Improved interfacial and electrical properties of GaSb metal oxide semiconductor devices passivated with acidic $(NH_4)_2S$ solution*

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(Received 10 November 2013; revised manuscript received 25 December 2013; published online 15 May 2014)

Surface passivation with acidic $(NH_4)_2S$ solution is shown to be effective in improving the interfacial and electrical properties of HfO_2/GaSb metal oxide semiconductor devices. Compared with control samples, the samples treated with acidic $(NH_4)_2S$ solution show great improvements in gate leakage current, frequency dispersion, border trap density, and interface trap density. These improvements are attributed to the enhancing passivation of the substrates, according to analysis from the perspective of chemical mechanism, X-ray photoelectron spectroscopy, and high-resolution cross-sectional transmission electron microscopy.

Keywords: GaSb, metal oxide semiconductor, sulfur passivation

PACS: 81.65.Rv, 73.20.At, 81.05.Ea, 77.55.dj **DOI:** 10.1088/1674-1056/23/7/078102

1. Introduction

To extend Moore's law of complementary metal oxide semiconductor (CMOS) scaling, high-mobility III–V semiconductor materials, such as GaAs and InGaAs, have been actively investigated as alternative channel materials to silicon.[1] Although these III–V materials possess high electron mobility,[2] their hole mobility is low.[3] Consequently, GaSb has attracted considerable attention as a channel material for p-type MOS devices because of its high hole mobility.[4] However, the interface trap density (D_{it}) of GaSb MOS devices is still too high for their wide application.[5] Although many methods have been proposed to improve the interfacial properties of high-mobility MOS devices, such as fluorine passivation,[6] post-deposition treatment,[7–9] plasma treatment,[10] insertion of an interfacial layer,[11,12] and sulfur passivation,[13] D_{it} of the GaSb MOS devices reported is still at $\sim 10^{12}$ $eV^{-1}\cdot cm^{-2}$ to $\sim 10^{13}$ $eV^{-1}\cdot cm^{-2}$ level.[3] Previous reports on sulfur passivation have mainly been focused on different solutes, such as Na_2S and $(NH_4)_2S$.[14] In this paper, a novel sulfur passivation technique using acidic $(NH_4)_2S$ solution is proposed. The effects of this passivation treatment with acidic $(NH_4)_2S$ solution on GaSb MOS capacitors (MOSCAPs) are systematically investigated. We find that treatment with acidic $(NH_4)_2S$ solution is superior to that with 20% $(NH_4)_2S$ solution, which has a pH of $\sim$11 and is hereafter referred to as basic $(NH_4)_2S$ solution. Compared with control samples, the samples treated with acidic $(NH_4)_2S$ solution show great improvements in frequency dispersion, gate leakage current, border traps, and interface traps.

2. Experimental

Te-doped (100)-oriented n-type GaSb wafers with a doping concentration of $\sim 10^{17}$ cm^{-3} were used as substrates. The substrates were first degreased by sequential immersion for 5 min each in acetone, ethanol, and isopropanol, and then cleaned with 9% HCl aqueous solution for 1 min. Sulfur passivation treatments were performed for 15 min using basic and acidic $(NH_4)_2S$ solutions for different groups of samples. An HfO_2 dielectric layer ($\sim$5.5 nm) was then deposited on each sample by atomic layer deposition (ALD) at 200 °C using tetrakis (ethylmethylamino) hafnium (TEMAH) and water as precursors. Finally, Al was evaporated and patterned to form MOSCAPs. The back metal contacts of Ti/Au were also deposited. Acidic $(NH_4)_2S$ solution was prepared by adding 37% HCl aqueous solution to 20% $(NH_4)_2S$ aqueous solution until the pH of the acidic $(NH_4)_2S$ solution was 5.5–6.0. It should be noted that $(NH_4)_2S$ solution was not stable at a pH lower than 5.5. High-resolution X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical states of the surface passivated with basic and acidic $(NH_4)_2S$ solution. The HfO_2/GaSb MOS stacks were physically characterized by high-resolution transmission electron microscopy (HRTEM). Capacitance–voltage (C–V), conductance–voltage (G–V), and gate leakage current–voltage (J–V) characteristics were recorded using an Agilent B1500A semiconductor device analyzer and a Cascade Summit 11000 AP probe system.

