Pergamon

CARBON

Carbon 37 (1999) 787–791

δ-Doping in diamond

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Received 17 June 1998; accepted 3 October 1998

Abstract

δ-Boron-doped homoepitaxial diamond films grown by microwave CVD were optimized for field effect transistor application to obtain steep profiles. The critical growth steps of the δ-doped device structures were analyzed and improved using mass spectrometry gas analysis, determining growth- and etch rates, hall-effect-measurements, elastic recoil detection and conductivity measurements. Optimized growth procedures were obtained and residual doping in the gate control layer was compensated using nitrogen. This results in a novel lossy dielectric Junction FET channel with high sheet charge activation and high drain current densities at moderate operation temperatures of 200°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Diamond; B. Chemical vapor deposition; Doping; C. Mass spectrometry; D. Electronic properties

1. Introduction

The characteristics of diamond field effect transistors have been limited in the past by a reduced free carrier density, due to the high activation energy of the boron acceptor (370 meV at low doping densities). To solve this problem δ- or pulse-doped layer structures have been proposed [1] and first promising results have already been reported [2,3]. At high doping levels ($>10^{20}$ cm^{-3}) the activation energy is reduced leading to almost 100% carrier activation. In a δ-doped structure the free carrier distribution is also expected to be considerably spread out beyond the doped layer, resulting in reduced ionized impurity scattering and high mobilities [1]. Therefore a δ-boron-doped channel field effect transistor with sheet concentration in the 10^{13} cm^{-2} range is expected to yield drain current densities even above 1 A/mm [3]. A schematic cross section of a δ-doped FET is shown in Fig. 1.

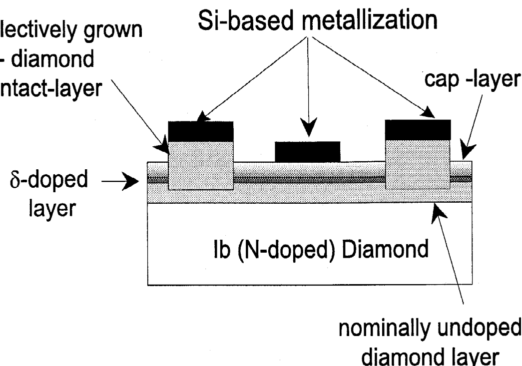

Fig. 1. Schematic cross section of a δ-doped-channel FET. The ohmic contact regions are defined by selective epitaxy of p^+-doped diamond [4].

2. Experimental

The investigated structures were grown in a commercial diamond microwave-CVD reactor (ASTEX™, Fig. 2). The substrate material was highly nitrogen (n-type) doped single crystal synthetic diamond. Definition of mesa-structures was performed by selective epitaxy, using SiO_2 masks. The growth was performed in using 1.5% CH_4 in H_2 at a total pressure of 30 torr. First a 500-nm thick, nominally undoped buffer layer was grown at a substrate temperature of ~650°C. The growth rate was about 5 nm/min. For p-type doping a boron rod was inserted into the plasma for a short time (≥3s). Finally a 100 nm thick cap-layer was grown at a higher temperature of 750°C (11 nm/min) in order to minimize memory effects from the residual boron in the growth chamber. The ohmic contacts

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PII: S0008-6223(98)00272-3

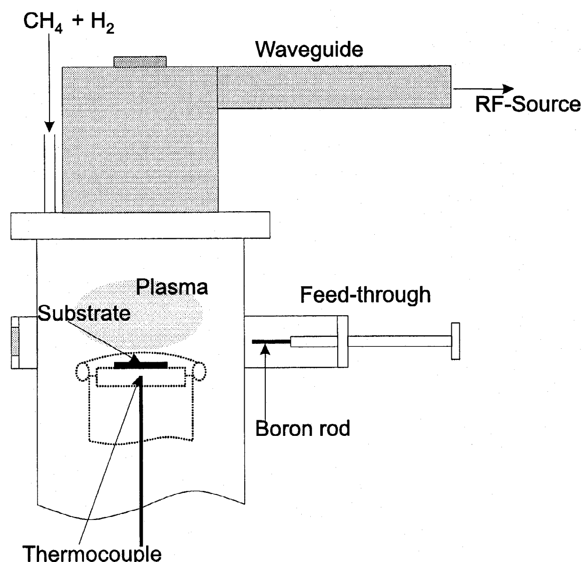

Fig. 2. CVD-System with solid boron rod as doping source. Typical growth conditions are 1.5% CH_4 in H_2 at a total pressure of 30 Torr, substrate temperature of approx. 650°C and 700 W RF-Power at 2.45 Ghz.

for this pulse doped structure were fabricated using selectively grown p^+-doped contact regions, as previously reported [4]. Both ohmic and Schottky contact metallization were sputter-deposited in a commercial ion beam reactor using highly temperature stable Si/WSi_xN_y/Ti/Au metals. The main growth conditions for the presented device structure are as follows.

