Extended Abstracts of the 2008 International Conference on Solid State Devices and Materials, Tsukuba, 2008, pp. 1062-1063

G-9-5

Improved electrical characteristics of atomic-layer-deposited Al_2O_3/GaAs MOS capacitors with $(NH_4)_2S$-C_4H_9OH sulfide treatment

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1. Introduction

GaAs metal-oxide-semiconductor (MOS) capacitors with different high-*k* gate dielectrics have been of more interest in recent years. Fermi-level-pinning is the most challenging issue, which arises from the remarkably high interfacial state density (D_{it}) at the interface. This problem casts some doubts on the anticipated superior electrical performance of NFETs with GaAs channel. In addition, relatively poor thermal stability needs to be cautiously tackled. As a result, additional surface passivation, such as surlfur chemical treatment, Si or Ge cap layer seems unavoidably required in order to effectively reduce native oxide and D_{it}. In this study, we found that the employed $(NH_4)_2S$-C_4H_9OH chemical treatment can significantly improve the high-*k*/GaAs MOS capacitor performance.

2. Experimental

MOSCAP structures were fabricated on high Si-doped (n-type, ~1 x 10^{18} cm^{-3}) GaAs(100) substrates. At first, the GaAs was rinsed in the diluted NH_4OH (1%) solution for 1min. Furthermore, we performed $(NH_4)_2S$ treatments in combination with either H_2O or C_4H_9OH solvent on GaAs surface prior to high-*k* deposition. Surface chemistry was analyzed by employing x-ray photoelectron spectroscopy (XPS) that Al $K\alpha$ is used as an excitation source. The Al_2O_3 thin film was then deposited by atomic-layer-deposited (ALD) system at 300 °C as gate dielectric followed by post deposition annealing (PDA) at 600 °C for 30 s in an O_2 ambient. Sputtered Pt dots were patterned as circular gate electrodes through the specific shadow mask with the Al for backside contact. The capacitance−voltage ($C-V$) and gate leakage current ($I-V$) curves on Pt/Al_2O_3/GaAs MOS capacitors were measured using an HP4284 and Keithley 4200, respectively.

3. Results and Discussion

Figure 1 displays As*2p3* and Ga*2p3* photoemission spectra with different wet-chemical cleaning processes (WCPs); the composition ratios were summarized in Table I. It was observed that both kinds of native oxides, especially for As_2O_x (x=3,5), were obviously reduced with using $(NH_4)_2S$ solutions; moreover, dissolving the sulfide in C_4H_9OH is more effective as compared to dissolving in (H_2O). The values of As_2O_x/As_{tot}(As-As/As_{tot}) were 97.8%(30.1%) for GaAs surface with deionized water (DIW) rinse only; its value can be reduced to 52.6%(22.6%) and 38.8%(20.1%) for the sulfide solution (H_2O) and the sulfide solution (C_4H_9OH) treatments, respectively. Increasing the concentration of the sulfide solution (C_4H_9OH) can further eliminate the formation of As oxides. The effects of these surface treatments on the $C-V$ characteristics of Al_2O_3/GaAs MOS capacitors are shown in Figs. 2(a) and 2(b), respectively. As can be seen, the $C-V$ frequency dispersion was improved by the sulfide treatments; subsequent 600 °C PDA further improved this dispersion behavior. Here, we qualitatively examine the interface properties through the variation of △C and △V values (Fig. 3) that are defined: △C(@V_g=4V) = 1 - C(@*100kHz*) / C(@*1kHz*) and △V(@C_{FB}) = V_g(@*1kHz*) - V_g(@*100kHz*), respectively. It was observed that the sample subject to sulfide solution (C_4H_9OH) revealed the smaller △C/△V and lower leakage current density (J_g) than that with sulfide solution (H_2O). The values of the △C and △V were 17-20% and 0.9-1.4 V for the as-deposited sample and we can improve these two values to 17-14% and 0.6-0.7 V by using 10% sulfide solution (C_4H_9OH). Fig. 4 shows the corresponding leakage current characteristics before and after 600 °C O_2-PDA. The result displayed that the GaAs capacitors through 10% sulfide solution (C_4H_9OH) treatment actually possessed the higher thermal stability due to the smaller amounts of the As-As species and As oxides. According to this chemical reaction: $As_2O_3 + GaAs \rightarrow Ga_2O_3 + 4As$, we suggested that the lower As oxides existed close to the dielectric interface should accompany with the reduced formation of the metallic As by-product after thermal processing, thus, a lower leakage current was characterized. The fabricated ALD-Al_2O_3/GaAs MOS capacitors in this work after optimized surface treatment showed the comparable insulating properties with respect to $HfSiO_x$ dielectrics reported on n-GaAs in Fig. 5.

