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Effects of HCl treatment and predeposition vacuum annealing on Al₂O₃/GaSb/GaAs metal–oxide–semiconductor structures

Takahiro Gotow^{1,2*}, Sachie Fujikawa¹, Hiroki I. Fujishiro¹, Mutsuo Ogura², Tetsuji Yasuda², and Tatsuro Maeda^{1,2}

¹Faculty of Industrial Science and Technology, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan

²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562, Japan

E-mail: takahiro-gotou@aist.go.jp

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The effects of HCl treatment and predeposition vacuum annealing (VA) on n-type GaSb/GaAs metal–oxide–semiconductor (MOS) structures with the atomic layer deposition (ALD) of Al₂O₃ dielectrics are studied. We obtained MOS structures with good Fermi level modulation by HCl treatment prior to the deposition of Al₂O₃. From X-ray photoelectron spectroscopy (XPS) analysis, we found that the Ga₂O₃ content increases during the Al₂O₃ deposition, whereas the amounts of Sb components are reduced. The excess growth of Ga₂O₃ is inhibited by the reductions in the amounts of Sb components by the HCl treatment. Further reductions in the amounts of Sb components are observed following predeposition VA, indicating a lower density of states (D_{it}). However, the frequency dispersion in the capacitance–voltage (C – V) characteristics increases with predeposition VA at higher temperatures. © 2015 The Japan Society of Applied Physics

1. Introduction

“6.1 Å III–V CMOS” devices have recently been proposed as potential candidates for high-performance/low-power complementary metal–oxide–semiconductor (CMOS) devices.^{1,2} 6.1 Å III–V materials such as InAs and GaSb have very high electron or hole mobility and saturation velocity, making them ideal III–V CMOS channel materials. GaSb has the highest hole mobility among all the III–V materials. The room-temperature hole mobility of GaSb is approximately $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is twice as high as that of Si.³ Thus, GaSb has been extensively studied as a channel material for pMOSFETs.^{4–7}

The nature of the GaSb surface prior to the deposition of dielectrics can directly affect the electrical properties of MOS structures. A native oxide layer composed of GaO_x and SbO_x is formed immediately on the GaSb surface after exposure to air.^{8,9} In order to remove the native oxide layer, HCl treatment has been widely used. However, the GaSb native oxide is not completely removed by the HCl treatment.¹⁰ Instead, the HCl treatment produces elemental Sb,¹¹ leading to series surface leakage. Therefore, the removal of the predeposition native oxide from the GaSb surface prior to dielectric growth is critical for the successful fabrication of MOS structures. It has been reported that high-temperature vacuum annealing (VA) is effective in removing native oxides from the GaSb surface,¹² whereas other studies have reported that GaO_x could not be removed after high-temperature VA.¹³

In this work, we study the effects of the HCl treatment and predeposition VA prior to atomic layer deposition (ALD)-Al₂O₃ deposition on the capacitance–voltage (C – V) characteristics of n-type Al₂O₃/GaSb/GaAs MOS structures and investigate the chemical states of the Al₂O₃/GaSb interface by X-ray photoelectron spectroscopy (XPS) analysis. For the preparation of a high-quality GaSb surface for GaSb pMOSFET operation, we employ an epitaxial n-type GaSb layer on a GaAs wafer obtained by metalorganic chemical vapor deposition (MOCVD) technique. In comparison with GaSb substrates, here, the topmost GaSb surface can be controlled with an Sb cap by an epitaxial growth technique, and a GaSb layer can be obtained on a relatively larger and semi-insulating wafer, which is favorable for the RF application and the integration of the photonic device.

