Diamond & Related Materials 38 (2013) 24–27

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Interfacial electronic band alignment of Ta_2O_5/hydrogen-terminated diamond heterojunction determined by X-ray photoelectron spectroscopy☆

Jiangwei Liu [a,*], Shaoheng Cheng [b], Meiyong Liao [a], Masataka Imura [a], Akihiro Tanaka [c], Hideo Iwai [c], Yasuo Koide [a,d,e,*]

[a] Optical and Electronic Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[b] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
[c] Materials Analysis Station, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[d] Nanofabrication Platform, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[e] Center of Materials Research for Low Carbon Emission, NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Available online 14 June 2013

Keywords:
H-diamond
Ta_2O_5
Band structure
XPS

ABSTRACT

Ta_2O_5 films have been deposited on hydrogen-terminated diamond (H-diamond) by a radio-frequency sputter-deposition technique at room temperature. Electronic band structure of Ta_2O_5/H-diamond heterojunction has been investigated by X-ray photoelectron spectroscopy. Based on the binding energies of core-levels and valence band maximum values, valence band offset has been found to be 1.5 ± 0.2 eV for the Ta_2O_5/H-diamond heterointerface. It shows a type-II band configuration with conduction band offset of 2.4 ± 0.2 eV. The large ΔE_V value makes the Ta_2O_5/H-diamond heterojunction probably suitable for the application of high power and high frequency field effect transistors.

1. Introduction

Compared to other wide band gap semiconductors (GaN, ZnO, and SiC, etc.), diamond has outstanding intrinsic electrical properties, such as a large thermal conductivity (22 W cm^{-1} K^{-1}), a high breakdown field (10 MV · cm^{-1}), large saturation velocity (2.7 × 10^7 cm s^{-1}), and high carrier mobility (2200 and 1800 cm^2 · V^{-1} · s^{-1} for electrons and holes, respectively) [1,2]. Therefore, diamond is considered to be a promising channel material for the fabrication of high power and high frequency metal-oxide-semiconductor field effect transistors (MOSFETs). However, due to large activation energies of dopants (boron, phosphorous, and nitrogen) at room temperature [3], carrier concentrations in the diamond are very low, which deteriorate electrical properties of the diamond-based semiconductor devices. Some studies have made great efforts to fabricate boron δ-doped diamond layers to resolve this problem [4,5]. However, the hole mobility is still behind expectation. Most studies by far have focused on the fabrication of diamond based devices with hydrogen-terminated diamond (H-diamond) as channel layers [6–14]. Holes are accumulated on the surface of the H-diamond with sheet carrier density and hole mobility of 1 × 10^{13} cm^{-2} and 10–150 cm^2 · V^{-1} · s^{-1}, respectively [15,16].

In order to fabricate the high performance H-diamond based MOSFETs, it is a critical issue to choose a suitable gate dielectric material. Compared to SiO_2, Ta_2O_5 has a large dielectric constant (>20) [17] and a large breakdown field (4 MV/cm) [18]. These characteristics can help to decrease device dimensions, reduce driving voltage, and suppress leakage current for the H-diamond based MOSFETs. In addition, because of large theoretical valence band discontinuity for the Ta_2O_5/diamond heterojunction [19], Ta_2O_5 was considered to be a potential interfacial layer for the ferroelectric/diamond structure, which has an application for metal-ferroelectric-diamond transistors [20].

The electrical properties of the Ta_2O_5/diamond MOS diode have been investigated in our previous report [21]. A low leakage current (10^{-8} A/cm^2 at gate bias of −3 V) for the MOS diode and a high dielectric constant for the Ta_2O_5 film (16–29) have been confirmed. Therefore, Ta_2O_5 would be a promising dielectric material for the application of the H-diamond-based MOSFETs. Although the interfacial band alignment of the Ta_2O_5/H-diamond heterojunction is considered as a material fundamental property, the experimental band offset values have not been investigated yet. In this paper, we have studied the interfacial behavior between Ta_2O_5 and H-diamond by means of X-ray photoelectron spectroscopy (XPS).

2. Experimental

We prepared three samples in order to clarify the electronic band structure of the Ta_2O_5/H-diamond heterojunction. The samples were

---

☆ Presented at the New Diamond and Nanodiamond (NDNC) Conference, Singapore, May 19-23, 2013.

* Corresponding authors at: Optical and Electronic Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
E-mail addresses: liu.jiangwei@nims.go.jp (J. Liu), koide.yasuo@nims.go.jp (Y. Koide).

0925-9635/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.diamond.2013.06.005

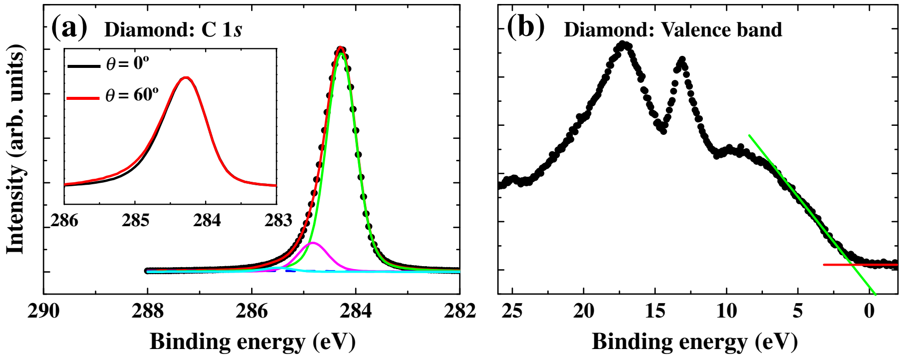

Fig. 1. C 1*s* and valence band photoelectron spectra for the H-diamond. The C 1*s* spectrum was fitted by Voigt (mixed Lorentzian–Gaussian) line shapes after the application of a Shirley background (dashed line). The solid line matched to the dots is the sum of Voigt line shapes and background. Inset in Fig. 1(a) shows the C 1*s* ARPES with the emission angles of 0° and 60° relative to the surface normal. *θ* refers to the emission angle relative to the surface normal. The C 1*s* main peak binding energy and VBM value for the H-diamond were summarized in Table 1.

