Thermal Atomic Layer Etching of Microelectronic Materials

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Abstract

Atomic layer control of microelectronic processing is required as critical dimensions are reduced below the 10 nm scale. Thermal atomic layer etching (ALE) has developed over the last 5 years to meet etching challenges. This paper will define thermal ALE in terms of sequential, self-limiting surface reactions. Thermal ALE can be viewed as the reverse of atomic layer deposition (ALD). Various microelectronic materials will be used to demonstrate thermal ALE including Ga_2O_3, Si, and Si_3N_4.

(Keywords: atomic layer etching, atomic layer processing, Ga_2O_3, Si, Si_3N_4)

Introduction

Thermal ALE is based on a binary reaction sequence [1]. The first surface modification reaction is able to alter the surface layer. The second volatile release reaction produces volatile etch products from the altered surface layer. An illustration of thermal ALE is shown in Figure 1. Ideally, both the surface modification and volatile release reactions are self-limiting. Thermal ALE is similar to the reverse of ALD.

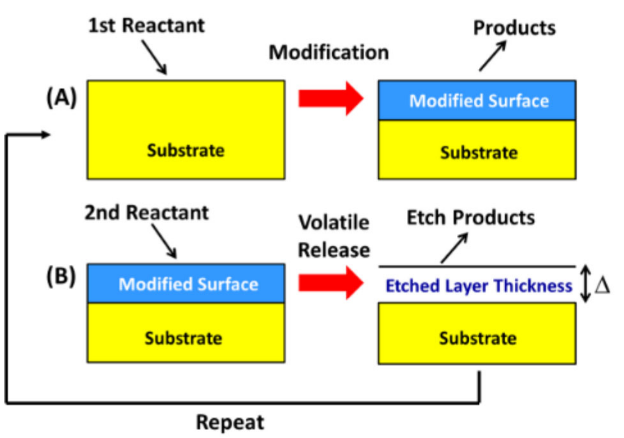

Figure 1. Schematic of thermal ALE process.

There are many mechanisms for thermal ALE [1]. Fluorination and ligand-exchange is one mechanism that is useful for the etching of metal oxides such as Ga_2O_3 [2]. The etching of silicon-based materials utilize oxidation mechanisms where the silicon material is oxidized to SiO_2 [3,4]. The etching of SiO_2 is then performed using a conversion mechanism where SiO_2 is converted to Al_2O_3 by trimethylaluminum [5]. This presentation will review the thermal ALE of Ga_2O_3, Si, and Si_3N_4.

Results and Discussion

A. Ga_2O_3 ALE

Gallium oxide is a transparent semiconducting oxide that has applications in power electronics and optoelectronics. The thermal ALE of Ga_2O_3 can be achieved using fluorination and ligand-exchange [2]. Ga_2O_3 is first fluorinated to GaF_3 using HF. The GaF_3 can then be removed by ligand-exchange using BCl_3. An illustration of these two sequential surface reactions is shown in Figure 2.

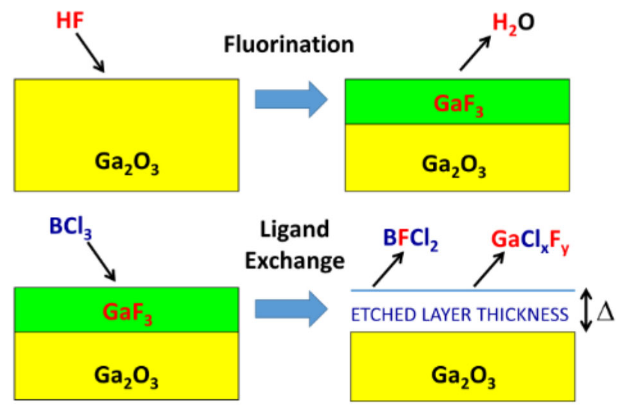

Figure 2. Schematic for Ga_2O_3 ALE using HF and BCl_3 as the reactants.

The thermal ALE of Ga_2O_3 can be monitored using in situ spectroscopic ellipsometry [2]. Results for Ga_2O_3 thermal ALE at 200°C are shown in Figure 3 [2]. The Ga_2O_3 film is removed with an etch rate of 1.38 Å/cycle. Additional experiments also reveal that the etch rate is self-limiting versus HF and BCl_3 pressure at constant exposure time [2].

