electronic applications. In this study, the effects of phosphorus in the gas phase on the morphological features of polycrystalline diamond films were investigated. The diamond films were prepared on n-type Si(100) substrates by the microwave plasma chemical vapour deposition. A trimethyl-phosphite vapour was introduced to the CH₄-CO₂ gas mixture as a dopant source. Surface morphology changed from well-defined facets to ball-like features by increasing the dopant concentration in the gas phase.

Phosphorus-doped diamond films of good quality and well defined facets could be obtained by reducing the carbon concentration of reactant gases. This reduction could be achieved by decreasing the CH₄ flow rates during the deposition process. An increase in the the dopant source caused the growth rate to become lower, the nucleation density to reduce drastically, and the relative intensity of XRD characteristic (110) peak to increase significantly.

Keywords: P-doped diamond films; Trimethyl-phosphite; XRD characteristic; Fourier transform infrared spectroscopy (FTIR)

1. Introduction

In general, the electronic properties of diamond films must be ensured before fabricating an electronic device. In addition, doped diamond films are a prerequisite for manufacturing diamond-based microelectronic devices. Doping of diamond films with boron during growth to obtain a p-type diamond has received extensive attention [1,2]. However, effective n-type doping remains elusive, partially by the inability to obtain an n-type diamond with reasonable conductivity. The problem is likely to originate from two sources: (1) whether the donor level yielded by the donor atoms is insufficient; and (2) whether these impurities can occupy electrically active sites in undamaged diamond lattices [3]. Potential n-type dopants including nitrogen, phosphorus, lithium, sodium and arsenic still present challenges to device fabrication. Phosphorus doping of both diamond-like carbon [4] and diamond films [5] has also been reported to yield conductive n-type material. However, the reproducibility of those results remains unclear. This is despite the fact that this technique was employed to fabricate of a p–n junction diode in 1991 [6]. Therefore, developing a reliable doping method and a suitable dopant source to incorporate impurities during growth becomes a relevant task.

In this study, an attempt is made to synthesize good and uniformly phosphorus-doped diamond films by microwave plasma CVD. Trimethyl-phosphite vapour is introduced to CH₄-CO₂ gas mixtures as dopant sources. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy results identify the deposited films as being a diamond.

2. Experimental details

The samples in this work were fabricated by standard microwave-plasma enhanced chemical vapour deposition processes [7]. N-type Si (100) substrates were scratched using a diamond powder (approximately 1–2 μm) to enhance the nucleation density of the deposits. Next, the scratched Si substrates were dipped into a solution of HF: H₂O = 1:100 for a few seconds to remove the native oxide of the silicon. A vapor source of trimethylborate was introduced into the CH₄-CO₂ gas mixtures. The flow rate of tri-methylborate was varied from 0 to 1 sccm using a mass flow controller.

The infrared absorption characteristics of the diamond films were studied using the Nicolet 510 FTIR spectrometer with a Michelson-type interferometer. Infrared data were taken with a resolution of 2 cm⁻¹ over the range

from 4000 to 400 cm^{-1} . Free-standing diamond films were produced from films grown on Si (100) substrate by dissolution of the silicon using a mixture of HF and HNO_3 acids (3:1) diluted by about 50% of DI water. Infrared spectra recorded by using pellets of free-standing diamond films compressed with KBr provided an enhanced resolution of the phosphorus-doped diamond films.

3. Results and discussion

The effects of phosphorus doping on the surface morphology of diamond crystallizations were investigated first. Various ratios of trimethyl phosphite as a dopant source were introduced into the CO_2 - CH_4 gas system. The flow ratio of $[\text{CO}_2]/[\text{CH}_4]$ was fixed at 30(sccm)/20.5(sccm) and the concentrations of trimethyl phosphite were varied at 0, 0.1, 0.5 and 1 sccm, respectively, as shown in Fig.1 (a)–(d). The surface morphology of diamond crystallites changed from well-defined facets to ball-like features with increasing trimethyl phosphite concentrations, indicating that the addition of trimethyl phosphite has a negative effect on the diamond crystallites morphology.