2. Experimental procedure

Te-doped GaSb layers were grown on a semi-insulating (SI)-GaAs substrate and a Te-doped n-type GaAs substrate by MOCVD using triethylgallium (TEGa), trimethylantimony (TMSb), and diethyltellurium (DETe) as the n-type dopant source. Before GaSb growth, GaAs buffer layers were grown on the GaAs substrate at 630 °C to provide a smooth GaAs surface free from polishing damage. To obtain highly crystalline GaSb layers, GaSb low-temperature (LT) buffer layers were grown at 440 °C. Then, GaSb layers were grown at 570 °C with a thickness of 400 nm. The substrate was then cooled below 200 °C in an Sb flux to passivate the GaSb surface, which is a well-known MOCVD technique to prevent Sb desorption at high temperatures.

n-type GaSb MOS structures were fabricated with an ALD-Al₂O₃ gate dielectric. The samples were degreased with acetone and isopropyl alcohol. To reduce GaSb native oxides, the samples were dipped in HCl (HCl : H₂O = 1 : 10) for 20 min. For the predeposition cleaning, VA at 350 °C for 30 min was performed in an ALD chamber. In order to determine the effects of various surface treatments, we fabricated GaSb MOS structures (1) without the HCl treatment, (2) with the HCl treatment but without the predeposition VA, and (3) with both the HCl treatment and predeposition VA. For GaSb MOS structures, ALD-Al₂O₃ films were deposited at 300 °C using trimethylaluminum (TMA) and water, and postdeposition annealing was performed at 400 °C for 2 min in the same ALD chamber. Au gate electrodes were created by electron beam evaporation. After back-side contact formation, postmetal annealing (PMA) was performed at 200 °C for 30 min.

3. Results and discussion

It is important to provide highly crystalline epitaxial GaSb layers on large GaAs wafers capable of fabricating III–V CMOS devices on the same substrates. Therefore, GaSb layers were grown on GaAs substrates by MOCVD. Figures 1(a) and 1(b) show transmission electron microscopy (TEM) images of the fabricated Au/Al₂O₃/GaSb/GaAs heterostructure for GaSb MOS structures. In Fig. 1(a), we clearly observe three layers of Au, Al₂O₃, and GaSb on the GaAs substrate, where the thicknesses of the Au, Al₂O₃, and

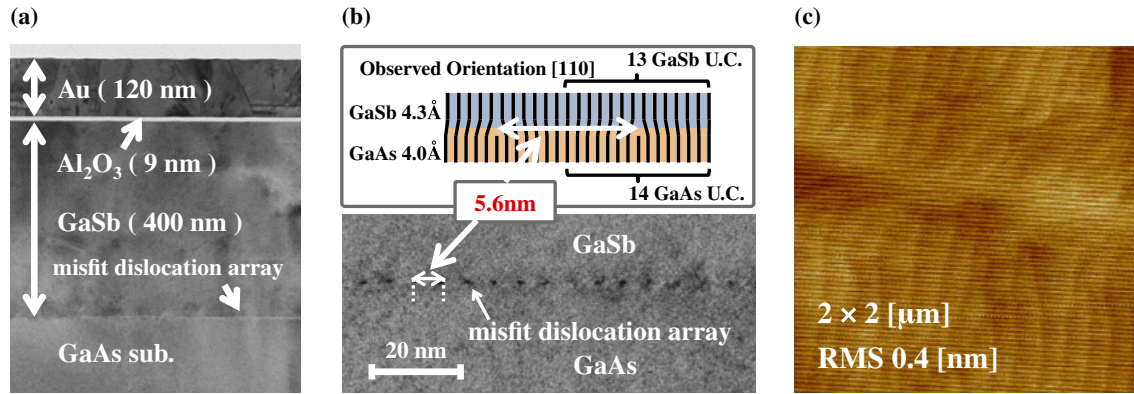


Fig. 1. (Color online) TEM images of (a) Au/Al₂O₃/GaSb/GaAs MOS structure, (b) GaSb/GaAs interface with periodic misfit dislocation array, and (c) AFM image of GaSb epiwafer surface.

