

Low Damage Atomic Layer Etching of ZrO_2 by Using BCl_3 Gas and Ar Neutral Beam

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This study examined the etch characteristics of ZrO_2 etched using an atomic layer etching (ALET) system with BCl_3 gas for adsorption and an Ar neutral beam for desorption. The effect of the BCl_3 gas pressure and Ar neutral beam dose on the etch characteristics was examined. The results showed that the ZrO_2 etch rate was maintained at a constant etch rate of $1.07 \text{ \AA}/\text{cycle}$ at a BCl_3 gas pressure $>0.15 \text{ mTorr}$ and an Ar beam flux $>1.485 \times 10^{16} \text{ atoms}/\text{cm}^2 \cdot \text{cycle}$. Under these constant etch rate conditions, the surface roughness of the etched ZrO_2 was similar to that of the as-received ZrO_2 . The surface composition of ZrO_2 etched by ALET was compared with that etched by BCl_3 inductively coupled plasma (ICP). The surface composition of ZrO_2 etched by ALET showed a similar composition to that of the as-received ZrO_2 while that etched by BCl_3 ICP showed a Zr-rich surface.

Keywords: Atomic Layer Etching, Neutral-Beam, High- k Etching, Zirconium Oxide.

Delivered by Publishing Technology to: Sung Kyun Kwan University
IP: 115.145.196.96 On: Thu, 25 Apr 2013 17:17:35
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1. INTRODUCTION

The size of metal oxide silicon field effect transistor (MOSFET) devices is shrinking to less than 100 nm. This means that the SiO_2 layer used as the gate oxide of these devices needs to decrease to 20 \AA , which at this thickness is reaching its physical limits. Consequently, for devices $<100 \text{ nm}$, SiO_2 needs to be replaced with other gate dielectrics.¹ In order to replace SiO_2 without decreasing the thickness of the gate oxide, high- k dielectric materials with a higher dielectric constant than SiO_2 (3.9) are being investigated and applied to some memory devices.^{2–5}

ZrO_2 has high thermal stability in the ZrO_2/Si structure and has been investigated as a gate dielectric material to replace SiO_2 owing to its high dielectric constant ($k = 20\text{--}254$) and wide bandgap ($5\text{--}7 \text{ eV}$).⁴ In the formation of MOSFET devices after depositing ZrO_2 as a gate dielectric material, the regions related to the source and drain need to be opened by etching to achieve ohmic-contact. Although damageless and selective etching of ZrO_2 is possible by wet etching, wet etching cannot be used to etch ZrO_2 due to the difficulty in the etching of the metal silicate formed at the ZrO_2 and silicon interface during annealing. Consequently, in the etching of a thin ZrO_2 gate oxide, there has been considerable interest in

plasma etching, such as reactive ion etching.^{6–10} However, the use of plasma etching to etch thin gate dielectric materials in nanoscale MOSFET devices could cause physical and electrical damage to the device. In addition, precise control of the gate dielectric etch depth is very important due to the very thin gate oxide thickness and shallow doping of the contact region.

Atomic layer etching (ALET) can be applied for precise control of the ZrO_2 etch depth and to minimize physical damage. This process is composed of four steps (1st step: adsorption of reactant molecules on the surface, 2nd step: evacuation of the excess reactant, 3rd step: energy irradiation of the reactant-adsorbed surface for desorption of the chemisorbed species, 4th step: evacuation of the etch product). Among the various energy irradiation methods, such as laser irradiation, thermal desorption, or low energy ion beam irradiation, low energy Ar^+ ion beam irradiation is used most extensively for the desorption of chemisorbed species in the third step on account its ability of anisotropic etch profile formation.

In this study, ALET of ZrO_2 was examined using BCl_3 gas for the adsorption step and Ar neutral beam for the desorption step, and the effects of the process variables on the ZrO_2 etch characteristics were examined. In particular, in this experiment, an Ar neutral beam was used instead of an Ar^+ ion beam to eliminate any possible charge-related damage during the desorption step. In addition, the degree

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of damage on the etched material surface by ALET was examined by comparing the surface composition of ZrO₂ etched by ALET with that of the as-received ZrO₂ and ZrO₂ etched by a BCl₃ inductively coupled plasma (ICP) etching.

