Thin Solid Films xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Improved depth resolution of secondary ion mass spectrometry profiles in diamond: A quantitative analysis of the delta-doping

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ARTICLE INFO

Available online xxxx

Keywords:
Diamond
Delta-doping
SIMS
Depth resolution function

ABSTRACT

In this work, we used the depth resolution function (DRF) of the secondary ion mass spectrometry (SIMS) to deconvolve the boron depth profile of nanometer-thin embedded diamond layers. Thanks to an isotopic change within a thin layer, where carbon-12 (^{12}C) and carbon-13 (^{13}C) are substituted, the DRF was evaluated by a self-consistent algorithm. In a second step, this DRF was used to deconvolve the boron depth profile of a double delta-doped diamond analyzed under the same ion beam condition. The expected position, thickness, and boron concentration of the embedded layers were confirmed. This technique has enhanced the SIMS performance, and the depth resolution reached the nanometer range. Interface widths of boron-doped diamond multilayers were resolved well below 1 nm/decade over a large doping range, from 3×10^{16} cm^{-3} to 1.2×10^{21} cm^{-3}, and confirmed a conformal growth layer by layer.

1. Introduction

The development of diamond growth technology has largely improved the fabrication of homo and heterostructures with abrupt interfaces such as superlattices and quantum wells [1]. Consequently, the request for a very accurate characterization has become more demanding even though the analysis of such structures is difficult and sometimes a challenge of its own (nanometer scale, low concentration of light atoms, hard material, and so on). Secondary ion mass spectrometry (SIMS) is commonly used to obtain depth profiles of dopants over many orders of magnitude in concentration. However, below 100 nm in thickness, SIMS induced ion mixing is no longer negligible; it affects strongly the depth profile measurements by broadening and distortion, so that the raw SIMS profile differs from the dopant profile, up to the point where thickness values and atom peak concentrations in multilayer stacks become erroneous. Other alternative and promising techniques like atom probe tomography [2] are not yet so commonly available, and in fact not yet demonstrated on the diamond material.

This work is dedicated to the potentiality of SIMS applied to the characterization of nanoscale diamond embedded heterogeneous structures. Diamond has several excellent properties, in most cases superior to those of other semiconductors, e.g., Si and SiC. Actually, two types of application require the availability of very thin layers (boron or nitrogen-doped) in the range of nanometer thickness, the so-called "delta structures" [3–5], as well as the possibility to characterize such ultrathin epilayers. These applications are related to high breakdown voltage/high temperature electronic devices [6] aimed at the development of next-generation high power devices, but also to colour centers, e.g., NV centers in diamond [3,7], a very active research field of photonics and spintronics, more in line with the optical properties of diamond.

Technically, during a SIMS analysis, the experimental depth profile is the convolution of the dopant depth profile and of the depth resolution function (DRF) [8]. Evaluation of this DRF (which depends on the probed atom) is a key issue in nm-range secondary ion mass spectrometry. Deconvolution analysis using such a DRF provides accurate measurements on abrupt dopant depth profiles over many orders of magnitude in concentration. The best tool to estimate quantitatively the influence of ion mixing during the SIMS analysis is the local isotopic substitution (or "isotopically pure growth"). This has already been demonstrated with silicon superlattices ($^{28}Si/^{30}Si$) [9]. The atomic substitution by an isotope is the best approach to extract the experimental response, i.e. the DRF, because it introduces only a negligible difference in mass (same recoiling effect) and ionization threshold as well as no additional crystalline strain (same lattice parameter). Once the DRF expression is known for carbon in diamond, we can apply this function to determine a genuine dopant depth profile for nitrogen, or boron, or phosphorus.

However, the requirements to record an accurate DRF are stringent. The embedded layer has to be in the same thickness range as the lattice parameter. The fabrication of such structure requires strict conditions such as flat interface, no chemical diffusion in the matter, and a single crystalline substrate [10]. Diamond epitaxial multilayer stacks fulfill these requirements.

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0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.10.076

2. Diamond sample growth

Two diamond single crystalline samples were grown in this study. A first sample, composed of a synchronized boron- and carbon-13-doped layer, was used to extract the DRF from the ^{13}C signal intensity. Furthermore, the fitting process was applied on the boron profile, in order to qualify the possibility to deconvolve the boron concentration and the layer thickness. The second sample was constituted of a double boron-doped delta layers in order to analyse the growth uniformity and the interface quality. The growth of the second sample was optimised to obtain delta layer thinness below the nanometer.

The strategy applied to grow an extremely thin embedded layer was to use a dedicated microwave plasma chemical vapor deposition (MPCVD) reactor, to work at high gas flow and at slow growth rate. This was explained in the literature, in the case of the diamond delta-doping without isotope enrichment [11]. Such equipment can grow step by step multilayer sample.

In theory, a delta structure is composed of the three layers, i.e. buffer, doped, and cap layer. In the particular case of the isotope-modulated sample, two distinct MPCVD reactors were employed in order to grow each layer with a specific carbon isotope source (Fig. 1). Standard methane (^{12}C: 98.9 % + ^{13}C: 1.1%), diborane and hydrogen were used at Institut Néel to grow the delta layer in a vertical quartz tubular (NIRIM-type) MPCVD reactor [12] modified for the diamond boron delta-doping [5]. ^{12}C-enriched methane (^{12}C: 99.999%) was used to grow the buffer and the cap layers in a high plasma density NIMS-type reactor developed at the National Institute for Material Science [13]. In order to minimize atomic diffusion from the delta layer to the cap layer, its homoepitaxy was made carefully; a lateral growth condition was applied. The second sample was continuously grown layer by layer in a modified NIRIM-type MPCVD reactor. Etching-back plasmas were applied after growth of the boron-doped layer in order to reduce its thickness to the nanometer scale [11].