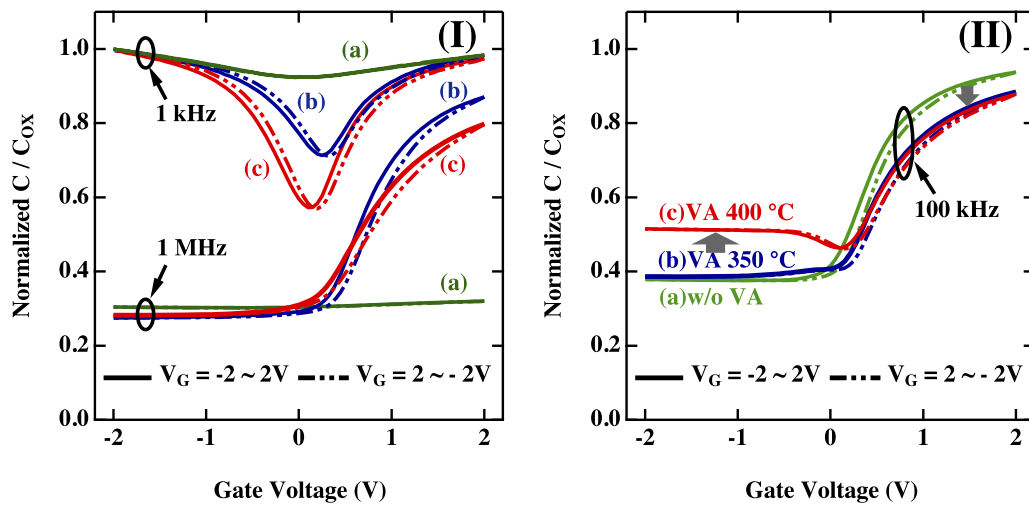


Fig. 2. (Color online) (I) Bidirectional C - V characteristics at frequencies of 1 kHz and 1 MHz for GaSb MOS structures (a) without HCl treatment, (b) with HCl treatment but without predeposition VA, and (c) with both HCl treatment and predeposition VA at 350 °C. (II) Bidirectional C - V characteristics at frequency of 100 kHz for GaSb MOS structures (a) without predeposition VA, and with predeposition VA at (b) 350 and (c) 400 °C.

GaSb layers are 120, 9, and 400 nm, respectively. We clearly identified the formation of the misfit dislocation array, as shown in Fig. 1(b). Despite a large lattice mismatch of 8%, the heteroepitaxy of high-quality GaSb layers on GaAs substrates has already been reported^{14,15} owing to the formation of a highly periodic array of 90° misfit dislocations at the GaSb/GaAs interface.¹⁶ The distance between two misfit dislocations is approximately 5.6 nm, which corresponds perfectly to 13 GaSb unit cells with 14 unit cells of GaAs substrates, as shown in Fig. 1(b). This misfit dislocation array leads to a significant decrease in crystal defect density in GaSb layers and to a suppression of the surface roughening of GaSb layers. In order to study the surface morphology of the epitaxial GaSb layer, ex situ atomic force microscopy (AFM) measurements were carried out. The AFM image in Fig. 1(c) shows the step-terrace structures on an epitaxially grown GaSb surface. The root-mean-square (RMS) surface roughness of the GaSb layers is 0.4 nm, which is sufficiently flat to fabricate a MOS device. Note that we could not observe the step-terrace structures without Sb passivation. Hence, Sb passivation is effective in preserving the surface structure. From Hall measurements, GaSb layers show an electron mobility of $\mu_e \sim 2400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a donor con-

centration of $N_D \sim 2 \times 10^{17} \text{ cm}^{-3}$. This electron mobility corresponds to a value of approximately 80% of the bulk mobility.¹⁷ The highly crystalline GaSb epitaxial layers on GaAs substrates were obtained for GaSb MOS structures. These GaSb epitaxial wafers have the capability to develop a 6.1 Å III-V CMOS in conjunction with InAs MOSFETs.

