Interfacial and electrical properties of HfAlO/GaSb metal-oxide-semiconductor capacitors with sulfur passivation*

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Interfacial and electrical properties of HfAlO/GaSb metal-oxide-semiconductor capacitors (MOSCAPs) with sulfur passivation were investigated and the chemical mechanisms of the sulfur passivation process were carefully studied. It was shown that the sulfur passivation treatment could reduce the interface trap density D_{it} of the HfAlO/GaSb interface by 35% and reduce the equivalent oxide thickness (EOT) from 8 nm to 4 nm. The improved properties are due to the removal of the native oxide layer, as was proven by x-ray photoelectron spectroscopy measurements and high-resolution cross-sectional transmission electron microscopy (HRXTEM) results. It was also found that GaSb-based MOSCAPs with HfAlO gate dielectrics have interfacial properties superior to those using HfO_2 or Al_2O_3 dielectric layers.

Keywords: HfAlO, GaSb, metal-oxide-semiconductor capacitors, interfacial properties

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1. Introduction

The III–V materials are promising candidates for channel materials in next-generation complementary metal-oxide-semiconductor (CMOS) technology because of their high electron mobility and saturation velocity.[1] Materials such as GaAs,[2] InAs,[3] GaN,[4] InP[5] and InGaAs[6–8] have been studied intensively. However, the hole mobility of most III–V materials is relatively low, making them unsuitable for p-channel metal-oxide-semiconductor (MOS) devices. GaSb is an exciting III–V material because its high hole mobility ($\sim 850\ cm^2 \cdot V^{-1} \cdot s^{-1}$) is nearly twice as high as that of silicon, while its electron mobility is five times higher than that of silicon. These two properties make it very suitable for the CMOS technology.[9] The lack of high quality, thermodynamically stable insulators with low interface states is the main obstacle impeding the widespread application of III–V MOS devices, making the high-k dielectric research increasingly urgent.[10] Although GaSb MOS devices with Al_2O_3 dielectrics have been studied intensively,[9,11–14] HfO_2/GaSb and HfAlO/GaSb MOS devices are rarely reported[15] and most of those have p-type substrates.[16] Al_2O_3 dielectrics are believed to form a higher quality interface with GaSb substrates than HfO_2. However, the dielectric constant of Al_2O_3 (~ 9) is not as high as that of HfO_2 (~ 25).[17,18] HfAlO is one of the most promising dielectrics, because it obtains a tradeoff between the good interfacial properties of Al_2O_3 and the high dielectric constant of HfO_2.

In this paper, we systematically investigate the effects of sulfur passivation on HfAlO/GaSb MOS capacitors (MOSCAPs) and compare the interfacial properties of the HfAlO/GaSb, HfO_2/GaSb and Al_2O_3/GaSb MOSCAPs with sulfur passivation. The HfAlO/GaSb MOSCAPs show a superior interface quality when compared with the HfO_2/GaSb and Al_2O_3/GaSb MOSCAPs.

2. Experiment

The wafers used in this work were Te-doped GaSb substrates (n-type) with doping concentrations of $\sim 1.5 \times 10^{17}\ cm^{-3}$, on which HfAlO was grown by atomic layer deposition (ALD) using a Beneq TFS 200 ALD system. The HfAlO dielectrics consisted of nine complete layers of HfAlO; each complete layer of HfAlO was deposited by three cycles of Al_2O_3 followed by three cycles of HfO_2. The Al_2O_3 was deposited by ALD at 200 °C using trimethylaluminum (TMA) and water, while HfO_2 was deposited by ALD at 200 °C using tetrakis (ethylmethylamino) hafnium (TEMAH) and water. Prior to the deposition, the substrates were degreased by sequentially rinsing for five minutes each in acetone, ethanol and isopropanol; they were then cleaned with 9% HCl for one minute. Sulfur passivation was then accomplished by immersing the substrates in a 15% aqueous $(NH_4)_2S$ solution for 15 min. Finally, 300-nm Al gate contacts were deposited by electron-beam evaporation. Back metal contacts of Ti/Au were also deposited. To investigate the effects of sulfur passivation (HCl-sulfur sample) on the HfAlO/GaSb interface, HfAlO/GaSb MOSCAPs without sulfur passivation (HCl-only samples) were also fabricated as control samples. GaSb MOSCAPs using HfO_2 or Al_2O_3 deposited by ALD for 50 cycles as dielectrics were fabricated for

