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The p-to-n-type conversion of boron-doped diamond layers by deuteration: New findings

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Abstract

The p-to-n-type conversion of particular B-doped homoepitaxially grown diamond layers upon deuterium plasma treatment was discovered three years ago. However, many questions regarding the reproducibility of the effect for samples of different origins remain unanswered up to now, in particular the role of the electrical contacts and the possibility of a surface inversion layer being responsible for the n-type conductivity, the thermal stability and origin of the donor.

Here we address the above questions. We show that the p-to-n conversion is closely related to the presence of defects, which can vary, on a macroscopic scale, in different regions of the same sample. The p-type regions containing a small concentration of defects are found to be converted to n-type upon deuteration. In contrast, the regions counting a high defect density exhibit very low p-type conductivity related to passivation of the boron acceptors by deuterium accompanied by a large uptake of D on defects. We show that the n-type conversion can be equally observed with three different kinds of contacts (silver paint, implanted and evaporated). We prove that the n-type conversion is a bulk effect and not a surface effect. We find that the thermal stability of the n-type complex is limited to temperatures lower than 200 °C. The temperature dependence of the carrier concentration measured by the Hall effect at different stages of the conversion process is fitted following the formalism describing the conduction mechanisms in a partially compensated semiconductor. The fact that the donor concentration in the as-deuterated state is very close to the boron concentration strongly suggests that the new-formed donor complexes contain both D and B.

Keywords: Hydrogen passivation; Doping; Defects; Electrical properties

1. Introduction

The recent discovery [1] of a new way to achieve n-type diamond with a rather shallow donor level raised much interest, both theoretically and experimentally [2–4]. Previous work of ours has shown [5–8] that deuteration in a microwave plasma of a p-type, boron-doped homoepitaxial diamond layer, results in the creation of a deuterium related donor complex with an ionization energy varying between 0.24 and 0.34 eV, depending on the doping level. The appearance of the n-type conduction was related to excess deuterium and the type conversion was explained by considering a two-step process. The first is a fairly slow one (diffusion coefficient at 475 °C is about 8×10^{-17} cm^2/s) and it is governed by the capture of deuterium by boron acceptors in the layer [5]. It causes the passivation of the boron atoms, as reflected by the disappearance of the characteristics 2450 and 2820 cm^{-1} IR absorption peaks of the neutral boron [9]. The second step is much faster (diffusion coefficient at 475 °C is about 1.5×10^{-14} cm^2/s) [5]; it seems to involve the capture of a second deuterium on the neutral (BD) complex in the already passivated layer. It is this step that is thought to be responsible for the appearance of the new donor state.

Computations investigating the possible formation of complexes involving a substitutional B and more than one hydrogen atom or B, H and native defects were published [2–4].

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Goss et al. [3] have calculated, using first-principles computations, the formation energies and energy levels of diamond samples with 64 and 216 atoms that contain a substitutional B atom with 2–4 hydrogen atoms placed next to it in several configurations. They find that one H attached to B passivates the acceptor level and that the complexes formed of (B,H) and the second, and subsequent H atoms are thermally instable, and none of the structures investigated are shallow donors. Dai et al. [4] have performed *ab initio* computations on a diamond sample composed of 32 C atoms containing a substitutional B atom with one two or three hydrogen atoms placed next to it. In contrast to the work of Goss and co-workers, Dai et al. conclude that BH_2 and BH_3 complexes in diamond do have donor levels at 1.2 and 0.7 eV below the conduction band, respectively, supporting our speculations. However, Dai et al. also conclude that (B, H) complexes behave as shallow acceptors, even shallower than isolated boron. This is in contradiction with well-established experimental results that prove that the B acceptor is passivated by an adjacent hydrogen atom.

In the same time, questions about the conversion process have been raised. Among them, (i) the reproducibility of the effect on samples originating from different laboratories, (ii) the influence of the electrical contacts on the determination of n-type conductivity by Hall measurements, (iii) the possibility that the measured n-type could be related to a surface conductivity effect, (iv) the similarity between D and H for the conversion process, (v) the thermal stability of the n-type dopant and, most importantly (vi) its origin.

Here we describe the results of most recent experiments, meant to answer several of the above questions and stress the current unsolved points. Special attention is given to the influence of various experimental stages on the final electrical properties of the samples.

