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Band Alignment Parameters of Al_2O_3/InSb Metal–Oxide–Semiconductor Structure and Their Modification with Oxide Deposition Temperatures

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From the Fowler–Nordheim (FN) current–voltage (*I*–*V*) characteristic and X-ray photoelectron spectroscopy (XPS) analysis, the conduction band offset of 2.73 ± 0.1 eV and the valence band offset of 3.76 ± 0.1 eV have been extracted for the atomic-layer-deposition (ALD) Al_2O_3/InSb structure. By these analyses, the parameters of an Al_2O_3 film including bandgap, electron affinity, and electron effective mass are also deduced. The capacitance–voltage and *I*–*V* characteristics of ALD Al_2O_3/InSb at different deposition temperatures indicate the modification of the Fermi level in InSb to 0.09 eV lower than that in metal side of the sample deposited at 250 °C as compared to the samples deposited at lower temperatures. © 2013 The Japan Society of Applied Physics

III–V compounds have been widely studied for future scaling down of low power, high speed field-effect transistors (FETs) due to their high electron mobility and saturation velocity. Among them, InSb has the highest electron mobility ($7.7 \times 10^4\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) and high hole mobility ($840\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) that has potential for both high speed n- and p-FETs.[1–3] Due to its narrow bandgap, InSb has been suggested to be applicable to quantum-well (QW),[2,3] nanowire (NW),[4–6] or tunnel (T) FET architectures.[7] For these kinds of application the determination of band alignment between InSb and the barrier layers (high-bandgap semiconductors or high-*k* dielectrics) is of critical importance. By using internal photoemission (IPE) measurement, the conduction band offset (ΔE_C) at the atomic-layer-deposition (ALD) Al_2O_3/(100)InSb interface was determined to be 2.9 ± 0.1 eV.[8] In the present work, we further investigate the band alignment of ALD Al_2O_3/(100)InSb structure including conduction and valence band offsets by using Fowler–Nordheim (FN) current–voltage (*I*–*V*) characteristic and X-ray photoelectron spectroscopy (XPS) analysis. The ΔE_C value determined from the FN characteristic is consistent with that determined by the IPE method.[8] Since the characteristics of high-*k*/InSb structure are very sensitive to the thermal process due to the low thermal budget in InSb,[1,9,10] the effect of oxide deposition temperatures on the band alignment modification of Al_2O_3/InSb is also investigated.

The wafers used in this work were n-type (100)InSb substrates with a donor concentration of $2.2 \times 10^{16}\,\mathrm{cm^{-3}}$ at room temperature (determined by Hall measurement). After decreasing in acetone and iso-propanol, the samples were dipped in diluted HCl (4%) solution for removing native oxides. The samples were then loaded into the ALD chamber (Cambridge NanoTech Fiji 202 DSC) for Al_2O_3 deposition using trimethylaluminium (TMA) and water as precursors. In the ALD chamber, 10 pulses of TMA/Ar were used to further removing native oxides before the deposition of 100 CYC (~9.2 nm) Al_2O_3. The use of in-situ TMA pre-cleaning before oxide deposition was proved to improve the Al_2O_3/InGaAs, Al_2O_3/InAs, Al_2O_3/InSb interfaces by self-cleaning effect.[11–16] Beside the effect on the reduction of III–V native oxides, the reduction of dangling bonds at Al_2O_3/InSb interface after using some pulses of TMA/Ar is also expected. For the fabrication of metal–oxide–semiconductor capacitors (MOSCAPs), Ni/Au gate metal was formed via photolithography/e-beam evaporation/lift-off process. Finally, the Au/Ge/Ni/Au was deposited for back side ohmic contact followed by post metal annealing at 200 °C in N_2 for 30 s.

