Selective composition modification deposition utilizing ion bombardment-induced interfacial mixing during plasma-enhanced atomic layer deposition

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We investigated the effects of low-energy (<15 eV) ion bombardment on the properties of Al2O3 plasma-enhanced atomic layer deposition (ALD) films. High-flux ion bombardment caused interfacial mixing with underlying material of Si, and AlSiOx films were formed instead of Al2O3 films. The interfacially mixed AlSiOx films were selectively formed on single-crystal and amorphous Si surfaces, whereas normal ALD Al2O3 films were formed on SiO2 surfaces. The interfacially mixed AlSiOx films possessed thin (~0.8 nm) SiO2 interlayers and abrupt interfaces. The interfacial mixing synthesis has the potential to realize simultaneous area and topographically selective depositions in combination with selective etching.

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With the continuous progress of the nanoscale integration of two- and three-dimensional electronic devices, the need for selective deposition is increasing because self-aligned patterning with selective deposition is advantageous over conventional patterning with lithography for improving pattern alignment and reducing patterning complexity.1,2) Area-selective deposition typically relies on the deactivation of certain areas of substrate by self-assembled monolayers (SAMs) or polymer films.2) Atomic layer deposition (ALD) is a suitable process for selective deposition because it depends strongly on surface chemistry. The main challenges for area-selective ALD are that the selectivity is lost after few nm thick films are deposited and coating defect-free SAMs generally takes extremely long times.2,13,14) Moreover, plasma-enhanced ALD (PE-ALD) cannot generally be used for selective deposition because the plasma exposure degrades SAMs or polymer films.2)

In our approach for overcoming these challenges, selective deposition process is conducted by combining selective composition modification deposition and postprocess selective etching as illustrated in Fig. 1. In the first deposition process, different composition films are simultaneously deposited on different material surfaces. This type of selective deposition has been categorized as chemical-composition-selective deposition.15) It may be realized by selective composition modification of deposited film utilizing ion bombardment during PE-ALD. The ions in plasma are accelerated by the voltage across plasma sheath and perpendicularly incident on substrate surface. Because the directional ions scarcely incident on vertical sidewalls, the modification does not occur on them. Therefore, different composition films may be simultaneously deposited on not only different material but also different topographical orientation surfaces. In the second etching process, the modified composition films are selectively removed through anisotropic etching or lift-off. Thus, it enables simultaneous area-selective and topographically selective depositions.16,17) The purpose of this study is to explore the possibility of selective composition modification PE-ALD of Al2O3 films by utilizing ion bombardment. The selective etching process will be developed in the future.

In Al2O3 ALD, films are generally grown sub-monolayer by sub-monolayer by sequentially repeating two half cycles.18–24) In the first half cycle, gas phase precursor such as trimethylaluminum (TMA) adsorbs on substrate surface in a self-limiting manner. In the second half cycle, the surface is exposed to reactive species such as O radicals produced in O2 plasma.24) The second half cycle includes an oxidation and purge steps. In the oxidation step, positive ions in plasma such as O2+ impinge on substrate surface. The momentum of ion is transferred to the surface, enhancing surface reaction, atom displacement, diffusion, migration, crystallization, bond breaking, and sputtering.23) which can affect the properties of deposited film.

Ion bombardment onto substrate surface often plays a crucial role during deposition processes.25–33) For example, we reported the effect of low-energy Ar+ ion bombardment on the properties of phosphorus-doped Si films deposited on single-crystal Si substrates utilizing a sputtering apparatus.25–27) At low substrate temperature below 350 °C and without ion bombardment, amorphous Si films were formed due to the lack of energy for epitaxial growth. The ion bombardment onto the growing film surface enhances the surface migration of Si adatoms and enables epitaxial growth.
even at low-temperatures below 300 °C. Total ion energy per Si adatom is the product of (individual) ion energy and ion dose ratio, which is defined by the number of bombarding Ar⁺ ions per deposited Si atom. We experimentally confirmed that the total ion energy is a main factor for the epitaxial growth at low-temperatures. Besides, for ion energy above 25 eV, ion bombardment causes physical damages and deteriorates film crystallinity. Thus, low-energy high-flux ion bombardment is effective to form high-quality films.