High-quality phosphorus-doped diamond films were next deposited by reducing the CH_4 flow rate to adjust the carbon concentration by increasing the amounts of trimethyl phosphite. Fig. 2 shows the surface morphology of the diamond films deposited with different

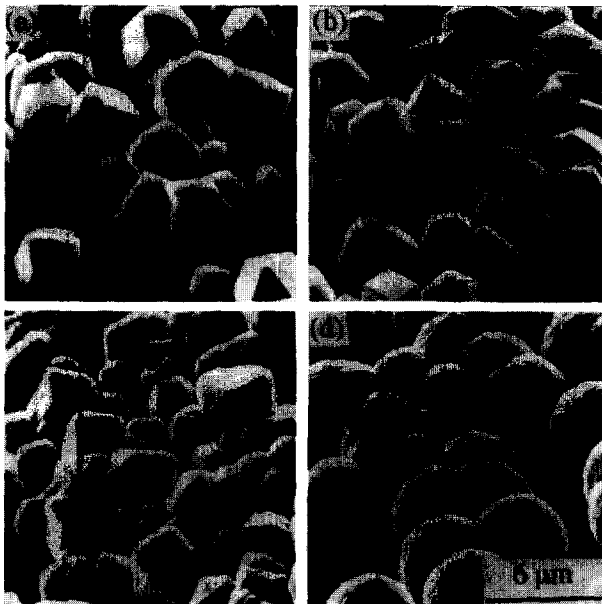


Fig. 1. Surface morphologies of diamond particles deposited with various trimethyl phosphite concentrations: (a) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.5$ sccm, $\text{P}(\text{OCH}_3)_3 = 0$ sccm; (b) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.5$ sccm, $\text{P}(\text{OCH}_3)_3 = 0.1$ sccm; (c) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.5$ sccm, $\text{P}(\text{OCH}_3)_3 = 0.5$ sccm; and (d) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.5$ sccm, $\text{P}(\text{OCH}_3)_3 = 1$ sccm.

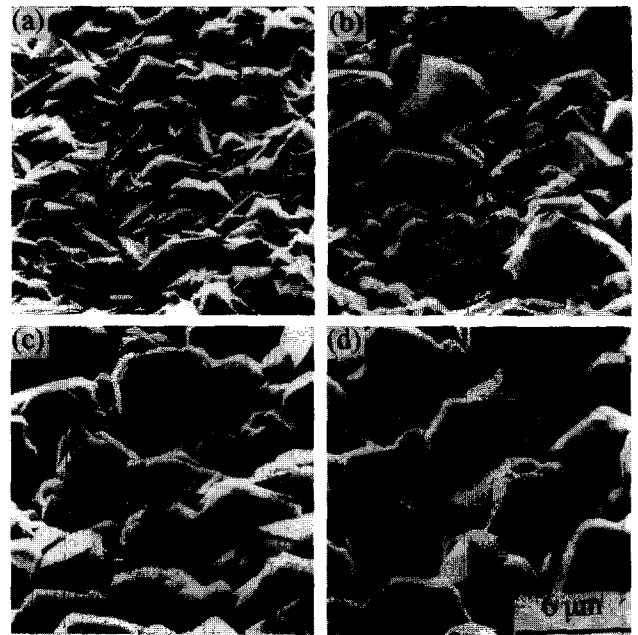


Fig. 2. SEM images of diamond films deposited with different trimethyl phosphite concentrations: (a) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.5$ sccm, $\text{P}(\text{OCH}_3)_3 = 0$ sccm; (b) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 20.0$ sccm, $\text{P}(\text{OCH}_3)_3 = 0.1$ sccm; (c) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 19.6$ sccm, $\text{P}(\text{OCH}_3)_3 = 0.5$ sccm; and (d) $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 18.1$ sccm, $\text{P}(\text{OCH}_3)_3 = 1$ sccm.

$\text{P}(\text{OCH}_3)_3$ concentrations. Moreover, the CH_4 flow rates were reduced from 20.5 to 18.1 sccm (the flow rate of CO_2 was fixed at 30 sccm) by increasing the addition of trimethyl phosphite. This figure clearly indicated that the diamond films present well-defined facets, even when the concentration of trimethyl phosphite reaches 2 sccm in the gas phase. Besides, the nucleation density significantly decreased and the grain size of deposited diamond films increased because of phosphorus doping. The surface morphology of undoped diamond films consisted mainly of the description (111) facets plus a few (100) facets as shown in Fig. 2 (a). Moreover, an increase in the concentration of trimethyl phosphite caused the surface morphology to transform from the randomly oriented triangular (111) facets to pyramidal (110) facets.

The distribution of phosphorus atoms in the diamond film was determined by SIMS depth profile (not shown here). It was confirmed that the phosphorus atoms was very uniformly distributed in diamond film by using trimethyl phosphite as a dopant source in the CO_2 - CH_4 gas mixtures. Moreover, the I-V characteristics of aluminum contacts on phosphorus-doped polycrystalline films with different trimethyl phosphite concentrations in the gas phase have been studied, which would be discussed in our next article. As the phosphorus concentration increased, the current did not rise sharply as expected.