The valence band offset (ΔE_V) of Al_2O_3/InSb was determined for the sample deposited at 200 °C by using XPS measurement via the following formula:[17–19]

$$\Delta E_V = E_{CL} + (E_{In4d}^{InSb} - E_{VBM}^{InSb}) - (E_{Al2p}^{AlO} - E_{VBM}^{AlO}), \quad (1)$$

where $E_{CL} = E_{Al2p}^{AlO/InSb} - E_{In4d}^{AlO/InSb}$ is the energy difference between Al 2p and In 4d core levels measured in 2 nm Al_2O_3/InSb interface, while $E_{In4d}^{InSb} - E_{VBM}^{InSb}$ and $E_{Al2p}^{AlO} - E_{VBM}^{AlO}$ are the differences between valence band maximum (VBM) energies and corresponding In 4d core level in InSb and Al 2p core level in 9.2-nm-thick Al_2O_3. XPS measurements were performed in a commercial Microlab 350 XPS system equipped with an Al Kα source in an ultrahigh-vacuum chamber (5×10^{-9} Torr) with a 60° take-off angle. The In 4d, Al 2p core levels and VBM spectra of the InSb, Al_2O_3/InSb interface and Al_2O_3 are shown in Fig. 1. The core levels were determined by using XPSPEAK software package (version 4.1) with Gaussian–Lorentz line shape and a Shirley background. The uncertainty of the core positions is 0.05 eV. The VBM positions were determined by the linear extrapolation of the leading valence band edge on the semiconductor and oxide. The uncertainty of determining VBM positions was also 0.05 eV. From the measurement values shown in Fig. 1 and Eq. (1), the value of $\Delta E_V \sim 3.76 \pm 0.1$ eV is extracted.

Figure 2(a) shows the current density–voltage (*J*–*V*) characteristics of the MOSCAP samples that were deposited at 150, 200, and 250 °C. *I*–*V* measurement was performed using a Keithley 4200 analyzer. All the samples exhibit a low leakage current with a breakdown field of above 7.2 MV/cm. In the FN regime, the current density can be expressed as[20]

$$J_{FN} = \frac{m}{m^*}\frac{q^3}{16\pi^2\hbar\phi_B}E^2\exp\left(-\frac{4\sqrt{2m^*}}{3q\hbar}\frac{\phi_B^{3/2}}{E}\right), \quad (2)$$

where m, m^*, q, $\hbar$, E, and ϕ_B are the electron mass, electron effective mass in Al_2O_3 oxide, elementary charge, Plank's

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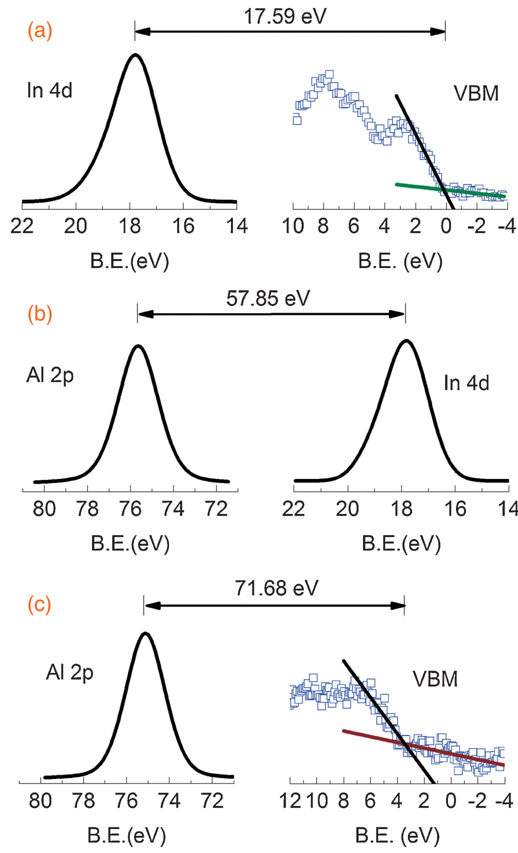

Fig. 1. XPS spectra of (a) In 4d core level and valence band of InSb surface (after HCl cleaning), (b) Al 2p and In 4d core levels at the 2 nm Al_2O_3/InSb interface, and (c) Al 2p and valence band of Al_2O_3 film.