1. The design with highly activated δ-channel imposes tight limits of the width of the δ-doped channel. For a sheet concentration of 10^{13} cm^{-2} a width of the δ-doped layer in the range of 1 nm is needed to achieve full activation. For both narrow doping profile and reproducible doping time (≥3 s to minimize error) small growth rates are required during the doping step. Analyzing the growth rates (Fig. 3), growth temperatures of $T_S = 600$°C at 1.75% CH_4 in H_2 will be needed or reduced CH_4-flux (for example 0.5% CH_4 in H_2 leading to a reduced growth rate of $r \approx 95$ nm/h). Therefore, the growth procedure of the doped layer determines the growth parameters of the nominally undoped buffer layer avoiding a growth interrupt. The activation energy of $E_a = 14.8$ kcal/mol (Fig. 3) indicates that dissociation of hydrogen from the diamond surface limits the growth rate [5].
2. A further critical feature of the structure lies in the cap layer. Here extremely low doping is needed to ensure a low leakage Schottky-gate contact. Also residual doping in the cap layer will inhibit modulation of the channel charge. Therefore after growing the doped layer a growth interrupt was performed to remove residual boron out of the chamber.

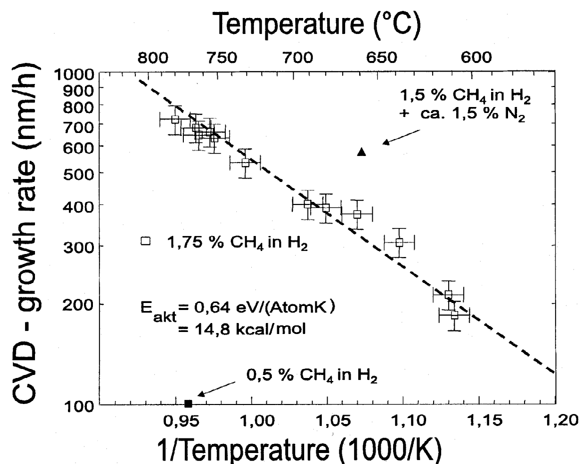

Fig. 3. Growth rates of the CVD-System.

The main influence on achieved activation energy of the devices can be seen in Fig. 4. Changing the doping time from 30 s down to 3 s leads to an increased activation energy from 0 meV up to 260 meV.

Optimization of the gate control layer requires a lot of research into growth conditions: usually each growth-start begins with some seconds or a few minutes of pure hydrogen plasma to ensure the required not-reconstructed, hydrogen saturated diamond surface [6]. The diamond-etching effect of such procedures are well known. At the growth-interrupt and at the restart after growth of the narrow pulse doped layer the etch rates and also gas flows have to be known to avoid any negative effect on the pulse

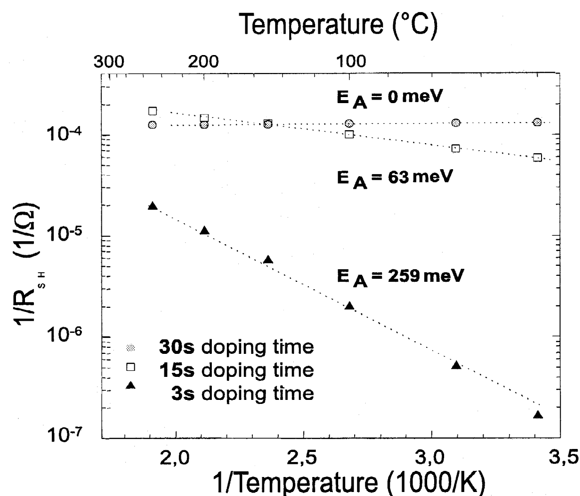

Fig. 4. Activation energies of pulse doped diamond films for different doping times.

