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Fabrication and electrical properties of $SrTiO_3$/diamond junctions

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ABSTRACT

Strontium titanate (STO) films were directly deposited on Ib (100) single crystal diamond by r.f. magnetron sputtering. The as-deposited STO film was in amorphous state. On the other hand, the crystalline STO film was obtained under the optimized condition of a deposition temperature of 250 °C and a post-annealing temperature of 650 °C. STO/diamond junctions were fabricated on boron-doped homoepitaxial layers grown on p^+-type single crystal diamond substrates. Electrical properties of the STO/diamond junction were investigated by changing the surface terminations of diamond with hydrogen or oxygen and the crystallinity of the STO film. It was found that the amorphous STO acted like a semi-insulator on H-diamond surface and that the amorphous STO/O-diamond junction behaved like a Schottky diode. The crystalline STO/O-diamond showed a complex rectifying behavior. The crystalline STO film possessed a higher dielectric constant as compared to that of the amorphous one.

1. Introduction

Diamond is a unique wide band gap semiconductor with many outstanding physical, chemical and mechanical properties, such as high carrier mobility, high thermal conductivity, and high breakdown field [1]. In recent years, significant progresses have been achieved on single crystal diamond growth and its semiconductor devices [2,3]. Heterojunctions formed by diamond and other materials would interestedly open novel applications and overcome some limitations in diamond such as shallow level doping. For example, Si, ZnO, AlN, and cBN have been deposited on diamond in pursue of novel type electronic or photonic devices [4–6]. The heterojunction formed by diamond and a liquid or other absorbates can be functioned as bio-chemical sensors [7].

Oxides materials, such as $SrTiO_3$ (STO), HfO_2, and Yb_2O_3, have attracted much interest for the chemical stability, high dielectric constant, and wide-bandgap [8–10]. The combination of oxides and diamond would find a lot of applications such as the gate in field-effect transistors, photodetectors with wide band selection, actuators and so on [11,12]. Strontium titanate ($SrTiO_3$) is cubic perovskite structure with a lattice constant of 3.91 Å at room temperature [13]. It has a high dielectric constant ($\varepsilon_r = 300$) [14], and high dielectric breakdown field (over 250 kV/cm) [15]. Furthermore, it can be n-type semiconductor with a wide-bandgap of 3.2 eV [16]. So far, however, there has been no work on the direct growth of STO on diamond. In this paper, we report the deposition of STO on single crystal diamond and the characterization of the electrical properties of metal/STO/p-diamond diode. Both hydrogen-terminated and oxygen-terminated diamond surfaces are utilized to understand the band discontinuity between the STO and diamond.

2. Experiment

Strontium titanate films were deposited on Ib HPHT (100) single crystal diamond substrates by an r.f. magnetron sputter-deposition method. Before sputtering, the substrates were cleaned in a boiling acid solution of $HCl:HNO_3:H_2SO_4 = 1:1:1$, and then, stirred by acetone and de-ioned water in turn in supersonic bath, finally, dried by Ar. The output power of sputtering was around 100 W. The sputtering chamber was evacuated down to 1.3×10^{-3} Pa as the background pressure, and it was 1 Pa of the working pressure. The feed gas for the sputtering was Ar with a 30 sccm flowing flux. The STO target was single crystalline $SrTiO_3$ with 25 mm in diameter. The deposition time was 30–60 min with a rate around 4 nm/min. The substrate temperature during the STO growth was from RT to 300 °C. The resultant STO films were annealing in a furnace with a quartz tube inside an oxygen atmosphere.

For the fabrication of the STO/diamond diode, unintentionally boron-doped single crystal diamond was utilized. The diamond

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epilayer was grown by microwave plasma enhanced chemical vapor deposition method (MPCVD) [17]. Boron was included inside the diamond epilayer due to the residual boron in the vacuum chamber. The substrate was heavily boron-doped single crystal p^+-diamond (100) from Technological Institute for Super-hard and Novel Carbon Materials (TISNCM) with $2.5\times2.5\times0.5$ mm in size and a boron concentration around 1×10^{20} cm^{-3}. The p^+-diamond substrate acts as a bottom electrode for the sandwich device structure. The boron concentration in the epilayer was around 3×10^{16} cm^{-3}, evaluated from the capacitance–voltage (C–V) measurement by using a metal/diamond Schottky diode. The oxygen-terminated diamond surface was achieved by boiling it in an acid solution of H_2SO_4 and HNO_3. Otherwise, the epilayer surface underwent the H-plasma treatment for 20 min in the same MPCVD environment at a substrate temperature of 800 °C to form the H-terminated surface. After the surface treatment, the samples were installed into the r.f. magnetron sputtering chamber to grow the STO layer. Tungsten carbide (WC) thin film was deposited on the STO layer with an area of 300 μm in diameter, and Ti/WC was deposited on the backside of the p^+-diamond substrate as the Ohmic contact [18].

The STO films on diamond were characterized by transmission electron microscopy (TEM) with a JEO+ system of JEM-2000EX and X-ray diffractometry with a RIGUKU system of RINT-2500. To fabricate the samples for TEM observation, focused ion beam technique (FIB) was used by a double beam FIB-SEM (Scanning Electron Microscope) hybrid system of Xvision200. The current–voltage (I–V) characteristics of the diodes were characterized by Advantest (R8340A) picoamperemeter and Advantest (R6144) DC voltage generator using a two-point probe method. The capacitance–voltage (C–V) characteristics were measured by Agilent LCR meter (4284A) at a frequency of 1 MHz. The bandgap of the STO was analyzed by photocurrent spectrum.