2. Experimental

For the investigations presented below, a boron-doped homoepitaxial diamond layer was grown by LEPES (CNRS—France) on a synthetic Ib diamond substrate at 890 °C by the microwave plasma chemical vapour deposition (MWPCVD) method, using a mixture of 0.25% methane and diborane in hydrogen with a B/C ratio of 60 ppm in the gas phase. For deuteration, the sample was placed in a microwave reactor and was exposed to a deuterium plasma at 550 °C for 20 min sufficient to ensure a diffusion of deuterium through the entire epilayer for such a low doping level. The sample temperature during deuteration (hydrogenation) was measured by a pyrometer focused onto the diamond surface. Surface electrical conductivity was avoided by oxidizing the sample surface by acid treatment prior to any electrical measurement. The electrical properties of the samples were determined by Hall effect measurements in the van der Pauw configuration. Prior to the Hall effect, three different kinds of contacts were applied to the deuterated layer: 1) silver paint contacts, 2) Pt/Ti/Au evaporated contacts and 3) 200 keV Ar implanted at 200 °C to a dose of 2×10^{16} cm^{-3}, yielding amorphous carbon conductive dots [10]. The depth profiles of boron, deuterium and carbon were measured in a Cameca ims-4f SIMS apparatus using a Cs^+ primary ion beam and monitoring the $^2H_2^-$, $^{11}B^-$, $^{12}C^-$ and $(^{12}C^{11}B)^-$ ions. Reactive ion etching using CF_4 followed by a short oxygen plasma exposure was applied to remove the first 100 nm of the deuterated p-to-n converted diamond. X-ray photoelectron spectroscopy (XPS) was used to check, after the dry etching process, the surface impurities that could influence the results of the electrical measurements. The XPS analysis was performed in a Thermo VG Scientific Sigma Probe fitted with a monochromatized X-ray Al Kα (1486.6 eV) source. A 100 W X-ray spot of 400 μm was used for surface scans with pass energies of 200 eV for maximum measurement sensitivity.

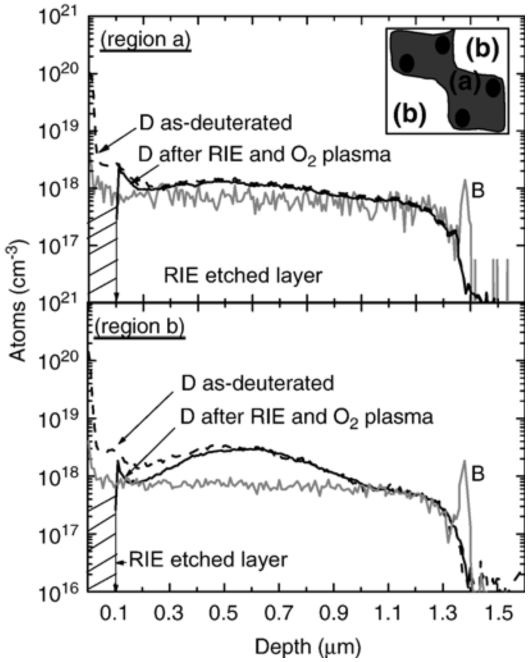

Fig. 1. Deuterium profiles in regions (a) and (b) directly after deuteration (dashed line) and after RIE and oxygen plasma (full line). A grey line represents the B profile. The insert shows a schema of the sample with the two types of regions (region (a) in grey and regions (b) in white). The four black circles represent the location of the four contacts in region (a).

3. Results

Upon deuteration, *I–V* curves obtained between sets of silver paint contacts located at various points on the sample revealed that the layer is composed of two regions. The regions labelled (a) are very conductive and have turned n-type while the regions labelled (b) exhibit extremely low conductivity and did not convert to n-type. Fig. 1 shows characteristic D and B SIMS profiles measured in region (a) and in region (b) of the B-doped film deuterated at 550 °C for 20 min. In both regions, the boron concentration is quite homogeneous throughout the whole layer thickness (1.3 μm) and equals to about 5×10^{17} cm^{-3}. In both regions, a strong accumulation of D is noticeable near the surface. However, the D profiles measured in the depth of the B containing layers are considerably different in regions (a) and (b). In region (a), the D profile is slightly above that of B throughout the entire layer while in region (b) it shows a pile up