The effects of phosphorus doping on the growth rate of diamond films were also investigated. The films growth rate was calculated using film thickness

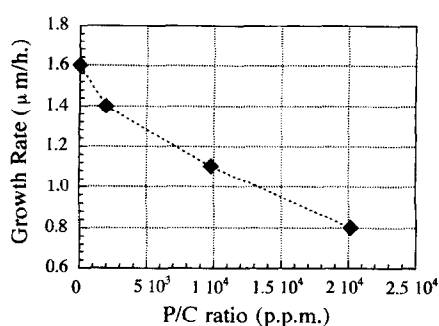


Fig. 3. Correlations between the growth rate of diamond films and various P/C ratio.

determined from the observations of SEM cross-sectional views. Fig. 3 shows the growth rate related to the phosphorus doping effects. Several investigations [8,9] have examined the roles of boron addition using B_2H_6 which was introduced to the plasma gas mixtures. Boron functions as a catalyst during the growth process, thereby increasing the growth rate. However, the effect of phosphorus on the growth rate of diamond films has only received limited attention. Bohr et al. [10] have studied the influence of phosphorus addition on the growth rate of diamond films by HF-CVD using PH_3 as a dopant source.

The statistical value graph calculated is shown in Fig. 3, indicating that the growth rate decreased with an increase in the phosphorus concentrations in the gas phase. The lower growth rate resulting from the higher amounts of trimethyl phosphite may be related to the reduction of CH_4 flow rate and the decrease in diamond growth precursors in the gas phase. Notably, trimethyl phosphite is a CH_3 -rich compound which would decompose in plasma and produce an equal amount of CH_3 radical to balance the carbon source in the gas phase. The most likely cause for the lower growth rates of heavily doped films or slightly doped films is the oxygen content involved in trimethyl phosphite molecules. The oxygen atom content was more than the phosphorus atom for trimethyl phosphite, which may be related to the etching of non-diamond carbon from the growing surface resulting in a lower growth rate. The same effects may also occur when adding O_2 to the CH_4 - CO_2 gas mixtures [11]. The Raman spectra of diamond films obtained with the same specimens as in Figs. 2(a)–(d), respectively, have been examined (not shown here). The Raman spectra present two main features: First, a sharp peak at 1332 cm^{-1} , denote the characteristic line of a crystalline diamond. Also, a broad peak centered at around 1550 cm^{-1} is characteristic of the diamond-like carbon [12]. In Fig. 5, the Raman spectra for the films obtained under three different deposition conditions are similar. However, the figure also reveals that the intensity of the broad peak centered at 1550 cm^{-1} increased with an increasing trimethyl phosphite concentration.

Restated, the diamond peak intensity at 1332 cm^{-1} decreased correspondingly to the intensity of the non-diamond feature at 1550 cm^{-1} . Moreover, the full width at half-maximum (FWHM) of 1332 cm^{-1} peak increased with the introduction of phosphorus dopants. The increase in FWHM values for a diamond peak reveals a diamond of reduced domain size, thereby implying a loss of diamond structural perfection. The methyl radicals (CH_3), i.e. a precursor of diamond growth, might increase with the addition of trimethyl phosphite because trimethyl phosphite is a CH_3 -rich compound. Thus, the etching rate decreased, and an increase in the amount of amorphous carbon or graphite remained in the resultant films. This widening can be accounted for by the lattice strain caused by phosphorus doping [13,14].

The effect of the dopant source during the nucleation steps using the deposition for 30 min was examined. Fig. 4 shows the variations of nucleation density and morphology presence of crystallites with various additions of trimethyl phosphite. The experimental conditions are the same as in Figs. 2(a),(b) and (c), respectively. These results demonstrate clearly that the nucleation

