



Precise Depth Control and Low-Damage Atomic-Layer Etching of HfO₂ using BCl₃ and Ar Neutral Beam

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The etch characteristics of HfO₂ by atomic-layer etching (ALET) were investigated using a BCl₃/Ar neutral beam. The effect of ALET on surface modification and etch-depth control was also examined. Self-limited etching of HfO₂ could be obtained using BCl₃ ALET. This was attributed to the absorption of BCl₃ by the Langmuir isotherm during the absorption stage and the vaporization of hafnium-chlorides/boron oxychlorides formed on the surface during the desorption stage. In addition, the surface composition of HfO₂ was not altered by etching during ALET.
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The downscaling of metal-oxide-semiconductor field-effect transistors (MOSFETs) has created the need for high-dielectric-constant (*k*) materials to replace SiO₂ for reducing the gate-leakage current while maintaining the gate-dielectric capacitance. Among the various high-*k* materials, hafnium oxide (HfO₂) is a potential material in next-generation MOSFETs due to its high-dielectric constant (25–30), wide bandgap, low leakage current, and superior thermal stability.^{1,2}

In order to apply HfO₂ to next-generation MOSFET devices, HfO₂ films should be patterned by dry etching, because the wet etching of HfO₂ has several disadvantages such as difficulty in controlling the etch rate, severe undercut, etc. Therefore, there have been many studies on the dry etching of HfO₂ using halogen-based plasma etching for applications to MOSFET devices. A precise etch rate is required in the plasma etching for HfO₂ instead of a high etch rate due to the low thickness of the material. Moreover, an extremely high etch selectivity over the underlayer material is required. In addition, the damage on the etched surface is intolerable. However, these conventional plasma-etching processes tend to physically damage the surface of the devices by creating surface defects, including structural disruption, an intermixing layer, or stoichiometry modification, and increasing surface roughness, due to use of energetic reactive ions to achieve vertical etch profiles.^{3,4} In addition, these halogen-based plasma etchings showed finite etch selectivity between HfO₂ and the underlying materials.^{5,6} These problems decrease the device performance.

Atomic-layer etching (ALET) may be the most suitable method for etching HfO₂ in next-generation MOSFET devices because it may etch HfO₂ with no physical damage and with atomic-scale etch controllability. Generally, ALET is a cyclic process that consists of four sequential steps: (i) adsorption of reactant molecules on the surface, (ii) evacuation of the remaining reactant molecules, (iii) Ar⁺ ion-beam irradiation to the reactant adsorbed surface for the desorption of chemisorbed species, and (iv) evacuation of the etch products.^{7,8} However, during step (iii) with Ar⁺ beam irradiation, the device can be damaged electrically due to the charged particles, such as positive ions generated in the plasma.

In this article, ALET of HfO₂ was carried out using BCl₃ adsorption, followed by Ar neutral-beam irradiation instead of Ar⁺ ion-beam irradiation to avoid possible charge-related damage, and the etch mechanism was examined. In addition, the effect of ALET on the properties of the etched material surface, such as surface modification and roughness, was investigated.

A low-energy Ar neutral beam was generated using a low-angle forward-reflected neutral (LAFRN) beam technique. In this tech-

nique, a neutral beam was formed by generating a parallel ion beam using a three-grid Ar inductively coupled plasma (ICP) ion source, followed by reflection of the ion beam on a low-angle reflector for the formation of a neutral beam. By applying 300 W of radio frequency power to the ion gun while supplying 30 sccm of Ar, and by applying 60 V to the first grid located close to the ion source (accelerator grid), –250 V to the second grid (extractor grid), and grounding the third grid, energy and flux of about 73 eV and 1.5×10^{15} ions/cm² s could be obtained, respectively, before the neutralization on the planar reflector. The neutralization efficiency of this neutral-beam source was estimated to be >99% using a Faraday cup. (However, the exact energy and flux of the neutral beam after reflection on the planar reflector are not currently known and are under investigation.) The details of the LAFRN beam source are described elsewhere.⁹

One cycle of the ALET process steps performed in this study are as follows. The reactant gas (BCl₃ or Cl₂) was supplied to the etch chamber for 20 s during the adsorption period in order to allow the reactant gas to be adsorbed on the HfO₂ surface. The neutral-beam source was turned on for several tens of seconds to desorb the adsorbed species. After each adsorption and desorption step, the etch chamber was evacuated for 3 s.

