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# Direct determination of the barrier height of Au ohmic-contact on a hydrogen-terminated diamond (001) surface

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ABSTRACT

The barrier height $\phi_B$ of Au ohmic-contact on hydrogen-terminated p-type surface conductive layer (SCL) made on a boron-doped diamond (001) substrate has been directly determined by X-ray photoelectron spectroscopy (XPS). For this purpose, thin layer (thickness ~ 3.6 nm) of Au was deposited on the p-type SCL. The formation of nm-size Au-islands was identified by scanning electron microscopy. It became therefore evident that C 1s XPS spectra originate from diamond in the gap areas among Au-islands but not from diamond underneath the Au-islands. Two-dimensional energy band simulation was performed to show that the diamond band diagram in the gap areas among Au-islands become effectively identical to that of diamond underneath the Au-islands when SCL is eliminated only in the gap areas. In order to eliminate SCL in the gap area only, a VUV/ozone irradiation process was applied on the Au-island-covered sample. C 1s and Au $4f_{7/2}$ XPS spectra were measured for the sample before and after the VUV/ozone irradiation process. The peak binding energies and widths of C 1s and Au $4f_{7/2}$ XPS spectra are carefully considered to reach to the conclusion that $\phi_B = 0.29 \pm 0.13$ eV. For the boron-doped present substrate, the current flow mechanism at the Au ohmic-contacts is expected to be thermionic emission and specific contact resistance $R_C$ is thus evaluated to be the order of $10^{-4}$ Ω cm$^2$.



## 1. Introduction

Ohmic metal-semiconductor contacts are essential elements of semiconductor devices and should have low specific contact resistances. For diamond as a semiconductor, p-type bulk doping is mainly obtained by boron impurity. Boron-doped diamonds are available either as natural diamonds or by chemical vapor deposition (CVD). For diamonds, another type of p-type conductivity is present, which is surface p-type conductivity. The surfaces of CVD grown or hydrogen-plasma/radical treated diamonds are terminated with hydrogen and show p-type conductivity only at the surface. In usual metal-semiconductor ohmic-contacts, the specific contact resistance ($R_C$) ranges between $10^{-6}$ and $10^{-8}$ Ω cm$^2$ at room temperature (RT) [1]. Mechanism of current flow at metal-semiconductor ohmic-contacts depends on the conditions of the contacts [1]. 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 is (thermal) field emission with a contact barrier height of 0.3–0.5 eV [1]. For boron-doped bulk p-type diamond, the latter mechanism is expected to hold and in fact it is the case [2].

The p-type surface conductivity (SC) is another type of conductivity of diamond and thus the notion of ohmic-contacts on wide band-gap semiconductors may not hold. The early stage of research endeavor on the surfaces and interfaces at SC layer (SCL) on hydrogen-terminated (H-terminated) diamonds may be viewed in Ref. [3]. The present status of research endeavor related to SCL may be viewed in Ref. [4]. A hypothetical energy band diagram at a metal/H-terminated diamond junction is shown schematically in Fig. 1a). The top ($E_V$) of diamond valence band is present at a certain energy position at the metal/diamond junction and the energy difference between $E_V$ and the Fermi level ($E_F$) is the barrier height ($\phi_B$). A small or negative value of $\phi_B$ means that the contact would be ohmic. The H-terminated diamond surface has essentially no dangling bonds at the surface, thus it is very stable. For this reason, chemical reaction between as-deposited metal and H-terminated diamond surface is not expected to happen. Thus, the barrier height ($\phi_B$) at the junction of metal/H-terminated diamond may follow the rule of Schottky-Mott, i.e. $\phi_B = \chi + E_G - \phi_M$ for p-type semiconductors, where $\chi$ is the electron affinity of semiconductor surface and $E_G$ is the band gap energy of the semiconductor and $\phi_M$ is the work function of the metal [5]. $E_G$ is ~5.5 eV for diamond and the electron affinities of H-terminated diamond surfaces were reported to be between −1.3 and −0.4 eV for diamond (001) surfaces [6,7]. The