In order to realize GaSb pMOSFETs, it is important to confirm an inversion response from the C - V curve with n-type GaSb substrates. Therefore, C - V measurements were conducted to characterize the Al₂O₃/n-type GaSb MOS structures. All C - V measurements were acquired at room temperature at frequencies of 1 kHz and 1 MHz. Figure 2-(I) shows the C - V characteristics of the Al₂O₃/GaSb MOS (a) without and (b) with the HCl treatment. The GaSb MOS structure without the HCl treatment shows strong Fermi level pinning in the C - V characteristics with a very fast interface trap density (D_{it}) response, whereas the MOS structure with the HCl treatment demonstrates good Fermi level modulation from the accumulation region to the inversion region. Therefore, the HCl treatment to remove native oxides is a critical step to reduce D_{it} . Figure 2-(I) shows the C - V characteristics of the Al₂O₃/GaSb MOS prepared (b) without and (c) with VA at 350 °C. The 1 kHz capacitance of the MOS

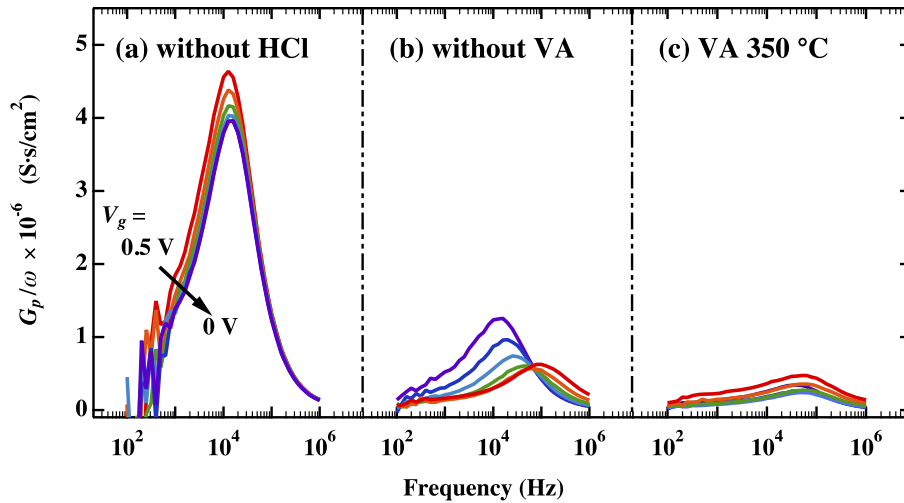


Fig. 3. (Color online) Conductance (G_p/ω) as a function of frequency of GaSb MOS structures (a) without HCl treatment and with predeposition VA at (b) 350 and at (c) 400 °C.

structure prepared with VA is a lower value than that without VA in the depletion region, which indicates that VA improves the interfacial properties, especially in the depletion region. On the other hand, the frequency dispersion in the accumulation region increased for the sample with VA. The frequency dispersion in the accumulation region of the C - V characteristics suggests the effect of a high D_{it} near the conduction band. Therefore, it is found that VA improved the interface property only in the depletion region and not in both the accumulation and inversion regions. Figure 2-(II) shows the difference between the C - V characteristics without and with VA at 350 and 400 °C. In addition to the capacitance reduction in the accumulation region, we observed a larger frequency dispersion in capacitance in the inversion region with the higher-temperature VA. The capacitance value in the inversion region in the C - V characteristics increases with increasing VA temperature. The inversion response accounts for the supply of minority carriers with the interface state contributions and bulk thermal generation across the space charge layer owing to bulk traps in the depletion layer.¹⁸⁾ It is expected that the higher-temperature VA will form the bulk traps in GaSb, which deteriorate the interface quality in the inversion region.

