ABSTRACT

Phosphorous-doping of predominantly (110) oriented polycrystalline CVD diamond films is presented. Incorporation of phosphorous into the diamond grains was accomplished by using novel microwave plasma enhanced chemical vapor deposition (MW PE CVD) growth conditions. The substitutional nature of the phosphorous atom was confirmed by applying the quasi-steady-state photocurrent technique (PC) and cathodoluminescence (CL) measurements at low temperature. Topographical information and the relation between substrate and P-doped film grain orientation was obtained with scanning electron microscopy (SEM) and electron back-scattered diffraction (EBSD). The optimized growth parameters for P-doped layers on (110) oriented polycrystalline diamond differ substantially from the standard conditions reported in literature for P-doping of single crystalline (111) and (100) oriented diamond surfaces.

INTRODUCTION

At present, the first report dealing with successful active n-type doping of CVD diamond is a decade old [1]. That breakthrough reinforced the position of diamond as the ideal future electronic material in "difficult" fields, such as high temperature, high frequency, and high power devices. Based on the availability of n-type doping and the realization of diamond pn-junctions, reports on devices making use of these achievements started to appear. Known demonstrators include light emitting diodes [2] and "solar blind" deep UV (VUV) detectors [3]. Since that time, many groups have proven that phosphorous doping can be reproducibly achieved by various deposition techniques and several precursor sources [4,5]. Phosphorous-doped layers of superior quality with high electron mobility [6] became available, and even the difficult problem to grow on (001) oriented substrates was tackled [7]. Recently, the use of such layers yielded a highly efficient UV-emitting p-i-n-junction [8] based on the superior quality of (001) oriented B-doped layers as opposed to the (111) counterpart. Even so, the amount of applications making use of n-type diamond remains limited up to now. Partly, the reason can be found in the rather deep nature of the P-donor, making it insufficiently ionized at room temperature, but it is clear that there are also more technical limitations that need to be overcome. Examples are the limited size of the samples, complicating processing, and the extremely low doping efficiency on (100) oriented diamond substrates [9]. In an attempt to overcome these problems a polycrystalline P-doped n-type diamond layer could prove to be beneficial. First results have proven that n-type conductivity and relatively high P-incorporation, comparable with (111) single crystalline doping can be obtained using similar conditions, but that unfavorable defects were also incorporated during growth [10]. This paper will deal with a new set of doping conditions that lead to the incorporation of P in microcrystalline CVD diamond films.

EXPERIMENT

To study the correlation between the used doping conditions and the incorporation of phosphorous in grains of different orientation, freestanding undoped polished microcrystalline diamond films were used. For this purpose a 2 inch Ø Si wafer was mechanically scratched with diamond powder as pretreatment, followed by exposure to a conventional hydrogen/methane plasma with a $[CH_4]/[H_2]$ ratio of 3 % in an ASTeX AX6500. Microwave power and pressure were kept at 6000W and 110 Torr, respectively. The substrate temperature varied between 850 and 900 °C during deposition, as measured by an optical. A growth rate of ~ 2.2 µm/h was calculated from the total growth duration of 550 hours and the obtained film thickness of 1.2 mm. After chemical removal of the Si substrate, 3 mm Ø round CVD diamond substrates were laser cut from the diamond wafer and subsequently polished. After a chemical acid treatment to remove all surface contaminants, P-doping experiments were performed in ASTeX (PDS 17) 5 kW reactor. The used source gases for the doping experiments were methane (4N) and PH_3 (5N), diluted in H_2 (9N). Two different series of growth parameters were used, as presented in detail in Table I.

Table I. Growth conditions used for the P-doping experiments.

Plasma parameters	Series A	Series B
Substrate temperature	900 °C	1140 °C
$[CH_4]/[H_2]$	0.05 %	1 %
$[PH_3]/[CH_4]$	1000 ppm	50 – 800 ppm
Pressure	100 Torr	180 Torr
H_2 gas flow	500 sccm	495 sccm
Growth duration	2h	
Microwave power	600 – 700 W	

The first series are the typically P-doping conditions that can be found in literature for the growth of n-type diamond films on single crystalline (111) oriented diamond surfaces [1]. When a higher $[PH_3]/[CH_4]$ ratio is used, these conditions can be used on (100) oriented substrates [7]. The focus of this work is on the second series. The most noticeable differences between these two series are the substrate temperature and the used amount of CH_4. For all experiments discussed here, the deposition time was fixed to 2 hours. However, for Series B this led to an approximate layer thickness of 20 µm, a substantially higher value than the 2 µm obtained for Series A.

