



**HAL**  
open science

## Sharp interfaces for diamond delta-doping and SIMS profile modelling

Christine Mer-Calfati, Nicolas Tranchant, P. Volpe, F. Jomard, Sylvain Weber, P. Bergonzo, Jean-Charles Arnault

► **To cite this version:**

Christine Mer-Calfati, Nicolas Tranchant, P. Volpe, F. Jomard, Sylvain Weber, et al.. Sharp interfaces for diamond delta-doping and SIMS profile modelling. *Materials Letters*, 2014, 115, pp.283 - 286. 10.1016/j.matlet.2013.10.053 . cea-01841354

**HAL Id: cea-01841354**

**<https://cea.hal.science/cea-01841354v1>**

Submitted on 17 Feb 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# Sharp interfaces for diamond delta-doping and SIMS profile modelling

C. Mer-Calfati <sup>a</sup>, N. Tranchant <sup>a</sup>, P.N. Volpe <sup>a</sup>, F. Jomard <sup>b</sup>, S. Weber <sup>c</sup>, P. Bergonzo <sup>a</sup>, J.C. Arnault <sup>a</sup>

<sup>a</sup> CEA LIST, Diamond Sensors Laboratory, F-91191 Gif-sur-Yvette, France

<sup>b</sup> GEMaC-CNRS/UVSQ, 1 Place Aristide Briand, 92195 Meudon, France

<sup>c</sup> Institut Jean Lamour, UMR CNRS 7198, Université de Lorraine, Parc de Saurupt - CS 50840, 54011 Nancy, France

## Abstract

Boron delta-doping of diamond has appeared as a promising viable approach for the fabrication of high performance RF power transistors taking advantage of diamond properties. Here structures based on  $p^-/p^+/p^-$  multilayers were synthesized on (100) HPHT Ib substrates using MPCVD. An original gas injector system was developed enabling to significantly improve the sharpness of both interfaces between  $p^+$  and  $p^-$  layers with a good reproducibility. SIMS profiles recorded on the doping transients still demonstrate an asymmetry of the interface sharpness from 7 nm/decade to 2 nm/dec on the  $p^-/p^+$  and the  $p^+/p^-$  interfaces, respectively. The observed differences are here explained and confirmed experimentally, and result from the combination of ion mixing with the effect of the surface roughness, thus limiting the SIMS resolution in depth. The Mixing Roughness Information (MRI) model then allows to evaluate the real value of the delta thickness achievable using this technique to 7 nm and the negative and positive gradients to identical values, namely of 1.4 nm/dec.

## Keywords

Boron delta doping, Single crystal diamond, SIMS, MRI model

## 1. Introduction

Diamond extreme properties make it a very attractive material for electronic applications (wide band gap, high electrical breakdown voltage and high thermal conductivity) [1], [2]. Single crystal diamond is an excellent candidate for high-voltage and high-power applications [3]. High frequency switches are based on “delta” MESFET architecture [4] that consists in a very thin  $p^+$  layer containing highly boron content (ideally 2 nm layer with  $[B]>3.10^{20}$  at/cm<sup>3</sup>) sandwiched between two “low boron doped”  $p^-$  layers (500 nm for the bottom layer and 20 nm for the top layer with  $[B]\approx 10^{16}$  at/cm<sup>3</sup>) [5], [6]. For such thin  $p^+$  layer, the conduction should occur in the  $p^-$  doped layers due to holes delocalization from the narrow delta layers [7]. The main experimental challenge is to control both the  $p^+$  thickness and the sharpness of the doping interfaces to allow carrier delocalization within the surrounding  $p^-$  layer that must exhibit high mobility.

We previously demonstrated the feasibility of ultra sharp  $p^+/p^-$  and  $p^-/p^+$  interfaces with doping gradient values above four decades using an original injection system [8]. This innovative configuration enables to inject the precursor gases at the very close vicinity of the holder via a retractable quartz tube (Fig. 1). Consequently, gradients of boron concentrations were significantly reduced, down to 7 nm/decade and 2 nm/decade for the  $p^+/p^-$  and  $p^-/p^+$  interface gradients, respectively.