3. Results and discussion

Figures 1(a) and 1(b) show XPS Ga 3d spectra of GaSb surfaces passivated with basic and acidic $(NH_4)_2S$ solutions,

*Project supported by the State Key Development Program for Basic Research of China (Grant No. 2011CBA00602) and the Major Project of the National Science and Technology of China (Grant No. 2011ZX02708-002).

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respectively. The Ga–O peak at 20.3 eV[15] is very intense for the sample treated with basic $(NH_4)_2S$ solution, and considerably reduces in intensity for the sample treated with acidic $(NH_4)_2S$ solution. This indicates that the acidic $(NH_4)_2S$ solution can effectively remove and prevent the further formation of Ga–O bonds. This happens because in the acidic solution, the chemical reaction $GaO_x+H^+ + S^{2-} \rightarrow GaS_x + H_2O$ takes place, preventing surface oxidation and promoting the sulfur passivation process. This reaction cannot occur in basic $(NH_4)_2S$ solution because the concentration of protons is much lower. The XPS Sb $3d_{3/2}$ spectra of the GaSb surfaces passivated with basic and acidic $(NH_4)_2S$ solutions are presented in Figs. 2(a) and 2(b), respectively. The Sb–O bonds at binding energies of 539.6 eV (Sb_2O_3) and 540.2 eV (Sb_2O_5)[16] do not change obviously for samples treated with acidic $(NH_4)_2S$ solutions, compared with those treated with basic $(NH_4)_2S$ solution. This happens because the residue oxides after basic $(NH_4)_2S$ solution treatment are mainly gallium oxide, and the intensities of the signals from Sb–O bonds are very weak. This is consistent with the fact that the Sb–O phase is not thermodynamically stable on the GaSb surface and the gallium oxide component of the native oxides on the GaSb surface is much higher than that of the antimony oxides.[17] The intensity of the Sb–S peak shown at 539.1 eV[16] is identical for each sample. The similarity of the XPS Sb $3d_{3/2}$ spectra for samples treated with basic and acidic $(NH_4)_2S$ solutions indicates that basic and acidic $(NH_4)_2S$ solutions have a similar effect on Sb related passivation.

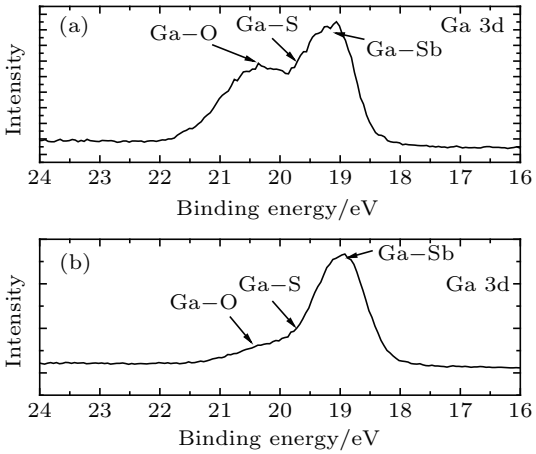


Fig. 1. XPS Ga 3d spectra of GaSb MOSCAPs passivated with basic (a) and acidic (b) $(NH_4)_2S$ solutions.

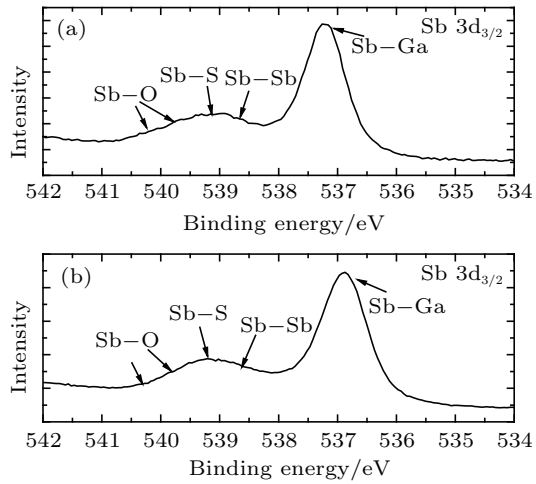


Fig. 2. XPS Sb $3d_{3/2}$ spectra of GaSb MOSCAPs passivated with basic (a) and acidic (b) $(NH_4)_2S$ solutions.