2. EXPERIMENTAL DETAILS

The Ar neutral beam used for the desorption step of ALET was formed using a low angle forward reflected neutral beam technique. In this technique, a parallel Ar neutral beam was produced by forming a parallel Ar⁺ ion beam using a three-grid ICP ion gun followed by reflection of the ion beam to a low angle using flat reflector. The ICP ion gun was operated at 300 W 13.56 MHz RF power. The energy on the ion beam was controlled by applying 60 V to the 1st grid and -250 V to the 2nd grid to direct the flux of the ion beam. The 3rd grid was grounded. More details of the neutral beam source can be found elsewhere.¹¹

A 70 nm thick ZrO₂ layer was deposited on silicon substrates using a reactive RF sputter deposition system. ZrO₂ was etched using ALET and the etch conditions are described in Table I. One cycle of ALET was composed of a BCl₃ adsorption step and a desorption step by Ar beam irradiation. Between the adsorption and desorption steps, the processing chamber was evacuated for 3 seconds for purging. For the adsorption step, the BCl₃ gas pressure was varied from 0 to 0.33 mTorr while the Ar beam dose was kept at 1.6×10^{16} atoms/cm²·cycle (by measuring the ion beam flux before reflecting on the reflector using a Faraday cup). For the desorption step, the Ar beam dose was varied from 0 to 2.673×10^{16} atoms/cm²·cycle while the BCl₃ pressure was maintained at 0.15 mTorr.

The etch depth of ZrO₂ was measured using a α -step profilometer (Tencor Instrument, Alpha Step 500), and the etch rate was estimated by dividing the etch depth by the number of etch cycles. The ZrO₂ RMS surface roughness after etching was measured using atomic force microscopy (AFM, Thero-microscopes, CP research). The surface composition of ZrO₂ was measured by X-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 2000, Mg K α source).

Table I. Typical experimental parameters for the ALET used in this experiment.

Parameter	Value
Base pressure	4.2×10^{-7} Torr
Working pressure	3.4×10^{-4} Torr
Inductive power	300 W
1st grid voltage	60 V
2nd grid voltage	-250 V
Ar flow rate	20 sccm
BCl ₃ gas supply time	20 s
Substrate temperature	RT

3. RESULTS AND DISCUSSION

Figure 1 shows the ZrO₂ etch rate and root-mean square (RMS) roughness measured as a function of the BCl₃ gas pressure while Ar beam irradiation dose was maintained at 1.6×10^{16} atoms/cm²·cycle. The energy of the Ar⁺ ion beam was maintained at 60 eV prior to neutralization at the reflector of the Ar neutral beam source. At this Ar beam energy, ZrO₂ was not etched when no BCl₃ gas was introduced during the adsorption step due to the insufficient energy of the Ar beam to sputter the deposited ZrO₂ during the desorption step. However, when the BCl₃ gas pressure was increased from 0 to 0.15 mTorr, ZrO₂ etching was observed and the ZrO₂ etch rate ($\text{\AA}/\text{cycle}$) was increased with increasing BCl₃ gas pressure. This was attributed to the formation of volatile ZrCl_x and BClO_x on the ZrO₂ surface. When the BCl₃ gas pressure was >0.15 mTorr, the ZrO₂ etch rate ($\text{\AA}/\text{cycle}$) became saturated at 1.07 $\text{\AA}/\text{cycle}$ and there was no increase in etch rate with further increases in BCl₃ gas pressure. In the case of the surface roughness of the ZrO₂ layers, with increasing BCl₃ gas pressure, the surface roughness increased initially to 68 \AA at 0.08 mTorr. However, the surface roughness decreased to that of the reference when the BCl₃ gas pressure was >0.15 mTorr, (as-received: 28 \AA).