4. Conclusions

In summary, we effectively improved the electrical properties of Pt/ALD-Al_2O_3/GaAs MOSCAP by dissolving $(NH_4)_2S$ in C_4H_9OH solvent for the chemical treatment. We found this solution did result in superior electrical characteristics than the conventional $(NH_4)_2S$ solution (H_2O). Further optimization of the sulfide solution (C_4H_9OH) conditions for the treatment of GaAs surface prior to high-*k* deposition is seems indispensable in pursuit of superior high-performance high-*k*/GaAs MOSFETs.

References

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Wet Clean	As-As/As_{Total}	As-S/As_{Total}	Ga-S/Ga_{Total}	As_2O_3/As_{Total}	Ga_2O_3/Ga_{Total}
D.I water only	30.1 %	–	–	97.8 %	54.3 %
NH_4OH only	23.5 %	–	–	73.4 %	25.8%
1% Sulf.(H_2O)	22.6 %	18.9 %	7.1 %	52.6 %	26.4 %
1%Sulf.(C_4H_9OH)	20.1 %	17.8 %	7.3 %	38.8 %	22.7 %
10% Sulf.(C_4H_9OH)	13.9 %	16.3 %	10.9 %	23.2 %	24.6 %

Table. 1 Chemical ratios calculated by XPS fitting results according to the different WCPs in Fig. 1.

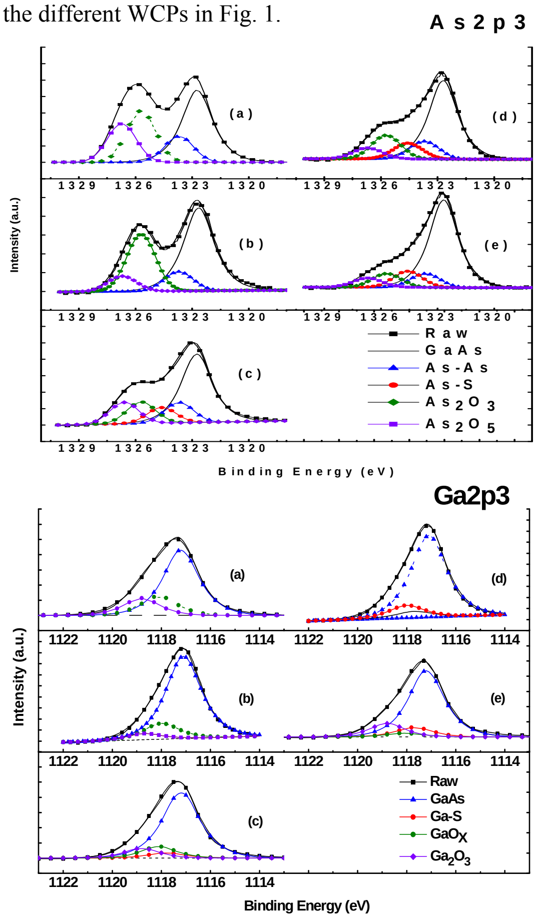
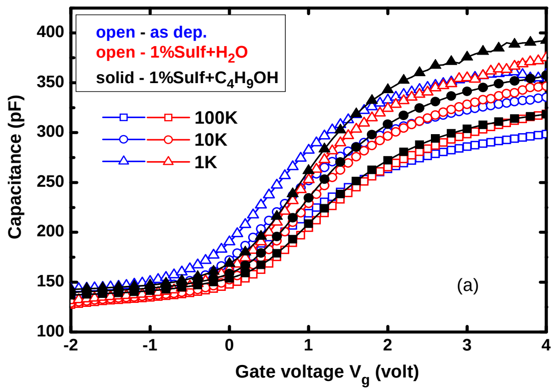


Fig. 1 As*2p3* and Ga*2p3* XPS spectra of GaAs surface receiving various WCPs: (a) DIW only, (b) NH_4OH only, (c)1%-Sulf.(H_2O), (d) 1%-Sulf.(C_4H_9OH), and (e) 10%-Sulf.(C_4H_9OH). Note that the cleaned surface was exposed to air for 30 min.



