



Direct determination of the barrier height of Ti-based ohmic contact on p-type diamond (001)

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ABSTRACT

Although Ti-based ohmic contacts are often used in the fabrication of diamond electronic devices, researches on the barrier height (ϕ_B) of this contact are very limited and no consistent values have been reached. In this study, a direct determination of ϕ_B was performed using X-ray photoelectron spectroscopy. An array of μm -size Ti/Au ohmic electrodes was made on a lightly boron-doped p-type diamond (001) surface, and C 1s and Au 4f_{7/2} XPS spectra were measured. The peak binding energies of the spectra from the sample and from reference samples were compared, and ϕ_B was determined to be -0.63 ± 0.13 eV for the p-type diamond (001). The result is compared with those of previous works and discussed.

Prime novelty statement: The Ti-based ohmic contacts are often used in the fabrication of diamond electronic devices. Although reasonably low specific contact resistances between 10^{-5} and $10^{-7} \Omega\text{cm}^2$ at room temperature have been obtained for the Ti-based ohmic contacts, the barrier height of the contact has not been determined consistently. In this study, the barrier height of the Ti-based ohmic contact on a p-type diamond (001) is directly determined by X-ray photoelectron spectroscopy to be 0.63 ± 0.13 eV.

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1. Introduction

Ohmic metal–semiconductor contacts are essential elements of semiconductor devices and should have low specific contact resistances without rectification properties. For diamond as a semiconductor, p-type bulk doping is mainly obtained by boron impurity. Boron-doped p-type diamonds are available either as natural diamonds or by chemical vapor deposition (CVD). In the usual metal–semiconductor ohmic contacts (OCs), the specific contact resistance (R_{SC}) ranges between 10^{-6} and $10^{-8} \Omega\text{cm}^2$ at room temperature (RT) [1]. Mechanism of current flow at metal–semiconductor ohmic contacts depends on the conditions of the contacts. For narrow band-gap semiconductors with lightly-doped contact layers, main current flow mechanism is the thermionic emission with a contact barrier height of 0.1–0.2 eV [1]. For wide band-gap semiconductors with heavily-doped contact layers, the main current flow mechanism at ohmic contacts is (thermal) field emission with a contact barrier height of 0.3–0.5 eV [1]. For diamond, the latter mechanism is expected to hold.

Historically, the OCs to p-type diamonds with low R_{SC} were difficult to obtain. The early stage of the development of OCs on diamond may be viewed in earlier works [2,3]. Nowadays, the commonly used OC on p-type diamond is titanium (Ti) based contact for several reasons,

such as good thermal and mechanical stabilities of the contacts [2–6]. A schematic energy band diagram near the Ti-based ohmic contact on p-type diamond is shown in Fig. 1. E_V stands for the valence band top of diamond and E_F is the Fermi level. The contact barrier height (ϕ_B) is the energy separation between E_F and E_V at the contact point. The method, that the Ti-based ohmic contact is formed, includes vacuum deposition of Ti and annealing of the diamond either during or after Ti-deposition. The cover layer of Au prevents oxidation of deposited Ti and the cover layer of Pt (or Mo) prevents diffusion of Ti toward the Au layer. The formation of titanium carbide (TiC) at the contact point has been confirmed [6,7]. Tables 1a and 1b summarize the characteristics of Ti-based OCs on p-type diamond so far reported to the authors' knowledge. A R_{SC} range between 10^{-5} and $10^{-7} \Omega\text{cm}^2$ at RT has been obtained depending on the conditions of the contacts [5,8–17]. Thus, the Ti-based OCs on p-type diamond are at the level of practical application to electronic devices.

In terms of the barrier height of Ti-based ohmic contact on p-type diamond, consistent results have not been obtained. The barrier height of a Ti-based OC on p-type polycrystalline diamond was first reported to be ~ 0.8 eV [4]. The method used for the ϕ_B estimation was X-ray photoelectron spectroscopy (XPS), which is supposed to be a direct method of determining relevant energy levels [18]. The value $\phi_B \sim 0.8$ eV was reported to be simply evaluated from the energy difference between the valence band top (E_V) of p-type diamond substrate and the Fermi-level of deposited and annealed titanium carbide layer. The C 1s binding was reported to be kept at 284.6 eV for compensation of charge-up of

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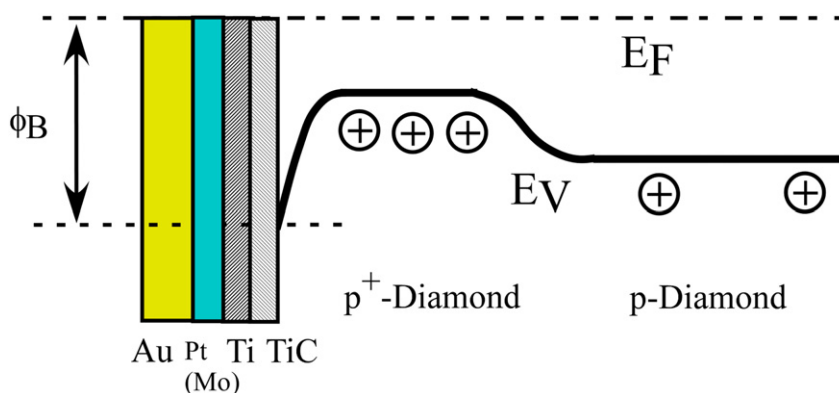


Fig. 1. Schematic energy band diagram for Ti-based ohmic contact on p-type diamond.