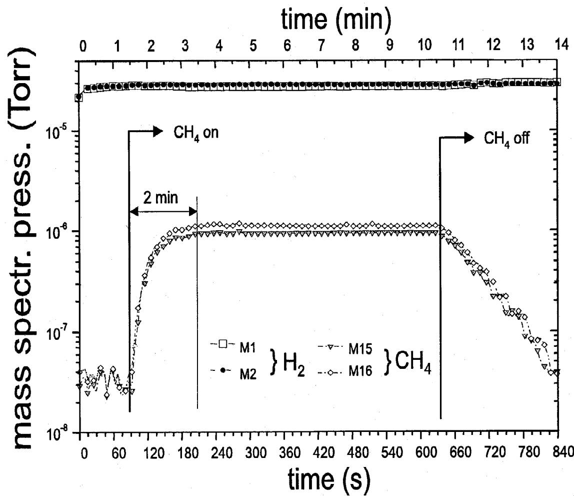

Fig. 5. Mass spectroscopy gas analysis during growth.

doped layer. Fig. 5 shows the mass spectroscopy analysis of CH_4 and H_2 during growth. After 3 min of stop of the CH_4-flux the concentration falls off at the background value and therefore further diamond growth occurs with starting of the etch process of diamond due to increasing hydrogen excess. The analysis of the etch rates of diamond in pure hydrogen (Fig. 6) reveals no significant effect on the pulse doped layer for the used 30 s 'outgrowth-time' and 30 s pretreatment in pure hydrogen before restart. Also variations on outgrowth time revealed no significant influence on activation energy of the devices.

3. Results

The conductivity profile of such a film is shown in Fig. 7 and was obtained by sequentially etching the top layer and measuring the conductivity after each step. A deep

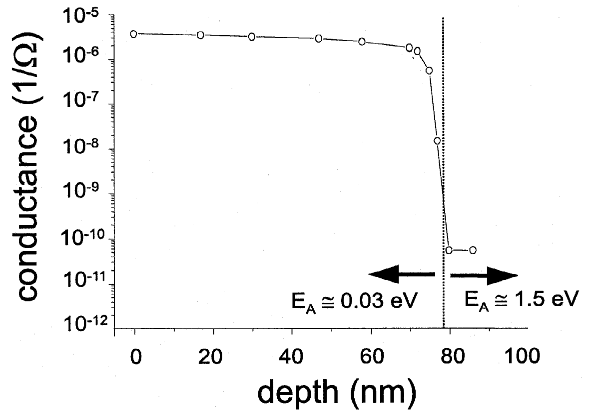

Fig. 7. Conductivity profile of a δ-doped structure.

decrease of conductivity over several orders of magnitude is observed over a depth range less than 15 nm, indicating that the conductivity is dominated by the doping pulse. This is confirmed by the activation energy, which remains basically constant at about 30 meV during the profiling. After etching the pulse doped layer, an activation energy of 1.3 eV for the undoped diamond buffer layer was extracted. Elastic recoil detection measurements have confirmed the steep doping profile, with a FWHM less than 10 nm. Elastic recoil detection on a pulse doped diamond film reveals similar results on the incorporated boron profile (Fig. 8). A full width at half maximum of only less than 6 nm was achieved. Nevertheless, not negligible residual doping in the cap layer leads to a sheet carrier concentration of $n_S \approx 1.6 \times 10^{13}$ cm^{-2}. The high sheet concentration towards the surface is already too high to modulate the peak carrier concentration and furthermore the high surface concentration limits the rectifying Schottky contacts. Similar results can be extracted from

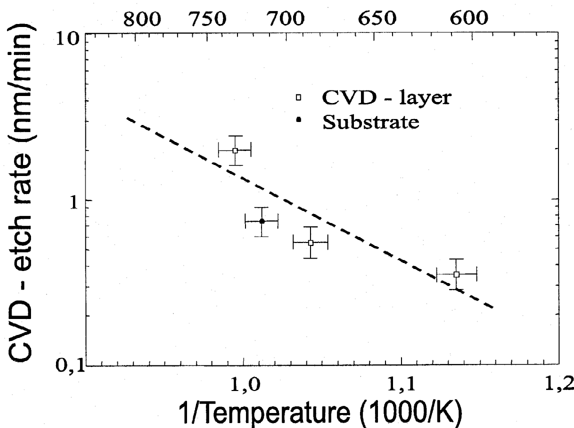

Fig. 6. Etch rates of diamond in pure hydrogen plasma.

