

Band offsets determination and interfacial chemical properties of the Al₂O₃/GaSb system

I. Geppert,^{1,a)} M. Eizenberg,¹ A. Ali,² and S. Datta²

¹Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

²Department of Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 26 August 2010; accepted 20 September 2010; published online 22 October 2010)

Band offsets of the Al₂O₃/GaSb system and various surface passivation treatments of the GaSb substrate by HCl, NH₄OH, and (NH₄)₂S solutions were investigated by x-ray photoelectron spectroscopy. The extracted conduction and valence band offsets values of Al₂O₃ relative to GaSb are 2.4 ± 0.1 eV and 3.4 ± 0.2 eV, respectively. The presence of Ga–O and Sb–O bonds was detected after NH₄OH surface treatment. In contrast, (NH₄)₂S and HCl solutions inhibit the Sb oxide formation. The lowest amount of Ga–O bands was obtained for (NH₄)₂S passivation. These results correlate with capacitance-voltage (C-V) measurements of Pd–Au/Al₂O₃/GaSb stacks which yielded the best characteristics for the S-based passivation. © 2010 American Institute of Physics. [doi:10.1063/1.3499655]

Further dimensional scaling of complementary metal oxide semiconductor devices requires the introduction of alternative materials, in order to overcome fundamental performance limitations.¹ Among these materials III–V semiconductors are potential replacements for silicon channels due to a high intrinsic carrier-mobility, which allows to increase the drive current in short- and long-channel devices. In recent years, III–V compounds coupled with high-k gate dielectrics have been widely investigated, however, many challenges remain. One of them is the formation of a high quality dielectric/substrate interface. Native oxides of III–V compounds lead to the formation of a high density of intrinsic defects with energy levels in the semiconductor band gap,² resulting in Fermi level pinning³ at the oxide-semiconductor interface. In addition, for the oxide to act as a barrier for both electron and hole injection, the chosen high-k material should have valence and conduction band discontinuities larger than 1 eV relative to the semiconductor.⁴

GaSb is an important III–V compound semiconductor for high speed⁵ and optoelectronic applications,⁶ the performance of which significantly depends on the chemical and electronic properties of the GaSb surface. However, GaSb is known to be highly reactive and easily oxidizes under atmospheric conditions forming an oxide layer, several nanometers thick, that is, not self limiting, stable, or abrupt.⁷ As a result of the oxidation process, a layer of elemental Sb is formed at the oxide/GaSb interface, which leads to a high leakage current.⁸ To overcome these problems, various surface passivation methods, including wet and dry chemical processes, were proposed in an effort to improve the GaSb interface characteristics.^{9,10} However, the growth of surface suboxides which degrades the quality of the surface was detected for all passivation techniques. Therefore, a study of the interfacial chemical properties and the band structure of the high-k/GaSb system is important for the development of advanced GaSb-based devices.

In this work, the conduction and valence band offset values of Al₂O₃ relative to GaSb were determined. In addition,

we investigated changes in the interfacial chemical bonding due to the various surface treatments applied prior to the Al₂O₃ deposition. Al₂O₃ films, 3 and 20 nm thick, were deposited by atomic layer deposition technique on top of GaSb(100) wafers. All the wafers were initially degreased in acetone, methanol, and isopropyl alcohol. Subsequently, each sample was immersed in one of the following solutions: hydrochloric acid (1HCl:10H₂O) for 5 min, ammonium sulfide [1(NH₄)₂S:45H₂O] for 5 min, and ammonium hydroxide [NH₄OH (29%)] for 3 min. X-ray photoelectron spectroscopy (XPS) measurements were used to determine the band structure and to characterize the chemical bonding of the dielectric films. These measurements were conducted in a Thermo VG Scientific Sigma Probe system using a monochromatic Al K α (1486.6 eV) x-ray source. Sb 4*d*, Ga 3*d*, and O 2*s* spectra were collected with a pass energy of 20 eV. O 1*s* and valence band spectra were collected using a pass energy of 50 eV. Curve fitting was done by the XPSPEAK 4.1 fitting program using a Gaussian–Lorentzian convolution with a Shirley-type background.