3. Results and discussion

Fig. 1 is the XRD results of STO layers on O-terminated surface of Ib HPHT (001) single crystal diamond substrate with different annealing temperatures and deposition temperatures. One can see that both amorphous and crystalline STO films can be obtained by the combined procedure of sputtering and post-annealing. Fig. 1a shows that the as-deposited STO film is amorphous state, and this amorphous state is not changed when the samples are annealed at the post-annealing temperature less than 650 °C. STO film becomes crystalline state when annealed at 650 °C. The X-ray diffraction peak at 32.7° is sharp and no other obvious peaks are found in the spectra, which indicates that (100) crystalline surface becomes the dominant crystalline surface in the film. The crystalline STO film can also be obtained by annealing at 720 °C. The position of diffraction peak from (100) shifts to 32.2°, and the width of the peak becomes broad. Meanwhile, another diffraction peak from (111) crystalline surface also appears near 40°. The results in Fig. 1a indicate that the post-annealing procedure is necessary to obtain crystalline STO (c-STO), and the high annealing temperature benefits the crystallization of STO. However, too high annealing temperature may induce stress into the STO film. As the XRD peak shifts to low angle, this kind of residual stress should be tensile type. The influence of deposition temperature on the crystallinity of STO is surveyed under the selected annealing temperature (650 °C). The results are summarized in Fig. 1b. It shows that the STO is amorphous when it is deposited at both higher (350 °C) and lower (from room temperature to 150 °C) temperatures. This indicates that crystalline STO can only be obtained within a limited deposition temperature window. The optimized conditions for achieving crystallized STO on diamond are: a growth temperature of around 250 °C and a post-annealing temperature of 650 °C in our case. It should be mentioned that the deposition of STO by sputtering in a pure Ar gas ambient may lead to the non-stoichiometric composition

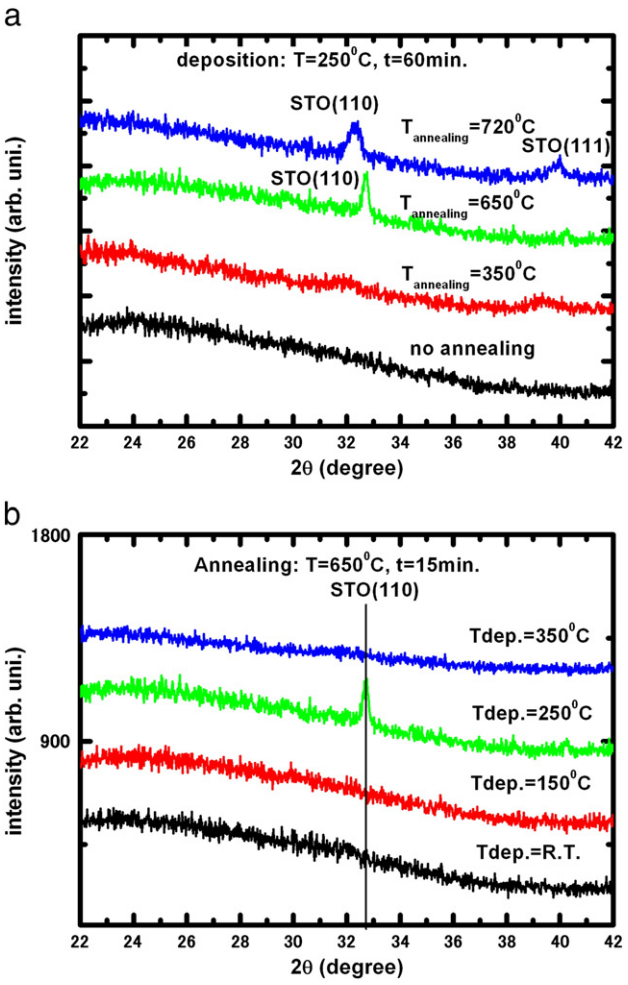

Fig. 1. XRD results of STO layers on O-terminated surface of Ib HPHT (001) single crystal diamond substrate. a. effect of annealing temperature; b. effect of deposition temperature.

of the resultant film due to preferential sputtering. The addition of O_2 in the work gas should improve the STO quality.

Fig. 2 is FIB and TEM results of the sample deposited under the optimized condition. Fig. 2a is the secondary electron image of ion-polished sample obtained in FIB-SEM hybrid system. There exists obvious layered structure, in which the bottom layer is diamond substrate, the interlayer is STO, and the upper layer is the coating to protect the sample during ion polishing. The thickness of STO layer is measured as about 260 nm. From the TEM result in Fig. 2b, one can see that the interface between STO and diamond is very abrupt and that there is no crack and vacancy found in this area. The STO film is dense near the interface, and seems like columnar crystal. Fig. 2c is the result of electron diffraction pattern of the area shown in Fig. 2b. There occur the discontinuous diffraction rings due to (110) of STO, scattered spots due to (111) of STO, and scattered spots due to (111) of single crystal diamond. It reveals that STO is poly-crystal, and the $(111)_{STO}$ tends to be parallel to $(111)_{Diamond}$. This result accords to the morphology shown in Fig. 2b.

The STO/diamond junction diode arrangement is schematically shown in Fig. 3a. WC and Ti/WC are the electrodes deposited on the top and backside of the junction, respectively. STO and p-diamond epilayer grown on p^+-diamond is the main part of the junction. In Fig. 3b, the I–V characteristics of different-type STO/diamond diodes are plotted. The diodes investigated include as-deposited amorphous STO (a-STO) on H-diamond surface, as-deposited a-STO on O-diamond surface and annealed c-STO on O-diamond surface. As can