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Measurement of barrier height of Pd on diamond (100) surface by X-ray photoelectron spectroscopy

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ABSTRACT

Barrier height (Φ_{BH}) values for Pd/hydrogen-terminated diamond (H-diamond) and Pd/oxygen-terminated diamond (O-diamond) have been investigated by X-ray photoelectron spectroscopy technique. H-diamond and O-diamond have been formed on the same diamond (100) layer grown by microwave plasma-enhanced chemical vapor deposition, on which Pd layers have been evaporated. The Φ_{BH} values for Pd/H-diamond and Pd/O-diamond are determined to be −0.27 eV and 1.73 eV, respectively. It indicates that Pd is a suitable metal for ohmic and Schottky contacts on H-diamond and O-diamond, respectively. The experimental Φ_{BH} values are in good agreement with the theoretical calculation results.

1. Introduction

Diamond exhibits attractive intrinsic properties, such as wide band gap energy (5.47 eV), high electric breakdown field (10 MV cm^{-1}), high carrier mobility (3800 cm^2 V^{-1} s^{-1} for holes), high thermal conductivity (22 W cm^{-1}) and low dielectric constant (~5.7), making it a promising material for future electronic devices [1,2]. Metal-semiconductor contacts play an important role in diamond electronic devices, such as Schottky diodes, metal-semiconductor field-effect transistors and deep-ultraviolet detectors [3–5]. For diamond, the type of surface termination strongly influences the properties of diamond surface, such as electron affinity, surface conductivity, and work function [6,7]. Contacts made by metal/hydrogen-terminated diamond (H-diamond) are likely to show ohmic characteristics or low Schottky barrier heights [8]. In addition, contacts made by metal/oxygen-terminated diamond (O-diamond) usually have Schottky barrier heights about 1–2 eV [8–10]. Recently, a new metal component of Pd/Ti/Au has been evaporated on H-diamond for ohmic contact which indicates very good stability [11]. However, the Pd/H-diamond interfacial properties such as contact resistivity and barrier height (Φ_{BH}) were still not very clear. The contact resistivity of the Pd/Ti/Au on H-diamond is easily to be measured by current-voltage characteristic. On the contrary, the Φ_{BH} of the Pd/H-diamond ohmic contact is difficult to be obtained directly by electrical measurements. Since X-ray photoelectron spectroscopy (XPS) technique can determine the electronic levels directly, it has been used to measure the band offsets for heterojunctions and the Φ_{BH} values for the Schottky junctions [12,13].

In this work, the Φ_{BH} for Pd/H-diamond ohmic contact have been investigated by the XPS technique. For comparison, the Φ_{BH} for Pd/O-diamond Schottky contact have also been measured. In the last section, the experimental Φ_{BH} values have been compared with the theoretical calculation results.

2. Experimental details

The II a-type high-temperature high-pressure diamond (100) substrate ($3 \times 3 \times 0.5$ mm^3) was used in this experiment. Before epitaxial layer growth, the substrate was cleaned in a nitric and sulfuric acids mixture solution at 250 °C for 1 h. Then, it was cleaned ultrasonically by deionized water, ethanol, acetone, ethanol, and deionized water sequentially. The H-diamond epitaxial layer with a thickness of 100 nm was grown by microwave plasma-enhanced chemical vapor deposition. In order to form the H-/O-diamond on one diamond sample, half of the H-diamond surface was treated by reactive ion etching (RIE) in an oxygen atmosphere. The oxygen flow rate, RIE chamber pressure, radio frequency power, and etching time were 100 sccm, 10 Pa, 50 W, and 60 s, respectively. The Pd layers with the thicknesses of 3 and 100 nm (3 nm-Pd and 100 nm-Pd) were deposited by thermal evaporation on the H-diamond and O-diamond surface, as shown in Fig. 1. A commercial X-ray

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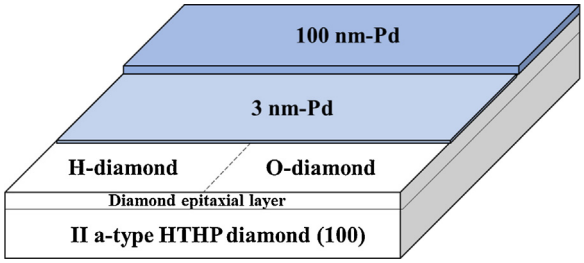