The band gap of the Al₂O₃ film was determined by XPS measurements analyzing the O 1*s* core level spectrum. The energy loss spectrum of O 1*s* photoelectrons supplies information about the value of the forbidden energy band gap (*E_g*) due to the fact that in dielectric films band-to-band transitions (from the valence band to the conduction band) require lower energy than plasmon losses.¹¹ Figure 1 shows the O 1*s* spectrum of the 20 nm thick Al₂O₃ film. The energy loss region can be seen in the inset, where the band gap is the energy difference between the middle of the peak and the beginning of the energy loss region, which was obtained by an intersection of following two lines: a linear fit line from a point near the onset of the loss signal and the line of the background level. The extracted band gap value is 6.5 eV, which is in a good agreement with the literature.¹²

The XPS measurements supply information about the core level and the valence electrons emitted from the films. This allows determining the valence band offset of Al₂O₃ relative to GaSb by the method described in Ref. 13. Using this approach, the XPS spectra were collected from the fol-

^{a)}Electronic mail: geppert@tx.technion.ac.il.

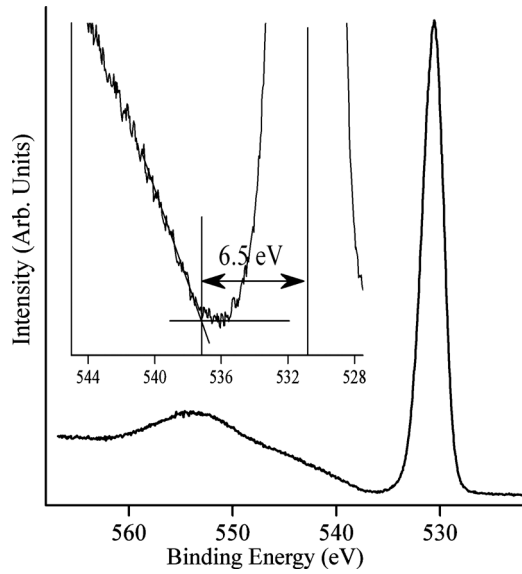


FIG. 1. O 1s energy-loss spectrum for 20 nm Al_2O_3 film. The inset is a magnified region of the energy loss spectrum.

lowing three samples: GaSb wafer, thin $\text{Al}_2\text{O}_3/\text{GaSb}$ (for each surface treatments), and thick $\text{Al}_2\text{O}_3/\text{GaSb}$. The valence band offset (ΔE_V) can be calculated by using the following equation:

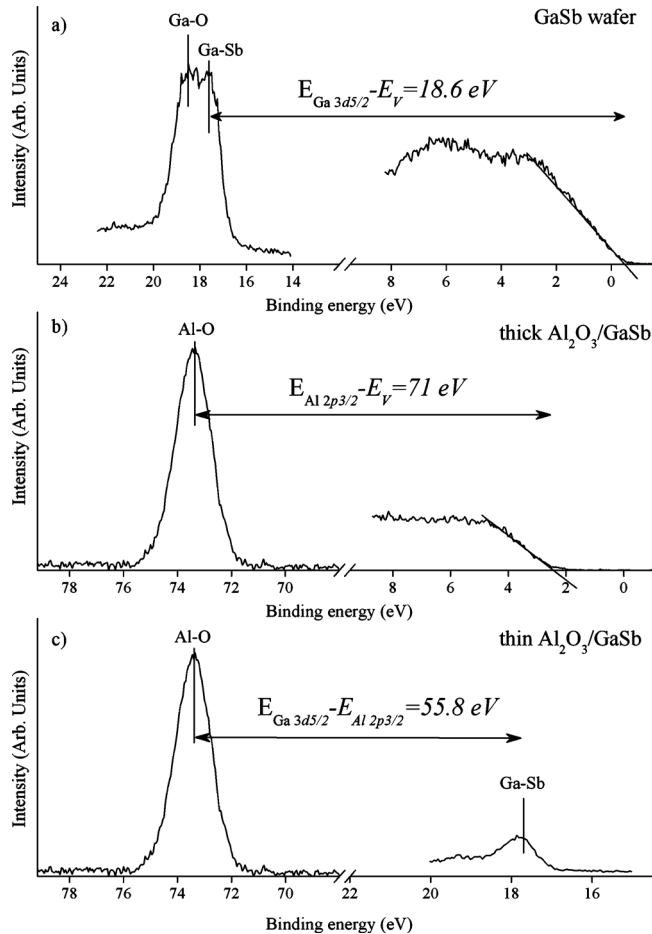


FIG. 2. XPS spectra of (a) Ga $3d_{5/2}$ core level and valence band of GaSb wafer, (b) Al $2p_{3/2}$ core level and valence band of thick $\text{Al}_2\text{O}_3/\text{GaSb}$ sample, and (c) Ga $3d_{5/2}$ and Al $2p_{3/2}$ core levels of thin $\text{Al}_2\text{O}_3/\text{GaSb}$ sample.

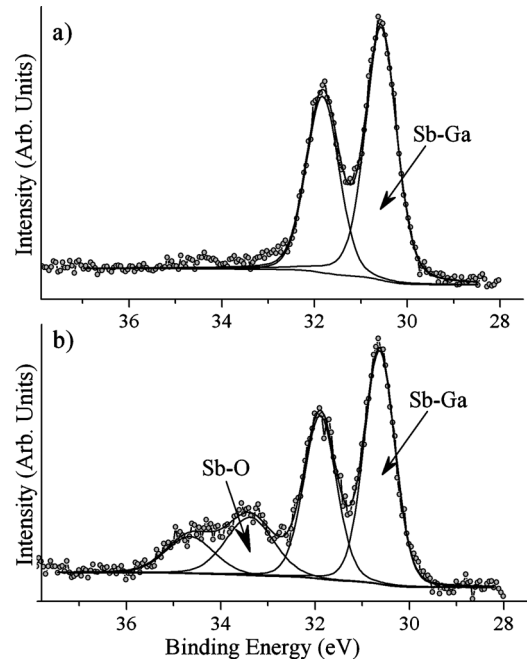


FIG. 3. XPS spectra of Sb $4d$ core level of $\text{Al}_2\text{O}_3/\text{GaSb}$ sample with various surface treatments applied prior to oxide deposition (a) $(\text{NH}_4)_2\text{S}$ and HCl and (b) NH_4OH .

$$\Delta E_V = (E_{\text{Ga } 3d} - E_V)_{\text{GaSb(wafer)}} - (E_{\text{Al } 2p} - E_V)_{\text{thick Al}_2\text{O}_3/\text{GaSb}} + (E_{\text{Al } 2p} - E_{\text{Ga } 3d})_{\text{thin Al}_2\text{O}_3/\text{GaSb}}, \quad (1)$$

where $E_{\text{Ga } 3d}$ and $E_{\text{Al } 2p}$ are the core levels of Ga $3d_{5/2}$ and Al $2p_{3/2}$, respectively. E_V is the valence band maximum of the involved samples and it can be determined by linearly fitting the leading edge of the valence electron spectrum. The energy differences between the core levels and the beginning of ejected valence electron spectrum can be seen in Fig. 2. The results show that the values of $(E_{\text{Ga } 3d} - E_V)_{\text{GaSb(wafer)}}$, $(E_{\text{Al } 2p} - E_V)_{\text{thick Al}_2\text{O}_3/\text{GaSb}}$, and $(E_{\text{Al } 2p} - E_V)_{\text{thin Al}_2\text{O}_3/\text{GaSb}}$ are 18.6 eV, 71 eV, and 55.8 eV, respectively, for the all samples with the surface passivation treatments mentioned above. The valence band offset of the Al_2O_3 relative to GaSb from the Eq. (1) is $3.4 \text{ eV} \pm 0.2 \text{ eV}$. The conduction band offset can be calculated from the following:

$$\Delta E_C = E_{g_{\text{Al}_2\text{O}_3}} - \Delta E_V - E_{g_{\text{GaSb}}}, \quad (2)$$

where $E_{g_{\text{Al}_2\text{O}_3}}$ and ΔE_V are the obtained band gap and valence band offset of Al_2O_3 , and $E_{g_{\text{GaSb}}}$ is the band gap of GaSb, which is 0.7 eV.¹⁴ The determined value of the conduction band offset of Al_2O_3 relative to GaSb is $2.4 \pm 0.1 \text{ eV}$. The obtained values of ΔE_V and ΔE_C indicate the potential use of Al_2O_3 as a high-k dielectric material for the GaSb based devices which require low leakage currents.