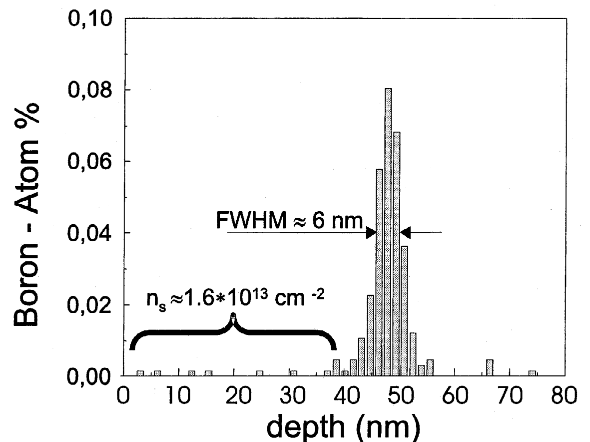

Fig. 8. Elastic recoil detection (ERD) analysis of boron profile in pulse doped diamond film.

the conductivity profile (Fig. 7) where the slow decrease before etching the δ-doped layer itself is due to the background doping in the cap layer.

Using the extracted doping profile from ERD-measurements and the conductivity-profiling, leading to a model with two conductivity paths, Hall measurements on such a pulse doped film (Fig. 9) can be approached. The first path with high carrier concentration (1.9×10^{21} cm^{-3}, assuming a pulse doping width of 10 nm), therefore low activation energy of $E_a\approx3$ meV and low mobility of $\mu\approx3$ cm^2/Vs dominates the range below $T=170$ K. These values are in good agreement with reported values extracted from highly doped samples [7], indicating hopping-conductivity. At the temperature range above $T=170$ K an activation energy of $E_a\approx180$ meV can be extracted. Using an active layer thickness of 100 nm, a film-thickness of 600 nm and from ERD-measurements determined nitrogen background-concentration of about 10^{18} cm^{-3} (therefore compensating factor $K\approx0.25$), a doping concentration of $N_A\approx10^{19}$ cm^{-3} results. Therefore no change in dominant conduction mechanism may be assumed, because of the different doping concentrations and activation energies. The small activation energy at $T<170$ K may be due to the highly doped δ-layer and the high activation energy at $T>170$ K with reduced carrier concentration due to the conductivity of the cap layer with parasitic doping concentration towards the surface.

From these investigations the properties of our δ-doped layers may be summarized as follows: (i) the peak doping concentration is above 10^{19} cm^{-3} or even higher leading to the desired reduction of the activation energy and dominating the conductivity of the whole structure. (ii) The residual doping in the cap layer contributes only negligibly to the overall conductivity, however it inhibits the formation of a good Schottky-gate and prevents modulation of the channel charge. This was actually confirmed in FET structures which showed only negligible current modulation using a Schottky-gate on the boron-contaminated cap-layer.

We propose a FET structure, where the doping tails towards the surface are cut by using the only choice of n-type doping nitrogen with an activation energy of 1.7 eV. In the presence of boron it compensates p-type doping and may therefore be used to adjust the doping profile and the effective doping concentration in the cap layer. Depending on the amount of built-in nitrogen concentration overcompensation may occur. This will lead to a transition region from p-δ-channel to n-type on top and therefore lead to a lossy dielectric region in between. Fig. 10 demonstrates the effect of nitrogen incorporation on the activation energy of the device changing only the purity of the used hydrogen. ERD-measurements revealed for the hydrogen with purity 5.3, a nitrogen concentration of about 16 ppm and for purity 6.0 a decreased concentration of about 2 ppm corresponding to dramatically reduced activation energy. Borst et al. have demonstrated in the past [7], that a structure consisting of a boron doped layer grown on n-type nitrogen doped single crystal substrates yield the electrical behaviour of a p/n-junction. It should therefore be possible to use such a diode in a Junction-FET instead of a Schottky-gate.