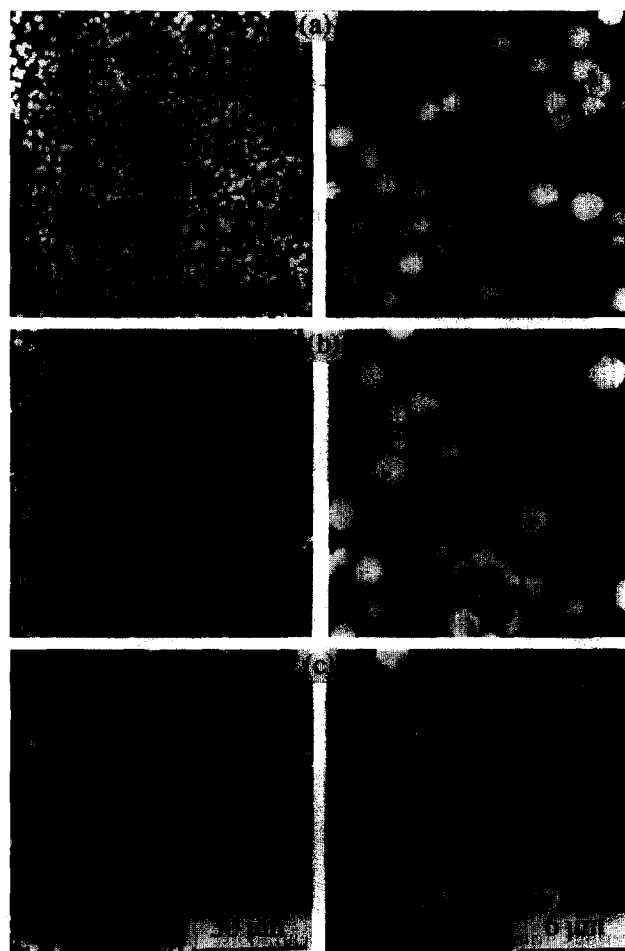


Fig. 4. Variations in nucleation density and morphology of crystallites obtained from the same conditions as Figs. 2 (a), (b) and (c) respectively.

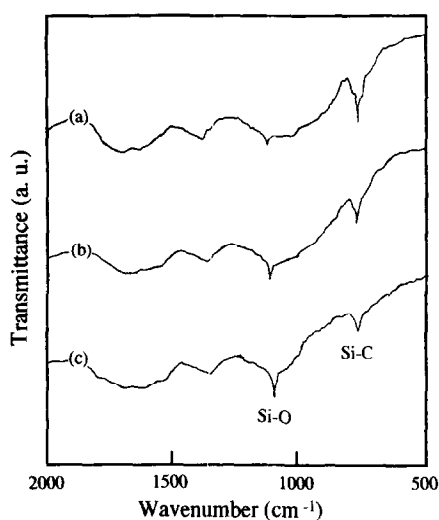


Fig. 5. Transmitted IR spectra obtained from the same specimens as Figs. 4 (a), (b) and (c) respectively.

density significantly reduced when the amount of trimethyl phosphite was increased.

From the above discussion, some performances are carried out during the nucleation step of a phosphorus-doped diamond film. The same specimens of Fig. 4 were also examined by FTIR and are shown in Figure 5. The latter figure obviously reveals that the two peaks appearing at about 800 cm^{-1} and 1100 cm^{-1} , respectively, were caused by Si-C and Si-O bonding. The IR spectra of three different deposition conditions all present the same features mentioned above. A comparison of the IR spectra for three different deposition conditions indicates that the Si-O peak intensity became stronger with increasing dopant concentrations. The stronger intensity of Si-O peak was due to the creation formation of a silicon oxide layer which would ultimately inhibit the diamond nucleation during the first step of diamond films growth. Moreover, optical emission spectroscopy (OES) measurement is also used to examine the chemical species and free radicals in the plasma during diamond film growth. Species identified in this study include CO (the positive and 5B bands system and the Ångström system), OH (3064 system, 306.9 and 308.9 nm), CH (387.1 and 431.4 nm), C_2 (Swan band, 516.5 and 563.5 nm), atomic oxygen (533 and 615.8 nm), excited O_2 (592.5 nm), and atomic hydrogen (Balmer series: $\text{H}\alpha$ 656.3 nm; $\text{H}\beta$ 486.1 nm) [15]. Based on the OES measurements, the primary differences between the plasmas of the gas mixtures were in the intensities of atomic oxygen, excited O_2^+ , OH, C_2 , CO, and CH radicals. Under these diamond film-formation conditions, the intensity of CH emission reduced markedly when the amount of trimethyl phosphite was increased. However, the opposite case occurred when the intensities of CO, C_2 , OH, atomic oxygen, and excited O_2 present an opposite manner, i.e. the CO, C_2 , OH, O, and excited

O_2^+ intensities increased. The increasing amounts of etching agents in the condition apparently blocked the nucleation of diamond films. The lower growth rate of diamond films with higher amounts of trimethyl phosphite addition was probably related to a decrease in CH emission, which is generally accepted to be a diamond growth precursor.

Another characterization of the deposited films was carried out by X-ray diffraction (using $\text{Cu K}\alpha$ radiation), which was the same specimens as in Fig. 2. The relations between the ratio of intensity from XRD diffraction peak with P/C ratio are shown in Fig. 6. The figure displays the expected (111), (220), (311) and (400) diffraction peaks for diamond films. The undoped layer showed the (111), (220), (311) and (400) diffraction lines of a diamond.