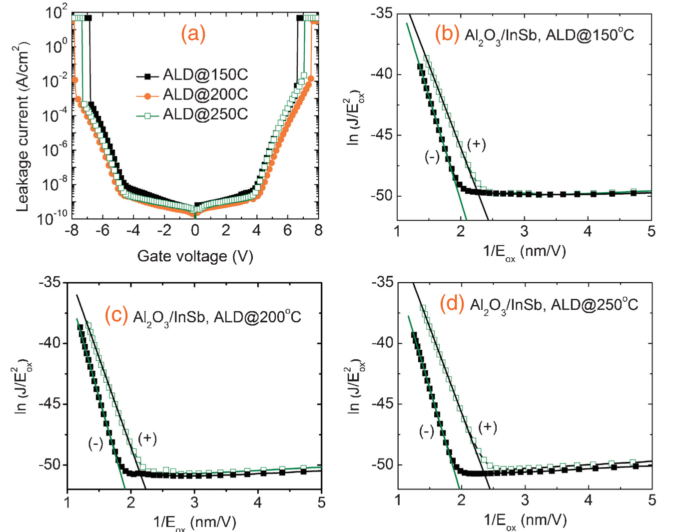

Fig. 2. (a) I–V characteristics of samples; (b) and (c) FN plots of samples deposited at 150 and 200 °C; (d) FN plots after revision of samples deposited at 250 °C.

constant, oxide electrical field ($E = V_g/t_{ox}$, V_g: gate bias and t_{ox}: oxide thickness), and tunneling barrier height, respectively. According to Eq. (2), the plot of $\ln J_{FN}/E^2$ versus $1/E$ (so-called FN plot) should be linear with slope S given by

$$S = \frac{d[\ln(J_{FN}/E^2)]}{d(1/E)} = -\frac{4\sqrt{2m^*}}{3q\hbar}\phi_B^{3/2}. \quad (3)$$

The barrier heights can be expressed as $\phi_B^+ = \chi_S - \chi$ under forward gate bias and $\phi_B^- = \phi_m - \chi$ under reverse gate bias, where χ_S, ϕ_m, and χ are semiconductor electron affinity, metal work function and oxide electron affinity, respectively. The FN plots of the three samples are shown in Figs. 2(b)–2(d). It can be seen that the curves exhibit a linear relationship at high electrical field, indicating the dominance of the FN mechanism. The slopes under forward and reverse bias (S_+ and S_-, respectively) can be extracted from these data and the values of m^*, ϕ_B^+, and χ can be determined using the following formulas:

$$\frac{m^*}{m} = \frac{9q^2\hbar^2}{32m}\frac{(S_-^{2/3} - S_+^{2/3})^3}{(\phi_m - \chi_S)^3},$$

$$\phi_B^+ = \left(-\frac{3q\hbar S_+}{4\sqrt{2m^*}}\right)^{2/3},$$

$$\chi = (\chi_S - \phi_B^+). \quad (4)$$

By taking the values of Ni work function $\phi_m = 5.05$ eV[21] and InSb electron affinity $\chi_S = 4.6$ eV,[1] the extracted parameters of the MOS structures are listed Table I. As

Table I. Band parameters of the samples extracted by FN characteristics.

	ϕ_B^+ (eV)	ϕ_B^- (eV)	m^*/m_0	χ (eV)
Sample at 150 °C	2.71	3.16	0.20	1.89
Sample at 200 °C	2.77	3.22	0.22	1.83
Sample at 250 °C (before revision)	*3.39*	*3.84*	*0.092*	*1.21*
Sample at 250 °C (after revision)	2.71	3.16	0.21	1.89

shown in the table, the extracted values of the two samples deposited at 150 and 200 °C are very similar. The conduction band offset ΔE_C values are found to be 2.71 and 2.77 eV, respectively. These values are in agreement and very close to that reported by Chou et al. by using the IPE method.[8] The values of m^* and χ are about 0.2–0.22m_0 and 1.8–1.9 eV, respectively. For the sample deposited at 250 °C, ΔE_C, m^*, and χ are 3.84 eV, 0.092m_0, and 1.21 eV, respectively, which are very different from those of the other samples.