The effects of ion bombardment on PE-ALD have been investigated using remote inductively coupled plasma (ICP) reactors.28–32 The properties of various material films formed with ALD were reported to be controlled by substrate biasing.28–32 For instance, the substrate bias voltages ranging from −100 to −200 V are effective to increase the mass densities of specific material films such as CoOₓ, TiO₂, HfO₂, and TiN.30,31 The effects of ion bombardment have been investigated mainly by varying the substrate bias voltage. The corresponding ion energy may be in the range 20–300 eV.28–30 However, for ion energies below 20 eV, there are no data on the effects of ion bombardment on PE-ALD. In this study, the effects of low-energy ion bombardment on the properties of Al₂O₃ PE-ALD films were investigated. Herein, the ion energy was maintained below 15 eV to suppress physical damages due to the ion bombardment.25–27,33,34 The effects of ion bombardment were investigated mainly by varying ion dose. The typical ion dose obtained in the remote ICP reactor is $10^{15}$ cm⁻² s⁻¹ and ion bombardment may have no effect at this level at such low ion energies. To confirm the effects of ion bombardment, it is necessary to increase the ion flux. We employed a direct ICP reactor in which the plasma was produced in the vicinity of the substrate while maintaining the ion energy at low level.

The ions are accelerated by the voltage across the sheath $\phi_s$ and impinge on the substrate surface. $\phi_s$ oscillates owing to the capacitive coupling between plasma and ICP coil. When a sinusoidal RF sheath voltage of amplitude $\tilde{\phi}_s$ is assumed, the average sheath voltage $\bar{\phi}_s$ is expressed as

$$\bar{\phi}_s = \frac{T_e}{2} + \frac{T_e}{2} \ln \left( \frac{m_i}{2\pi m_e} \right) + \frac{T_e}{2} \ln \left[ I_0 \left( \frac{\tilde{\phi}_s}{T_e} \right) \right].$$

where $T_e$ is an electron temperature in eV, $m_i$ is an ion mass, $m_e$ is an electron mass, and $I_0$ is a zeroth-order modified Bessel function. When the ion mean free path is shorter than the sheath thickness, the accelerated ions collide with the neutral gas species in the sheath and lose kinetic energy. Therefore, the ion energy is distributed with $\bar{\phi}_s$ as the maximum. The maximum ion energy $\varepsilon_{im}$ is expressed by

$$\varepsilon_{im} = e\bar{\phi}_s.$$ 

From Eq. (1), $\varepsilon_{im}$ is decreased by lowering $\tilde{\phi}_s$. We employed an electrically balanced self-resonant coil to reduce the capacitive coupling, thereby realizing low $\varepsilon_{im}$. No RF bias was applied to the substrate to realize lowest $\varepsilon_{im}$.

The energy and flux of O₂⁺ ions were evaluated using RF-compensated Langmuir and planar probes. Selected data are summarized in Table I. The ion flux $\Gamma_i$ can be varied over a wide range by changing O₂ pressure. The value of $\Gamma_i$ at 1 Torr was 1/289 of that at 0.01 Torr. The significant decrease of $\Gamma_i$ with the increase of O₂ pressure is owing to the decrease of electron density in upstream plasma for intensifying electron energy loss caused by inelastic collisions and decrease of an ambipolar diffusion coefficient in the downstream plasma. A low ion energy of 14.9 eV and a high-ion flux of $4.68 \times 10^{15}$ cm⁻² s⁻¹ were simultaneously realized at 10 mTorr. The ion dose ratio $\Gamma_{i/Al}$ denotes the number of bombarding ions per deposited Al atom. Reported typical values of $\Gamma_{i/Al}$ are 0.01—1.28 The values of $\Gamma_{i/Al}$ at 10 mTorr were more than two orders of magnitude higher than the typical values. In this study of PE-ALD, the ion dose ratio was widely controlled by changing O₂ pressure and oxidation time while keeping the ion energy at low value.

