



In situ spectroscopic ellipsometry monitoring of diamond multilayers grown by microwave plasma enhanced chemical vapor deposition

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ABSTRACT

Thanks to its unique properties, diamond is intensively investigated for the development of optical and electronic devices. These applications, such as pseudo-vertical Schottky diodes or Bragg mirrors, rely on the synthesis of boron-doped (p^+) and non-intentionally doped (*nid*) stacked epilayer with well-controlled thicknesses, doping level and sharp interfaces. Such structures require a time-consuming optimization of the growth processes throughout the use of destructive techniques such as Secondary Ion Mass Spectroscopy (SIMS), Transmission Electron Microscopy (TEM) or transport measurements. From this perspective, the use of an *in situ* characterization tool is a considerable asset.

In this paper, we demonstrate that spectroscopic ellipsometry, implemented to be used *in situ* during the Plasma Enhanced Chemical Vapor Deposition (MPCVD) process, is a powerful and non-destructive technique to characterize diamond based devices. Moreover, it can also be sensitive enough to access the gas flow dynamics in the reactor. To this aim, two doped and *nid* multilayer stack have been investigated. The doping profile of a doped layer, extracted from the optical spectra is compared to the one obtained by SIMS and the growth rate of *nid* epilayers grown under various flow rate, is derived based on this technique.

1. Introduction

The fabrication of diamond-based power or optical devices such as n/i/p and Schottky pseudo-vertical diodes [1–3] or Bragg mirrors [4,5], requires the growth of boron-doped and intrinsic diamond layers with sharp interfaces, well-controlled thicknesses and doping levels. In most cases, an optimization of the growth conditions is needed, requiring the growth of a large number of samples and the use of destructive and time-consuming techniques such as Secondary Ion Mass Spectroscopy (SIMS) or Transmission Electron Microscopy (TEM).

In situ spectroscopic ellipsometry has already been reported to be an efficient way to characterize the nucleation and coalescence of polycrystalline diamond grown on silicon thanks to the substantial index contrast between the two materials [6–12]. However, in spite of several papers [13,14] indicating a significant decrease of the refracting index in doped epilayers induced by free holes absorption in the infrared region, very few studies were undertaken to characterize diamond single crystal by using *ex situ* spectroscopic ellipsometry. And all of them concern pristine semi-infinite layers [15,16]. Thus, contrary to a large number of materials, the very first *ex situ* measurement to

precisely assess the thickness and doping level of boron doped diamond monolayers was only demonstrated in 2013 [17]. Recently, the same technique has been used *in situ* on the reactor to monitor in real time the fabrication of Bragg mirrors [5].

This paper aims at going one step further by showing that substantial information can be extracted from an on-line treatment of the spectra recorded during the growth of p^+ or *nid* diamond layers. First, we show that a proper free carrier concentration depth profile of a metallic heavily boron doped (p^+) layer can be deduced from *in situ* spectra by comparing our measurements with SIMS profiles. Then, the sensitivity of the technique is assessed. By studying the transient regime of the growth of a stack of *nid* epilayers synthesized under various gas flow rates we will also demonstrate that this technique can give access to the transit time of gases inside the reactor, a considerable asset for the elaboration of new growth recipes for thin film such as boron [18,19] or nitrogen delta-doped layers [20].

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Table 1
Details of the growth conditions of the metallic sample and the *nid* epilayer stack.

	Pressure (torr)	CH ₄ /H ₂ (%)	B/C (ppm)	Gas flow rate (sccm)	Growth time (min)
p ⁺	33	3.54	2000	100	7
<i>nid</i> stack	50	1	0	70, 100, 150, 200 and 1000, 1500, 2000	1.5 and 1

2. Experimental

2.1. Sample preparation

All samples were grown by MPCVD in a vertical silica tube NIRIM type reactor on 3 × 3 mm² and [100]-oriented diamond substrates (purchased from Sumitomo Electric). Prior to each growth, pure hydrogen plasma was performed to stabilize the temperature and the pressure inside the chamber. Then a *nid* buffer layer was grown by injecting a H₂ + CH₄ gas mixture. The microwave power was adjusted at 280 W to keep a surface temperature around 910 °C as measured by a pyrometer, and the metallic layers were synthesized at 830 °C by adding B₂H₆ to the gas mixture. The growth conditions of the p⁺ layer and the *nid* epilayer stacks are detailed in Table 1.

A thick doped layer ([B] > 10²⁰ cm⁻³), covered by a *nid* film, was grown on each substrate to get a sufficient index contrast. Acting as a mirror, this p⁺ is needed to measure the second *nid* layers (for the *nid* stack case) and can be used to increase the sensitivity of the measurement by maximizing the amplitude of the reflected beamlight in the first experiment (p + doping profile assessment).

2.2. Secondary ion mass spectroscopy

The SIMS measurements were performed in a CAMECA IMS7F system with collection of a negative secondary ¹¹B and ¹²C ions or their compounds. A O₂⁺ primary ions beam at 5 keV, reduced to 0.5 keV for thin layers, was used.