Saturation of the ZrO₂ etch rate at a BCl₃ gas pressure >0.15 mTorr is related to the degree of BCl₃ adsorption coverage (θ) on the ZrO₂ surface. The coverage of BCl₃ on the ZrO₂ surface can be represented by the dissociative Langmuir isotherm, i.e., the coverage (θ) can be expressed by the following equation; ($\theta = \sqrt{kp}/(1 + \sqrt{kp})$),¹² where, k is the reactive gas adsorption constant and p is the gas pressure. When the substrate temperature was maintained at room temperature, the surface coverage of the adsorbed BCl₃ was dependent on the BCl₃ gas pressure only. Therefore, incomplete BCl₃ coverage was obtained on the ZrO₂ surface when the BCl₃ gas pressure was not high enough (0~0.15 mTorr), while a monolayer coverage of BCl₃ was

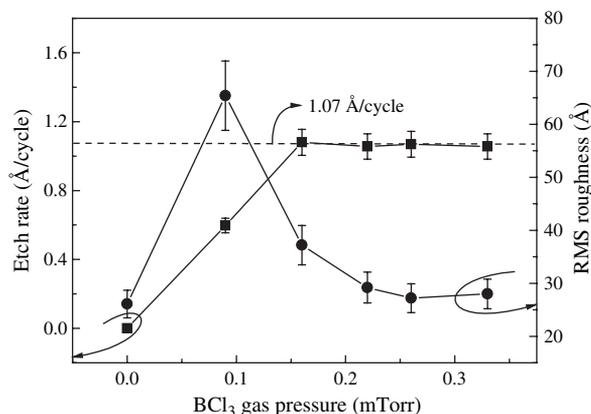


Fig. 1. The etch rate ($\text{\AA}/\text{cycle}$) and RMS roughness of ZrO₂ ALET measured as a function of the BCl₃ gas pressure at the Ar neutral beam irradiation dose of 1.6×10^{16} atoms/cm²·cycle.

obtained when the BCl_3 gas pressure was >0.15 mTorr. In addition, when BCl_3 gas covered the ZrO_2 surface, zirconium chloride (Zr-Cl) and boron oxychloride (BCl-O) bonds were formed by the chemisorption of BCl_3 on ZrO_2 . In addition, the binding energy of the Zr-O binding beneath the Zr-Cl and BCl-O was weakened due to transfer of the electron cloud from Zr-O bonds to Zr-Cl and BCl-O .¹³ Consequently, during the desorption step, ZrCl_x and BClO_x are easily removed from the ZrO_2 surface without removing the ZrO_2 located below the chemisorbed surface layer. Therefore, the ZrO_2 etch rate increases with increasing BCl_3 coverage on the ZrO_2 surface during the adsorption step but the ZrO_2 etch rate is saturated when BCl_3 surface coverage approaches 1.

In the case of the ZrO_2 surface roughness, when the BCl_3 gas pressure is <0.15 mTorr, due to the incomplete BCl_3 coverage on the ZrO_2 surface, only a portion of the surface layer is removed during each cycle. Consequently, the ZrO_2 surface roughness increases initially with increasing BCl_3 gas pressure. However, more than a half of the surface layer is removed when the BCl_3 surface coverage is >0.5 . Moreover, when the entire surface layer is covered with BCl_3 at pressures >0.5 mTorr, a surface roughness close to that of the reference is obtained due to the complete removal of one surface layer per cycle.

Figure 2 shows the ZrO_2 etch rate ($\text{\AA}/\text{cycle}$) measured as a function of the Ar beam irradiation dose during the desorption step at a BCl_3 gas pressure of 0.4 mTorr. A BCl_3 gas pressure of 0.4 mTorr corresponds to a gas pressure higher than the critical pressure (0.15 mTorr) for full surface coverage ($\theta = 1$). As shown in the figure, at full BCl_3 coverage on ZrO_2 , no ZrO_2 etching was observed when no Ar beam was irradiated indicating no spontaneous etching of ZrO_2 through the adsorption of BCl_3 only. However, when the Ar beam dose was increased from 0 to 1.485×10^{16} atoms/ $\text{cm}^2 \cdot \text{cycle}$, the ZrO_2 etch rate increased with increasing Ar beam irradiation dose due to the increased removal of the chemisorbed species, such as Zr-Cl and

