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Phosphorus incorporation and activity in (100)-oriented homoepitaxial diamond layers

G. Frangieh, M.-A. Pinault*, J. Barjon, T. Tillocher, F. Jomard, and J. Chevallier

Groupe d'Etude de la Matière Condensée (GEMaC), Université Versailles St Quentin, CNRS, 1 place Aristide Briand, 92195 Meudon Cedex, France

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*Corresponding author: e-mail marie-amandine.pinault@cnrs-bellevue.fr, Phone: +00 33 (0)1 45 07 53 29, Fax: +00 33 (0)1 45 07 58 41

In this work, we present a study about the homoepitaxial growth of phosphorus-doped diamond on (100) substrates. The growth was performed by microwave plasma assisted chemical vapor deposition (MPCVD) adding an organic precursor for phosphorus (tertiarybutylphosphine: TBP) in the gaseous phase. We show that phosphorus is incorporated in (100) chemical vapor deposition (CVD) diamond as proved by

secondary ion mass spectrometry (SIMS). The recombination of excitons bound to phosphorus donors is observed by cathodoluminescence (CL) spectroscopy. The influence of the growth parameters on the phosphorus donor activity is investigated. We show that the $[C^*]/[H_2]$ ratio is a key parameter for controlling the P-donor activity when diamond is grown on (100) surfaces.

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1 Introduction Diamond exhibits unusual physical properties. Among them, its high breakdown electric field ($2 \times 10^7 \text{ V cm}^{-1}$), its high thermal conductivity ($20 \text{ W cm}^{-1} \text{ K}^{-1}$) [1] and its high mobility for both holes and electrons ($\sim 2500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [2, 3] make diamond a promising wide band gap semiconductor for high power, high frequency, and high temperature electronic devices. To develop such applications, achieving an efficient n-type doping is one of the difficulties to overcome. Nowadays, phosphorus is the only well established substitutional donor in chemical vapor deposition (CVD) diamond. Until recently, the discovery of phosphorus doping was limited to (111)-oriented diamond lattice structure [4]. For actual technological applications, the growth of n-type diamond films on (100) substrates is a basic requirement [5]. The (111) diamond surface is difficult to polish mechanically [6], whereas it is easier to achieve smooth (100) surfaces. In the case of undoped and/or B-doped diamond films, it has been reported that the performance of metal/diamond junction properties as well as electrical and optical properties on (100) surfaces are indeed better than those on (111) substrates [6]. In addition, (111)-oriented diamond substrates are difficult to produce, which makes them expensive, and their size is currently limited ($2 \times 2 \times 2 \text{ mm}^3$), which

generates significant technological problems with respect to photolithography, etching, metallization, and throughput. To bring diamond electronic applications closer to the actual market and to manufacture bipolar devices for a wide range of applications, it is necessary to control n-type doping using phosphorus on (100)-oriented crystals [6]. From these viewpoints, there is a strong need for the development of n-type doping on (100)-oriented diamond. In 2005, Kato et al. [5] overcame this difficulty by optimizing the conditions for CVD growth, where the parameters differ significantly compared with those for (111) growth. They succeeded in producing n-type (100) phosphorus doped diamond films. A phosphorus donor level of $\sim 570 \text{ meV}$ was confirmed, and the compensation ratio of their samples was in the range 50–80% [6]. The maximum electron mobility at room temperature is $780 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [7] and the maximum phosphorus donor activity $\sim 65\%$ [8].

In this paper, we present a study about the homoepitaxial diamond growth on (100) substrates with a misorientation between 2.4° and 2.9° . The growth was performed by microwave plasma assisted chemical vapor deposition (MPCVD) adding an organic precursor for phosphorus in the gaseous phase. A wide range of growth conditions is

used (growth temperature, $[CH_4]/[H_2]$, $[TBP]/[H_2]$ ratios etc.) to investigate their influence on the phosphorus donor activity.

2 Experimental procedure The homoepitaxial diamond films were grown in a stainless steel microwave plasma assisted MPCVD reactor associated with a dopant-gas injection line using the metal organic CVD (MOCVD) technology. In previous works, we successfully used this MO-MPCVD combination to dope (111)-oriented diamond with phosphorus using TBP for the liquid organic precursor of phosphorus, reaching the state of the art for the electron mobilities [9, 10].

In this paper, we present our first results for n-type doping of MPCVD (100)-oriented diamond using liquid TBP (tertiarybutylphosphine, TBP: $P(C_4H_9)_3$) as an alternative to phosphine. The film depositions were performed on (100)-oriented Ib HPHT ($3 \times 3 \times 0.5 \text{ mm}^3$) Sumitomo and IIa CVD ($3 \times 3 \times 0.3 \text{ mm}^3$) Element6 substrates. The substrates were polished to have a specific miscut angle ($2.4\text{--}2.9^\circ$). The miscut angles of diamond substrates have been checked by X-ray diffraction. Before growth, the substrates were cleaned in a boiled (200°C) acid mixture ($HClO_4$, H_2SO_4 , and HNO_3) to remove the organic and metallic contaminations from their surfaces. They were placed on a molybdenum holder in the growth reactor. The substrate temperature was measured by using a bichromatic pyrometer. Samples were grown with TBP added to the conventional CH_4 (6N) diluted with H_2 (9N) mixture. In the low pressure regime used in this study, it is known that diamond growth is governed by atomic hydrogen and methyl radicals containing carbon atoms [11]. The reactive carbon species come from the decomposition of the gas mixture CH_4 and PC_4H_{11} into the plasma. Then $[C^*]$ defined as the total concentration of carbon atoms involved in growth is given by the sum of the carbon atoms coming from CH_4 and those from TBP. As a result: $[C^*] = [CH_4] + 4[TBP]$. The growth conditions are summarized in Table 1.