For further investigation of the effect of VA in GaSb MOS structures, the D_{it} distribution was evaluated by the conductance method in the depletion region. All conductance peaks were acquired at room temperature at frequencies ranging from 100 Hz to 1 MHz. The range of the gate voltage is from 0 to 0.5 V in 0.1 V steps, which corresponds to the energy level of the upper half of the bandgap near the midgap. Figure 3 shows the conductance (G_p/ω) of $\text{Al}_2\text{O}_3/\text{GaSb}/\text{GaAs}$ MOS structures as a function of frequency, which is indicative of the interface state response. Clear G_p/ω peaks were observed from all samples prepared (a) without the HCl treatment, (b) with the HCl treatment but without VA, and (c) with both the HCl treatment and VA. The comparison of the G_p/ω values of the GaSb MOS structures without and with VA showed that the values of the G_p/ω peaks are reduced by VA because of the suppression of the slow $\text{Al}_2\text{O}_3/\text{GaSb}$ interface state response. From the ob-

served G_p/ω peaks, we estimated the time constants to be $0.7\text{--}2.5 \times 10^{-5}$ s, which are comparable to those obtained from previous studies.¹⁹⁾ Minimum interface states of $\sim 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ were estimated for the sample without VA, whereas D_{it} for the sample with VA was on the order of $\sim 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, a value that is comparable to those obtained from previous studies.⁸⁾

We observed various modulations in the C - V characteristics resulting from different surface treatments. The maximum capacitance of $\sim 0.7 \mu\text{F}/\text{cm}^2$ and hysteresis in the C - V characteristics for each sample showed almost no variation. Therefore, it is reasonable that the cause of the different C - V characteristics is in the $\text{Al}_2\text{O}_3/\text{GaSb}$ interface rather than in the Al_2O_3 dielectrics because all gate dielectrics were deposited by the same process. In order to clarify the chemical properties of the $\text{Al}_2\text{O}_3/\text{GaSb}$ interface, XPS analyses of Ga and Sb spectra utilizing Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) were conducted for the samples with various treatments on the GaSb surface. Structures of 1 nm $\text{Al}_2\text{O}_3/\text{GaSb}$ were fabricated for XPS measurement by the same procedures used for the GaSb MOS structures. Figure 4 shows (I) Sb 3d_{3/2} and (II) Ga 3d XPS spectra of 1 nm $\text{Al}_2\text{O}_3/\text{GaSb}$ structures as received on the (a) GaSb/GaAs epiwafer, (b) without the HCl treatment, (c) with the HCl treatment but without VA, with both the HCl treatment and VA at (d) 350, and (e) 400 °C. The spectral analysis of the Sb 3d_{3/2} core level reveals five separate core-level features, which have been assigned to Sb 3d_{3/2} (537.6 eV), Sb-Sb (538.4 eV), Sb₂O₃ (540.0 eV), Sb₂O₅ (540.8 eV), and the plasmon loss feature according to previous studies.²⁰⁾ Note that a clear Sb-Sb peak in the as-received GaSb/GaAs epiwafer is clearly detected because excess Sb is absorbed on the surface of the as-received GaSb/GaAs epiwafer through the substrate cooling process. The Ga 3d core level can be resolved into three components, Ga 3d_{3/2,5/2} (19.4 eV), GaO (20.4 eV), and Ga₂O₃ (21.0 eV).²¹⁾ Figure 4 shows the ratios of the fitted peak areas of (III) Sb-Sb, Sb₂O₃, and Sb₂O₅, and (IV) GaO and Ga₂O₃ to those of the bulk peak from the Ga 3d and Sb 3d_{3/2} core-level spectra. The comparison of the data shown in Figs. 4(a) and 4(b) reveals that there is a