BCl-O on the ZrO_2 surface. At Ar beam irradiation doses $>1.485 \times 10^{16}$ atoms/ $\text{cm}^2 \cdot \text{cycle}$, the ZrO_2 etch rate was saturated at $1.07 \text{\AA}/\text{cycle}$ due to complete removal of the chemisorbed species on the ZrO_2 surface at an irradiation dose of 1.485×10^{16} atoms/ $\text{cm}^2 \cdot \text{cycle}$ without etching the ZrO_2 exposed after removing the chemisorbed species. In the case of surface roughness, the surface roughness decreased continuously with increasing Ar beam irradiation dose from 0 to 1.485×10^{16} atoms/ $\text{cm}^2 \cdot \text{cycle}$. A minimum surface roughness close to that of the reference could be obtained at 1.485×10^{16} atoms/ $\text{cm}^2 \cdot \text{cycle}$. Further increases in Ar beam irradiation dose $>1.485 \times 10^{16}$ atoms/ $\text{cm}^2 \cdot \text{cycle}$ did not alter the surface roughness. The change in surface roughness with Ar beam irradiation dose is also related to the removal of Zr-Cl and BCl-O on the ZrO_2 surface. When the Ar irradiation dose was low, the surface roughness was higher than that of the reference due to the partial removal of chemisorbed species per desorption step. This is despite the fact that an increase in Ar beam irradiation dose decreases the surface roughness due to the removal of chemisorbed species from the ZrO_2 surface. On the other hand, the surface roughness was close to that of the reference when the Ar beam irradiation dose was high enough to remove all the chemisorbed species on the ZrO_2 surface due to the complete removal of one surface chemisorbed layer per cycle.

Figures 1 and 2 show that constant monolayer etching of $1.07 \text{\AA}/\text{cycle}$ is obtained if the BCl_3 gas pressure is higher than the critical gas pressure of 0.15 mTorr during the adsorption step and if the Ar beam irradiation dose is higher than the critical dose of 1.485×10^{16} atoms/ $\text{cm}^2 \cdot \text{cycle}$ during the desorption step of the ALET process. Figure 3 shows the constant monolayer etching parameter region measured as a function of the BCl_3 gas pressure and Ar beam irradiation dose. The constant etch rate

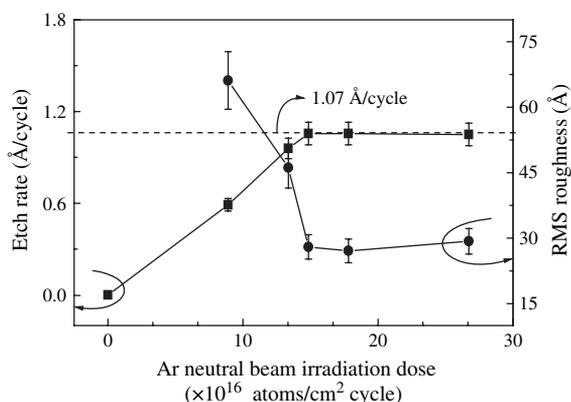


Fig. 2. The etch rate ($\text{\AA}/\text{cycle}$) and RMS roughness of ZrO_2 ALET measured as a function of the Ar neutral beam irradiation dose at a BCl_3 gas pressure of 0.4 mTorr.

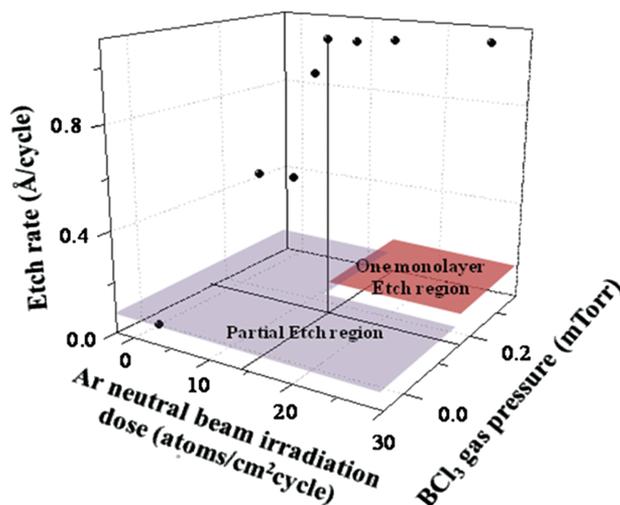


Fig. 3. ZrO_2 ALET process window measured as a functions of the BCl_3 gas pressure and Ar neutral beam irradiation dose. The Ar beam energy measured before the reflection to the reflector was 60 V.