Secondary ion mass spectrometry (SIMS) using a Cameca IMS 4f equipment was performed onto the samples to measure the incorporation of impurities and the depth distribution of P atoms into the diamond films. Cs^+ primary ions were accelerated at 10 keV and the impact energy was

Table 1 Growth conditions investigated for phosphorus doping of (100) homoepitaxial layers.

$[CH_4]/[H_2]$	0–1%
$[TBP]/[C^*]$	300–250 000 ppm
$[C^*]/[H_2]$	0.06–1.14%
growth rate	$0.02\text{--}0.76 \mu\text{m h}^{-1}$
$[TBP]/[H_2]$	340–62 500 ppm
microwave power	490–580 W
T_{growth}	$850\text{--}930^\circ\text{C}$
growth duration	3–7 h
pressure	50 mbar
total gas flow	65–250 sccm

14.5 keV. The concentrations of P atoms were quantified using reference implanted samples. Cathodoluminescence (CL) spectroscopy was performed to analyze the optical activity of the dopant (the experimental details are given in Ref. [12, 13]). The surface morphology of the layers was observed by a scanning electron microscope (SEM).

3 Results and discussion Figure 1 shows the SIMS depth profile of P detected in the sample grown with $[TBP]/[C^*] = 250\,000$ ppm without methane. The P profile shows a very clear interface with no P accumulation or gradual P incorporation. The P incorporation ($8 \times 10^{18} \text{ cm}^{-3}$) is relatively homogeneous in the whole epilayer.

The range of phosphorus concentration reached in this study is 4.4×10^{17} to $2.0 \times 10^{19} \text{ P cm}^{-3}$. The phosphorus incorporation efficiency, η , defined as the ratio between the P atoms in the gas phase and the P atoms into the diamond lattice, is given by the following expression:

$$\eta = \frac{([P]/[C])_{\text{Solid}}}{([TBP]/[C^*])_{\text{Gas}}} \quad (1)$$

We deduce that the efficiency of the P incorporation, η , increases up to 0.84% when varying the growth parameters. A clear influence of the $[C^*]/[H_2]$ ratio is observed in Fig. 2 (improvement of η when $[C^*]/[H_2]$ increases). However, no tendency is seen for the other growth parameters ($[TBP]/[C^*]$, T_{growth} , misorientation etc.).

A SEM image of the epilayer surface is shown in Fig. 3. It exhibits the characteristics of bi-dimensional growth steps, typical of surface morphologies of (100) P-doped diamond epilayer grown on diamond substrates with a misorientation angle higher than 2° [6]. This morphology may depend on the (100)-oriented substrate misorientation angle, θ . In general, toward lower θ , the density of non-epitaxial crystallites and pyramidal hillocks increases, leading to a degradation of surface properties. Increase in misorientation angle to ($\theta > 2^\circ$) is claimed to be necessary for reproducible phosphorus doping of (100)-oriented diamond [6].

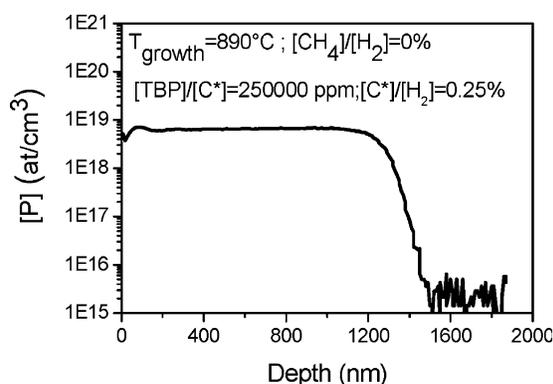


Figure 1 SIMS depth profile of the phosphorus concentration for a (100)-oriented CVD diamond layer grown at $T_{\text{growth}} = 890^\circ\text{C}$ with $[TBP]/[C^*] = 250\,000$ ppm, (equivalent $[C^*]/[H_2] = 0.25\%$).

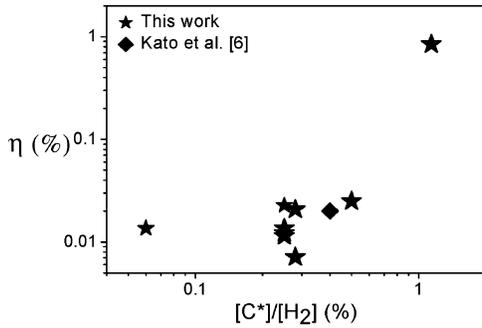


Figure 2 Relationship between the phosphorus incorporation efficiency and $[C^*]/[H_2]$.