Fig. 1. Configuration of the injection gas system using a retractable quartz tube.

In the present paper, we report on the growth of reproducible delta-doped layers ( $p^-/p^+/p^-$ ) with nanometric  $p^+$  layer. Secondary Ion Mass Spectrometry (SIMS) phenomena inherent to the technique such as mixing and roughness effects were taken into account to extract the real  $p^+$  thickness from SIMS profiles using the Mixing Roughness Information model (MRI model) [9].

## 2. Experimental

Boron doped diamond layers were grown using Microwave-Plasma-enhanced Chemical Vapor Deposition (MPCVD) on Ib (100) HPHT diamond substrates purchased from Sumitomo. The dopant gas used is trimethylboron (TMB). Oxygen was added during growth (with an optimum for a  $[O_2]/[H_2]=0.25\%$ ) to achieve  $p^-$  layers with a boron content below the residual one in the reactor ( $<5 \times 10^{16}$  at  $cm^{-3}$ ) [10], [11]. Such  $p^-$  layers exhibit high carrier mobility values ( $1250 \text{ cm}^2/V \text{ s}$ ) according to the RT Hall effect measurements [12].

For CVD growth, the temperature, the pressure and the microwave power were respectively at  $850 \text{ }^\circ\text{C}$ , 120 mbar and 600 W. Other CVD parameters are summarized in the Table 1. Boron concentrations were measured by SIMS in a secondary negative ion detection using  $Cs^+$  ions primary of 14.5 keV and an incidence angle of  $27^\circ$ .

Layer type	$CH_4/H_2$ (%)	$O_2/H_2$ (%)	$(B/C)_{\text{gas}}$ (ppm)	Injection time (sec)	Growth rate ( $\mu\text{m/h}$ )
$p^-$	1	0.25	residual	–	0.55
$p^+$	0.6	–	21400	45-90-105	–

Table 1. Diamond growth conditions.