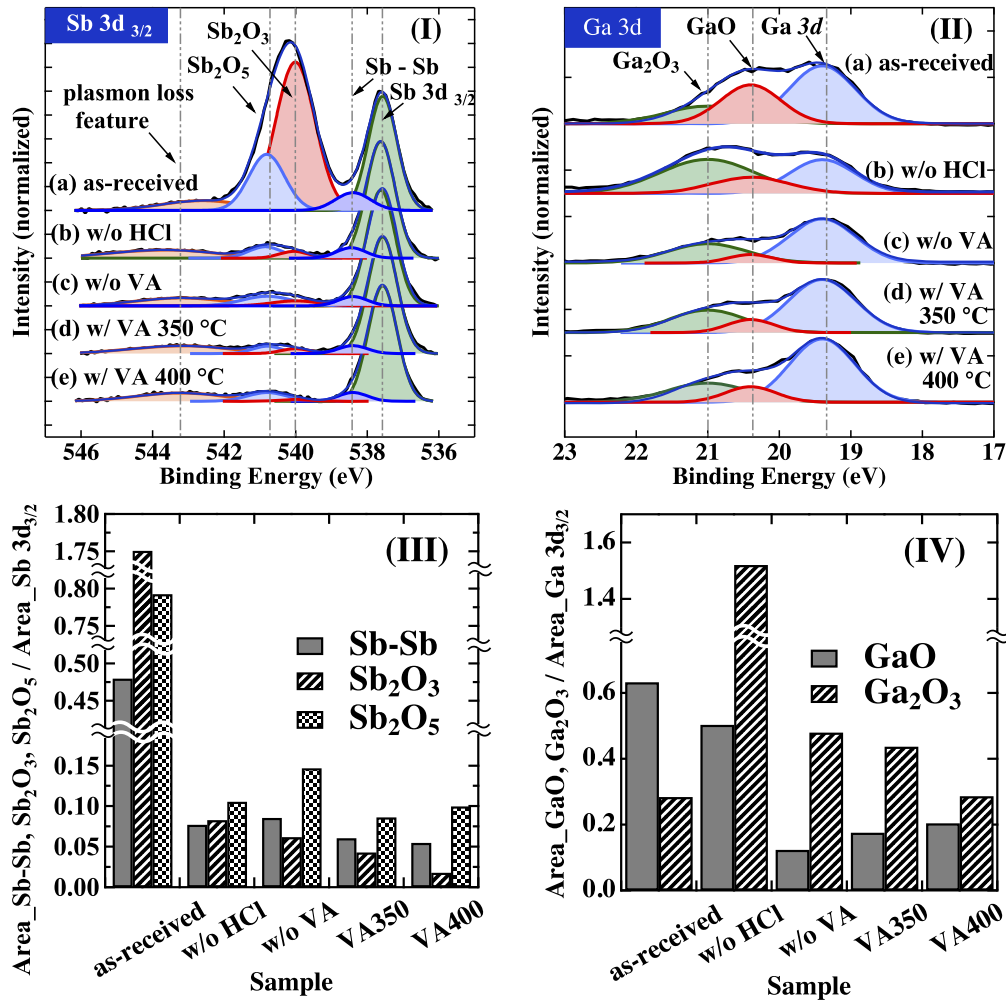
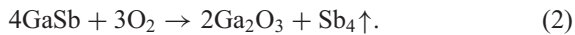
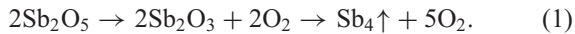


Fig. 4. (Color online) (I) Sb 3d and (II) Ga 3d XPS spectra of (a) as-received GaSb epiwafer, (b) sample without HCl treatment, (c) sample with HCl treatment but without predeposition VA, and samples with predeposition VA at (d) 350 and at (e) 400 °C; ratios of the fitted oxide peak areas of (III) Sb-Sb, Sb₂O₃, and Sb₂O₅, and (IV) GaO and Ga₂O₃ to those of the bulk peaks from the Sb 3d and Ga 3d core-level spectra.

considerable reduction in the amounts of both Sb-Sb and Sb oxides. Through the Al₂O₃ deposition at 300 °C, elemental Sb and Sb oxides can be desorbed thermally. There is a significant amount of Ga₂O₃ of 0.3 nm thickness, which is thicker than the layer of native Ga oxides, as shown in Fig. 4-(IV). This means that the Sb oxide desorption process leads to substantial Ga₂O₃ growth, with mechanisms of the thermal desorption of Sb oxides on GaSb as follows:¹³⁾