Fig. 1. The schematic sample diagram for the H-diamond, O-diamond, Pd/H-diamond, and Pd/O-diamond.

photoelectron spectrometer (ESCALAB 250Xi) was used. The excitation source of the XPS was a monochromatic Al $K\alpha$ line with the energy of 1486.6 eV. The vacuum pressure of the chamber was above 1.0×10^{-7} Pa. The X-ray spot size, analyzer pass energy, and the scanning step were 500 μm, 20 eV, and 0.1 eV, respectively.

3. Results and discussion

The Hall measurement showed that the hole sheet concentration and mobility of the H-diamond are 1.04×10^{13} cm^{-2} and 92 cm^2 V^{-1} s^{-1}, respectively. The sheet resistivity of O-diamond was measured to be over 10^{12} Ω/□. Fig. 2(a) shows a scanning electron microscopy (SEM) image of the diamond sample with both O-diamond (on the left side) and H-diamond (on the right side) on the surface. Since the electrical conductivities for the O-diamond and H-diamond are quite different, a clear boundary line can be seen in the SEM image. Fig. 3 shows the wide spectra of the H-diamond (red line) and the O-diamond (black line). There are O 1s (around 532 eV) and O KLL (around 984 eV) peaks in weak intensities for the H-diamond, which are attributed to the absorption of impurities in the air. After oxygen plasma treatment for H-diamond to form O-diamond, the intensities of O 1s and O KLL peaks increased obviously.

In the study of the Φ_{BH} by XPS, photoelectrons from both diamond and the metal electrode must be measured. As the electron attenuation length of photoelectrons is only 1–2 nm at XPS energies, discontinuous metal layers should be deposited so that photoelectrons of diamond can be collected from diamond surface among the metal islands [14]. Fig. 2(b) shows a SEM image of the 3 nm-Pd area which has been deposited by thermal evaporation. Since the Pd layer is extremely thin, the deposited layer is not a uniform layer but consists of islands, which can be clearly seen in the SEM image.

Fig. 4(a) shows the schematic electron energy diagram of Pd/diamond junction under thermal equilibrium. The Φ_{BH} which is the junction energy separation between the Fermi level (E_F) and valence band maximum (VBM). As the advantage of XPS is its direct determination of electronic levels, the C 1s core levels of diamond can be detected by XPS. The $\Delta E_{diamond}$ is the energy separation between the VBM and C 1s for the diamond epitaxial layer, which has been obtained by the previous report of 284.01 ± 0.12 eV [13]. Thus, the Φ_{BH} is the difference of E_{C1s} and $\Delta E_{diamond}$. During the actual measurements of XPS, the sample is not necessarily under thermal equilibrium as shown in Fig. 4(b). Since the diamond and the 3 nm-Pd no longer have a unified Fermi level, the determination of E_F under the measurement conditions must be performed by using a thick Pd layer as a reference [13,15]. Then, the Φ_{BH} can be calculated by the following equation [12],

$$\Phi_{BH} = E_{C1s}^{3nm-Pd/diamond} - \Delta E_{diamond} - (E_{metalcore}^{3nm-Pd/diamond} - E_{metalcore}^{100nm-Pd/diamond}) \quad (1).$$

The $E_{C1s}^{3nm-Pd/diamond}$ values are the C 1s binding energies for the 3 nm-Pd/H-diamond and 3 nm-Pd/O-diamond samples. The $E_{metalcore}^{3nm-Pd/diamond}$ and $E_{metalcore}^{100nm-Pd/diamond}$ are binding energies of Pd $3d_{5/2}$ for the 3 nm-Pd/diamond and the 100 nm-Pd/diamond, respectively. Since there is possibly photovoltage effect or/and charge accumulation during the XPS measurement for the 3 nm-Pd/diamond samples [13], the spectra for them were calibrated by using Pd $3d_{5/2}$ spectrum for the 100 nm-Pd film at the binding energy of 335.55 eV. It should be noted that the binding energy of C 1s for the thin-metal/diamond is no longer an absolute value but a relative value. However, according to Eq. (1), the value of Φ_{BH} does not change after the calibration, as the variation of values of the $E_{metalcore}^{3nm-Pd/diamond}$ and $E_{metalcore}^{100nm-Pd/diamond}$ are same. Fig. 4(c) shows the schematic electron energy diagram of Pd/diamond junction after calibration. Moreover, after calibration the Eq. (1) has been simplified to the following equation:

$$\Phi_{BH} = E_{C1s}^{3nm-Pd/diamond} - \Delta E_{diamond} \quad (2).$$

Fig. 5 shows the C 1s spectra obtained from the 3 nm-Pd/O-diamond [Fig. 5(a)] and 3 nm-Pd/H-diamond [Fig. 5(b)]. The backgrounds of all experimental spectra have been corrected with a nonlinear Shirley function. Then, each of the spectra have been fitted with Voigt functions. The components of the C 1s spectrum for the 3 nm-Pd/O-diamond sample [Fig. 5(a)] are situated at the energies of 284.20 ± 0.02 and 285.74 ± 0.02 eV, respectively. The main component at 285.74 eV is attributed to sp^3 C—C bonds. The component at 284.20 eV stems from carbon-containing impurities, which has been proved by our previous work [15]. The C 1s spectrum for the 3 nm-Pd/H-diamond sample [Fig. 5(b)] is situated at energies of 283.74 ± 0.02 and 284.20 ± 0.02 eV, respectively. The main component at 283.74 eV is attributed to sp^3 C—C bonds. The component at 284.20 eV stems from carbon-containing impurities, which is the same with that for the 3 nm-Pd/O-diamond.

It should be noted that the binding energy of carbon-containing impurities is not shifted whereas those of the others components are all shifted, which means that the impurities are located at the metal surface and not at the interface [15]. They are independent components in the C 1s spectra, as they do not join the Schottky junctions. However, the sp^3 C—C bonds near the 3 nm-Pd/diamond interface are affected by the Schottky barriers. After calibration mentioned in the previous paragraph, the binding energy of C 1s for the 3 nm-Pd/diamond changes and becomes a relative value.

Based on the Eq. (2), the Φ_{BH} values for the Pd/O-diamond can be calculated as $\Phi_{BH} = (285.74 \pm 0.02) - (284.01 \pm 0.12) = 1.73 \pm 0.14$ eV. The Φ_{BH} values for the Pd/H-diamond can be calculated as $\Phi_{BH} = (283.74 \pm 0.02) - (284.01 \pm 0.12) = -0.27 \pm 0.14$ eV. Fig. 6 shows schematic band diagrams for the Pd/O-diamond and Pd/H-diamond interfaces. The Φ_{BH} values for the Pd/H-diamond and Pd/O-diamond junctions are negative and positive, respectively. Thus, Pd is a suitable metal for ohmic and Schottky contacts on the H-diamond and O-diamond, respectively.

The theoretical Φ_{BH} (Φ_{BH_TH}) values for the Pd/H-diamond and Pd/O-diamond can be calculated by the following equation [16],

$$\Phi_{BH\_TH} = S(E_{g,diamond} - \Phi_{Pd} + \chi_{diamond}) + (1 - S)\Phi_{CNL,diamond} \quad (3),$$

where $E_{g,\,diamond}$ is the bang gap energy of 5.47 eV for the diamond, and $\Phi_{CNL,\,diamond}$ is "charge neutrality level" of diamond, which is defined as the energy level above which the states are empty. The $\Phi_{CNL,\,diamond}$ energy for the H-diamond is 1.4 eV [17]. The electron affinity $\chi_{diamond}$ for H-diamond and O-diamond are −1.3 and 1.7 eV, respectively [7]. Φ_{Pd} is the work function for Pd metal of 5.6 eV [18]. S is the "pinning factor", which is in the range from 0 to 1. The value of "1" indicates no pinning effect at the Pd/diamond interface, while "0" stands for complete pinning at the Pd/diamond interface. The