### 3. Results and discussion

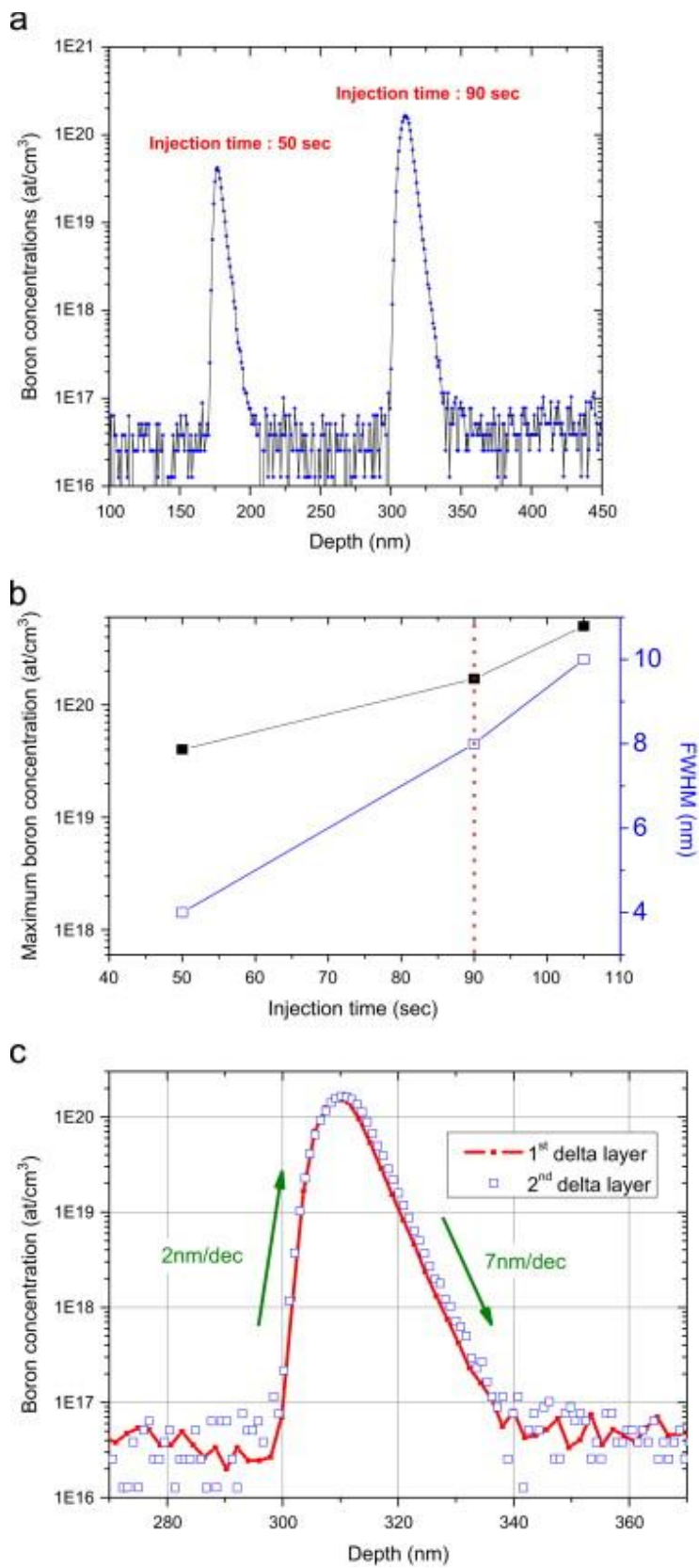


Fig. 2. (a) SIMS profiles of two p+ layers grown with injection times of 50 sec and 90 sec. (b) [B]max concentration and FWHM of the p+ layers for injection times ranging from 50 to 105 s. (c) SIMS profiles recorded on two p-/p+/p- delta layers grown on different substrates.

The effect of injection time was first investigated to determine the best compromise to achieve the highest boron content and the thinnest full width at half maximum (FWHM) of the  $p^+$  layer. Two  $p^+$  layers were deposited on the same substrate (Fig. 2a) while a third  $p^+$  layer was grown on another substrate with an injection time of 105 s. For the three  $p^+$  layers, the maximum boron concentration and the FWHM measured from SIMS profiles are plotted on Fig. 2b versus injection time. The best compromise is obtained for an injection time of 90 s leading to a maximum boron content of  $2 \times 10^{20}$  at/cm<sup>3</sup> and a FWHM of 8 nm. Indeed, for a longer injection time, the FWHM becomes too broad to obtain a functional  $p^+$  layer for delta MESFET architecture (Fig. 2b). The boron concentration is lower than  $5 \times 10^{19}$  at/cm<sup>3</sup> for the shortest injection time. The reproducibility of the  $p^-$  layers is confirmed from the SIMS analysis, as they exhibit a residual boron concentration of  $3 \times 10^{16}$  at/cm<sup>3</sup> (Fig. 2a).

Two  $p^-/p^+/p^-$  structures were synthesized with the same injection time (90 s) on two different HPHT Ib (100) substrates to check the reproducibility of the process. SIMS profiles provided on Fig. 2c is identical exhibiting the same positive and negative gradients (2 nm/decade and 7 nm/decade) and a FWHM of 8 nm. The two samples exhibit the same boron concentrations,  $3.10^{16}$  at/cm<sup>3</sup> and  $2 \times 10^{20}$  at/cm<sup>3</sup> for the  $p^-$  and  $p^+$  layers, respectively. The high reproducibility and control of boron concentrations for  $p^-/p^+/p^-$  multilayers were demonstrated.

When nanometric layers (<10 nm) are characterized by SIMS, several artefacts may affect the depth resolution, and namely mostly ion mixing and the effect of the surface roughness [13], [14]. These effects can here explain the asymmetry of the observed SIMS profiles and the lower dynamic for the negative gradient (7 nm/decade instead of 2 nm/decade).