The thinner surface oxide layer present in samples treated with acidic $(NH_4)_2S$ solution than those treated with a basic $(NH_4)_2S$ solution was also confirmed by HRTEM, as shown in Fig. 3. An oxide layer, which is about 1.8 nm thick, can be clearly observed between the HfO_2 dielectric and GaSb substrate for the sample treated with basic $(NH_4)_2S$ solution (see Fig. 3(a)). In contrast, this surface oxide layer is about 0.5 nm thick for the sample treated with acidic $(NH_4)_2S$ solution, as illustrated in Fig. 3(b). The thinner surface oxide layer for the sample treated with the acidic $(NH_4)_2S$ solution indicates that the acidic $(NH_4)_2S$ solution has a more favorable effect on surface passivation than the basic $(NH_4)_2S$ solution. According to the XPS results presented in Figs. 1 and 2, the main component of this surface oxide layer is gallium oxide.

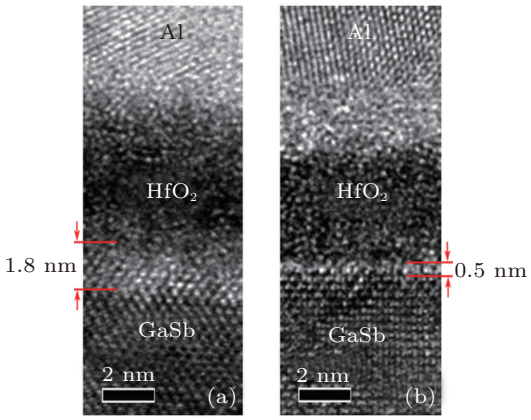


Fig. 3. (color online) HRTEM images of GaSb MOSCAPs passivated with basic (a) and acidic (b) $(NH_4)_2S$ solutions.

Figure 4 displays the gate leakage current–voltage (J–V) characteristics of samples treated with basic and acidic $(NH_4)_2S$ solutions. The gate leakage current for samples treated with acidic $(NH_4)_2S$ solution is significantly reduced compared with that of samples treated with basic $(NH_4)_2S$ solution. The gate leakage current density of samples treated with acidic $(NH_4)_2S$ solution at ± 4 MV/cm is about one order of magnitude lower than that of samples treated with basic $(NH_4)_2S$ solution. This might be caused by the reduction of trap-assisted current owing to the reduction of border traps and interface traps,[18] which is confirmed by the C–V and G–V measurements below.

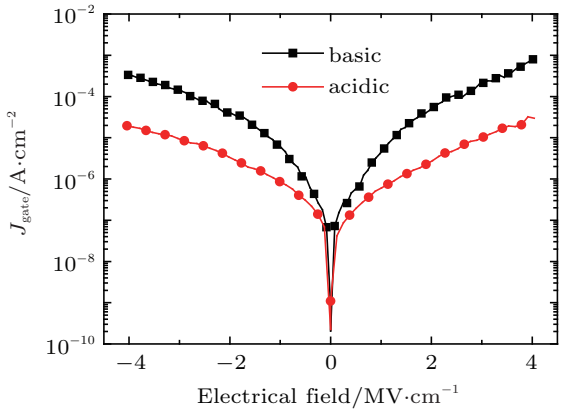


Fig. 4. (color online) Comparison of gate leakage current characteristics of MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions.

