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Surface electronic properties on boron doped (111) CVD homoepitaxial diamond films after oxidation treatments

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Abstract

Surface electronic properties on oxidized boron (B) doped (111) homoepitaxial diamond films are investigated by Hall effect measurements and Schottky junction characterizations. Surface electronic properties on (111) diamond strongly depend on annealing treatments after wet-chemical oxidation, whereas for those on (001) diamond no change due to annealing can be detected. Hall effect results show that a p-type surface conductive layer (SCL) exists on (111) diamond surface in air after wet-chemical oxidation followed by annealing in Ar atmosphere (WO–AN) above 300 °C, but does not if only wet-chemical oxidation or air-oxidation is applied. This SCL disappears at annealing temperature above 350 °C in air. Schottky junction characteristics suggest that the Fermi level is unpinned at the (111) surface after WO–AN. Surface electronic characteristics on (111) diamond after WO–AN are similar to those generated by hydrogen termination.

Keywords: (111) diamond surface; Oxidation treatments; Annealing effects; Surface electronic properties; Surface states; Adsorbates

1. Introduction

Diamond is an attractive material due to its superior physical properties for power electronic devices requiring high power density, high frequency, low power loss and high thermal conductivity. In general, surface electronic properties of semiconductors affect all kinds of devices. Therefore, it is important to understand and control surface electronic properties for device applications. Especially, surface electronic properties for diamond strongly depend on surface terminations. For example, a p-type surface conductive layer (SCL) exists on as-grown chemical vapor deposited (CVD) and hydrogen terminated poly- and single-crystalline diamond surfaces independent of crystal orientations after air exposure [1–8]. On the other hand, the SCL can be removed by oxidation treatments [1,2,9] and a high resistive diamond is generated for undoped and intrinsic diamonds. Therefore, many researchers have pointed out that hydrogen atoms play an important role for the formation of SCL. Recently, we have found that an SCL exists on oxidized (111) diamond surfaces, which is sensitive to adsorbates in air, but no SCL can be detected on oxidized (001) diamond surfaces [10]. In this previous report, the oxidation process to obtain an SCL was as follows: (1) Sample was boiled in a mixed acid of HNO_3:H_2SO_4 (1:3) at 230 °C for 1 h (wet-chemical oxidation treatment). (2) Sample was annealed at 420 °C for 30 min in Ar atmosphere after ohmic contact deposition (Au/Pt/Ti) in Van der Pauw configuration for Hall effect measurements.

In this paper, we report about the origin of surface conduction on oxidized (111) diamond, taking into account different treatments like oxidation/annealing cycles and apply Hall effect measurement and Schottky junction characterization to discuss formation mechanisms.

2. Experiments

Boron (B) doped CVD homoepitaxial diamond films were deposited on high-pressure, high-temperature (HPHT) synthetic

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Ib (111) and (001) single-crystal diamonds using an end-launch type microwave plasma CVD system. The following process parameters were used for deposition: 0.05–0.3% CH_4/H_2 ratio, 5–10 ppm B_2H_6/CH_4 gas flow rate, 400 sccm total gas flow, 50 Torr total gas pressure, 1200–1300 W input microwave power, and 920–1050 °C substrate temperature. The space charge densities of B doped (111) and (001) diamond films determined by capacitance–voltage (*C*–*V*) characteristics were in the range of $2–30\times10^{15}$ cm^{-3}, which are corresponding to boron densities in the films.

Table 1 shows oxidation treatment and annealing procedures in our experiments. The initial oxidation treatment is wet-chemical oxidation (WO). Samples were boiled in a mixed acid of HNO_3:H_2SO_4 (1:3) at 230 °C for 1 h. After that, three kinds of annealing were carried out. One is annealing at 420 °C for 30 min in Ar atmosphere or vacuum below 7.5×10^{-7} Torr (WO followed by annealing: WO–AN), the other is annealing at 400 °C for 30 min in air (air-oxidation: AO). Ohmic electrodes (Au/Pt/Ti) with Van der Pauw configuration and Ni for Schottky electrodes with diameter of 200 μm were deposited on samples by using electron beam evaporator. All Hall effect measurements and *I*–*V* characteristic measurements of ohmic and Schottky contacts were carried out at room temperature in air.