Ion mixing traditionally occurs under the bombardment of primary ions, as part of the atoms is sputtered from the sample while a fraction is pushed into the diamond lattice. As a consequence, when a  $p^-$  to  $p^+$  interface is probed, most of the “implanted” atoms are carbon atoms prevailing over boron atoms because the  $p^-$  layer is probed. Conversely, for  $p^+$  to  $p^-$  interface, a significant amount of boron atoms is present at the surface leading to an artificial increase of the boron concentration. The implanted boron atoms are pulled over the lattice and can be re-implanted in the  $p^-$  layer (Fig. 3a and b).

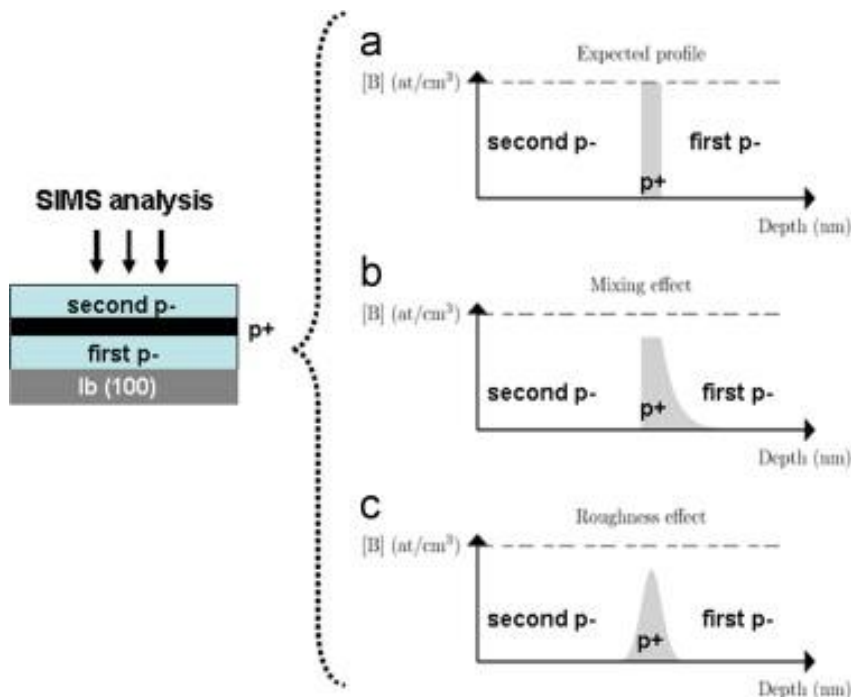


Fig. 3. (a) Expected SIMS profile without artefacts, Influence of mixing (3b) and roughness effects (3c) on SIMS profiles.

This effect was experimentally confirmed. A second SIMS analysis was realized on the same sample with a new generation set-up. For this experiment,  $O_2^+$  ions were used with a lower incident kinetic energy (2 keV) and an incident angle of  $44^\circ$ . Both SIMS profiles are compared on Fig. 4, an improvement of the negative gradient is observed: 4 nm/dec instead of 7 nm/dec. A slight decrease from 2 nm/dec to 1.4 nm/dec of the positive gradient can be noticed. This result can be explained by a better sputtering control using lighter ions with lower kinetic energy that reduces the ion mixing effect.

