Band offsets determination and interfacial chemical properties of the Al$_2$O$_3$/GaSb system

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Band offsets of the Al$_2$O$_3$/GaSb system and various surface passivation treatments of the GaSb substrate by HCl, NH$_4$OH, and (NH$_4$)$_2$S solutions were investigated by x-ray photoelectron spectroscopy. The extracted conduction and valence band offsets values of Al$_2$O$_3$ 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 NH$_4$OH surface treatment. In contrast, (NH$_4$)$_2$S and HCl solutions inhibit the Sb oxide formation. The lowest amount of Ga–O bands was obtained for (NH$_4$)$_2$S passivation. These results correlate with capacitance-voltage (C-V) measurements of Pd–Au/Al$_2$O$_3$/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. 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 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, resulting in Fermi level pinning 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.

GaSb is an important III–V compound semiconductor for high speed and optoelectronic applications, 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. 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. 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. 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 Al$_2$O$_3$ 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 Al$_2$O$_3$ deposition. Al$_2$O$_3$ 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:10H$_2$O) for 5 min, ammonium sulfide [1(NH$_4$)$_2$S:4H$_2$O] for 5 min, and ammonium hydroxide [NH$_4$OH (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 Ka (1486.6 eV) x-ray source. Sb 4d, Ga 3d, and O 2s spectra were collected with a pass energy of 20 eV. O 1s 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 Al$_2$O$_3$ film was determined by XPS measurements analyzing the O 1s core level spectrum. The energy loss spectrum of O 1s 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. Figure 1 shows the O 1s spectrum of the 20 nm thick Al$_2$O$_3$ 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 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.

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 Al$_2$O$_3$ relative to GaSb by the method described in Ref. 13. Using this approach, the XPS spectra were collected from the fol-
following three samples: GaSb wafer, thin Al₂O₃/GaSb (for each surface treatments), and thick Al₂O₃/GaSb. The valence band offset ($\Delta E_V$) can be calculated by using the following equation:

$$\Delta E_V = (E_{Ga\ 3d} - E_V)_{GaSb\ wafer} - (E_{Al\ 2p} - E_V)_{thick\ Al₂O₃/GaSb} + (E_{Al\ 2p} - E_{Ga\ 3d})_{thin\ Al₂O₃/GaSb}$$

where $E_{Ga\ 3d}$ and $E_{Al\ 2p}$ 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 $(E_{Ga\ 3d} - E_V)_{GaSb\ wafer}$, $(E_{Al\ 2p} - E_V)_{thick\ Al₂O₃/GaSb}$, and $(E_{Al\ 2p} - E_{Ga\ 3d})_{thin\ Al₂O₃/GaSb}$ are 18.6 eV, 71 eV, and 55.8 eV, respectively, for all samples with the surface passivation treatments mentioned above. The valence band offset of the Al₂O₃ relative to GaSb from the Eq. (1) is 3.4 eV ± 0.2 eV. The conduction band offset can be calculated from the following:

$$\Delta E_C = E_{G₃Al₂O₃} - \Delta E_V - E_{G₃GaSb}$$

where $E_{G₃Al₂O₃}$ and $\Delta E_V$ are the obtained band gap and valence band offset of Al₂O₃, and $E_{G₃GaSb}$ is the band gap of GaSb, which is 0.7 eV. The obtained value of the conduction band offset of Al₂O₃ relative to GaSb is 2.4 ± 0.1 eV. The obtained values of $\Delta E_V$ and $\Delta E_C$ indicate the potential use of Al₂O₃ as a high-k dielectric material for 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 $4d$ core level of Al₂O₃/GaSb sample with various surface treatments applied prior to oxide deposition (a) (NH₄)₂S and HCl and (b) NH₄OH.

$\Delta E_V = (E_{Ga\ 3d} - E_V)_{GaSb\ wafer} - (E_{Al\ 2p} - E_V)_{thick\ Al₂O₃/GaSb} + (E_{Al\ 2p} - E_{Ga\ 3d})_{thin\ Al₂O₃/GaSb}$

where $E_{Ga\ 3d}$ and $E_{Al\ 2p}$ 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.

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$$\Delta E_C = E_{G₃Al₂O₃} - \Delta E_V - E_{G₃GaSb}$$

where $E_{G₃Al₂O₃}$ and $\Delta E_V$ are the obtained band gap and valence band offset of Al₂O₃, and $E_{G₃GaSb}$ is the band gap of GaSb, which is 0.7 eV. The obtained value of the conduction band offset of Al₂O₃ relative to GaSb is 2.4 ± 0.1 eV. The obtained values of $\Delta E_V$ and $\Delta E_C$ indicate the potential use of Al₂O₃ 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 Al₂O₃ deposition. The identical spectrum was obtained for the sample with the (NH₄)₂S surface treatment. The spectrum is represented by one doublet at 31.5 eV with
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$_4$OH surface treatment before the oxide deposition completely removes the Sb oxide while the presence of an addition doublet in the Sb 4d spectrum of the NH$_4$OH 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$_2$O$_3$ 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$_{Ga-O}$/I$_{Ga-Sb}$ for each sample with different surface treatments is plotted in Fig. 4(b). Since the Al$_2$O$_3$ thickness is the same for all samples the change in the ratio of I$_{Ga-O}$/I$_{Ga-Sb}$ reflects the variation in the amount of Ga–O bonds at the GaSb/Al$_2$O$_3$ 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 (NH$_4$)$_2$S surface treatment while the biggest one is in the sample with the NH$_4$OH surface treatment.

Capacitance-voltage (C-V) measurements were carried out on Pd–Au/Al$_2$O$_3$/GaSb stacks with various surface treatments applied prior to the Al$_2$O$_3$ deposition. A better modulation (C$_{max}$/C$_{min}$) in the C-V curves was obtained for the (NH$_4$)$_2$S treated sample compared to the NH$_4$OH 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 (NH$_4$)$_2$S surface passivation treatment.

In conclusion, the band parameters and the interfacial chemical properties of the Al$_2$O$_3$/GaSb system, which are important for future device design, were studied. Surface treatments in (NH$_4$)$_2$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$_2$O$_3$ interface relative to the other treatments. In contrast, the presence of Ga–O and Sb–O bonds was detected after the NH$_4$OH surface treatment.

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