To find out the reason for this difference, the capacitance–voltage (C–V) measurement was performed using an HP4284A meter for further study. Figure 3(a) shows the C–V curves at 1 kHz of the three samples. While the C–V curves of the two samples deposited at 150 and 200 °C are very similar, that of the sample deposited at 250 °C shifts positively to $\Delta V = 0.09$ V. In the previous work, we found that there was an In, Sb out diffusion layer with a thickness of 1.5 nm at the Al_2O_3/InSb interface when the sample was deposited at 250 °C [see the transmission electron microscopy (TEM) image of the sample with 7.5 nm ALD Al_2O_3/InSb at 250 °C in Fig. 3(b)].[9] This out diffusion layer might cause a negative fixed charge which results in lowering the Fermi level in InSb side to $\Delta\phi = 0.09$ eV below that in the metal side [Fig. 3(b)]. The root cause of negative charge layer needs further investigating but it may attribute to the dominant diffusion of Sb at low thermal temperature

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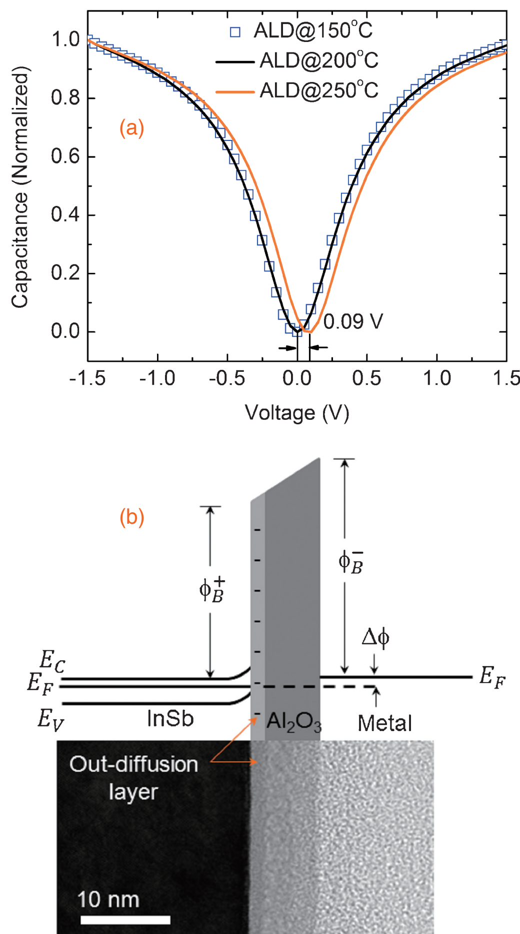

Fig. 3. (a) C–V curves of samples, and (b) the band modification diagram of the sample deposited at 250 °C caused by In, Sb out diffusion layer as indicated by TEM image.

process as compared to the diffusion of In.[10] Due to this modification, the determination of band alignment parameters of the sample deposited at 250 °C was not accurate. We then revised the electrical field for the FN plot of this sample by adding a revisional factor ΔV:

$$E = \frac{V_g - \Delta V}{t_{ox}}. \tag{5}$$

The FN plot after revision is also linear as indicated in Fig. 2(d). The band alignment parameters were extracted again and interestingly, all the parameters became very similar to those of others samples (see Table I). By this revision, one can conclude that the conduction band offset of Al_2O_3/InSb is $\Delta E_C \sim 2.73 \pm 0.1$ eV. Combining this value of conduction band offset with the valence band offset ΔE_V extracted above and the InSb band gap of 0.17 eV at room temperature,[1] the band gap of the Al_2O_3 film can be deduced to be $E_g \sim 6.66 \pm 0.1$ eV. This value is consistent with that reported by Huang et al. (6.8 ± 0.1 eV) by using energy loss spectra analysis.[19]

In conclusion, the band alignment parameters of Al_2O_3/InSb structures have been evaluated by using XPS analysis and FN characteristics. The conduction band offset $\Delta E_C \sim 2.73 \pm 0.1$ eV, and valence band offset $\Delta E_V \sim 3.76 \pm 0.1$ eV are extracted. For the ALD Al_2O_3 film parameters, an energy band gap of 6.66 ± 0.1 eV, an electron affinity of 1.8–1.9 eV, and an electron effective mass of 0.2–0.22m_0 were deduced. The I–V and C–V analyses also indicated the band modification of the sample deposited at 250 °C caused by the In, Sb out diffusion layer at the Al_2O_3/InSb interface. These results would be useful for the future study of high-k/InSb MOS devices.

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