2.3. Spectroscopic Ellipsometry

In Spectroscopic Ellipsometry, the change of the polarization state of the beam light is measured throughout the two ellipsometric angles ψ and Δ which are defined by the ratio ρ of the two complex reflection coefficients as followed [21]:

$$\rho = \frac{r_p}{r_s} = \tan(\psi) \exp(i\Delta) \quad (1)$$

with r_p and r_s the complex reflection coefficients for the electric field which are respectively parallel and perpendicular to the incidence plane.

Our *in situ* measurements were performed over a spectral range of 210–1690 nm, with a J. A. Woolam M2000 ellipsometer running under the Complete Ease software. The source and the detector were placed on each side of the quartz tube and aligned with the sample so that the polarized beam light coming through the silica tube *via* the waveguide slits is reflected by the sample toward the center of the detector with an angle of around 75° (see Fig. 1a). Note that the overall surface of the sample impacted by the beam light is about 2.4 × 4 mm² *i.e.* along the sample diagonal. All optical measurements are thus averaged over the surface of the sample.

The *in situ* configuration requires considering the influence of the different interfaces crossed by the beam light (here the silica tube) but also of the temperature on the ellipsometric angles. To that aim, the same protocol was followed before each growth. First, an *ex situ* spectrum of the substrate was recorded and modeled. Then, a second

measurement was carried out *in situ* at room temperature. A shift of the Δ angle, induced by the silica tube, was then estimated from the comparison of the two spectra. This shift, presented in blue in Fig. 1b, was taken into account by adding the “Prism” function of the software (4 parameters Cauchy formula) to the model defined from the *ex situ* spectrum. The same procedure was followed during the hydrogen plasma at around 880 °C. For all *in situ* measurements, a strong shift of Δ has been observed whereas almost no change in the spectral dependence of ψ could be noticed tending to indicate that the influence of the temperature on the dielectric constants of the substrate is negligible in comparison to the transmittance change induced by the silica tube heating. Thus, at this stage, the new Δ offset is taken into account by fitting the new spectrum and adjusting the 4 parameters previously introduced (see red curve in Fig. 1b). Note that a final spectral dependence of the Δ shift, quite similar whatever the substrate, has been observed, pointing again to the quartz tube as a possible origin for this shift.

As mentioned elsewhere [5], the substrate, considered as a semi-infinite medium, and the *nid* diamond layers of finite thickness, could be simulated by a Cody-Lorentz model. In this latter, the direct E_g⁰ and indirect E_g^{ID} band gap absorptions of diamond were simulated by fixing the energy of the principal oscillator at 7.3 eV and adjusting the amplitude and the tail of the Lorentzian contribution whereas the E₂ peak absorption was taken into account by fixing the UV Pole energy at 11 eV.

A Drude component (ε_{Drude}) was added to this UV oscillator (ε_{nid}) in order to model the boron-doped samples. The thickness of the epilayer was extracted from the spectral oscillation of the ellipsometric angles. The electronic properties were deduced from the modeling of the optical absorption at low energy using two independent sets of parameters; respectively the resistivity at zero frequency (ρ₀) and the scattering time (τ_{opt}), or the renormalized free carrier concentration (N_{opt}/m_{opt}^{*}) and mobility (μ_{opt}).

Since our previous report [17] the spectral range of our ellipsometer has been extended allowing a more accurate extraction of the holes effective mass. The recent comparison of the optical parameters with SIMS and transport measurements gave a new optical effective mass of around m* = 0.4 m₀ (with m₀ the electron mass), within the error bar of the previous value.

Considering 3 bands degenerated at the Γ point, the total density of state effective mass can be approximated by the expression

$$m_{opt}^* = \frac{m_{hh}^{3/2} + m_{lh}^{3/2} + m_{so}^{3/2}}{m_{hh}^{1/2} + m_{lh}^{1/2} + m_{so}^{1/2}} \quad (2)$$

m_{hh}, m_{lh} and m_{so} being the effective masses of the heavy, light and spin-orbit holes in the diamond band structure. This value of 0.4 m₀ is thus in good agreement with the recent measurements by electron cyclotron resonance (m_{opt}^{*} = 0.47 m₀) [22] and Angle Resolved Photoemission Spectroscopy (m_{opt}^{*} = 0.41 m₀) [23] but also with earlier LMTO calculation of Willatzen [24] (m_{opt}^{*} = 0.45 m₀) or Eremets [25]. Note that our value is however lower than the one predicted by other earlier works [26–28].

3. Results

3.1. Boron-doped layer

On top of providing real-time feedbacks about the layer properties, the use of *in situ* Spectroscopic Ellipsometry enable an easy extraction of its doping profile without the need of a complex model.

In the following example, the p⁺ epilayer of a multilayer stack was measured in real time by recording one spectrum every 2.4 s. After the growth of a *nid* epilayer, the metallic film was deposited during 7 min under the conditions detailed in Table 1. Then, a short rinsing hydrogen plasma was used before capping with a *nid* film and continuing the

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