In the growth of Al₂O₃ films, TMA was used as a precursor, O₂ plasma as a reactant, and Ar as a purge gas. The time taken for one ALD cycle comprises $T_1$, $T_2$, $T_3$, and $T_4$, where $T_1$ is the precursor exposure time, $T_3$ is the oxidation time, and $T_2$ and $T_4$ are the purge times.36 $T_1$, $T_2$, and $T_4$ were fixed at 30, 60, and 60 s, respectively, and were not optimized. During $T_3$, O₂ plasma was excited with an RF power of 1000 W. $T_3$ was varied in the range 5—60 s. The Al₂O₃ films were grown on moderately doped p-type Si (100) and thermally grown SiO₂ surfaces. Additionally, Al₂O₃ films were formed on line-and-space nanostructures to investigate the influence of topographical face orientation. The line-and-space nanostructures were formed of amorphous Si in order to suppress the influence of crystal orientation on the properties of deposited films. The line width, line pitch, and aspect ratio were ∼130 nm, ∼260 nm, and ∼1.3, respectively. The amorphous Si films were formed on thermally grown SiO₂ surfaces in a low-pressure chemical vapor deposition reactor at 450 °C using SiH₄. The properties of films deposited under the conventional low ion-dose ($4.85 \times 10^{14}$ cm⁻² s⁻¹, $\Gamma_{i/Al} = 0.83$) condition are shown in Figs. 2(a)—2(d). Figures 2(a) and 2(b) show cross-sectional TEM images of Al₂O₃ films formed on single-crystal Si and SiO₂ surfaces, respectively. Figures 2(c) and 2(d) are the corresponding energy dispersive X-ray spectroscopy (EDS) profiles. The deposited Al₂O₃ films were amorphous over a wide range of ion doses.37,38 The thicknesses of the Al₂O₃ films formed on both Si and SiO₂

| Pressure (mTorr) | Oxidation time (s) | Maximum ion energy $\varepsilon_{im}$ (eV) | Ion flux $\Gamma_i$ (cm⁻² s⁻¹) | Ion dose per cycle (cm⁻² cycle⁻¹) | Ion dose ratio $\Gamma_{i/Al}$ |
|-----------------|-------------------|-----------------------------------------------|--------------------------------|----------------------------------|-----------------------------|
| 1000            | 10                | 11.8                                         | $1.62 \times 10^{13}$           | 0.30                             |                              |
| 1000            | 30                | $\uparrow$                                    | $\uparrow$                      | $4.85 \times 10^{14}$           | 0.83—1.0                    |
| 1000            | 60                | $\uparrow$                                    | $\uparrow$                      | $9.70 \times 10^{14}$           | 1.7                         |
| 260             | 30                | 6.7                                          | $1.32 \times 10^{14}$           | 6.8                             |                              |
| 10              | 5                 | 14.9                                         | $4.68 \times 10^{14}$           | 46—49                           |                              |
| 10              | 30                | $\uparrow$                                    | $\uparrow$                      | $1.40 \times 10^{17}$           | 240—310                     |
were 3.3 nm, where a growth per cycle (GPC) was 0.17 nm/cycle. It corresponds to 0.56 monolayer/cycle.\(^{39}\)

The values of GPC obtained were greater than those for thermal ALD (0.10–0.13 nm/cycle).\(^{40,41}\) This may be because highly reactive O radicals produce higher density adsorption sites for TMA molecules than H\(_2\)O molecules. The thickness, morphology, and composition of the Al\(_2\)O\(_3\) film deposited on the Si surface were the same as those deposited on the SiO\(_2\) surface. As seen in Fig. 2(a), an interlayer with a thickness of 4.8 nm is clearly observed. The abrupt EDS profiles indicate that the interlayer is composed of SiO\(_x\). The oxide film was likely formed by highly reactive O radicals in the first few cycles. The interlayer obtained was thicker than reported values of 1–3 nm due to the relatively long oxidation time of 30 s.\(^{41–43}\) As seen in Fig. 2(d), the composition ratio of Al\(_2\)O\(_3\) and SiO\(_2\) from the EDS profiles is not identical to stoichiometric ratio. This may be due to the deviation of each atom sensitivity because of various factors in TEM-EDS analysis.