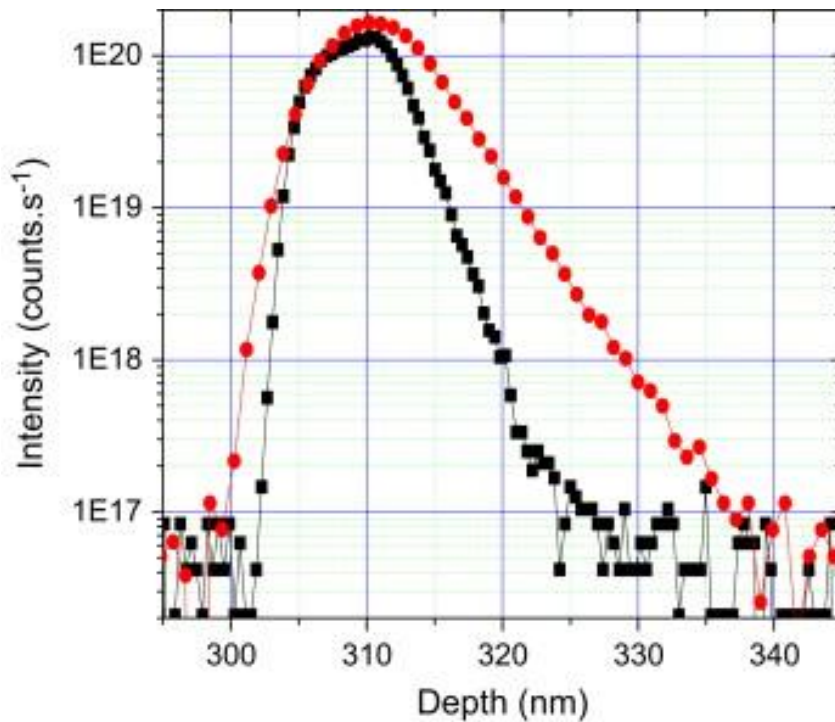


Fig. 4. SIMS profiles probed on the same delta layer using two SIMS set-ups, Curves were normalized for comparison. (Circle):  $Cs^+$ , 14.5 keV.  $O_2^+$ , 2 keV, (square):  $O_2^+$ , 2 keV.

The surface roughness comes as a second effect that can alter the sharpness of the SIMS profiles (Fig. 3c). It can be resulting directly from polishing scratches of the HPHT substrate or also from crystalline defects present in the diamond lattice: e.g. such as pyramidal hillocks or unepitaxial crystallites [15]. A typical  $5 \times 5 \mu m^2$  AFM scan has been performed on the sample after the delta layer structure was been grown. An average RMS roughness of 1.5 nm was measured.

The MRI model [9] takes into account the two previous effects: the ion mixing and the surface roughness. Ion mixing is computed with an exponential function: the fit of the interface slope in log scale provides a corresponding measured value of 6 nm/decade on the down interface was determined giving for the atomic mixing parameter  $w=0.38$  nm (of the MRI model [9]). On the other hand, a Gaussian function is used to take into account the surface roughness in the MRI model [16]. It affects both the up and down gradients. Using the MRI fitting model, the best agreement was found for a roughness of  $\sigma=1.6$  nm which closely matches the measured AFM value (Fig. 5 – (circle)). According to SIMS profiles, the best positive gradient is equal to 1.4 nm/decade. If the SIMS mixing effect artefact is subtracted, the calculated negative gradient drops to 1.4 nm/dec. This suggests that both  $p^-/p^+$  and  $p^+/p^-$  interfaces present the same gradient. This result looks more consistent because the

same experimental protocol was used for each interface. After fitting, the width of the  $p^+$  layer is estimated at 7 nm (Fig. 5 – (square)).