In a processed device structure a 100-nm thick nitrogen doped layer was placed on top of the δ-doped layer. This was done by selective epitaxy and by adding nitrogen to the process gas during the growth of the cap layer. The resulting output characteristics of this FET structure is shown in Fig. 11 for a gate length of 20 μm. Due to the

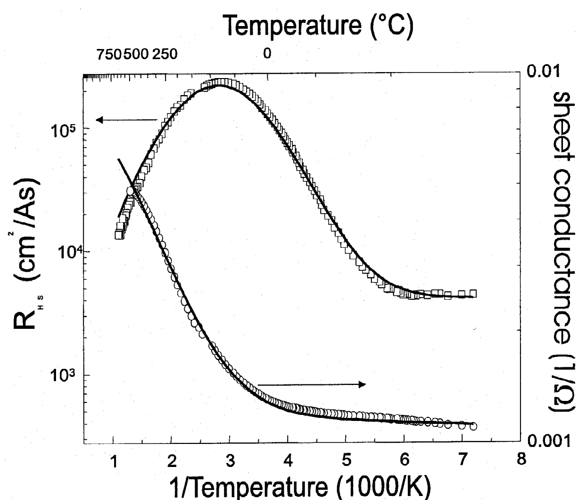

Fig. 9. Hall effect measurement and fit curves for pulse doped diamond film.

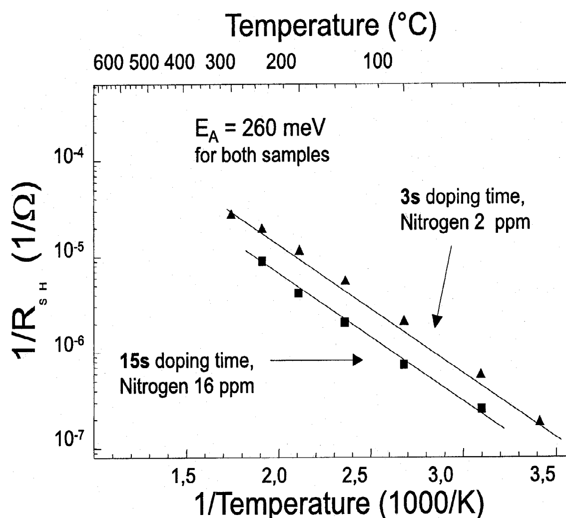

Fig. 10. Analysis of the effect of nitrogen incorporation on the activation energy of pulse doped devices using different hydrogen purity. (ERD-data by A. Bergmaier, Techn. University of Munich).

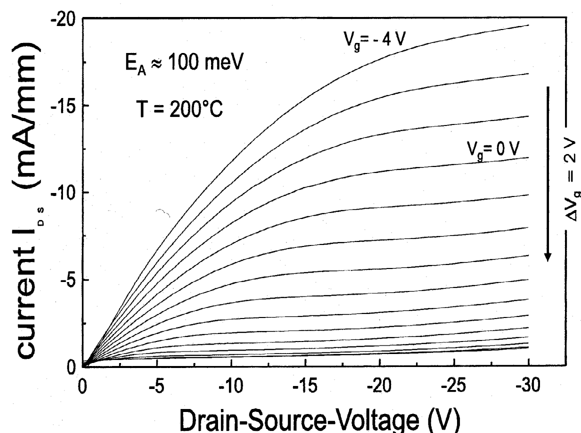

Fig. 11. Output characteristics of a Junction FET with nitrogen doped cap layer, with a gate length of 20 μm.

short doping time of only 3 s, the activation energy is slightly increased to 140 meV. Nevertheless a maximum drain current density of 20 mA/mm can be achieved already at 200°C. The device can be completely turned off, indicating that in this structure the complete channel charge in the δ-peak can be depleted. At 10 μm gate length the maximum drain current reaches even 40 mA/mm, however pinch off could not be achieved. The maximum extrinsic transconductance is 1.4 mS/mm. To our knowledge these are the highest values reported so far for boron doped diamond field effect devices at this gate length and such low temperatures. Scaling these results down to a gate length of 1 μm we expect that the current densities may be increased above 200 mA/mm and therefore comparable to other wide band-gap semiconductors.

In conclusion these preliminary results demonstrate clearly that using an *n*-dopant like nitrogen, a Junction FET may be realized on diamond films. The undesired residual doping in the gate control layer can be reduced and problems related to the formation of a Schottky-gate eliminated. Using this concept together with a δ-boron-doped channel the activation energy can be considerably reduced, leading to high current densities. The performance may be further increased by reducing the gate resistance using more shallow *n*-type doping. Therefore phosphorous may be an alternative. Recently published results on phosphorous as a donor in diamond [8], indicate a reduced activation energy around 0.5 eV.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, carried out under the frame of the trinational 'D-A-CH' consortium.

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