In addition to desired band offsets, effective passivation of the surface defects is necessary. The XPS spectra of Sb $4d$, Ga $3d$, O $2s$, and Al $2p$ were examined. The binding energies for all samples were calibrated by correcting the position of the Al $2p_{3/2}$ peak to 73.4 eV. Figure 3(a) shows the Sb $4d$ spectrum for the sample with the HCl immersion before the Al_2O_3 deposition. The identical spectrum was obtained for the sample with the $(\text{NH}_4)_2\text{S}$ surface treatment. The spectrum is represented by one doublet at 31.5 eV with

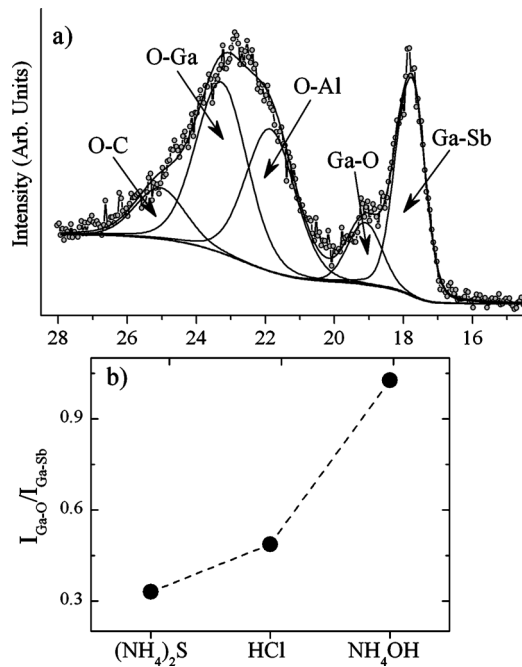


FIG. 4. (a) XPS spectra of Ga $3d_{5/2}$ and O $2s$ for $\text{Al}_2\text{O}_3/\text{GaSb}$ sample with HCl surface treatment applied prior to oxide deposition and (b) The ratio of $I_{\text{Ga-O}}/I_{\text{Ga-Sb}}$ for the various surface treatments.

a spin orbit splitting of 1.25 eV, which is related to Sb–Ga bonds from the substrate. In comparison, the Sb $4d$ of the sample with the NH_4OH surface treatment before the oxide deposition is fitted by two doublets, as can be seen in Fig. 3(b). The second doublet at 33.6 eV, with the same spin orbit splitting, corresponds to Sb–O bonds. Namely, the surface treatment of $(\text{NH}_4)_2\text{S}$ or HCl before the Al_2O_3 deposition completely removes the Sb oxide while the presence of an additional doublet in the Sb $4d$ spectrum of the sample with the NH_4OH surface treatment indicates the formation of Sb–O bonds.

Figure 4(a) illustrates the O $2s$ and Ga $3d_{5/2}$ spectra of the sample with the HCl surface treatment applied prior the Al_2O_3 deposition. The O $2s$ spectrum consists of the following three peaks: O–Al bonds at 21.5 eV, O–Ga bonds at 23.0 eV, and a peak of O–C bonds at 24.8 eV attributed to surface contamination. The O $2s$ spectra of the samples with the other surface treatments are similar to this one. The Ga $3d_{5/2}$ spectrum of the HCl surface treated sample is deconvoluted into two doublets. The doublet splitting cannot be observed for these two peaks due to a large full width at half maximum value (1.5 eV) and small spin orbit splitting (0.45 eV). The first doublet of Ga $3d_{5/2}$ at 17.6 eV is related to Ga–Sb bonds. The second doublet at 18.9 eV is attributed to Ga–O bonds. In the Ga $3d_{5/2}$ spectra of the other samples the same two types of bonding were observed. For the sake of comparison, the ratio of $I_{\text{Ga-O}}/I_{\text{Ga-Sb}}$ for each sample with differ-

