Atomic layer etching of Al₂O₃ using BCl₃/Ar for the interface passivation layer of III–V MOS devices

K.S. Min a, S.H. Kang a, J.K. Kim a,c, Y.I. Jhon b, M.S. Jhon b, G.Y. Yeom a,⇑

a Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, South Korea
b Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, PA 15213, USA
c Technology Team, Semiconductor R&D Center Samsung Electronics Co. Ltd., Hwasung, Gyeonggi-do 445-701, South Korea

ABSTRACT

The atomic layer etching (ALET) of Al₂O₃ has been studied for possible application in precise etch control and low damage etching of the Al₂O₃ layer for use as the interface passivation layer (IPL) between the high-κ dielectric and the III–V compound semiconductors. Under the ALET condition, about 1 Å/cycle of Al₂O₃ corresponding to one monolayer per etch cycle and surface roughness similar to that of the reference, regardless of the number of etch cycles, were obtained. Therefore, etch depth could be controlled with atomic scale precision. In addition, during the ALET, the stoichiometry of Al₂O₃ and the Al/O ratio were maintained the same as those of the reference. Therefore, it is believed that the ALET of Al₂O₃ can reduce the plasma induced damage at the edge of an IPL because it can decrease the sidewall leakage by maintaining the stoichiometry of the sidewall Al₂O₃ surface, in addition to, precisely controlling the etch depth and minimizing the amount of substrate recess.

1. Introduction

High-κ dielectrics have been studied for silicon metal–oxide–semiconductor (MOS) devices. Recently, it has been extended to different channel materials such as GaAs, InGaAs, etc. for III–V compound MOS devices because of the high electron mobility of III–V materials [1,2]. However, unlike the silicon, one of the main problems in applying high-κ dielectric to III–V compound semiconductors is the deficiency of a stable native, which would passivate the interface states between the high-κ dielectric and the substrate. To address this problem, various high-κ dielectrics, such as SiO₂, Al₂O₃, Ga₂O₃, etc. have been considered as interface passivation layer (IPL) materials for III–V MOS devices [3–5].

In the patterning of the IPL, as the critical dimension (CD) is scaled down to 22 nm node and below, plasma etching has become important because of the difficulty in etching the IPL with the minimal recess of the III–V compound semiconductor substrate due to the very thin physical thickness of the IPL ranging from about 0.5 to 1 nm, even when the gate stacks can be etched anisotropically for accurate CD control. Therefore, a precise etch rate, rather than a high etch rate, and a very high etch selectivity between the IPL and the III–V compound semiconductor substrate are required. Plasma etching of the IPL has been studied in many groups [6,7]. During the IPL etching, however, conventional plasma etching techniques tend to physically damage the etched surface of the substrate because of the energetic reactive ions they use to make anisotropic gate profiles. Additionally, these reactive ions can degrade the electric characteristics of MOS and memory devices [8–10].

Previously, atomic layer etching (ALET) has been introduced as the most suitable method for extreme nanoscale device patterning because it can etch a material at an atomic scale without physically and chemically damaging the substrate. ALET is a cyclic process similar to atomic layer deposition (ALD), but after the one cycle, ALET etches exactly one atomic layer whereas ALD deposits one atomic layer. ALET consists of four steps: (1) adsorption of reactive atoms and molecules on the surface for chemisorption, (2) evacuation of un-reacted gas species, (3) desorption by energetic Ar beam bombardment from a beam source to chemisorbed compounds, and (4) evacuation of the desorbed species. The details of ALET can be found elsewhere [11,12].

This article presents the first time study of the ALET of Al₂O₃ as the IPL for III–V MOS devices. The monolayer etching of Al₂O₃ for ALET is investigated. By using the optimized ALET condition, the etch depth of a very thin Al₂O₃ can precisely be controlled with minimal surface roughness and without stoichiometric change during the ALET of Al₂O₃.

2. Experimental

Al₂O₃ was deposited to a thickness of 3 nm on a GaAs substrate using atomic layer deposition (ALD) using commercial ALD equip-
ment with trimethyaluminium (TMA) and O2. In the ALET of Al2O3, one cycle was composed of four steps, and each step carried out under the following conditions. In the 1st step, 0–100 sccm of BCl3 gas was supplied for 30 s to adsorb the reactive gas (chemisorption) on the surface of Al2O3. In the 2nd step, the ALET system was evacuated to the base pressure of 5 × 10−7 Torr for 30 s to remove the non-reacted BCl3 gas. In the 3rd step, a low energy Ar beam from a beam source was applied to desorb the chemisorbed compounds for 125 s. For the Ar beam source, an energetic Ar neutral beam was used to avoid possible charge-related damage during the etching and, to form an energetic Ar neutral beam, a three-gridded inductively coupled plasma (ICP) ion gun and a neutralizer installed in front of the ICP ion gun were used. To extract Ar+ ion beam from the ICP ion gun, 300 W of 13.56 MHz rf power and 50 sccm of Ar gas flow rate were used to generate an Ar plasma in the ICP source while 50–150 V, −250 V, and 0 V were applied to the 1st grid of the ion gun for the energy of the Ar+ ions, the 2nd grid for focusing the ions, and the third grid for grounding, respectively. After the extraction of the Ar+ ion beam, the beam was reflected to the neutralizer composed of parallel reflecting plates having 5° tilted to the ion beam direction to form a near-parallel and energetic Ar neutral beam. In the final step, the ALET system was evacuated again for 30 s to the base pressure of 5 × 10−7 Torr. Therefore, the ALET experimental condition is composed of 30 s of BCl3 adsorption time, 30 s of evacuation time, 125 s of desorption time, and 30 s of evacuation time, so it requires 215 s for one cycle of ALET.