As the samples, HfO₂ films (100 nm) were deposited on Si by reactive sputtering and patterned by a photoresist to estimate the etch rate. The etched step height was measured using a step profilometer (Tencor Instrument, Alpha Step 500). The measured step height was divided by the total number of ALET cycles to yield the etch amount per cycle. Atomic force microscopy (Thermomicroscope, CP Research) was used to measure the surface roughness. X-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 2000, Mg K α source) was used to analyze the stoichiometric modification of the HfO₂ surface after etching.

Figure 1 shows the HfO₂ etch rate ($\text{\AA}/\text{cycle}$) and root-mean-square (rms) roughness of the etched HfO₂ surface measured as a function of the reactant gas pressure during the adsorption stage of the etch cycle. BCl₃ and Cl₂ were used as the reactant gas and the pressure was varied from 0 to 0.33 mTorr. At that time, the Ar neutral-beam irradiation dose was maintained at 1.48×10^{17} atoms/cm² cycle. As shown in the figure, the HfO₂ etch rate increased with increasing BCl₃ pressure (P_{BCl_3}) up to 0.22 mTorr. However, there was no further increase in the HfO₂ etch rate with further increases in P_{BCl_3} due to surface saturation. The saturated HfO₂ etch rate was 1.2 $\text{\AA}/\text{cycle}$. In the case of the rms roughness of the HfO₂ surface, the increase in P_{BCl_3} to 0.09 mTorr increased the roughness rapidly to 70.3 \AA , but a further increase of P_{BCl_3} decreased the roughness. When the P_{BCl_3} was >0.22 mTorr, the rms roughness remained at 28.5 \AA , which is similar to that of the refer-

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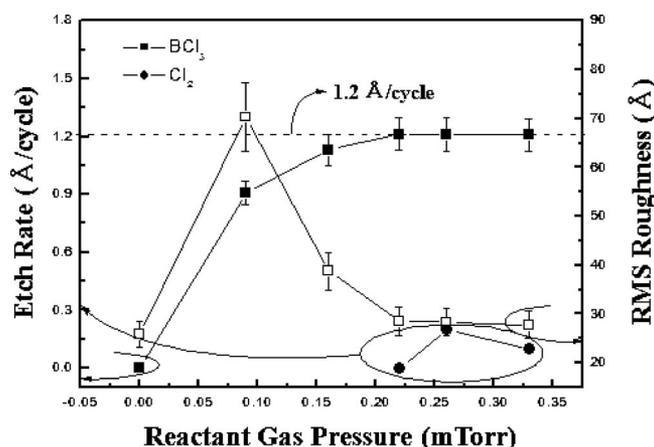


Figure 1. HfO₂ etch rate (Å/cycle) by ALET and change in rms surface roughness as a function of the reactant gas pressure of Cl₂ and BCl₃. [Process condition: inductive power (300 W), 1st grid voltage (60 V), 2nd grid voltage (-250 V), Ar neutral-beam irradiation dose (1.5×10^{17} atoms/cm² cycle), and reactant gas supply time (20 s)].

ence sample (25.5 Å). No etching of the HfO₂ surface was observed when Cl₂ was used as the reactant gas instead of BCl₃ at the pressures investigated, as shown in the figure.

The difference in the HfO₂ etching behavior observed for different reactant gases was attributed to the difference in binding energy with oxygen. For the ALET process, the reactant gas needs to be adsorbed on the HfO₂ surface, and a volatile compound needs to be formed between HfO₂ and the reactant gas before desorption of the compound by Ar neutral-beam bombardment. The bond strength of Cl–O formed on the HfO₂ surface was approximately 2.8 eV, which is smaller than that of Hf–O (8.2 eV).¹⁰ Therefore, for the etching with Cl₂ gas, when an Ar neutral beam is irradiated on a Cl₂-adsorbed HfO₂ surface, oxygen in HfO₂ cannot be removed from the HfO₂ surface in the form of Cl–O because oxygen is bonded more strongly to Hf than to Cl. Hence, no etching of the HfO₂ surface can occur. However, in the case of BCl₃ etching, the bonding strength of B–O is 8.4 eV,¹⁰ which is greater than that of Hf–O. Therefore, the oxygen in HfO₂ is removed in the form of boron oxychlorides during Ar neutral-beam irradiation, which makes HfO₂ etching possible.