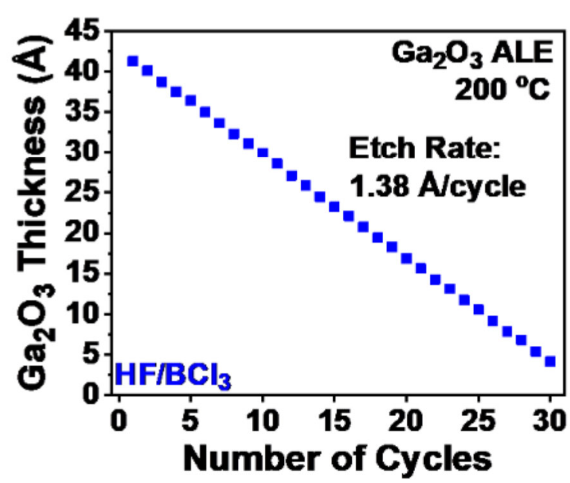

Figure 3. Ga_2O_3 film thickness versus number of cycles of Ga_2O_3 ALE using HF and BCl_3 as the reactants.

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Other experiments revealed that a number of precursors could etch Ga_2O_3 after fluorination using HF [2]. These precursors were $AlCl(CH_3)_2$, $Al(CH_3)_3$, $TiCl_4$ and $Ga(N(CH_3)_2)_3$. Some of these precursors, such as $TiCl_4$, are believed to etch Ga_2O_3 through a conversion mechanism. The $TiCl_4$ can convert Ga_2O_3 to TiO_2 prior to the spontaneous etch of TiO_2 by HF [2].

B. Si ALE

Silicon is one of most ubiquitous semiconductor materials in microelectronics. Si thermal ALE can be performed using oxidation, fluorination, ligand-exchange and conversion [3]. Silicon is initial oxidized to SiO_2 using O_2. Subsequently, trimethylaluminum (TMA) is able to convert SiO_2 to Al_2O_3. After fluorination of Al_2O_3 to AlF_3 by HF, TMA can volatilize the AlF_3 by ligand-exchange. The reaction sequence for Si thermal ALE is displayed in Figure 4 [3].

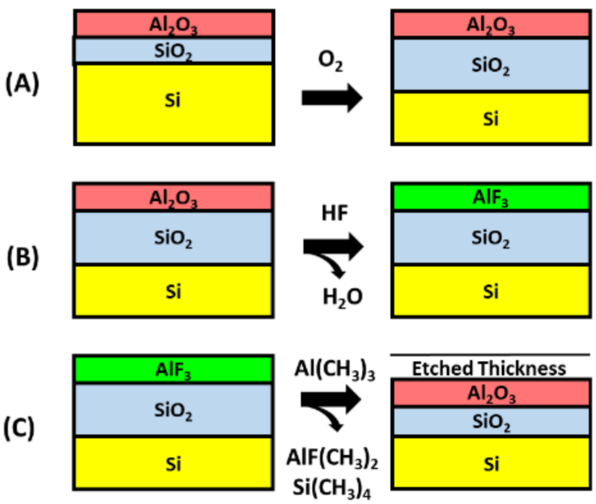

Figure 4. Schematic of Si ALE using O_2, HF and $Al(CH_3)_3$ as the reactants.

Si thermal ALE is dependent on the conversion of SiO_2 to Al_2O_3. SiO_2 by itself is not etched by HF and TMA when these reactants are at low pressure of < 100 mTorr [6]. However, at higher TMA pressures of > 1 Torr, the TMA is able to convert SiO_2 to Al_2O_3 [5] This conversion to Al_2O_3 provides a pathway for Al_2O_3 to be etched using HF and TMA [7].

In situ spectroscopic ellipsometry was employed to monitor the Si film thickness during Si thermal ALE. The ellipsometry could simultaneously monitor the thicknesses of both the SiO_2 layer on top of the Si film and the Si film itself. Ellipsometry results for Si ALE at 290°C are shown in Figure 5 [3]. The SiO_2 layer thickness is approximately constant at 10 Å while the underlying Si film is etched at a rate of 0.4 Å/cycle [3].

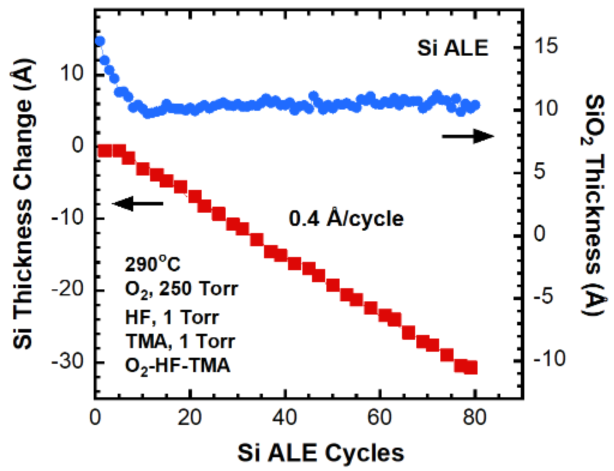

Figure 5. Si thickness change and SiO_2 film thickness versus number of Si ALE cycles using O_2, HF and TMA as the reactants.