After the ALET, the etch depth was measured using a step profilometer (Tencor Instrument, Alpha Step 500). The measured etch depth was divided by the total number of cycles to obtain the etch rate per cycle (Å/cycle). Atomic force microscopy (AFM, Thermomicroscope, CP Research) was used to measure the surface roughness. X-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 2000, Mg Kα source) was used to measure the surface composition.

3. Results and discussion

To etch one monolayer of Al2O3 per each cycle in ALET, one monolayer of BCl3 needs to be adsorbed on the Al2O3 surface during the 1st adsorption step and BCl3-reacted one monolayer of Al2O3 needs to be etched away during the 3rd desorption step by energetic Ar bombardment without sputtering the Al2O3 layers under BCl3-reacted one monolayer of Al2O3. The adsorption of BCl3 tends to form one monolayer of chemisorbed species such as AlCl/BCl-O on the Al2O3 surface, due to the electron transfer from the Al-O 1st sub-layer (or Al2O3 1st sub-layer) to the Al-O/BCl-O chemisorbed surface layer, the binding energy (Ea) between the chemisorbed layer and the Al-O 1st sub-layer is weakened. By using the energy, which is higher than the binding energy (Eb) between the chemisorbed layer and the Al-O 1st sub-layer, but lower than the binding energy (Ea), which is the binding energy of natural Al2O3 between the Al-O 1st sub-layer and the Al-O 2nd sub-layer, only the chemisorbed layer can be etched during the 3rd desorption step without sputtering the Al-O 1st sub-layer [13]. Therefore, for one-monolayer etching, it is important to supply the appropriate Ar bombardment energy (Eb) during the 3rd desorption step. Fig. 1 shows the etch depth of Al2O3 per cycle (Å/cycle) for Ar sputtering and ALET, measured as a function of the 1st grid voltage from 50 to 150 V of the Ar+ ion beam source (the 1st grid voltage of the Ar+ ion beam source controls the energy of the Ar+ ion beam and determines the final Ar neutral beam energy for desorption during ALET). During the 1st adsorption step, one monolayer of BCl3 covered the Al2O3 surface at BCl3 flow rate of 100 sccm. Without sputtering the Al-O sub-layer under the chemisorbed layer, the 1st grid voltage was varied to determine the optimum Ar neutral beam energy for desorption of the chemisorbed species such as Al-Cl and BCl-O on the Al2O3 surface. ALET without the BCl3 adsorption step was also carried out to find out whether Al2O3 is etched just by Ar sputtering (without BCl3 adsorption), not by ALET (with BCl3 adsorption). As shown in the figure, when the 1st grid voltage was less than about 105 V, no sputtering of Al2O3 was observed, but when the 1st grid voltage was higher than 105 V, the sputtering of Al2O3 was observed and the sputter rate increased almost linearly with increasing 1st grid voltage. This indicates that, the threshold voltage for the sputtering of Al2O3 is about 105 V (the actual threshold voltage would be lower because the Ar+ ions lose some energy during neutralization by the reflection on a parallel reflector to form an Ar neutral beam); therefore, if the 1st grid voltage is lower than 105 V, then no sputtering of Al2O3 would be observed during the ALET.

When the ALET was carried out with different 1st grid voltages, as shown in Fig. 1, the etch depth/cycle was divided into three regions. In region 1 (1st grid voltage (1st G) < 95 V), the etch depth/cycle is low and increases abruptly with increasing 1st grid voltage, indicating that the beginning of partial layer etching of Al2O3 because of the insufficient energy transfer from the bombarding Ar beam to the Al2O3 surface for the removal of the chemisorbed layer due to the lower Eθ than both Eθ and Ep. On the other hand, in region 3 (105 V < 1st G < 150 V), the etch rate of ALET is constant with the largest differences between the Ar sputter and the ALET indicating that the optimum ALET condition, which removes one monolayer/cycle is obtained because Eθ is between Eθ and Ep.