The change in HfO₂ etch rate and rms roughness obtained as a function of P_{BCl₃} is related to the amount of compounds formed between HfO₂ and BCl₃ (i.e., Hf–Cl/BCl–O: hafnium chlorides and boron oxychlorides) on the HfO₂ surface. When HfO₂ is exposed to BCl₃, due to the Langmuir isotherm, a single layer of Hf–Cl/BCl–O is formed on the HfO₂ surface and the surface coverage of the compound ($\theta_{\text{Hf-Cl/BCl-O}}$) is determined by P_{BCl₃}.¹¹ When Hf–Cl/BCl–O is formed on the HfO₂ surface during the BCl₃ adsorption stage, the electron moves from Hf–O to the Hf–Cl and BCl–O bonds, and the bond strength of Hf–O is lower than the bond strength of Hf–Cl and BCl–O.¹² Therefore, during Ar neutral-beam irradiation on the BCl₃-adsorbed HfO₂ surface, only Hf–Cl/BCl–O bonds formed on the HfO₂ can be removed by desorption, because the Hf–O bond located immediately below the Hf–Cl/BCl–O bond is broken more easily compared with the Hf–Cl/BCl–O bonds by supplying an adequate Ar bombardment energy somewhere between the Hf–O and Hf–Cl/BCl–O bond energies (i.e., approximately 73 eV in this experiment). In addition, when the Ar beam dose is higher than the HfO₂ surface atomic density, the HfO₂ etch rate is determined by the surface coverage of Hf–Cl/B–O ($\theta_{\text{Hf-Cl/BCl-O}}$), which is varied by P_{BCl₃}. If the P_{BCl₃} is less than a certain value, i.e., 0.22 mTorr, Hf–Cl/BCl–O bonds do not completely cover the HfO₂ surface due to the lower coverage ($\theta_{\text{Hf-Cl/BCl-O}} < 1$). Hence, only a portion of

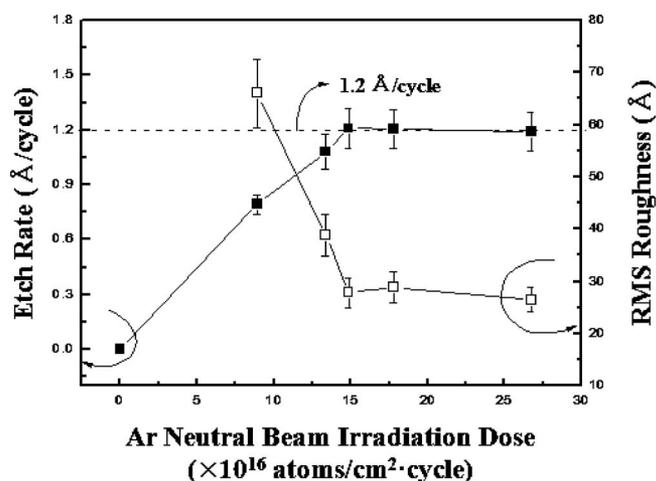


Figure 2. HfO₂ etch depth and etch rate (Å/cycle) by ALET and rms surface-roughness variation as a function of the Ar neutral-beam irradiation dose. [Process condition: inductive power (300 W), 1st grid voltage (60 V), 2nd grid voltage (-250 V), BCl₃ pressure (0.33 mTorr), and BCl₃ gas supply time (20 s).]

the surface layer is etched, and the etch rate (Å/cycle) increases with increasing P_{BCl₃}. In addition, at this etch condition, the surface roughness is higher than that before etching (reference) due to the removal of the partial surface layer during each etch cycle. When the P_{BCl₃} reaches 0.22 mTorr, the entire surface is covered with Hf–Cl/BCl–O bonds. Therefore, one monolayer (ML) layer is etched during each cycle (1.2 Å/cycle), and a further increase in P_{BCl₃} does not alter the etch rate. In addition, the surface roughness remains similar to that of the reference due to the removal of a single ML layer per etch cycle, as shown in Fig. 1.