Figure 3 shows the thickness of deposited films on flat single-crystal Si and SiO\(_2\) surfaces and on the top faces of amorphous Si line-and-space patterns as a function of \(\Gamma_{i/Al}\). The films were formed under various oxidation conditions of pressure in the range of 0.01–1 Torr and oxidation time in the range of 5–60 s over 20 cycles. The corresponding values of \(\Gamma_{i/Al}\) were ranging from 0.30 to 310. The films deposited on SiO\(_2\) surfaces, the thickness was around 3.1 nm and almost constant over a wide range of \(\Gamma_{i/Al}\). For the films deposited on single-crystal and amorphous Si surfaces, when \(\Gamma_{i/Al} < 49\), the thickness was also around 3.1 nm. In contrast, when \(\Gamma_{i/Al} \geq 240\), the thickness suddenly increased to around 5.5 nm. There seems to be a certain threshold of the ion dose at which the film thickness significantly changes. The reason why the thicker films were obtained is described below.

The properties of films deposited under a high-ion-dose (1.40 \(\times\) 10\(^{17}\) cm\(^{-2}\) cycle\(^{-1}\), \(\Gamma_{i/Al} = 240\)) condition are shown in Figs. 4(a)–4(d). The morphology of the Al\(_2\)O\(_3\) film formed on SiO\(_2\) are the same as those for the case of low ion dose (\(\Gamma_{i/Al} = 0.83\)). By contrast, those formed on Si were entirely different. As shown in Fig. 4(c), the Si profile overlaps the Al profile, indicating that the film is composed of AlSiO\(_x\). As shown in both TEM image and EDS profiles [see Figs. 4(a) and 4(c)], the AlSiO\(_x\) film has a layered structure of Al-/Si-/Al-rich layers. In addition, a thin (~0.8 nm) interlayer composed of SiO\(_x\) exists between the
The interface between the SiO film and the Si substrate. There exists an abrupt interfacial mixing with the underlying Si into the deposited film.

The mechanism of interfacial mixing is hypothesized as follows. In this study, the first step in PE-ALD process was oxidation, where Si substrate surface was oxidized by O₂ plasma. A several nm thick SiO film was formed in a time shorter than the oxidation time per cycle (5–60 s), and then the thickness of SiO film was almost saturated. The oxidation conditions were not optimized for obtaining high-quality SiO₂ film. In particular, the substrate ALD temperature of 150 °C was too low, and the ion energy of 14.9 eV was too high for plasma oxidation.** Non-optimized oxidation condition may result in the formation of degraded SiO film containing many defects. When the imperfect SiO film is exposed to high-flux O²⁺ ion bombardment, energetic ions can create new defects into the film, and some of the O₂⁺ ions can penetrate into SiO film. The Si–O–Si network of SiO₂ film may become weaker gradually, and then suddenly partially collapses when a certain threshold is exceeded. Consequently, low-density SiO film may appear under very-high-flux ion bombardment. In subsequent oxidation step, adsorbed Al atoms on SiO₂ surface are knocked-on by the momentum transfer from energetic O₂⁺ ions and penetrate into SiO₂ film. In SiO₂ film, multiple collisions associated with Al atoms can occur and Al atoms penetrate deeper. The low-density SiO film may lead to a significant increase of Al penetration depth. As a result, Al atoms are taken into SiO₂ films resulting in AlSiO₃ film. In the initial few cycles, where Al concentration and film density is still low, some of the Al atoms may pile up near the interface between SiO₂ and Si substrate. After relatively high-density AlSiO₃ film is formed by the incorporation of Al atoms, normal Al₂O₃ film is deposited on it. In this way, AlSiO₃ film having the layered structure of Al/Si-Al-rich layers may be formed. On the other hand, when ion dose is below a certain threshold, the Si–O–Si network of SiO₂ film is still maintained. On thermally grown SiO₂ surface, such surface modification by O₂⁺ ion bombardment cannot occur owing to its inherent robust Si–O–Si network. Thus, normal Al₂O₃ films were deposited. However, this potential mechanism is speculation at this stage. Further analyses are necessary to clarify the mechanism of interfacial mixing as a result of ion bombardment.