In the Langmuir isotherm, the adsorption of BCl3 on the Al2O3 surface forms one monolayer of BCl3 on the Al2O3 surface. Its surface coverage (θ) is dependent on the operating pressure, which can be determined by the gas flow rate. Therefore, BCl3 gas flow rate is an important factor in obtaining one monolayer etching per cycle during ALET [14]. Fig. 2 shows the etch depth per cycle (Å/cycle) of Al2O3 and the AFM root mean square (rms) roughness of the etched Al2O3 surface measured as a function of BCl3 gas flow rate from 0 to 100 sccm during the 1st adsorption step. Based on previous results, as the 1st grid voltage for Ar+ ion beam, 100 V was used because it ranges between Eθ and Ep, which results in etching the chemisorbed layer without sputtering the Al-O...
As shown in the figure, the etch depth/cycle of Al₂O₃ increased with BCl₃ gas flow rate up to 50 sccm, and saturated at higher BCl₃ gas flow rates. The saturated etch rate for Al₂O₃ was about 1 Å/cycle, consistent with the deposition rate of Al₂O₃ by ALD, suggesting one monolayer etching per cycle during ALET [15]. In the case of the partial layer etching condition, in which less than one monolayer is etched per cycle, the rms roughness of the etched Al₂O₃ surface was higher than that of the reference (unetched Al₂O₃ sample) whereas in the case of the ALET condition, the rms roughness was similar to that of the reference. This is attributed to the coverage of adsorbed reactive molecules on the Al₂O₃ during the 1st adsorption step, which forms chemisorbed compounds between BCl₃ and Al₂O₃ (i.e., Al-Clₓ/BCl-Oₓ). As shown in the figure, when the gas flow rate (Pbc) is lower than 50 sccm, the surface coverage of the reactive gas (θAl₂O₃) is lower than 1, which results in partial layer etching per cycle, and the random partial layer etching during each cycle increases the surface roughness. However, when the gas flow rate (Pbc) is higher than 50 sccm, the surface coverage (θAl₂O₃) is about 1, reaching the one monolayer self-limiting coverage of the Langmuir isotherm, which results in one monolayer etching per each cycle, a surface roughness similar to the reference is obtained after the ALET.

Fig. 3 shows the etch depth (Å), etch depth per cycle (Å/cycle) of Al₂O₃, and AFM root-mean-square (rms) roughness of the etched Al₂O₃ surface measured as a function of the number of ALET etch cycles. As the Al₂O₃ ALET condition, BCl₃ flow rate of 100 sccm during the 1st adsorption step and 1st grid voltage of 100 V during the 3rd desorption step were used. As shown in the figure, the Al₂O₃ etch depth/cycle maintained constant at about 1 Å/cycle, regardless of the number of etch cycles. Therefore, the etch depth (Å) increased linearly with increasing number of etch cycles, enabling us to control the etch depth of the Al₂O₃ with atomic scale precision. Also, the rms roughness of the etched Al₂O₃ surface remained similar to that of the reference regardless of etch cycles.

Fig. 4 shows (a) the atomic percentage of the etched Al₂O₃ surface and (b) the Al/O ratio of the etched surface of Al₂O₃ measured by X-ray photoelectron spectroscopy (XPS) for the reference, the Al₂O₃ etched by partial layer etching (θAl₂O₃ < 1), and the Al₂O₃ etched by ALET (θAl₂O₃ = 1).

Please cite this article in press as: K.S. Min et al., Microelectron. Eng. (2013), http://dx.doi.org/10.1016/j.mee.2013.03.170
and the Al/O ratio was lower than that of the reference possibly due to the preferential removal on the exposed Al₂O₃ surface during the partial layer etching. However, in the case of the ALET, the stoichiometry of Al₂O₃ surface and the Al/O ratio remained the same as those of the reference because one monolayer was fully etched during each cycle.

4. Conclusions

The ALET of Al₂O₃ as the IPL for III–V MOS devices, which is composed of four steps (BCl₃ adsorption for chemisorption, Ar desorption of the chemisorbed layer, and the evacuation steps between adsorption and desorption), has been studied. To obtain one monolayer etching per cycle during ALET, energetic Ar bombardment with energy between the binding energies of \( E_a \) (the binding energy of Al-O 1st sub-layer under the chemisorbed layer) and \( E_b \) (the binding energy of Al-O 2nd sub-layer or natural Al-O binding energy) at the 1st grid voltage of 95–105 V for the Ar⁺ ion source and one monolayer coverage of BCl₃ during the 1st adsorption step at BCl₃ gas flow rate over 50 sccm were required. When the ALET condition was used, the etch depth per cycle remained the same at about 1 Å/cycle and the surface roughness remained the same as that of reference, regardless of the number of etch cycles. Therefore, the etch depth could be controlled precisely with atomic scale precision while maintaining the surface roughness the same as that of the reference. Also, during the ALET, not only the stoichiometry of Al₂O₃ surface but also the Al/O ratio remained the same as those of the reference because one monolayer was fully etched during each cycle. Therefore, the ALET is promising for etching Al₂O₃ for use as the IPL for III–V MOS devices because plasma induced damage at the edge of IPL can be minimized. In addition, the etch depth can be precisely controlled, and the amount of III–V substrate recess can be minimized to further improve device characteristics.

Acknowledgments

This work was supported by Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012M3A7B4035323) and was supported in part by the World Class University program of National Research Foundation of Korea (Grant No. R32-10124) and was supported by MKE/KOTEF through the Human Resource Training Project for Strategic Technology.

References