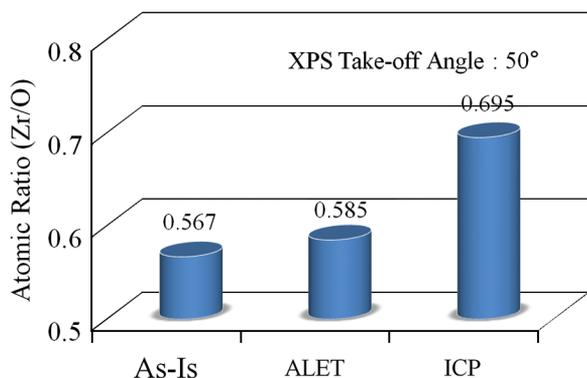


Fig. 4. The ratio of Zr/O measured using XPS after the Ar neutral beam ALET. The ratio of Zr/O measured after the etching by a BCl₃ ICP and that of ZrO₂ reference sample are also shown. ALET condition: Ar neutral beam irradiation dose of 1.6×10^{16} atoms/cm² · cycle, BCl₃ gas pressure of 0.4 mTorr. Process condition of ICP etching: inductive power of 600 W, dc bias voltage of -150 V, and BCl₃ (100 sccm)/Ar (30 sccm) at 10 mTorr.

parameter region is quite large. Hence, the monolayer etch rate condition of 1.07 Å/cycle can be easily obtained, even though the process variables, such as Ar beam dose and BCl₃ gas pressure are varied during processing. Theoretically, perfect etch uniformity is possible over a large wafer surface for ALET processing if the energy of the Ar beam is maintained at a constant level.

The use of ALET technology in this experiment did not damage the surface physically or electrically (using Ar neutral beam), and precise etch rate control and possible perfect etch uniformity was achieved. The surface composition of ZrO₂ etched by ALET was compared with that of the reference sample and that etched by conventional BCl₃ ICP. The following ICP etching conditions were used: 600 Watts of 13.56 MHz RF power, -150 volts of dc-bias voltage, and 13 mTorr by flowing BCl₃ (100 sccm)/Ar (30 sccm). Under these etch conditions, ZrO₂ was etched at 150 Å/min. One of the single monolayer etching conditions (Ar neutral beam irradiation dose: 1.485×10^{16} atoms/cm² · cycle, BCl₃ gas pressure: 0.4 mTorr) was used for the ALET condition. For both etch conditions, the ZrO₂ etch depth was maintained at 50 Å. Therefore, ZrO₂ was etched for 20 seconds and 50 cycles for ICP and ALET etching, respectively. The etched ZrO₂ surfaces and reference sample were examined by XPS with a take-off angle at 50°. The results are shown in Figure 4. The Zr/O ratio of the reference ZrO₂ sample was 0.57. The Zr/O ratio of the ZrO₂ etched by ALET was 0.58. Therefore, the ZrO₂ surface composition etched by the ALET was not changed after etching. On the other hand, the ratio of ZrO₂ etched by ICP was 0.69. Therefore, a Zr-rich surface was formed after ICP etching. This was attributed to differences in the volatility of ZrCl_x and BClO_x, i.e., the lower volatility of ZrCl_x than BClO_x.¹⁴ However, in the case of ALET, the surface composition remained the

same as that of the reference for ALET due to exactly one monolayer being removed per cycle.

4. CONCLUSIONS

In this study, ZrO₂ was etched by ALET using BCl₃ as the adsorption gas and an Ar neutral beam during the desorption step, and its etch characteristics were investigated as a function of the BCl₃ gas pressure and Ar neutral beam irradiation dose. The results showed that one monolayer etching condition of 1.07 Å/min could be obtained when both BCl₃ gas pressure and Ar neutral beam irradiation dose were higher than the critical values of 0.15 mTorr and 1.485×10^{16} atoms/cm² · cycle, respectively. In addition, if the monolayer etching condition is satisfied, the surface roughness after etching was similar to that of the reference (as-received) sample. The surface composition after etching by ALET was similar to that of the reference sample due to complete removal of the surface layer per cycle for the ALET condition while the surface composition after ICP etching was modified significantly due to differences in the volatility of chemisorbed species. In addition, due to the wide window of the ALET condition, it is believed that perfect etch uniformity can be easily obtained over a large area wafer surface if a constant Ar bombardment energy can be maintained during the desorption step.

Acknowledgments: This work supported by the National Program for Tera-Level Nano devices of the Korea Ministry of Education, Science and Technology (MEST) as a 21st Century Frontier Program.

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Received: 9 October 2008. Accepted: 17 March 2009.