We checked *I*–*V* characteristics of ohmic contacts on films after different treatments before Hall effect measurements and Schottky junction characterizations. Fig. 1 shows *I*–*V* characteristics of ohmic contacts on B doped (a) (111) and (b) (001) diamond films after application of hydrogenation, WO, WO–AN, and AO. Each symbol and line represent *I*–*V* characteristics at different direction biases. For (111) surface, all *I*–*V* characteristics showed ohmic properties with a slope of 1 and with symmetry in both biases, as shown in Fig. 1(a). On the other hand, for (001) surface, only the sample exposed to WO shows an *I*–*V* characteristic with non-linear properties. Treatments of WO–AN and AO result in ohmic properties, as shown in Fig. 1(b). It is known that good ohmic properties on oxidized B doped (001) diamond films can be achieved by annealing at 400 °C after the deposition of Ti, but not for as-deposited Ti [11]. Therefore, the results for B doped (001) diamond films, as shown in Fig. 1(b), are consistent with the literature. On the other hand, for B doped (111) diamond films, good ohmic properties were obtained for all cases as shown in Fig. 1(a). After the above checking, we have started the characterization of surface electronic properties.

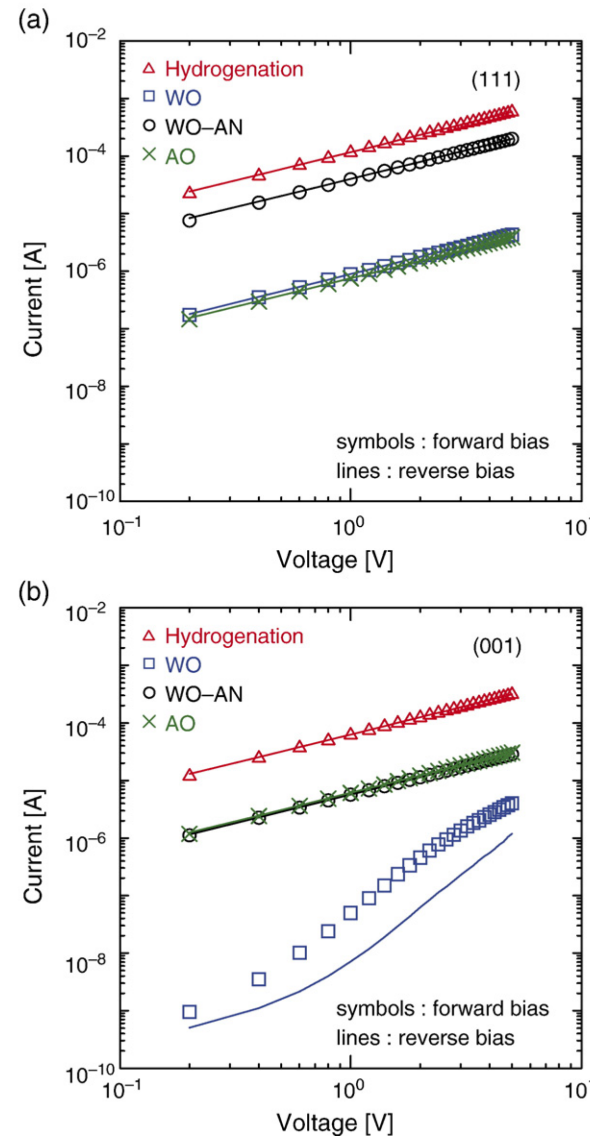

Fig. 1. *I*–*V* characteristics of ohmic contacts on B doped (a) (111) and (b) (001) diamond films after different treatments. Open triangles, squares, circles, and crosses represent *I*–*V* characteristics after hydrogenation, wet-chem, wet-chem and annealing, and air-ox treatments, respectively. Each symbol and line represent *I*–*V* characteristics at forward and reverse biases, respectively. *I*–*V* characteristic measurements were carried out in air at RT.

Table 1
Oxidation treatment and annealing procedures used for measurements of surface electronic properties

Treatment	Procedure
Wet-chemical oxidation (WO)	Boiling in mixed acid of HNO_3:H_2SO_4 (1:3) at 230 °C for 1 h (WO) → Deposition of ohmic metal → Deposition of Schottky metal
Wet-chemical oxidation + annealing in Ar or vacuum (WO–AN)	WO → Deposition of ohmic metal → Annealing in Ar atmosphere or vacuum at 420 °C for 0.5 h → Deposition of Schottky metal
Air-oxidation (AO)	WO → Deposition of ohmic metal → Annealing in air at 400 °C for 0.5 h → Deposition of Schottky metal

3. Results and discussions

Fig. 2 shows sheet resistivity (ρ_s), sheet carrier concentration (p_s), and Hall mobility (μ_H) of B doped (111) and (001) diamond films after different treatments. Filled and open circles represent (111) and (001) diamond films, respectively. For hydrogenated surfaces, ρ_s of about 10 kΩ/□ was detected for both samples in air. For (111) surface, after WO, SCL disappeared and bulk properties of boron doping were detected. After