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comparison to evaluate the interfacial properties of HfAlO dielectrics for GaSb MOS devices. Capacitance–voltage (C–V), conductance–voltage (G–V) and current–voltage (I–V) measurements were carried out using an Agilent B1500A semiconductor device analyzer and a Cascade Summit 11000 AP probe system. X-ray photoelectron spectroscopy (XPS) measurements were also performed using the Thermo Scientific ESCALAB 205 Xi to investigate the chemical bonding conditions of the surface.

3. Results and discussion

XPS measurements were performed to investigate the GaSb surfaces treated with HCl only and treated with HCl and $(NH_4)_2S$, using the Thermo Scientific ESCALAB 205 Xi XPS system equipped with an Al $K\alpha$ source. Figures 1(a) and 1(b) illustrate the Sb $3d_{3/2}$ core level spectra of the HCl-only sample and the HCl-sulfur sample, respectively.[19–22] The reduced area of the Sb–O feature in the Sb $3d_{3/2}$ core-level spectra indicates that the interlayer between GaSb and HfAlO is reduced. The binding energy of Sb–O shifts towards smaller binding energy, which shows that the Sb–S bond is formed. This is because the electronegativity of S is smaller than that of O.

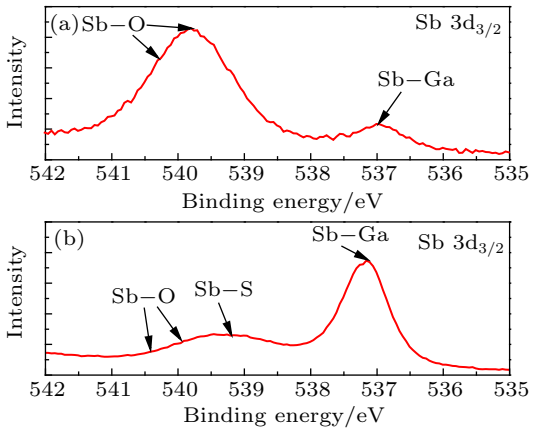


Fig. 1. (color online) The Sb $3d_{3/2}$ XPS spectra of (a) the HCl-only GaSb sample surface and (b) the HCl-sulfur GaSb sample surface.

The Ga 3d core level spectrum of the HCl-only sample is shown in Fig. 2(a).[23,24] The Ga 3d core level signals of the HCl-sulfur sample are shown in Fig. 2(b).[25] It is clearly shown in Fig. 2(a) that, for the HCl-only treatment substrate, the Ga–O feature occupies most of the area in the Ga 3d core-level spectrum, which indicates that the Ga–O bond is formed immediately after the HCl treatment. However, with sulfur passivation treatment after the HCl etch, as Fig. 2(b) shows, almost no Ga–O bonds exist, being replaced by Ga–S, indicating that the use of S passivation can effectively prevent the formation of Ga–O bonds.

The details of the sulfur passivation process are analyzed as follows. When the samples are exposed to air, the reactions between oxygen and the bulk GaSb are as follows:[26]

$$2GaSb + 3O_2 \rightarrow Ga_2O_3 + Sb_2O_3, \quad (1)$$

$$2GaSb + Sb_2O_3 \rightarrow Ga_2O_3 + 4Sb, \quad (2)$$

$$Sb_2O_3 + O_2 \rightarrow Sb_2O_5. \quad (3)$$

The natural oxides (Ga_2O_3, Sb_2O_5 and Sb_2O_3) protect the bulk GaSb surface from further oxidation. Reaction (2) will proceed until Sb_2O_3 no longer exists at the GaSb surface.