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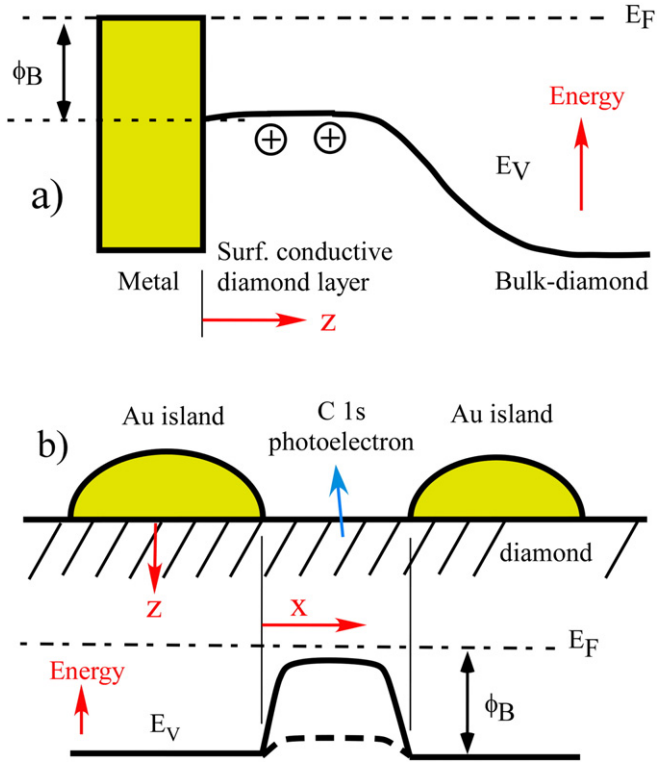


**Fig. 1.** a) A hypothetical energy band diagram at a metal/H-terminated diamond junction with surface conductivity. $E_V$ and $E_F$ represent the top of diamond valence band and the Fermi level, respectively. Coordinates are explained in red. b) The upper part is schematic cross-sectional view of the junction at Au-island/H-terminated diamond. A blue arrow indicates that C 1s XPS photoelectrons come from the gap areas among Au-islands but not from underneath the Au-islands. The lower part shows schematic $E_V$ band diagrams around the Au-islands with SC in the gap (solid line) and without SC in the gap (dashed line). Coordinates are explained in red.

variation in $\chi$ for H-terminated diamonds may be the consequence of surface conditions/perfections. Thus, metals with $\phi_M$ larger than 4.2–5.1 eV would cause negative $\phi_B$ leading to ohmic-contacts.

Electric characteristics of metal/H-terminated polycrystalline diamond were studied and ohmic characters were found for Au (5.10), Ag (4.26), Cu (4.65), Pt (5.65) but not for Al (4.28), Ni (5.15), Ta (4.25), Ti (4.33), In (4.12), Sn (4.42), and Zn (4.33) [8]. Here, the values in the parentheses are work functions (in eV) of polycrystalline metals [9]. Similar study was performed on metal/H-terminated diamond (001) crystal and ohmic characters were obtained for Au and Pt but not for Al, Cu, Fe (4.5), In, Mg (3.66), Ni, Pb (5.12), Ta, W (4.55), and Zn [10,11]. It can be seen that these results of Refs. [8,10,11] do not follow the rule of Schottky-Mott. The barrier heights of the 10 non-ohmic-contact metals were evaluated electrically to be ~0.5–1.0 eV [10,11]. A linear correlation of the barrier height $\phi_B$ to the electronegativities ($\varepsilon$) of contact metals has been reported [10,11]. The barrier heights of the ohmic-Au and -Pt contacts are assumed to be almost zero simply because they are ohmic and because it may be extrapolated from the $\phi_B$-$\varepsilon$ relationship [10,11]. Recently, electric characteristics of metal/H-terminated (001) crystal were studied and ohmic characters were obtained for Ag, Au, Cu, and Pt but not for Al, Co, Ni, Pb, Ti, and Zn [12]. The barrier heights of the 6 non-ohmic-contact metals were evaluated electrically (by Richardson-plot) to be ~0.2–0.6 eV and a linear correlation in $\phi_B$-$\varepsilon$ curve was also reported and discussed in detail [12]. The barrier heights of the ohmic-Ag, -Au, -Cu and -Pt contacts are assumed to be almost zero [12] for the same reasons of [10,11]. It may be noted here that those metals of non-ohmic characters are reactive and oxidized components are very likely to exist at the metal-diamond contacts. In fact, an oxidized component of Al was reported for the contact of Al/H-terminated diamond (001) crystal even for ultra-high-vacuum in-situ deposition Al [6]. In this sense, noble metals of Ag, Au, and Pt are expected not to be oxidized. This may be one of the reasons why ohmic-contacts were consistently observed for these three noble metals in the previous studies [8,10–12]. This is the reason why we restrict our attention in this study to the Au ohmic-contact on a H-terminated diamond (001) crystal. Very recently, ohmic-contact of another noble/stable metal Pd (work function ~ 5.12 eV) on H-terminated diamond is reported and used as ohmic electrodes [13,14].