Figure 2 shows the HfO₂ etch rate and rms roughness of the etched HfO₂ surface as a function of the Ar neutral-beam irradiation dose during the desorption stage of the etch cycle. The BCl₃ pressure was maintained at 0.33 mTorr, and the Ar neutral-beam irradiation dose was varied from 0 to 2.67×10^{17} atoms/cm² cycle. As shown in the figure, the HfO₂ etch rate increased with increasing Ar neutral-beam irradiation dose up to 1.5×10^{17} atoms/cm² cycle, and a further increase in the Ar neutral-beam irradiation dose saturated the etch rate at 1.2 Å/cycle. In the case of the rms roughness of the HfO₂ layer, an increase in the Ar neutral-beam irradiation dose decreased the surface roughness continuously until saturation of the etch rate had been reached. Further increases in the Ar neutral-beam irradiation dose did not alter the surface HfO₂ roughness significantly. The increase in HfO₂ etch rate with increasing Ar neutral-beam irradiation dose is the result of the increased Hf–Cl/BCl–O removed from the surface by the increased energetic particle dose. Saturation of the HfO₂ etch rate is related to the removal of a single-layer HfO₂ by the sufficient flux of Ar energetic particles. The HfO₂ etching characteristics with the Ar neutral-beam irradiation dose can also be understood by the measured surface roughness. The decrease in HfO₂ rms roughness with increasing Ar neutral-beam irradiation dose is related to the removal of more Hf–Cl/BCl–O formed on the surface, which is related to the suppression of HfO₂ rms roughness caused by the partial removal of Hf–Cl/BCl–O on the surface during the etch cycle. The surface roughness was finally minimized at approximately 28 Å for HfO₂ as a result of the complete removal of Hf–Cl/BCl–O during each cycle. This roughness is similar to that measured for the nonetched reference. Therefore, it is believed that the etching is controlled by the removal of Hf–Cl/BCl–O formed on the surface through the Ar neutral-particle bombardment, not by sputter etching of HfO₂ or the spontaneous vaporization of Hf–Cl/BCl–O.

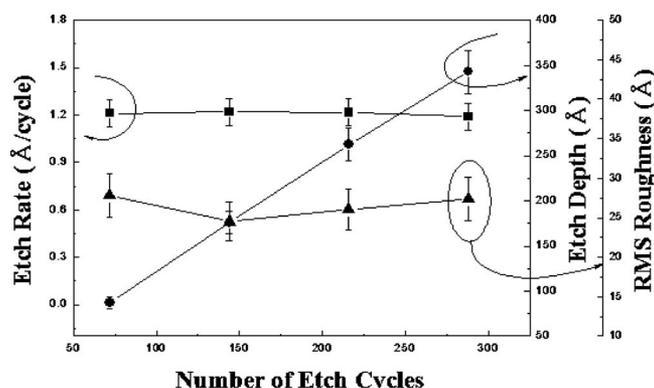


Figure 3. HfO₂ etch depth and etch rate (Å/cycle) by ALET and rms surface-roughness variation as a function of the number of etch cycles. [Process condition: inductive power (300 W), 1st grid voltage (60 V), 2nd grid voltage (−250 V), Ar neutral-beam irradiation dose (1.5×10^{17} atoms/cm² cycle), BCl₃ pressure (0.33 mTorr), and BCl₃ gas supply time (20 s).]

Figure 3 shows the HfO₂ etch rate, rms roughness of the etched HfO₂ surface, and the etch depth measured as a function of the etch cycle for a single ML layer etch condition (1.2 Å/cycle), which is 0.33 mTorr of P_{BCl₃} and an Ar neutral-beam irradiation dose of 1.5×10^{17} atoms/cm² cycle. As shown in the figure, the HfO₂ etch rate and rms roughness remained the same at 1.2 Å/cycle and approximately 28.5 Å, respectively, regardless of the number of etch cycles, and the etch depth increased linearly with increasing etch cycles. Therefore, using ALET, the etching of HfO₂ could be achieved with etch-depth controllability on the atomic scale by adjusting the etch cycles.