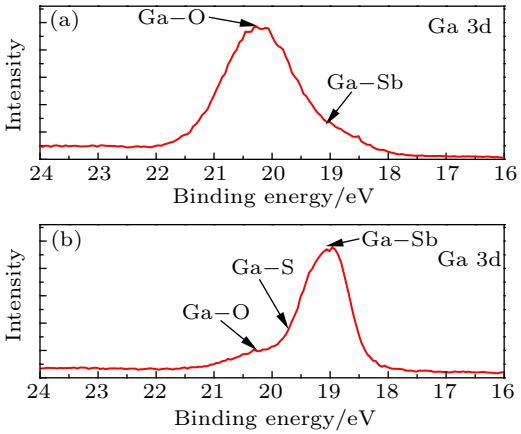


Fig. 2. (color online) The Ga 3d XPS spectra of (a) the HCl-only GaSb sample surface and (b) the HCl-sulfur GaSb sample surface.

During etching in dilute HCl, the HCl removes the oxides[27]

$$Ga_2O_3 + 6HCl \rightarrow 2GaCl_3 + 3H_2O, \quad (4)$$

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O. \quad (5)$$

Sb_2O_5 cannot react with dilute HCl. Reactions (1) and (2) occur repeatedly after the substrates are removed from the dilute HCl. When treated with $(NH_4)_2S$, the possible reactions that may take place are

$$(NH_4)_2S + H_2O \rightarrow NH_4OH + NH_4SH, \quad (6)$$

$$SbO_x + NH_4SH \rightarrow SbS_y + NH_4OH, \quad (7)$$

$$GaO_x + NH_4SH \rightarrow GaS_y + NH_4OH, \quad (8)$$

$$GaSb + NH_4OH \rightarrow GaO_x + SbO_y + NH_3 + H_2. \quad (9)$$

As a result, after the sulfur treatment, the surfaces of the samples are passivated by forming Ga–S and Sb–S bonds, which will improve the electrical properties of the MOSCAPs.

Figures 3(a) and 3(b) show the typical multi-frequency capacitance–voltage (C–V) characteristics of the HCl-only and the HCl-sulfur GaSb MOSCAPs, respectively. The frequency dispersion in the accumulation region is reduced from 22.5% to 3.4% by the sulfur treatment, which indicates that the border traps are greatly reduced.[28] The equivalent oxide thickness (EOT) of the HCl-sulfur GaSb MOSCAPs is calculated to be 4 nm, much less than the 8 nm EOT of the HCl-only treated GaSb MOSCAPs. This indicates that oxide layer re-growth on

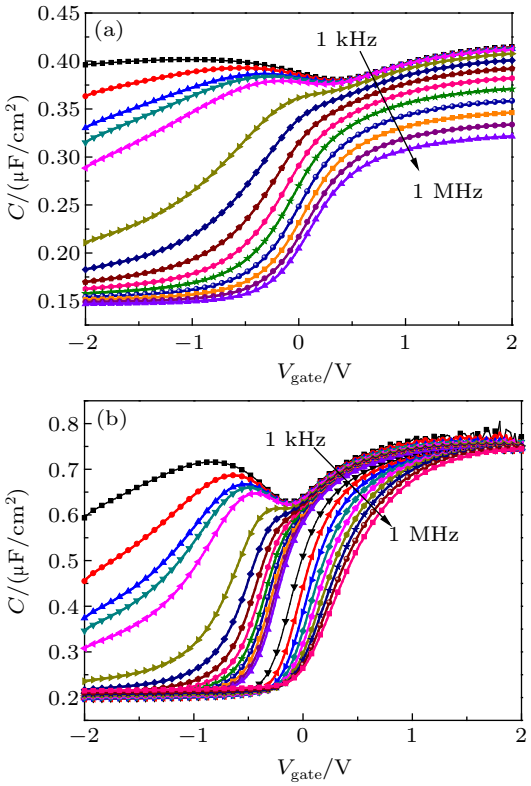


Fig. 3. (color online) The *C*–*V* curves of (a) the HCl-only GaSb MOSCAPs and (b) the HCl-sulfur GaSb MOSCAPs.