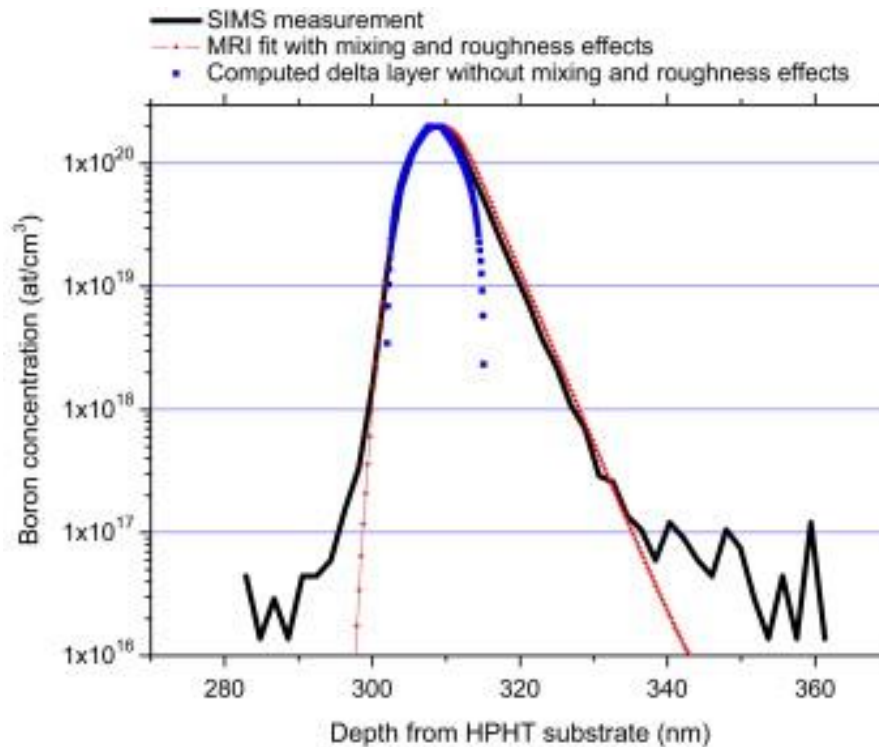


Fig. 5. Delta layer SIMS. (Black line): SIMS measurements. (Circle): MRI fit with roughness and mixing effect. (Square): Computed Delta Layer without mixing and roughness effect.

#### 4. Conclusion

We reported on the controlled growth of  $p^-/p^+/p^-$  multilayers with a high reproducibility for boron concentrations. This was achieved using an innovative gas injector. SIMS profiles were fitted with the MRI model to take into account the ion mixing and the surface roughness effects. As these effects are considered,  $p^-/p^+$  and  $p^+/p^-$  interfaces present the same gradient of 1.4 nm/dec.

#### Acknowledgments

The authors would like to thank the ANR for its financial support through the Deltadiam-ANR-08-BLAN-0195 contract.

#### References

- J. Butler, et al. *Semicond Sci Technol*, 18 (2003), p. S67
- R. Kalish, et al. *J Phys D: Appl Phys*, 40 (2007), p. 6467
- R.S. Balmer, et al. *Phil Trans R Soc A*, 366 (2008), pp. 251-265
- Kobayashi T. et al., *J Appl Phys* 76, 1977 (1994).
- El-Hajj, A Denisenko, A Kaiser, R.S. Balmer, E Kohn. *Diamond Relat Mater*, 17 (2008), pp. 1259-1263
- A. Aleksov, et al. *Diamond Relat Mater*, 12 (2003), pp. 391-398
- A. Fiori, T.N. Tran Thi, G. Chicot, F. Jomard, F. Omnès, E. Gheeraert. *Diamond Relat Mater*, 24 (2012), pp. 175-178

- P.N. Volpe, N Tranchant, J.C. Arnault, F Jomard, P. Bergonzo. *Phys Status Solidi RRL*, 6 (2012), pp. 59-61
- S. Hofmann, et al. *J Surf Anal*, 13 (2) (2006), pp. 142-147
- I. Sakaguchi, M. Nishitani-Gamo, K.P. Loh, K. Yamamoto, H. Haneda, T. Ando. *Diamond Relat Mater*, 7 (1998), pp. 1144-1147
- M. Kadri, D. Araujo, M. Wade, A. Deneuveille, E. Bustarret. *Diamond Relat Mater*, 14 (2005), p. 566
- P.N. Volpe, et al. *Diamond Relat Mater*, 22 (2012), pp. 136-141
- Hayashi S. et al., *Appl Surf Sci* 203.204 298–301 (2003)
- A. Takano, et al. *Appl Surf Sci*, 203–204 (2003), pp. 294-297
- N. Habka, et al. *Phys Status Solidi A*, 205 (9) (2008), pp. 2169-2172
- S. Hoffmann, et al. *Surf Interface Anal*, 27 (1999), pp. 825-834