Figure 5 shows the multi-frequency *C*–*V* characteristics of GaSb MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions. The frequency dispersion in the accumulation region is reduced considerably by passivation with acidic $(NH_4)_2S$ solution instead of the basic solution, which indicates that the interfacial properties are improved using the acidic solution.[19] The EOT for the samples treated with basic and acidic $(NH_4)_2S$ solutions is 3.46 and 2.60 nm, respectively. Compared with the EOT of samples treated with basic $(NH_4)_2S$ solution, the lower EOT of samples treated with acidic $(NH_4)_2S$ solution indicates that the acidic solution can remove the surface oxide layer and prevent further oxidization more effectively than the basic one, which is consistent with the XPS and TEM results. It should be noted that the *C*–*V* characteristics show an obvious frequency-dependent *C*–*V* hump behavior in the depletion region. The decrease in measurement frequency increases the *C*–*V* hump. It is believed that the *C*–*V* hump is attributed to the charges generated through near-midgap located interface states,[20] which will be discussed in detail when analyzing the D_{it} below. The insets in Fig. 5 show the *C*–*V* hysteresis characteristics of samples treated with basic and acidic $(NH_4)_2S$ solutions, respectively. A large hysteresis is observed for samples treated with basic $(NH_4)_2S$ solution, which indicates large border traps.[21] This might be due to the intermixing of the high-*k* and the interfacial layer.[18] The *C*–*V* hysteresis for samples treated with acidic $(NH_4)_2S$ solution is reduced significantly, which indicates that border traps are considerably reduced.

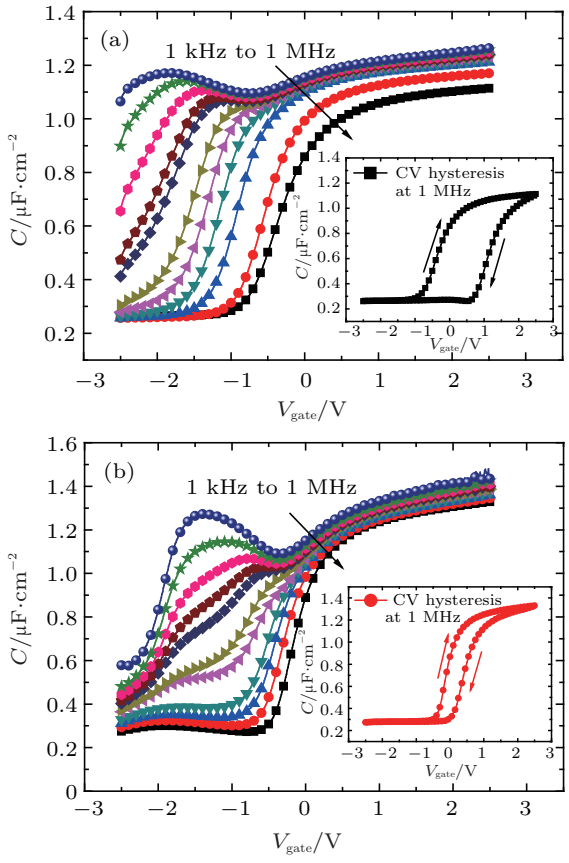


Fig. 5. (color online) Multi-frequency *C*–*V* characteristics of GaSb MOSCAPs passivated with basic (a) and acidic (b) $(NH_4)_2S$ solutions. The insets show the CV hysteresis characteristics of the samples.

A measure of the total effective border traps density (ΔN_{bt}) can be obtained by investigating the *C*–*V* hysteresis characteristics.[18,21] Figure 6 plots the border traps estimation curves of the GaSb MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions, which is calculated from the difference in *C*–*V* hysteresis from reverse to forward bias direction (ΔC) divided by the electronic charge.[18] The ΔN_{bt} of GaSb MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions is extracted by integrating the border traps estimation curves. Compared with the samples treated with basic $(NH_4)_2S$ solution, ΔN_{bt} of the GaSb MOSCAPs passivated with acidic $(NH_4)_2S$ solutions is significantly reduced from $\sim 7.58 \times 10^{12}$ cm^{-2} to $\sim 3.56 \times 10^{12}$ cm^{-2}.