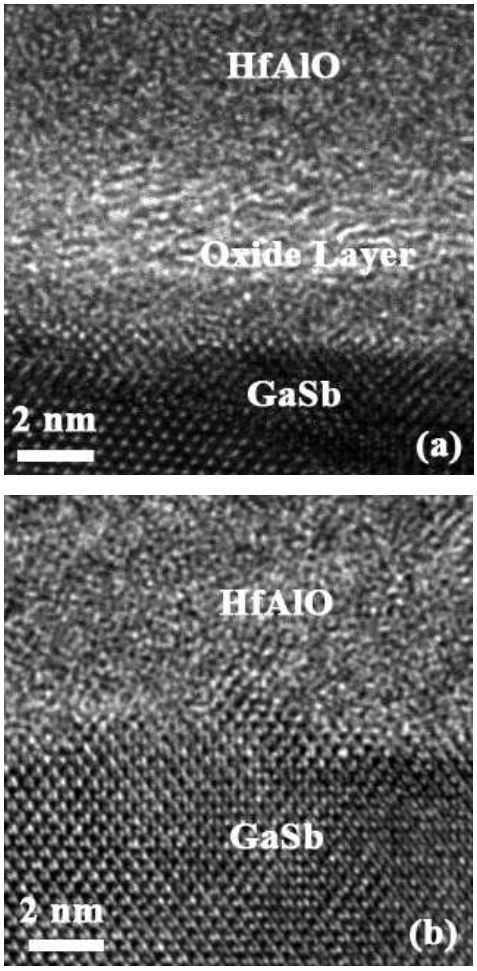


Fig. 4. HRXTEM images of (a) the HCl-only GaSb MOSCAPs and (b) the HCl-sulfur GaSb MOSCAPs.

the GaSb surface is efficiently prevented by the sulfur passivation treatment after the HCl treatment, while the oxide layer re-grows easily on surfaces without sulfur passivation. This is confirmed by the high-resolution cross-sectional transmission electron microscopy (HRXTEM) results, as shown in Fig. 4. An oxide layer exists for the HCl-only samples, while there is nearly no oxide layer for the HCl-sulfur samples. This result is consistent with the XPS results shown in Figs. 1 and 2.

Figure 5 shows the gate leakage current characteristics of the HCl-only and the HCl-sulfur GaSb MOSCAPs. When the applied gate voltage V_{gate} is small, the HCl-only sample has a lower gate leakage current. This is because of the additional oxide layer of the HCl-only sample, as discussed above. When the applied gate voltage is large, the gate leakage current of the HCl-sulfur sample is lower than that of the HCl-only sample, which indicates that sulfur passivation can improve the gate leakage current characteristics, especially when the applied gate bias is large.[29] The gate leakage current in the inversion region is mainly due to the minority carrier generation from the interface states and the bulk traps.[30] Consequently, the reduced gate leakage in the inversion region for the HCl-sulfur samples indicates the improved interfacial properties.

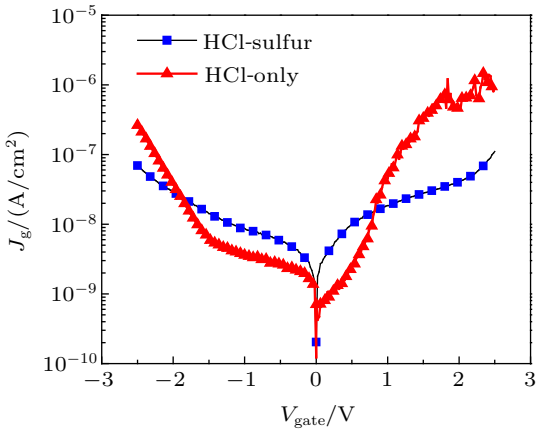


Fig. 5. (color online) Gate leakage current characteristics of the HCl-only and HCl-sulfur GaSb MOSCAPs.

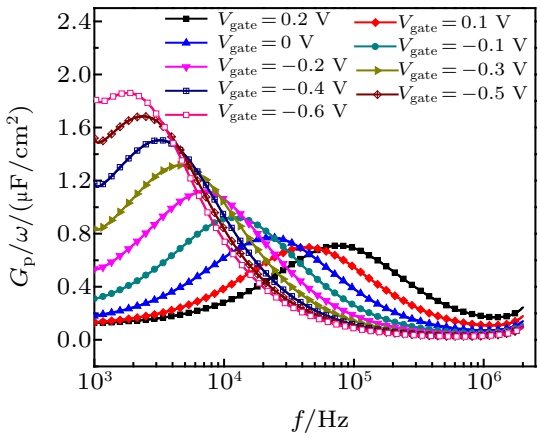


Fig. 6. (color online) Typical measured parallel G_p/ω versus frequency characteristics for different gate bias voltages of the HCl-sulfur HfAlO/GaSb MOSCAPs.