To further investigate the effects of ion bombardment, thin (~3 nm) ALD films were formed on line-and-space nanostructures of amorphous Si. Figures 5(a) and 5(b) present cross-sectional TEM images of deposited films under an intermediate-ion-dose (Γᵢ/Al = 49) and high-ion-dose (Γᵢ/Al = 310) conditions, respectively, between which deposited film thickness on Si substrate fairly changed as seen in Fig. 3. The pressure in the oxidation steps was 10 mTorr, at which an ion mean free path was much longer than the shear width. Owing to the collisionless sheath, directional ions with a kinetic energy of around εᵢm = 14.9 eV were perpendicularly incident on the substrate. The directional ions were densely incident on the horizontal top and bottom faces, whereas scarcely incident on the vertical sidewalls. In the intermediate-ion-dose (Γᵢ/Al = 49) case, conformal Al₂O₃ films and SiO₂ interlayers are observed over the entire surface, including the corners of the pattern. This result clearly indicates that for Γᵢ/Al < 49 and low-energy (εᵢm = 14.9 eV) ion bombardment has no effect on the morphology, thickness, or composition of the deposited films and interlayers, regardless of the underlying materials. By contrast, in the case of high-ion dose (Γᵢ/Al = 310) conditions, no interlayer was observed at the top and bottom faces, indicating that interfacially mixed AlSiO₃ films were formed on the horizontal faces due to the ion bombardment, whereas relatively thick interlayers were observed at the sidewalls, indicating that normal ALD Al₂O₃ films were deposited on the vertical faces. The difference in the film morphology is apparently due to the directional ion bombardment. In addition, there is a certain ion dose threshold above which interfacial mixing occurs. The value of this threshold is in the range 2.34 × 10¹⁶–1.40 × 10¹⁷ cm⁻² cycle⁻¹ (49 < Γᵢ/Al < 240) at εᵢm = 14.9 eV. The thickness and morphology of deposited films on amorphous Si surfaces were the same as those on single-crystal Si surfaces regardless of the ion dose. It seems that there is no influence of the crystallinity of underlying Si on the properties of deposited films.

In summary, the effects of low-energy (<1.5 eV) ion bombardment on Al₂O₃ PE-ALD were investigated using a direct ICP reactor with a self-resonant planar coil. The properties of the Al₂O₃ films formed on single-crystal Si, amorphous Si and SiO₂ surfaces were compared over a wide range of ion doses from 1.62 × 10¹⁴ to 1.40 × 10¹⁷ cm⁻² cycle⁻¹ (0.30 ≤ Γᵢ/Al ≤ 310). Under a low-ion-dose condition, ion bombardment had no identifiable effect on the morphology, thickness, and composition of the deposited Al₂O₃ films irrespective of the substrate material used. By contrast, under a high-ion-dose condition of 1.40 × 10¹⁷ cm⁻² cycle⁻¹, which is over two orders of magnitude higher than typical values, ion bombardment yielded significant effects on the properties of the film. We determined that AlSiO₃ films several nm thicker than normal ALD Al₂O₃ films were selectively formed on the single-crystal and amorphous Si surfaces owing to interfacial mixing with the underlying material of Si, whereas normal ALD Al₂O₃ films were formed on the SiO₂ surfaces. The interfacially mixed AlSiO₃ films had thin (~0.8 nm) SiO₂ interlayers and abrupt interfaces. The ALD films were also
formed on line-and-space nanostructures. The interfacially mixed AlSiO films were selectively formed on the horizontal top and bottom faces, whereas normal ALD Al2O3 films were formed on the vertical sidewalls, where the ions scarcely impinge.

The notable feature of the interfacial mixing ALD relates to selective deposition. In this study, it was demonstrated that the interfacial mixing ALD realizes material and topographical orientation selective composition modificiation deposition as illustrated in Fig. 1. Silicate compound films, such as AlSiO, may be selectively removed by etching or lift-off. Therefore, the combination of interfacial mixing ALD on the patterned substrate and selective etching enables area-selective deposition. In the same manner, the interfacial mixing ALD on 3D structures leads to the topographically selective deposition. Thus, the interfacial mixing ALD has the potential to realize simultaneous area-selective and topographically selective depositions, which are becoming important techniques for next-generation nanoelectronics.

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