Additional experiments explored the etching of ultrathin silicon films on SOI wafers. These silicon films had thicknesses <100 Å. These ultrathin silicon films were etched linearly from 100 Å until reaching the underlying SiO_2 film on the SOI wafer [3]. These experiments demonstrate that quantum confinement effects in silicon that are present at <100 Å do not influence the etching.

C. Si_3N_4 ALE

Silicon nitride is an important dielectric, barrier and spacer material in microelectronics. In similarity with Si thermal ALE, the thermal ALE of Si_3N_4 can be achieved using oxidation, fluorination, ligand-exchange and conversion [4]. Si_3N_4 is initial oxidized to SiO_2 using O_2 or O_3. Afterwards, TMA is able to convert SiO_2 to Al_2O_3. After fluorination of Al_2O_3 to AlF_3 by HF, TMA can volatilize the AlF_3 by ligand-exchange. The reaction sequence for Si_3N_4 thermal ALE is displayed in Figure 6 [4].

In situ spectroscopic ellipsometry was again used to monitor the Si_3N_4 film thickness during Si_3N_4 thermal ALE. Similar to the results in Figure 5, the ellipsometry could simultaneously monitor the thicknesses of both the SiO_2 layer on top of the Si_3N_4 film and the Si_3N_4 film itself. Ellipsometry results for Si ALE at 290°C are shown in Figure 7 [3]. The

SiO_2 layer thickness is approximately constant at 9 Å while the underlying Si_3N_4 film is etched at a rate of 0.25 Å/cycle [3].

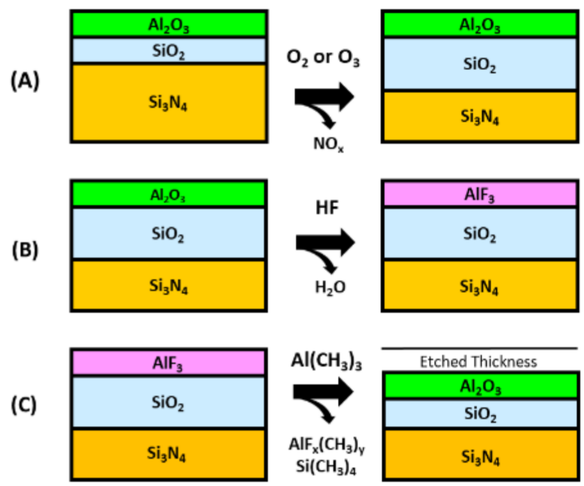

Figure 6. Schematic of Si_3N_4 ALE using O_2 or O_3, HF and $Al(CH_3)_3$ as the reactants.

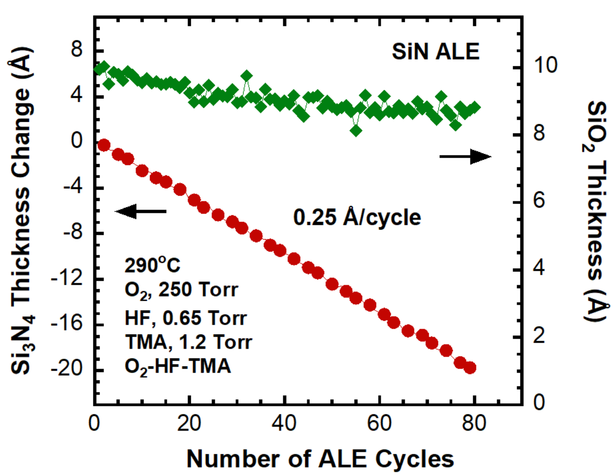

Figure 7. Si_3N_4 thickness change and SiO_2 film thickness versus number of Si_3N_4 ALE cycles using O_2, HF and TMA as the reactants.

Si_3N_4 thermal ALE was also conducted using O_3 as the oxidation reactant. Under the same reaction conditions as the above Si_3N_4 ALE thermal process using O_2, the O_3 produced a higher Si_3N_4 thermal ALE etch rate of 0.47 Å/cycle [4].

Conclusions

Thermal ALE should be useful in the processing of microelectronic materials. Thermal ALE is a gas phase process analogous to the reverse of ALD. Thermal ALE should be able to etch isotropically and conformally. This paper has highlighted the thermal ALE of Ga_2O_3, Si and Si_3N_4.

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