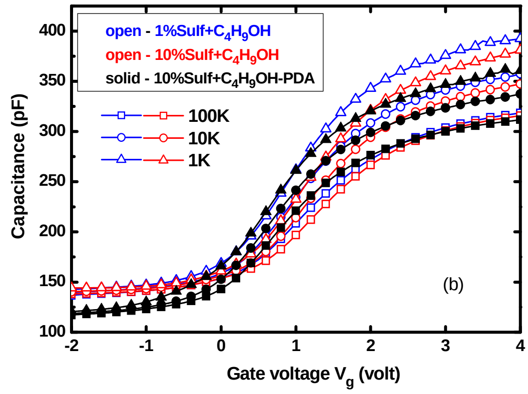


Fig. 2 Multi frequency *C-V* curves of Pt/Al_2O_3/n-GaAs capacitors with (a) different WCPs and (b) different WCPs and O_2 annealing.

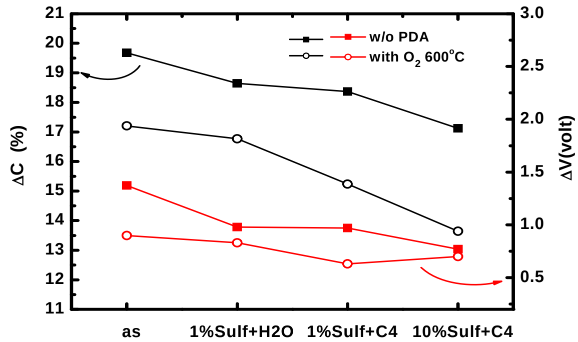


Fig. 3 variations of △C and △V values of Pt/Al_2O_3/n-GaAs capacitors after different WCPs and post annealing.

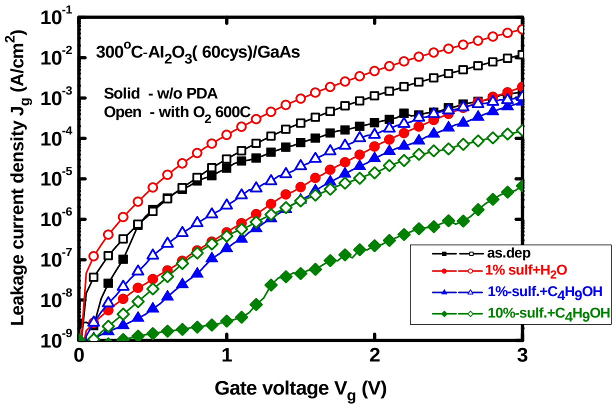


Fig. 4 Gate leakage current characteristics of Pt/Al_2O_3/n-GaAs capacitors with different WCPs. The Al_2O_3 thin films were deposited at 300 °C for 60 cycles.

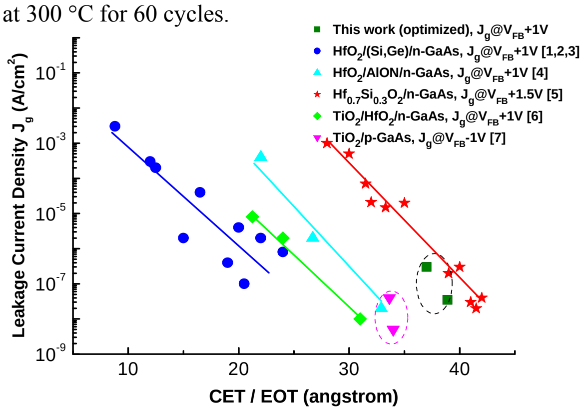


Fig. 5 Comparison of J_g versus CET or EOT characteristics in this work with other's published data.