The intensities of XRD (311) and (400) decreased and that of XRD (220) peak increased. Consequently, the (111) peak dominated the spectrum when the P/C ratio was 965 p.p.m. Moreover, an increase in the intensity of (220) diamond diffraction line caused an increase in the P/C ratios, indicating that the diamond growth was favored in the $\langle 110 \rangle$ direction.

4. Conclusion

Various characteristics of phosphorus-doped diamond films were of primary concern in this study. Based on those results, we can conclude the following:

1. Trimethyl phosphite vapour was successfully introduced to the $\text{CH}_4\text{-CO}_2$ gas mixtures as a dopant source. The diamond films surface morphology transformed from well-defined facets to ball-like features with an increase trimethyl phosphite concentrations. Phosphorus-doped diamond film of good quality could be obtained by reducing the CH_4 flow rate to adjust the carbon concentration when the trimethyl phosphite concentrations increased.
2. The nucleation density of deposits significantly reduced and the growth rate of films decreased with an

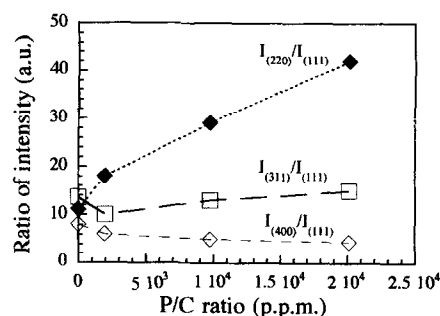


Fig. 6. The intensity relations of the XRD diffraction peaks varying with the P/C ratio from the same specimens as Figs. 2 (a), (b), (c) and (d) respectively.

increase in the amounts of trimethyl phosphite. X-ray diffraction analysis of phosphorus-doped diamond films revealed that the intensity of (110) peak increased markedly. However, the (311) and (400) peaks remained less sensitive with an increase in the P/C ratio.

Acknowledgments

The authors would like to express their thanks to the National Science Council of the ROC for the financial support of this work under Contract No. NSC 84-2221-E009-036.

References

- [1] K. Okano, Y. Akiba, T. Kurosa, M. Iida, and T. Nakamura, *J. Cryst. Growth*, **99** (1990) 1192.
- [2] K. Okano, Y. Akiba, T. Kurosa, and M. Iida, *Diamond Relat. Mater.*, **3** (1993) 35.
- [3] C. Cytermann, R. Brenner and R. Kalish, *Diamond Relat. Mater.*, **3** (1994) 667.
- [4] V.S. Veerasamy, G.A.J. Amaratunga, C.A. Davis, A.E. Timbs, W.I. Milne and D.R. Mckenzie, *J. Phys. Condens. Matter.*, **5** (1993) L169.
- [5] K. Okano, H. Kiyota, T. Iwasaki, Y. Nakamura, Y. Akiba, T. Kurosu, M. Iida and T. Nakamura, *Appl. Phys. A* **51** (1990) 334.
- [6] K. Okano, H. Kiyota, T. Iwasaki, Y. Nakamura, Y. Akiba, T. Kurosu, M. Iida and T. Nakamura, *Solid-State Electron.*, **34** (1991) 139.
- [7] K. Okano, H. Kiyota, T. Iwasaki, Y. Nakamura, Y. Akiba, T. Kurosu, M. Iida and T. Nakamura, *Appl. Phys. Lett.*, **58** (1991) 840.
- [8] M.W. Geis, Growth of Device-quality Homoepitaxial Diamond Thin Films, in *Proc. Fall 1989, MRS Meeting, Vol. 162*, Boston MA, 1989, p.15.
- [9] R. Meiluns and R.P.H. Chang, The Physical and Electrical Properties of Boron-Doped Diamond Films, *Proc. 2nd Int. Conf. on Elect. Mats., Mat. Res. Soc.*, 1990, p. 609.
- [10] S. Bohr, R. Haubner and B. Lux, *Diamond Relat. Mater.*, **4** 1995, 133.
- [11] C.F. Chen, T.M. Hong and S.H. Chen, *J. Appl. Phys.*, **74** (1993) 4483.
- [12] D.S. Knight and W.B. White, *J. Mater. Res.*, **4** (1989) 4385.
- [13] P.K. Bachmann and W.V. Enchevort, *Diamond Relat. Mater.*, **1** (1992) 1021.
- [14] K. Nishimura, K. Das, J.T. Glass, K. Kobashi and R.J. Nemanich, *Proc. NATO Adv. Res. Workshop on Phys. and Chem. of Carbides, Nitrides and Borides*, Manchester, UK, (1989).
- [15] R.W.B. Pearse and A.G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 1976.