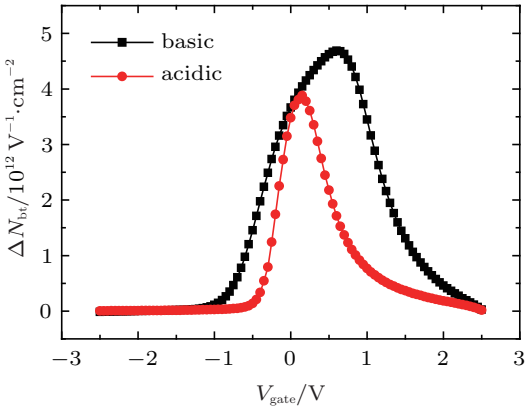


Fig. 6. (color online) Border traps estimation curves of GaSb MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions.

Figure 7(a) shows typical measured parallel G_p/ω versus frequency curves for different gate biases of the MOSCAPs passivated with acidic $(NH_4)_2S$ solution. The observed peak

shift indicates the efficiency of the surface Fermi level movement over the energy gap. The D_{it} distribution in the upper half of the band gap was determined using the conductance method,[22,23] as plotted in Fig. 7(b). Low temperature (77 K) measurement was performed to investigate the D_{it} distribution over a wider range of the band gap. The extracted D_{it} distribution is consistent with previously reported results.[5] Compared with the samples treated with basic $(NH_4)_2S$ solution, D_{it} is reduced by ~53% for the samples treated with acidic $(NH_4)_2S$ solution, from $\sim 16 \times 10^{12}$ $eV^{-1}\cdot cm^{-2}$ to $\sim 7.5 \times 10^{12}$ $eV^{-1}\cdot cm^{-2}$, which is also lower than previously reported D_{it} of the HfAlO/GaSb gate stacks treated with basic $(NH_4)_2S$ solution.[24] D_{it} can be further reduced by optimizing the process parameters of the acidic $(NH_4)_2S$ solution treatment, such as passivation time and pH value, which may also reduce the *C*–*V* hump behavior. It should be noted that, no thermal annealing was performed in this work. It is believed that forming gas annealing can further improve the interfacial properties of GaSb devices.[25]

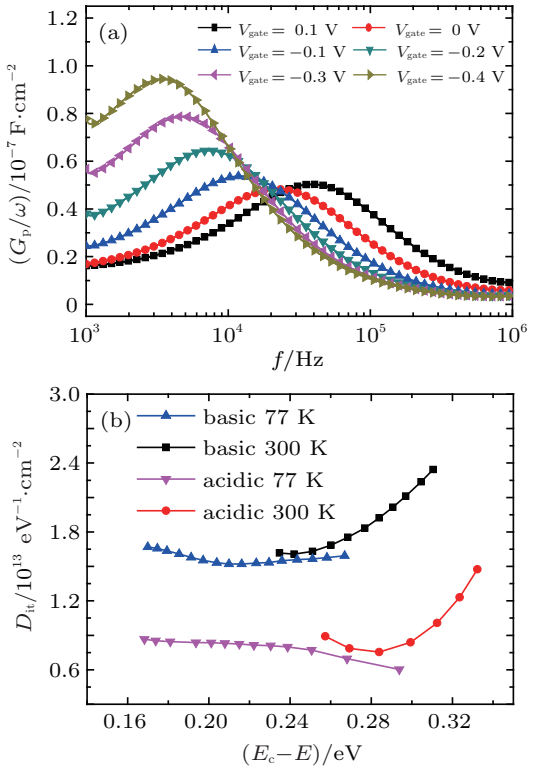


Fig. 7. (color online) (a) Typical measured parallel G_p/ω versus frequency curves for different gate biases of the MOSCAPs passivated with acidic $(NH_4)_2S$ solution. (b) D_{it} distributions of MOSCAPs passivated with basic and acidic $(NH_4)_2S$ solutions.

4. Conclusions

In summary, sulfur passivation with acidic $(NH_4)_2S$ solutions was found to be a promising method to improve the properties of GaSb MOS devices. Gate leakage current, frequency dispersion, border traps, and interface traps are all reduced for samples treated with acidic $(NH_4)_2S$ solution, compared with those treated with basic $(NH_4)_2S$ solution. These improvements can be explained by acidic $(NH_4)_2S$ solution reducing GaO_x interfacial layer and enhancing sulfur passivation on the surface of the GaSb substrates compared with basic $(NH_4)_2S$ solution.

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