ent surface treatments is plotted in Fig. 4(b). Since the Al_2O_3 thickness is the same for all samples the change in the ratio of $I_{\text{Ga-O}}/I_{\text{Ga-Sb}}$ reflects the variation in the amount of Ga–O bonds at the GaSb/ Al_2O_3 interface. The higher the ratio, the higher is the amount of the Ga–O bonds. Based on these XPS results, the smallest amount of Ga–O bonds is detected in the sample with the $(\text{NH}_4)_2\text{S}$ surface treatment while the biggest one is in the sample with the NH_4OH surface treatment.

Capacitance-voltage (C-V) measurements were carried out on Pd–Au/ $\text{Al}_2\text{O}_3/\text{GaSb}$ stacks with various surface treatments applied prior to the Al_2O_3 deposition. A better modulation ($C_{\text{max}}/C_{\text{min}}$) in the C-V curves was obtained for the $(\text{NH}_4)_2\text{S}$ treated sample compared to the NH_4OH and HCl surface passivations. This finding can be correlated with the XPS analysis, which shows the absence of Sb–O and the lowest amount of Ga–O bonds after the $(\text{NH}_4)_2\text{S}$ surface passivation treatment.

In conclusion, the band parameters and the interfacial chemical properties of the $\text{Al}_2\text{O}_3/\text{GaSb}$ system, which are important for future device design, were studied. Surface treatments in $(\text{NH}_4)_2\text{S}$ or HCl inhibit the Sb oxide formation. In addition, the sulfidization of GaSb surface reduces the amount of Ga–O bonds at the GaSb/ Al_2O_3 interface relative to the other treatments. In contrast, the presence of Ga–O and Sb–O bonds was detected after the NH_4OH surface treatment.

This work was supported by the Russell Berrie Nanotechnology Institute at the Technion.

- ¹R. M. Wallace, P. C. McIntyre, J. Kim, and Y. Nishi, *MRS Bull.* **34**, 493 (2009).
- ²W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, *Phys. Rev. Lett.* **44**, 420 (1980).
- ³P. Chiaradia, M. Fanfoni, P. Nataletti, P. De Padova, L. J. Brillson, M. L. Slade, R. E. Viturro, D. Kilday, and G. Margaritondo, *Phys. Rev. B* **39**, 5128 (1989).
- ⁴J. Robertson and B. Falabretti, *J. Appl. Phys.* **100**, 014111 (2006).
- ⁵K. F. Longenbach, L. F. Luo, S. Xin, and W. I. Wang, *J. Cryst. Growth* **111**, 651 (1991).
- ⁶Y. Wei, A. Gin, M. Razeghi, and G. J. Brown, *Appl. Phys. Lett.* **81**, 3675 (2002).
- ⁷P. S. Dutta, H. L. Bhat, and V. Kumar, *J. Appl. Phys.* **81**, 5821 (1997).
- ⁸Z. Y. Liu, D. A. Saulys, and T. F. Kuech, *Appl. Phys. Lett.* **85**, 4391 (2004).
- ⁹E. Papis, A. Piotrowska, E. Kaminska, K. Golaszewska, R. Kruszka, T. T. Piotrowski, W. Rzdokiewicz, J. Szade, A. Winiarski, and A. Wawro, *Phys. Status Solidi C* **4**, 1448 (2006).
- ¹⁰Z. Y. Liu, T. F. Kuech, and D. A. Saulys, *Appl. Phys. Lett.* **83**, 2587 (2003).
- ¹¹S. Miyazaki, *Appl. Surf. Sci.* **190**, 66 (2002).
- ¹²M. L. Huang, Y. C. Chang, C. H. Chang, T. D. Lin, J. Kwo, T. B. Wu, and M. Hong, *Appl. Phys. Lett.* **89**, 012903 (2006).
- ¹³E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, *Phys. Rev. Lett.* **44**, 1620 (1980).
- ¹⁴*Semiconductor Material and Device Characterization* edited by D. K. Schroder (Wiley & Sons, New Jersey, 1998), p. 781.