Figure 6 presents the typical measured parallel conductance divided by ω (G_p/ω) versus the frequency characteristics for different gate biases of the HCl-sulfur GaSb MOSCAPs. The observed peak shift indicates the efficiency of the surface Fermi level movement over the energy gap. Figure 7 shows the interface trap density (D_{it}) distribution that is extracted with the conductance method.[31] It is clear that D_{it} near the mid-gap is reduced by 35%, which might be due to a reduction in dangling bonds.

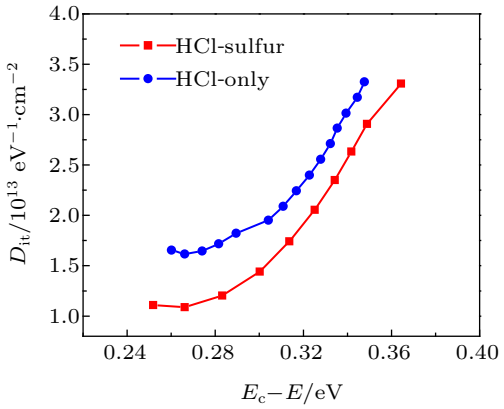


Fig. 7. (color online) The D_{it} distribution extracted by the conductance method for the HCl-only and the HCl-sulfur HfAlO/GaSb MOSCAPs.

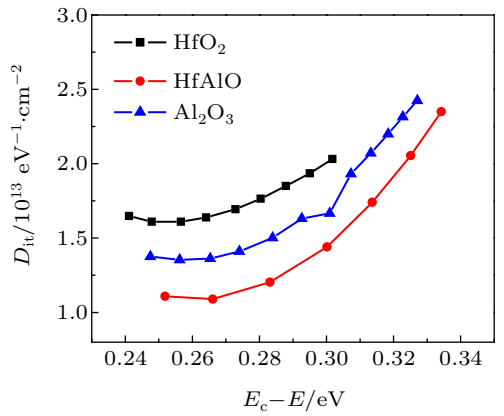


Fig. 8. (color online) The D_{it} distributions of the GaSb MOSCAPs using HfAlO, HfO_2 and Al_2O_3 as dielectrics.

We also examined the interfacial properties of GaSb MOSCAPs with different high-k dielectrics. Figure 8 shows the D_{it} distributions of GaSb MOSCAPs using HfAlO, HfO_2 or Al_2O_3 as dielectrics. These samples were all treated by sulfur passivation before the dielectrics were deposited. The D_{it} of HfAlO/GaSb MOSCAPs is $\sim$ 33% lower than that of HfO_2/GaSb MOSCAPs and $\sim$ 20% lower than that of Al_2O_3/GaSb MOSCAPs, indicating the promising performance of HfAlO/GaSb MOS devices. The mechanism of HfAlO's superior interface qualities has not been fully understood yet.[32–34] One possible explanation can be illustrated from the perspective of the length and energy of the chemical bond. Three different chemical bonds (Hf–O bond, Al–O bond and Hf–Al bond) exist in the HfAlO film. The combined effect of different bond lengths and different bond energies may reduce the number of dangling bonds at the HfAlO/GaSb interface, which would lead to a lower D_{it}.

4. Conclusion

In conclusion, we have systematically investigated the interfacial and electrical properties of the HfAlO/GaSb MOSCAPs. The chemical mechanisms of the sulfur passivation process are also carefully examined. XPS results show that with sulfur passivation, the native oxides (Sb_2O_3, Sb_2O_5 and Ga_2O_3) are mostly removed; the Sb–S and Ga–S bonds are then formed. When compared with the samples without sulfur passivation, it is found that the sulfur passivation can reduce the D_{it} of the HfAlO/GaSb interface near the mid-gap by 35% and reduce the equivalent oxide thickness from 8 nm to 4 nm. It is also found that HfAlO/GaSb MOSCAPs with sulfur passivation have interface properties superior to those of HfO_2/GaSb and Al_2O_3/GaSb MOSCAPs.

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