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# Engineering of AlON interlayer in  $Al_2O_3/AlON/In_{0.53}Ga_{0.47}As$  gate stacks by thermal atomic layer deposition



Woo Chul Lee $\mathrm{^{a,b}}$  $\mathrm{^{a,b}}$  $\mathrm{^{a,b}}$  $\mathrm{^{a,b}}$ , Cheol Jin Cho $\mathrm{^{a,b}}$  $\mathrm{^{a,b}}$  $\mathrm{^{a,b}}$ , Suk-In Park $\mathrm{^c}$  $\mathrm{^c}$  $\mathrm{^c}$ , Dong-Hwan Jun $\mathrm{^d}$  $\mathrm{^d}$  $\mathrm{^d}$ , Jin Dong Song $\mathrm{^c}$ , Cheol Seong Hwang<sup>[b](#page-0-1)</sup>, Seong Keun Kim<sup>a,\*</sup>

<span id="page-0-0"></span><sup>a</sup> Center for Electronic Materials, Korea Institute of Science and Technology, Seoul, 02792, South Korea

<span id="page-0-1"></span><sup>b</sup> Department of Materials Science and Engineering, Inter-university Semiconductor Research Center, College of Engineering, Seoul National University, Seoul, 08826, South Korea

<span id="page-0-2"></span><sup>c</sup> Center for Opto-Electronic Materials, Korea Institute of Science and Technology, Seoul, 02792, South Korea

<span id="page-0-3"></span><sup>d</sup> Korea Advanced Nano Fab Center, Suwon, 16229, South Korea

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# ABSTRACT

The presence of an AlN interfacial layer in high-k/In<sub>0.53</sub>Ga<sub>0.47</sub>As gate stacks improves the interfacial properties and enhances the electrical performance of devices. However, pure AlN is rarely grown by atomic layer deposition (ALD) because of the low reactivity of  $NH<sub>3</sub>$  toward the common Al-precursor and the predisposition to oxidation of the grown AlN layer. Although a plasma-enhanced ALD technique significantly suppresses the oxygen content in the grown AlN layer, the deterioration of the interface properties by plasma-damage is a critical issue. In this work, an AlON interlayer was engineered by optimizing the NH3 feeding time in thermal ALD to improve the interface quality in  $\text{Al}_2\text{O}_3/\text{AlON}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  capacitors. It was determined that a mere increase in the NH3 feeding time during the ALD of the AlON film resulted in a higher nitrogen incorporation into the AlON interlayer, leading to a reduction in the interface trap density. Furthermore, the out-diffusion of elements from the In<sub>0.53</sub>Ga<sub>0.47</sub>As layer was effectively suppressed by increasing the NH<sub>3</sub> feeding time. This work demonstrates that simple process optimization can improve the interface quality in high-k/In<sub>0.53</sub>Ga<sub>0.47</sub>As gate stacks without the use of any plasma-activated nitrogen source.

### 1. Introduction

Group III-V semiconductors, such as  $In<sub>0.53</sub>Ga<sub>0.47</sub>As$  are promising channel materials beyond Si, which can overcome the challenges of continuous scaling of metal-insulator-semiconductor field effect transistors (MISFETs) in logic devices because of their high electron mobility [[1](#page--1-0)]. However, the integration of III-V materials with high-k dielectrics is currently limited. This is because a considerably large number of defects at the high-k oxide/ $In<sub>0.53</sub>Ga<sub>0.47</sub>As$  interface pose a significant challenge in the implementation of high-k oxide/  $In<sub>0.53</sub>Ga<sub>0.47</sub>As structures. The oxidation of III-V materials results in the$ further creation of As-As dimers and  $Ga_{As}$  antisite defects, significantly increasing the interface trap density  $(D_{it})$  and inducing Fermi level pinning [\[2,](#page--1-1)[3](#page--1-2)]. Considerable efforts have been dedicated to the improvement of interface quality of high-k/In<sub>0.53</sub>Ga<sub>0.47</sub>As structures [4–[10](#page--1-3)]