In addition to Ga₂O₃ growth, the elemental Sb formed through an Sb oxide thermal reduction process may remain at the interface. Actually, the reduction in the amount of Sb-Sb is smaller than that in the amounts of Sb oxides. Even if the amounts of Sb oxides are significantly reduced thermally at the interface through the Al₂O₃ deposition, the sample with excess Ga₂O₃ growth shows strong Fermi level pinning [Fig. 2-(I) (a)]. Therefore, the suppression of Ga₂O₃ growth is the key to obtaining a high-quality GaSb MOS interface. By performing the HCl treatment just before the Al₂O₃ deposition, the growth of Ga₂O₃ is clearly suppressed, as shown in Fig. 4(c), demonstrating superior gate modulation in the *C-V* characteristics. Hence, it is important to remove

the Sb oxide by HCl treatment before the Al₂O₃ deposition in order to suppress the growth of Ga₂O₃ because oxygen in the Sb oxide is the cause of the oxidation of GaSb that results in the formation of Ga₂O₃. The HCl treatment before the Al₂O₃ deposition is effective in removing the Sb oxide and inhibiting the growth of Ga₂O₃, but both oxides still remain.

Next, we investigate the effect of the VA at 350 °C [Fig. 4(d)]. There are decreases in the amounts of both Sb oxides or Sb-Sb following VA at 350 °C. The amount of Ga₂O₃ is reduced, whereas the amount of GaO is increased; thus, the total amount of Ga oxides is unchanged. Consequently, it is possible that the decrease in the minimum of *D_{it}* can be attributed to the reductions in the amounts of Sb components. It is reported that the existence of elemental Sb is a major issue contributing to *D_{it}*, and the Fermi level pinning can be mitigated by the absence of elemental Sb at the Al₂O₃/GaSb interface.⁸⁾ Further elemental Sb removal is expected by following higher-temperature VA. However, elemental Sb and Sb oxides are not removed completely at a higher temperature of 400 °C. Ga oxides also remain and are thermally stable up to 400 °C [Fig. 4(e)]. We observed the increase in the amount of GaO and the decrease in the amount of Ga₂O₃ following predeposition VA at 400 °C and interface roughening in TEM images. These phenomena

could thereby result in fast traps near the conduction band, indicating frequency dispersion with a positive bias. Higher-temperature VA also generates bulk traps by Sb desorption, leading to an inversion response,¹⁸⁾ as shown in Fig. 3. Therefore, it is difficult to remove the Sb oxide or elemental Sb by VA, and it is inevitable that the thermal deoxidation process of Sb oxides forms elemental Sb. It is important to remove the Sb source before a thermal process such as Sb thermal desorption or high-temperature deposition. To avoid the formation of elemental Sb, a low-temperature reduction atmosphere, such as hydrogen plasma, and low-temperature dielectric deposition are favorable for obtaining a high-quality GaSb MOS interface.⁶⁾

4. Conclusions

We confirmed by XPS analysis that the Sb oxide desorption process leads to substantial Ga₂O₃ growth. GaSb MOS structures with an unpinning Fermi level were demonstrated by the HCl treatment prior to the deposition of Al₂O₃ because the growth of Ga₂O₃ was inhibited by the reduction in the amount of an Sb component by the HCl treatment. We clearly observed that predeposition VA is effective for reducing D_{it} . Because the amounts of elemental Sb and Sb₂O₃ decrease with predeposition VA, the reduction in the amount of an Sb component is the key to obtaining good Fermi level modulation. Increasing the VA temperature results in lower D_{it} ; however, there is an increase in frequency dispersion in the C - V characteristics at the same time. Therefore, it is crucial to find appropriate conditions for native oxide removal and to prevent the formation of elemental Sb.

Acknowledgements

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