Particularly flat samples were selected to minimize surface roughness effects. The surface was ultra-polished in Japan by Syntek Co., Ltd.; the resulting surface root mean square roughness was below 0.3 nm before overgrowth.

3. SIMS profile fitting

Several authors have reported that a SIMS profile can be modelled by convolving the genuine atom profile with the SIMS depth resolution function, a response which depends on instrumental and fundamental aspects as well (convolution model). In the 90s, Dowsett et al. [10] have demonstrated that for delta-doped layers characterized by few atomic layers and hence below the SIMS resolution, an excellent approximation of depth resolution function (DRF) can be obtained by convolving a double exponential with a Gaussian distribution.

The edges of the measured SIMS signal have an exponential behavior characterized by a leading edge decay length λ_{up} (upslope during the sputtering process) and a trailing edge decay length λ_{down} (downslope). The σ parameter is related to the full width at half maximum of a Gaussian function, characteristic of the surface roughness, mostly generated by the ion beam/solid matter interaction. It depends of the incidence angle between the ion beam and the crystalline system, and the scanning velocity.

The following analytical expression of this DRF was employed for this study, similarly to past experiments performed in the silicon technology [14]:

$$\mathrm{DRF}(z) = \frac{1}{2\left(\lambda_{up}+\lambda_{down}\right)} \times \left\{ exp\left(\frac{z-z_0}{\lambda_{up}} + \frac{\sigma^2}{2\lambda_{up}^2}\right) \times \left[1 + \frac{1}{\sqrt{2}} \cdot \mathrm{erf}\left(\frac{-(z-z_0)}{\sigma} - \frac{\sigma}{\lambda_{up}}\right)\right] + exp\left(\frac{-(z-z_0)}{\lambda_{down}} + \frac{\sigma^2}{2\lambda_{down}^2}\right) \times \left[1 + \frac{1}{\sqrt{2}} \cdot \mathrm{erf}\left(\frac{z-z_0}{\sigma} - \frac{\sigma}{\lambda_{down}}\right)\right]\right\}$$

, where z_0 represents the position of the delta layer. This expression has the advantage to be simple to use. The procedure describing the extraction of the DRF and the removal of the ion mixing effect in a boron depth profile is given on Fig. 2.

3.1. Initialization

The initialization (arrows labeled "Init." on Fig. 2) was used to extract the set of variable parameters (λ_{up}, λ_{down}, and σ) and to localize the position z_0 of the layer. In practice, parameters λ_{up}, λ_{down}, and σ were evaluated separately, by local fits, in order to initialize the self-consistent fitting process. In agreement with many other works in the literature regarding SIMS depth profiling of delta-doped distributions, the edges of the measured isotopes signals have an exponential behavior characterized by an upslope length λ_{up} and a downslope length λ_{down}. Their initial values were measured on 3–4 points, on the 1×10^{17}–1×10^{20} cm^{-3} range. The initial value of σ, more dependent on the surface roughness, was measured by 3D optical microscope to lie within the 0.1–1 nm range.

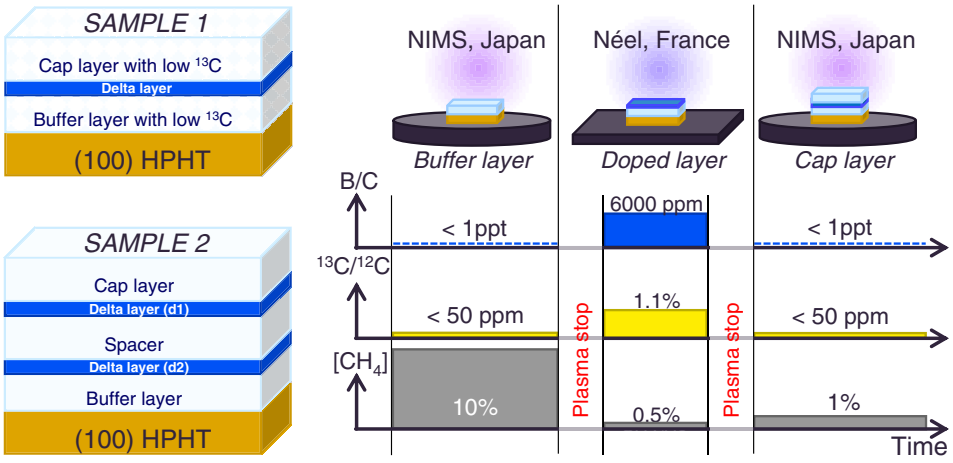

Fig. 1. Stacking structure of samples 1 and 2 together with the flowchart used to grow sample 1. One MPCVD reactor employed low ^{13}C methane source for intrinsic growth and another allowed a boron doped growth with a standard methane source.

Please cite this article as: A. Fiori, et al., Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2013.10.076