the H-diamond epitaxial layer with thickness of 150 nm and Ta_2O_5 films with thicknesses of 2 nm and 30 nm deposited on the H-diamond epitaxial layers with thickness of 150 nm. The H-diamond was homoepitaxially grown by a microwave plasma-enhanced chemical vapor deposition method on Ib-type single crystalline diamond (100) substrate. The deposition temperature is in the range of 900–940 °C. The chamber pressure, H_2 flow rate, and CH_4 flow rate are 80 Torr, 500 sccm, and 0.5 sccm, respectively. The 2 nm and 30 nm thick Ta_2O_5 films were deposited by the RF sputter-deposition technique in the atmosphere of Ar (95%) and O_2 (5%) at room temperature. Details for the formation of the H-diamond and Ta_2O_5 films were reported elsewhere [21,22]. The core level and valence band spectra for the samples were performed by a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV) with a 0.05 eV step and a 55 eV pass energy. All the core-level peaks were fitted using a Shirley background and Voigt (mixed Lorentzian–Gaussian) line shapes. Valence band maximum (VBM) values of the H-diamond and 30 nm thick Ta_2O_5 film were determined by extrapolating a linear fit of the leading edge for the valence band photoelectron spectra to the baseline [23].

3. Results and discussion

Fig. 1 shows C 1*s* and valence band photoelectron spectra for the H-diamond sample. The inset in Fig. 1(a) shows the C 1*s* angle-resolved photoelectron spectra (ARPES) with the emission angles of 0° (bulk sensitive) and 60° (surface sensitive) relative to the surface normal. The C 1*s* spectrum [Fig. 1(a)] consisted of three peaks, which were possibly attributed to C–C, CH_x, and C–OH [24]. Binding energy difference between the C–C and CH_x was 0.6 eV, and that between the C–C and C–OH was 1.2 eV [24,25]. The ARPES results showed that the CH_x and C–OH peaks had surface sensitivity property, which corresponds to the surface components. However, there is not a big difference for the ARPES spectra, which imply that the content of surface components is low. The VBM value for the H-diamond [Fig. 1(b)] was determined to be 1.2 ± 0.2 eV. Fig. 2 shows C 1*s*, Ta 4*f*, and O 1*s* spectra for the 2 nm thick Ta_2O_5 sample. Two components with an energy difference of 2.0 eV [26] were used to fit the Ta 4*f* spectrum [Fig. 2(b)]. Due to existence of oxygen vacancies in the Ta_2O_5, the lower binding energy component with a small content was probably ascribed to the tantalum suboxide (Ta^{3+}/Ta^{4+}) [26]. The O–Ta and O–H bonds were used to fit the O 1*s* spectrum [Fig. 2(c)]. The O–H peak, considered as a surface component, was located at a higher binding energy. The binding energy difference between the O–Ta and O–H peaks was 1.5 eV [26]. Fig. 3 shows Ta 4*f*, O 1*s*, and valence band spectra for the 30 nm thick Ta_2O_5 sample. The Ta 4*f* and O 1*s* peak fittings [Fig. 3(a) and (b)] for the 30 nm thick Ta_2O_5 sample were similar with those for the 2 nm thick Ta_2O_5 sample [Fig. 2(b) and (c)]. The VBM of the 30 nm thick Ta_2O_5 sample was determined to be 3.8 ± 0.2 eV. There was a broad peak in the binding energy between 3.8 and 11.0 eV, which was composed by Ta 5*d* hybridized with O 2*p* orbitals. A small broad peak in the binding energy between 1.0 and 2.2 eV was probably attributed to Ta 5*d* orbitals in the defects like tantalum in a metallic state due to the effect of the oxygen vacancies [27]. Table 1 summarized the main peak binding energies of the XPS core level spectra for all the samples and the VBM values for the H-diamond and Ta_2O_5 (30 nm). The error in the peak positions and the VBM values is ±0.2 eV.

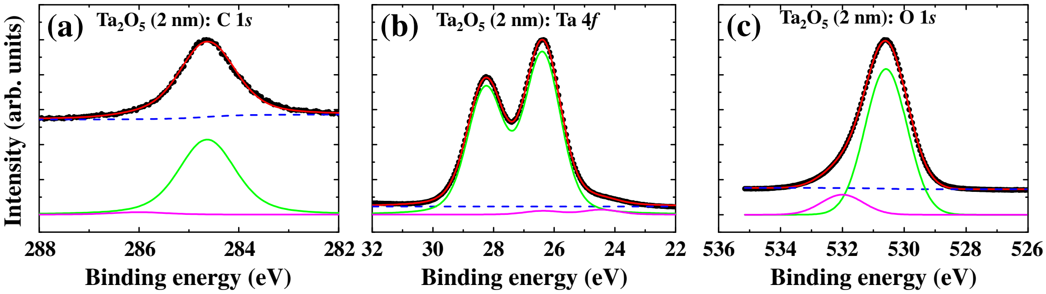

Fig. 2. C 1*s*, Ta 4*f*, and O 1*s* photoelectron spectra for the Ta_2O_5 (2 nm)/diamond sample. Experimental data were fitted by Voigt (mixed Lorentzian–Gaussian) line shapes after the application of a Shirley background (dashed line). The solid lines matched to the dots are the sums of Voigt line shapes and background. The main peak binding energies were summarized in Table 1.