Aluminum oxide  $(Al_2O_3)$  has been reported to form better interfaces with In<sub>0.53</sub>Ga<sub>0.[4](#page--1-3)7</sub>As than HfO<sub>2</sub> and ZrO<sub>2</sub> [4[,5\]](#page--1-4). This is because Al<sub>2</sub>O<sub>3</sub> acts as an oxygen diffusion barrier and suppresses oxidation of the underlying  $In<sub>0.53</sub>Ga<sub>0.47</sub>As layer. In addition, trimethylaluminum$ (TMA), the most common Al precursor for atomic layer deposition (ALD) of  $Al_2O_3$ , has a self-cleaning effect on  $In_{0.53}Ga_{0.47}As$  [[11\]](#page--1-5). It has been reported that TMA helps in the removal of As-As dimers by the formation of Al-As bonds [\[12](#page--1-6)]. However,  $Al_2O_3/In_{0.53}Ga_{0.47}As$  stacks still exhibit poor interface qualities compared with high-k/Si stacks; therefore, further passivation is necessary.

Aluminum nitride (AlN) has been considered as an alternate interfacial layer for the passivation of the  $In<sub>0.53</sub>Ga<sub>0.47</sub>As surface [13,14]$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As surface [13,14]$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As surface [13,14]$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As surface [13,14]$ . Its dielectric constant is comparable to that of  $Al_2O_3$ . It has been reported theoretically that formation of nitrogen bonds with the  $In<sub>0.53</sub>Ga<sub>0.47</sub>As$ surface does not introduce interface states in the bandgap of  $In<sub>0.53</sub>Ga<sub>0.47</sub>As [15].$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As [15].$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As [15].$  A notable reduction in the  $D_{it}$  was also experimentally observed by the implementation of an AlN interfacial passivation layer [\[13](#page--1-7)].

The growth of AlN films by ALD is generally performed at a very high temperature ( $> 340$  °C) because of the low reactivity of NH<sub>3</sub>. It is a significant challenge to form an oxygen-free AlN layer using ALD because Al atoms are easily oxidized by reaction with residual oxygen in

E-mail address: [s.k.kim@kist.re.kr](mailto:s.k.kim@kist.re.kr) (S.K. Kim).

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<span id="page-0-4"></span><sup>∗</sup> Corresponding author.

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Fig. 1. C−V curves of (a) Al2O3/In0.53Ga0.47As and Al2O3/AlON/In0.53Ga0.47As prepared at NH3 feeding times of (b) 5, (c) 20, (d) 40, and (e) 60 s during the growth of AlON interlayer. (f) Variation in the V<sub>FB</sub> of the MIS capacitors as a function of the NH<sub>3</sub> feeding time.

the reactor rather than with  $NH<sub>3</sub>$  at such high temperatures. Although NH3 plasma is effective in suppressing the oxygen content of aluminum oxynitride (AlON) films, the activated species in the plasma could significantly deteriorate the interface properties.

In this study, engineering of the AlON interlayer was performed to suppress the  $D_{it}$  of  $Al_2O_3/AlON/In_{0.53}Ga_{0.47}As$  stacks without the use of any activated species. The chemical and the electrical properties of the stacks were examined at various  $NH<sub>3</sub>$  feeding times.

#### 2. Materials and methods

A 1 µm-thick n-type Si-doped (3  $\times$   $10^{17}$  cm<sup>-3</sup>) In<sub>0.53</sub>Ga<sub>0.47</sub>As layer was grown on an insulating InP (001) substrate by metal-organic chemical vapor deposition. The substrate was degreased with methanol, acetone, and isopropanol, respectively. It was then cleaned with an HF solution and an NH4OH solution for 1 min each and loaded in the ALD reactor (CN-1 Co., Atomic Classic). The  $\text{Al}_2\text{O}_3$  and the AlON layers were grown on the  $In<sub>0.53</sub>Ga<sub>0.47</sub>As layer by ALD at a growth temperature of$ 350 °C. TMA was used as the Al source, and  $H_2O$  and  $NH_3$  were used as the reactant for the growth of  $Al_2O_3$  and AlON, respectively. The detailed experimental conditions are reported elsewhere [[16\]](#page--1-10). The flow rate of  $NH<sub>3</sub>$  was fixed at 500 sccm, and the  $NH<sub>3</sub>$  feeding time was varied from 5 to 60 s.

The film thickness was measured by spectroscopic ellipsometry. The chemical binding states in the films were examined by X-ray photoelectron spectroscopy (XPS). The binding energy was calibrated using the C 1s peak (248.8 eV) of adventitious carbon. The depth profile of elements was examined by time of flight secondary-ion mass spectroscopy (ToF-SIMS) using  $Cs<sup>+</sup>$  sputtering ions (with an acceleration energy of 3 keV).