On the contrary to the above notion that the barrier height of ohmic-contact of Au/H-terminated diamond can be assumed to be almost zero, the barrier height of an Au ohmic-contact to H-terminated polycrystalline diamond surface was reported to be 0.41 eV [15] and that on a H-terminated diamond (001) surface to be 0.49 eV [16]. These values were obtained from the analyses of measured specific contact resistance $R_C$ by the thermionic emission theory [15,16]. Characteristics (at RT) of Au ohmic-contact on H-terminated diamond so far published in literature (to the authors' knowledge) are summarized in Table 1. Although it was not specifically stated that the specimen surface was H-terminated, a similar analysis of Au ohmic-contact on an as-grown polycrystalline diamond gave a barrier height of ~0.55 eV based on thermal field emission theory [17]. In these studies, specific contact resistances of Au ohmic-contacts were reported to be ~0.1 [17], ~0.04 [15], and ~0.5 [16] $\Omega$ cm$^2$ at RT. The other studies of $R_C$ at RT resulted in various values of ~$1 \times 10^{-6}$, ~$1 \times 10^{-5}$, 0.04 $\Omega$ cm$^2$ [18–20]. Barrier heights were not evaluated in the later three studies [18–20].

No direct determination of the barrier height of Au ohmic-contact to H-terminated diamond has been reported; a direct determination by X-ray photoelectron spectroscopy (XPS) of the barrier height of an Au ohmic-contact to H-terminated diamond (111) was intended but no conclusion was drawn [6]. To the authors' knowledge, even the specific contact resistances and the barrier heights of Ag and Pt ohmic-contacts on H-terminated diamonds are not yet reported. In this study, we apply the direct method of XPS to determine the barrier height for Au ohmic-contact on a H-terminated boron-doped diamond (001) surface. The method is based on determining diamond C 1s XPS binding energy and the principle is described fully in a previous paper [21] (c.f. Eq. (1)). However, the special property of SCL of H-terminated diamond forces us to modify the method. The scheme of modification is explained in the next section.

## 2. Modified scheme of XPS barrier height determination of Au ohmic-contact on H-terminated diamond

For the XPS barrier height determination of a Ti-based ohmic-contact, a lightly boron-doped CVD diamond substrate was used [2]. This made the photovoltaic effect to happen during XPS measurement and made nearly flattening of the valence band of boron-doped diamond. This in turn made it possible to use thick and μm-size metal electrodes in XPS determination of barrier height [21]. For ohmic-contacts on H-terminated boron-doped diamond, the surface conductivity is present in addition to conductivity due to B-doped layer, and this surface conductivity is much higher than that of the boron-doped substrate diamond. Therefore, the photovoltaic effect is not expected to happen and thus the band flattening do not happen during XPS measurement. When the band flattening is absent, the diamond energy band position underneath the metal electrodes is generally different from that of diamond in the gap areas among the metal electrodes. This forces us to use very thin layer of metal over the H-terminated diamond in order to detect C 1s photoelectrons from diamond underneath the metal layer. The thinness of the metal layer should be of the same order of C 1s photoelectron escape depth which is a few nm [7,21]. Thin metals deposited on stable substrates such as the H-terminated diamond do not form a uniform layer but form islands [22,23]. In fact, for 3.6 nm thick Au deposited on a H-terminated diamond, Au-islands of 10–20 nm size