Study of TMB/CH_4/O_2/H_2 Plasmas for Diamond Doped Multilayers

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Introduction Sharp transitions from heavily doped (p^{++}, [B] > 5×10^{20} cm^{-3}) to lightly doped (p^-, [B] < 10^{17} cm^{-3}) diamond films are essential to build power transistors (delta-doping) [1], or in optical systems (superlattice) [2]. Important challenges concern the accuracy and reproducibility of doping levels and deposition rates. Therefore, understanding the mechanism supporting the incorporation of boron in diamond is mandatory. However, that mechanism is very complex; many parameters are operating. Among them, the feed gas composition of plasma-enhanced CVD has the larger impact. In this study, we estimated the influence of methane and oxygen flows on the boron doping, and we adjusted plasma mixtures to obtain sharp boron transitions in diamond multilayers.

Experiment Optical emission spectroscopy (OES) has been employed to make a diagnostic of CVD plasmas composed of trimethylboron (TMB), methane, and oxygen, diluted into hydrogen. The comparison of H_α, H_β, H_γ, OH*, BH*, CH*, and C^2* emission lines provided a semi-quantitative characterization of the plasma composition in real time. We performed continuous plasma-enhanced CVD of diamond multilayers following a process in four steps (ML4), as follow: #1 deposition of a p^{++} layer, #2 rinsing mixture to reduce the residual of boron, #3 deposition of a p^- layer with typically oxygen flow, and #4 rinsing mixture to remove oxygen from the plasma mixture.

Results & discussion Reliable trends between BH*/CH* peaks ratio and boron concentration, and between C^2/H_β peaks ratio and carbon concentration have been drawn based on systematic experiments. We also identified a specific BH* super-intensity associated with diamond in-situ etching. Fig. 1 shows OES chronograms of C^2/H_β, BH*/CH*, OH*/CH* peaks ratios recorded during a ML4 deposition. In this example, plasmas #2 and #4 have the same feed gas composition (0.5% CH_4 + 0.1% O_2 to the total flow), but different OES features are observed. The OES highlights the consequence of residual boron during rinsing (#1: 6% CH_4 + 0.7% B/C, #3: 1% CH_4 + 0.2% O_2). Red arrows, visible on Fig. 1, indicate an irregular optical emission of boron, carbon, and oxygen in rinsing #2 compared to the case of a simple dilution in #4. In this example, boron and carbon OES signals increased and oxygen OES signal decreased during rinsing #2. We explain this irregularity by the in-situ etching of diamond during rinsing #2, after p^{++} deposition, while no etching happened in step #4, after p^- deposition. However, we suppose that etching is responsible of larger surface roughness and worse crystallinity, which are detrimental for high quality and nano-scale multilayers. Therefore, we established specific plasma mixtures to avoid etching during rinsing at doping transitions, by adjusting precisely methane and oxygen flows, supported by the real time OES technique.

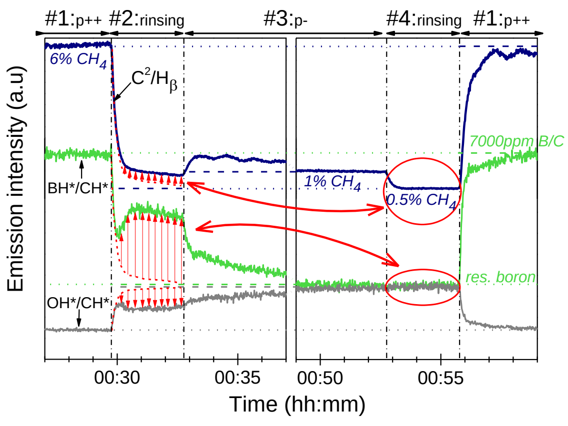

Fig. 1 OES chronograms of C_2/H_β, BH*/CH*, OH*/CH* peaks ratios recorded during ML4 deposition. Feed gas mixtures are composed as following: #1 (20’): 6% CH_4 + 0.7% B/C, #2 & #4 (3’): 0.5% CH_4 + 0.1% O_2, #3 (20’): 1% CH_4 + 0.2% O_2, and plasma condition: 140 Torr, and 280 $W.cm^{-3}$.

References
[1] A. Fiori et al, *Appl. Phys. Express* **6** (2013), 045801
[2] A. Fiori et al, *Appl. Phys. Lett.* **105** (2014), 081109