Automated electron back-scattered diffraction (EBSD) and Scanning Electron Microscopy (SEM) pictures were acquired using a Quanta 200 FEG Scanning Electron Microscope. The quasi-steady-state photocurrent (PC° measurements were obtained on a home made set-up. The excitation source was a 100 W halogen lamp, monochromatised and chopped at low frequency (~7 Hz) to enable the use of lock-in detection techniques. Spectra were taken with a 5 meV step size. For the cathodoluminescence (CL) experiments, the samples were excited with a 200 µm wide 8 keV electron beam using 500 nA beam current, leading to a resolution of about 8 meV in the spectral range involved. PC as well as CL data were taken at liquid nitrogen temperature, i.e. 77.4 K.

DISCUSSION

SEM and EBSD results

To enable the influence of the doping conditions on the grain orientation of the used substrates, those were fully characterized with SEM and EBSD. Figure 1 shows pole figures obtained on the undoped diamond substrates used for the P-doping experiments. It is clear that the described conditions for the undoped diamond substrates, lead to a mainly (110) oriented morphology.
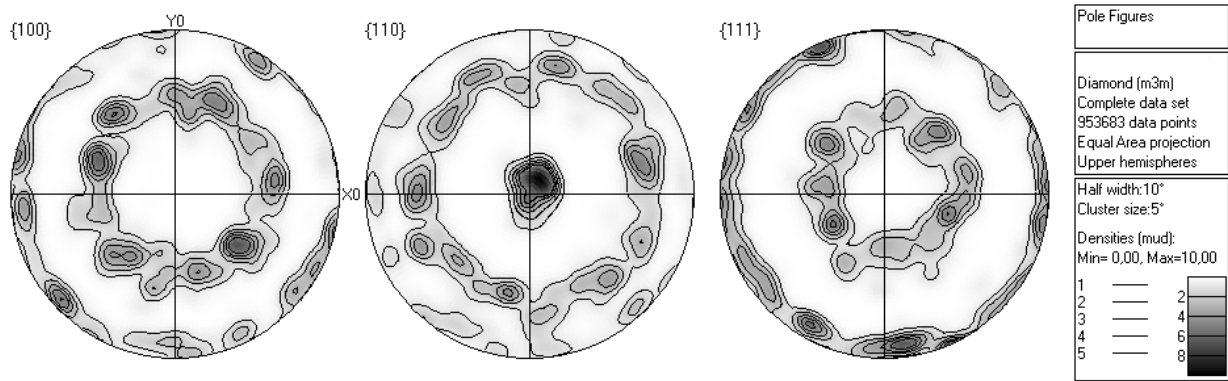

Figure 1. Pole figures obtained by EBSD on a freestanding undoped polished microcrystalline diamond substrate. The dark spot in the centre of the middle pole figure points to the (110) oriented nature of the used substrates.
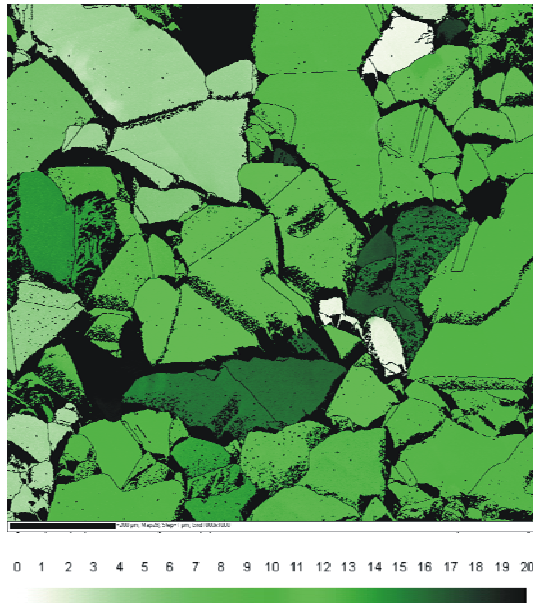

Figure 2. EBSD texture component map (1 x 1 mm^2) of a polycrystalline diamond film grown using the series B growth parameters with 800 ppm [PH$_3$]/[CH$_4$]). The scale bar indicates that the majority of grains have a tilt of less than 12° with respect to the perfect (110).

Figure 2 shows an EBSD texture component map for the (110) orientation of a sample grown using the doping conditions described as Series B in Table I. The darker the grain, the larger the off-angle of that grain is with respect to the perfect (110) orientation. First of all, every grain shows a continued growth when compared to the substrate surface before growth. Hence, the phosphine containing gas mixture does not prohibit growth of the (110) oriented surfaces. Moreover, the grain orientation after growth remains unmistakably (110) with the majority of grains having a tilt of less than 12°.