The use of ALET can minimize the etch damage formed during etching. Figure 4 shows the surface composition of HfO₂ measured by XPS before (as is) and after ALET. The XPS measurements were carried out at the take-off angle of 25° to measure the surface composition. At the take-off angle of 25°, the analysis depth was estimated to be about 10 Å. In comparison, the surface composition of

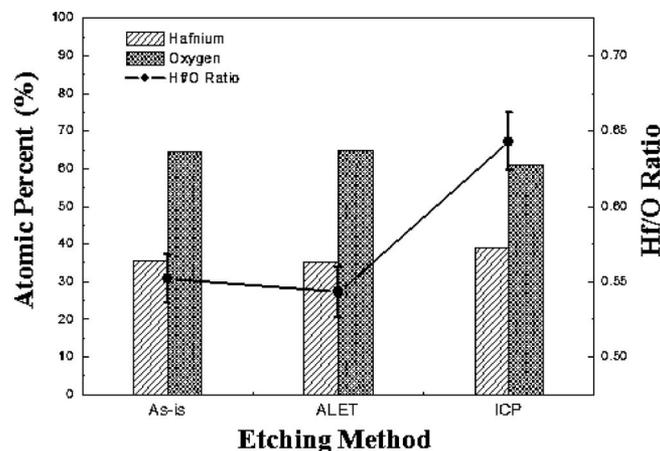


Figure 4. Atomic percentage of the HfO₂ surface and the Hf/O ratio measured using XPS with the different etching methods. [Process condition: ALET—1st grid voltage (60 V), Ar neutral-beam irradiation dose (1.5×10^{17} atoms/cm² cycle) and BCl₃ pressure (0.33 mTorr), ICP etching—inductive power (300 W), dc bias voltage (−60 V), BCl₃ (50 sccm)/Ar (50 sccm), and working pressure (12 mTorr).]

HfO₂ measured after BCl₃-based ICP etching was also included. Figure 3 shows the one ML layer etching condition of 1.2 Å/cycle under ALET conditions. An inductive power of 300 W, a dc bias of −60 V, and 12 mTorr of BCl₃ (50 sccm)/Ar (50 sccm) were used for the ICP etching conditions. Under these conditions, an approximately 105 Å/min HfO₂ etch rate could be obtained. In order to maintain the same etch depth, 85 ALET etch cycles were used, and a 60 s etch time was used for ICP etching. The etched samples were loaded to the XPS chamber immediately after etching (less than 5 min) to minimize the contamination of the surface by air exposure.

As shown in the figure, after ICP etching, the atomic percentage of Hf and O were changed from Hf—35.56% and O—64.44% (as is) to 39.15 and 60.85%, respectively. Therefore, the etched HfO₂ surface became Hf-rich (a Hf/O from 0.552 to 0.643). However, after ALET, the surface composition remained relatively constant at an Hf and O composition of 35.19 and 64.81%, respectively. The Hf-rich surface obtained after ICP etching is believed to be due to the preferential removal of oxygen as a result of the differences in the sputter yield of Hf and O as well as by the formation of volatile compounds such as BCl_xO_y using BCl₃.¹³ The lack of change in the surface composition after ALET was attributed to the removal of all Hf—Cl/BCl—O bonds formed on the surface by the Ar neutral-beam bombardment during each ALET cycle without the removal of HfO₂ located under the Hf—Cl/BCl—O bonds.

This study examined the etch characteristics of HfO₂ by ALET. In addition, the surface characteristics after etching by ALET were compared with those after ICP etching. The ALET of HfO₂ could be achieved using BCl₃ as the adsorption reactive gas, while no etching was observed using Cl₂ as the reactive gas. Moreover, a 1.2 Å/cycle of a self-limited one monolayer etch rate could be obtained by supplying a BCl₃ pressure >0.22 mTorr at an Ar beam flux of 1.5×10^{17} cm²/cycle with an energy of 73 eV, which enabled the etch depth to be controlled with atomic precision. When the surface composition after HfO₂ etching by ALET and ICP etching were compared, there was no change in the surface composition observed on the sample surface after ALET, while there was a change in the surface composition to an Hf-rich surface after ICP etching. Therefore, it is believed that etch damage can be minimized using ALET.

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