MIS capacitors were fabricated to test the electrical properties of the films. Pt top electrodes were prepared on the  $Al_2O_3/AlON/$  $In<sub>0.53</sub>Ga<sub>0.47</sub>As stack by sputtering with a shadow mask. Post-metalli$ zation annealing was performed at 400 °C for 30 min in a forming gas [H2 (4.5%) and Ar (95.5%)] atmosphere. The capacitance−voltage (C−V) measurements were performed in a shielded probe station using an Agilent 4294 A Precision Impedance Analyzer.

## 3. Results and discussion

The  $NH<sub>3</sub>$  feeding time during the thermal ALD of AlON films was varied to engineer the interfacial AlON layer on  $In<sub>0.53</sub>Ga<sub>0.47</sub>As.$  The physical thickness of the AlON layers was approximately 2 nm irrespective of the NH<sub>3</sub> feeding time. The thickness of the upper  $Al_2O_3$  layer was approximately 7 nm.

[Fig. 1 \(a\)](#page-1-0)–(e) show the C−V curves of the Al<sub>2</sub>O<sub>3</sub> and the Al<sub>2</sub>O<sub>3</sub>/ 2 nm-thick AlON layers grown on  $In<sub>0.53</sub>Ga<sub>0.47</sub> As at different NH<sub>3</sub>$ feeding times. Two distinct features are observed in the C−V curves. First, the C−V curves shift to positive bias with an increase in the NH3 feeding time. [Fig. 1\(](#page-1-0)f) shows the variation in the flat band voltage ( $V_{FB}$ ) of the C−V curves as a function of the NH<sub>3</sub> feeding time. The V<sub>FB</sub> value is extracted using the second derivative method suggested by Winter et al. [[17\]](#page--1-11). The  $V_{FB}$  value increases from 0.6 to 1.1 V when the NH<sub>3</sub> feeding time is increased from 5 to 60 s. A positive shift in the C−V curve is primarily attributed to the increase in the negative fixed charge density at the dielectric/semiconductor interface. Choi et al. have recently reported, using ab-initio calculations, that nitrogen acts as a source of negative fixed charge in an  $Al_2O_3$ /semiconductor system [\[18](#page--1-12)]. Negara et al. also experimentally demonstrated that negative fixed charges are generated by the incorporation of nitrogen ions in the  $Al_2O_3$ gate insulator on III-V semiconductors [[19\]](#page--1-13). This suggests the possibility that a longer feeding time of  $NH<sub>3</sub>$  results in a higher incorporation of nitrogen and suppression of oxygen content in the AlON interlayer grown by thermal ALD.

The second distinct feature in the C−V curve is that the weak inversion hump in the C−V curves is suppressed with an increase in the NH<sub>3</sub> feeding time. [Fig. 2 \(a\)](#page--1-14) shows the C-V hump area (Q<sub>hump</sub>) [\[20](#page--1-15)], which is used to compare the change in the inversion hump quantitatively. Krylov et al. reported that the Qhump represents inversion charges, which are generated from the interfacial trap states near the mid-gap [\[20](#page--1-15)]. [Fig. 2 \(b\)](#page--1-14) shows the variation in the  $Q_{\text{hump}}$  as a function of the NH<sub>3</sub> feeding time. The  $\text{Al}_2\text{O}_3/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  stack exhibits a large  $Q_{\text{hump}}$  of 0.45 µC/cm<sup>2</sup>. The  $Q_{\text{hump}}$  value is drastically reduced even at a short  $NH<sub>3</sub>$  feeding time of 5 s; a longer feeding time of  $NH<sub>3</sub>$  leads to further reduction in the Qhump (0.07  $\mu$ C/cm<sup>2</sup> at 60 s). The D<sub>it</sub> of the MIS capacitors was determined using a conductance method; [Fig. 2 \(c\)](#page--1-14) shows the variation in the  $D_{it}$  of the  $Al_2O_3/AlON/In_{0.53}Ga_{0.47}As$  stack with the NH<sub>3</sub> feeding time. The D<sub>it</sub> of the Al<sub>2</sub>O<sub>3</sub>/AlON/In<sub>0.53</sub>Ga<sub>0.47</sub>As

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