Quasi-steady-state photocurrent results

To study the incorporation of phosphorous and possible unwanted defects, quasi-steady-state photocurrent measurements (PC) were performed at liquid nitrogen temperature. For a more detailed description of the technique, the reader is referred to [11]. First, a comparison is made between two PC spectra taken on a (111) single crystalline layer deposited on a synthetic type Ib HTHP crystal (Sumitomo Electric Ltd.), and a polycrystalline film. Both layers were deposited with the first set of plasma parameters. The successful incorporation of the phosphorous donor is evidenced by the presence of the photoionization onset related to substitutional phosphorous situated around 0.6 eV [12], as can be seen in Figure 3. However, for the polycrystalline sample the oscillatory conductivity is obviously less pronounced, while photothermal ionization peaks cannot be seen on the rising edge of the photocurrent [13]. Moreover, the Series A conditions lead to the presence of an extra absorption edge around 1.5 eV for the microcrystalline sample. A similar level with ionization energy ~ 1.5 eV has been seen in several CVD diamond films from different origin [14], making a P-related complex unlikely. Even so, the nature of this defect remains unknown.
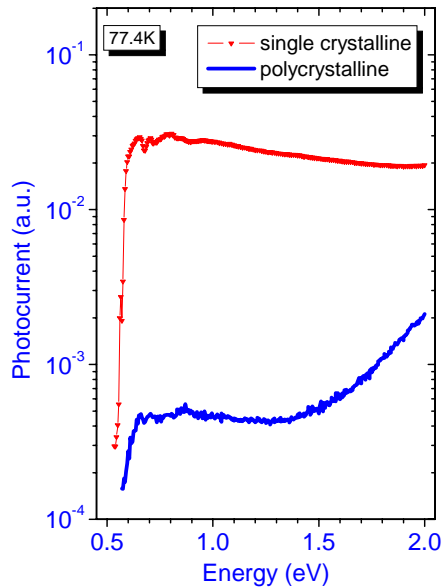

Figure 3. Comparison of PC spectra taken on a (111) oriented single crystalline and a mainly (110) oriented polycrystalline diamond layer grown using the Series A plasma parameters.

Surprisingly, when Series B is used, the subsequent photocurrent signals become much richer in details, while the defect level at high energy has completely disappeared. This is a direct proof that the novel doping conditions presented here lead to an incorporation of substitutional phosphorous on (110) oriented substrates. Comparing the photoresponse obtained at identical electric fields for different doping levels also reveals that an increase of the dopant concentration in the gas phase leads to a shift of the photocurrent onset towards lower energy values (Figure 4). For the 800 ppm doped sample, photocurrent can be detected as low as 485 meV, more than 100 meV below the ionization energy of the phosphorous donor. This result can be explained by impurity-assisted electron tunneling, i.e. in samples with a higher incorporation of phosphorous, the donor atoms are closer to each other facilitating tunneling of the electrons [15]. In addition, the signal intensity also increases with the dopant concentration sustaining the statement that more P can be found in these layers.
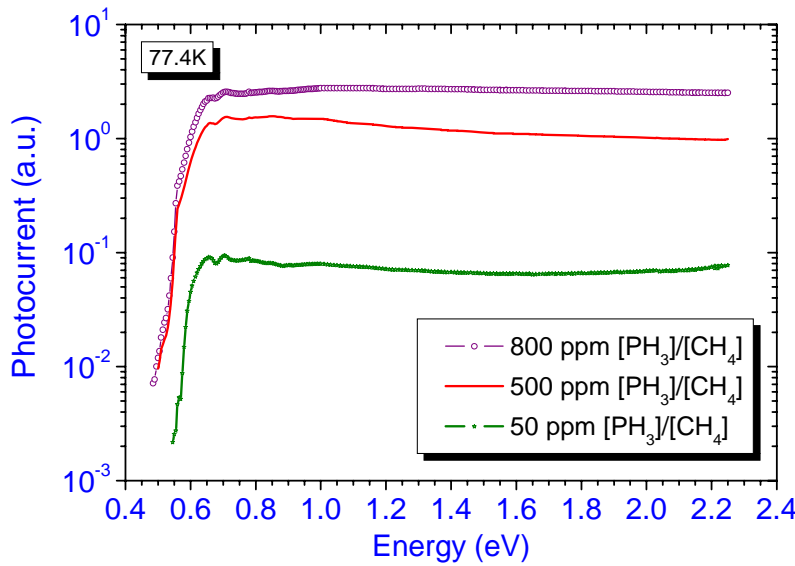

Figure 4. PC spectra measured on (110) oriented microcrystalline layers grown using the second set of plasma parameters with different $[PH_3]/[CH_4]$ ratios.