the sample [4]. The above procedure might have led to an erroneous value in the light of the difficulty of determining valence band top position of diamond in XPS and the photovoltaic effect experienced in diamond XPS [18]. The barrier height of a Ti-based OC on polycrystalline p-type diamond was roughly estimated to be ~0.6 eV by the slope of a curve of R_{SC} vs. acceptor concentration [10]. The barrier heights of 5 metal (Ti, Mo, Cr, Co, and Pd) ohmic contacts on polycrystalline p-type diamonds were evaluated to be ~0.5 eV by fitting the curves of R_{SC} vs. acceptor concentration and temperature with thermal field emission theory [11–12]. This work was quite elaborate but the method was not direct in the determination of ϕ_B ; the results might be affected by the input parameters used in the fitting procedure and by the range of applicability of thermal field emission theory. Further, the results were obtained for polycrystalline diamond samples, thus the effects of single-crystal domains and domain boundaries might be involved. Two years later, the barrier height of Ti-based ohmic contact on single crystal p-type diamond (001) was evaluated by the direct method of internal photoemission [13]. They compared the results for B and/or Si implanted and un-implanted cases and ϕ_B values were ~1.2 and ~2.0 eV for the implanted and un-implanted cases, respectively claiming the barrier height lowering by the implantation [13]. Looi et al. [19] estimated the barrier height of a Ti/Au ohmic contact on an annealed hydrogen-terminated non-doped polycrystalline diamond to be ~0.4 eV. However, this Ti/Au ohmic contact may not be regarded as the Ti-based ohmic contact on p-type diamond since the substrate diamond was non-doped and the conductivity was carried by a re-hydrogenated surface conductive layer.

Thus, ϕ_B of Ti-based ohmic contact on p-type diamond has been reported essentially in only two works [11–12,13], and ϕ_B differs very much, either ~0.5 eV [11–12] or ~2.0 eV [13]. In the present study, we apply the direct method of XPS of determining barrier height for Ti-based ohmic contact on homoepitaxial p-type single crystal diamond (001). The method is based on the established principle as described fully in a previous paper [18]. In short, a lightly boron-dope CVD

diamond substrate was used, which makes the photovoltaic effect to happen during XPS measurement and makes nearly flattening of the valence band of boron-doped diamond. This in turn makes it possible to use thick and μm -size Ti-based ohmic electrodes in XPS determination of barrier height [18]. Namely, ϕ_B is determined as,

$$\phi_B = E_{C1s} - E_{VBM-C1s} - \Delta E_{Au4f}, \quad (1)$$

where, E_{C1s} is the C 1 s XPS peak binding energy at the Ti-based ohmic electrodes, $E_{VBM-C1s}$ is the energy difference between E_V and C 1 s core-level of diamond and calibrated to be 284.01 ± 0.12 eV, and ΔE_{Au4f} is the difference of Au 4f_{7/2} XPS peak binding energies between the Au-layer of Ti-based electrodes and a Au-reference sample [18]. The binding energies are all reference to the Fermi-level E_F of the sample holder.

2. Experimental procedures

A high pressure high temperature (HPHT) synthetic diamond (001) type-Ib commercial (Sumitomo) crystal ($3 \times 3 \times 0.5 \text{ mm}^3$) was used as a substrate. An additional finer polishing (Syntek) was applied to have an off-angle of ~3° from the surface normal along <110> direction, thus a nominal 3° vicinal (001) surface was created. The reason for having the vicinal surface is to obtain better surface flatness of homoepitaxial diamond films [20]. The boron-doped layer was deposited by microwave-assisted (MW) CVD under the following conditions; total gas pressure, microwave power, methane concentration (flow ratio of CH₄ to the total gas flow), oxygen concentration (flow ratio of O₂ to the total gas flow), boron concentration (flow ratio of trimethyl boron to CH₄), total flow rate, substrate temperature, and duration were 130 Torr, 1.0 kW, 10%, 2%, 0.4 ppm, 50 sccm, 1050 ± 10 °C, and 1 h, respectively. The growth condition with the high oxygen concentration is suitable to grow high-quality homoepitaxial diamond film [20]. The thickness of the p-type layer was ~3 μm with a boron

Table 1a

Characteristics (at room temperature) of Ti-based ohmic contact on p-type diamond for the period in 1990s. The figure 1e-5, for example, in the table is equal to 1×10^{-5} and (C)TLM stands for (circular) transmission line model.

Type of contact metal	Refer.	R_{sc} (Ωcm^2)	Type of R_{sc} meas.	Type of diamond	Dopant type & concentration (cm^{-3})	Barrier height (eV)	Comments
Ti/Au	[8]	$1\text{e}-6$ for poly, $1\text{e}-5$ for natural dia.	TLM	CVD poly and IIb natural dia.	B, ~7e–20, ion impla.		
Ti/Au	[9]	~5e–5 ~1.4e–5 ~1.8e–3	TLM w/o mesa TLM with mesa CTLM	CVD poly	B, 1.5e–21, ion impla.		R_{sc} differs very much for different meas.
Ti/Mo/Au	[10]	1.0e–6	CTLM	Poly CVD	B, ~3e–20		
Ti/Mo/Au	[11,12]	~1e–1 at B ~2.5e–18, ~1e–5 at B ~2e–20	TLM	Poly CVD	B, 2.5e–18, 2e–20	~0.5	Barrier height by thermal field theory
Ti/Au	[13]	~1e–5 for no impla., ~1e–7 for Si and B impla.	TLM	CVD (001)	B ~1e–17 for no-impla. B ~2e–20 & Si ~8e–20 by B & Si impla.	~2.0 w/o impla. ~1.2 with impla.	Barrier height by internal photo-emission

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