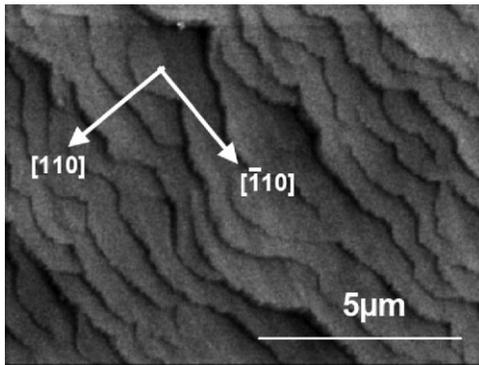


Figure 3 Surface image obtained by SEM for a (100)-oriented homoepitaxial layer grown at $T_{\text{growth}} = 890^\circ\text{C}$, with $[TBP]/[C^*] = 250\,000$ ppm (equivalent $[C^*]/[H_2] = 0.25\%$) and without CH_4 .

The optical signature of P-donors has been investigated by CL. For P-doped layers, the presence of the free exciton recombination associated with a transverse optical phonon, FE_{TO} (5.27 eV), is observed. The neutral phosphorus bound exciton recombination signatures, BE_p , confirm that at least a fraction of the P atoms act as donors. Their main characteristics are the no-phonon recombination BE_p^{NP} at 5.33 eV and the transverse optical phonon recombination BE_p^{TO} at 5.18 eV [14, 15] (Fig. 4).

The coexistence of free and bound exciton populations can be described through the capture of free excitons by P impurities and the thermal dissociation of phosphorus bound-excitons. The P-donor concentration is calculated by the following equation defined from the ratio between the BE_p^{TO} and FE_{TO} luminescence intensities [13]: $N_D (\text{cm}^{-3}) = 1 \times 10^{17} \times I(\text{BE}_p^{\text{TO}})/I(\text{FE}_{\text{TO}})$.

The P-donor activity is then given by:

$$\text{P-donor activity (\%)} = \frac{N_D}{[P]_{\text{SIMS}}} \quad (2)$$

Figure 5 shows the evolution of the P-donor activity in the films as a function of the $[C^*]/[H_2]$ ratio in the gas phase. When we increase the $[C^*]/[H_2]$ ratio, the optical activity of the P-donor activity increases up to 50%. At low

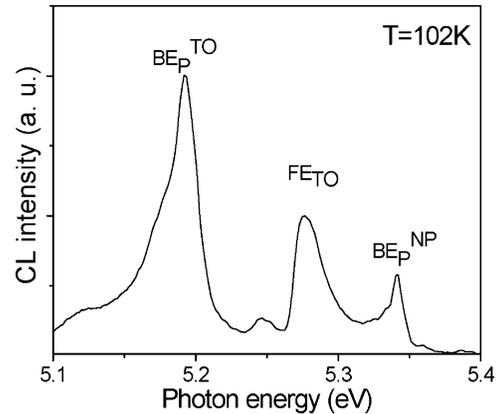


Figure 4 CL spectrum of the sample grown at $[C^*]/[H_2] = 1.14\%$, $T_{\text{growth}} = 850^\circ\text{C}$ with $[TBP]/[C^*] = 300$ ppm.

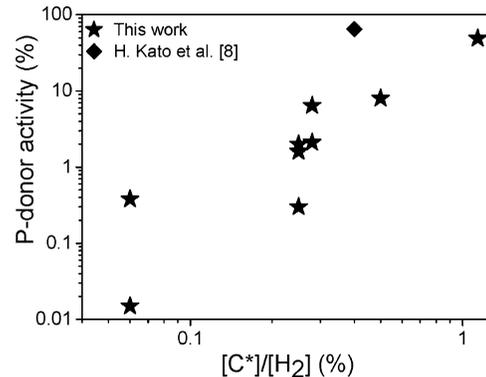


Figure 5 P-donor activity dependence with $[C^*]/[H_2]$ obtained from Eq. (2) for P-doped diamond films.

$[C^*]/[H_2]$, the activity is low, possibly due to (P,H), (P,V), (P,P) complexes or/and P in interstitial sites.

4 Conclusion The incorporation of phosphorus into (100) homoepitaxial diamond layers was controlled by the methane ratio in the case of miscut angles in the range $2.4\text{--}2.9^\circ$. Phosphorus is successfully incorporated (up to $2 \times 10^{19} \text{P cm}^{-3}$) with high incorporation efficiency (up to 0.84%) in good crystalline quality films.

The observation of BE_p emissions reveals that the P atoms act as donor atoms. From the BE_p^{TO} and FE_{TO} intensities obtained from CL spectra, we have calculated the P-donor activity. High $[C^*]/[H_2]$ ratio leads to high P-donor activity (up to 50%).

In comparison with the (111) homoepitaxy, only half of the P-atoms act as donor. In perspective, the origin of such a low activity on (100) is still an open issue to investigate.

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