Cathodoluminescence results

CL spectroscopy is an excellent tool to confirm the just described results. Figure 5 displays two CL spectra taken on two P-doped polycrystalline samples with different doping concentration. Two important peaks in the excitonic region are visible in the CL spectra: the free exciton (FE^{TO}) peak at 5.27 eV and the P-bound exciton (BE^{TO}) peak at 5.18eV [16]. Both recombination events are assisted with the emission of transverse optic phonons. Also several replicas are visible. Note that the peak labeled BE_P^{NP} in the left side of Figure 4 is actually the sum of free exciton recombination assisted by a transverse acoustic phonon (FE^{TA}) and the P-bound exciton assisted by no-phonon (BE_P^{NP}) transitions. However, as the intensity of the FE^{TA} peak is usually a couple of times smaller then the intensity of the FE^{TO} peak, the contribution of FE^{TA} is deemed to be of minor importance. As could be expected, the incorporation of P is higher in the layer grown with 500ppm as confirmed by the amplitude of the P-bound exciton

signal. This is corroborated as well by significant broadening of the spectral when comparing the right and left parts of Figure 4.On single crystal diamond one can quantify the substitutional phosphorous concentration found in the diamond layer from the ratio between the BE and FE luminescence intensities [17], but due to the presence of grain boundaries complementary analyses making use of spot selected CL are requested for a precise estimation on these microcrystalline films. Nevertheless, it is safe to conclude that the intensity of the CL BE peak confirms the behavior seen in the PC spectra, which showed that a higher PH_3 concentration in the gas phase leads to higher active P-incorporation in the obtained diamond layer.
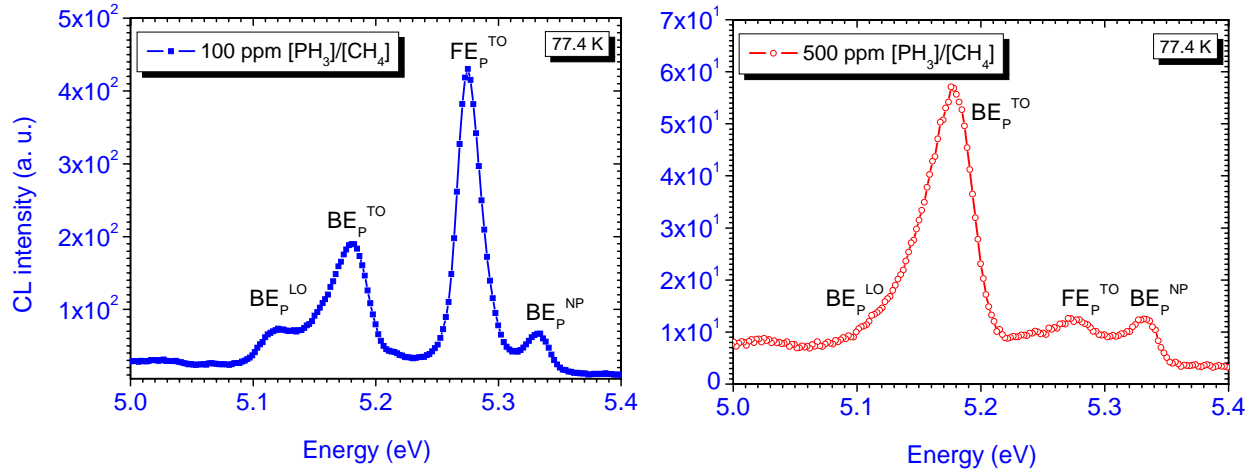

Figure 5. Cathodoluminescence spectra taken at 77.4 K for two microcrystalline samples grown with the second series of plasma conditions: (left) 100 ppm $[PH_3]/[CH_4]$. (right) 500 ppm $[PH_3]/[CH_4]$. Note that the peak attributed to the BE_P^{NP} likely contains a contribution of the FE^{TA} exciton.

CONCLUSIONS

Innovative MW PE CVD conditions for P-doping were discussed. These conditions clearly lead to the incorporation of phosphorous in polycrystalline P-doped CVD diamond films. The grain orientation of these films, as confirmed by SEM and EBSD, proved to be primarily (110), with the majority of the grains being within a 15° off-angle of the perfect (110) direction. PC and CL spectra undoubtedly confirm the successful incorporation of substitutional phosphorous.

ACKNOWLEDGMENTS

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