PAPER

Enhanced interfacial reaction of precursor and low temperature substrate in HfO₂ atomic layer deposition with highly Ar diluted O₂ plasma

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Abstract

The internal energy of metastable oxygen atoms in highly Ar diluted oxygen plasma was utilized in the initial stage of the atomic layer deposition of HfO₂ on SiO₂/Si(100) at low temperature of 150 °C. The highly Ar-dilute oxygen plasma enhanced the oxidation of the incomplete chemisorption state of the precursor at low temperature, successfully formed Hf silicate interface, and decreased the impurity nitrogen atoms in the HfO₂ film compared to the pure oxygen plasma ALD. Residual nitrogen atoms in the film were found to cause excessive precursor adsorption. The results of plasma emission spectroscopy and ion saturation current measurements show that the highly Ar-diluted O₂ plasma can increase the O radical formation rate for ion fluxes at pressures above 100 Pa. The relatively high metastable oxygen atom irradiation is thought to be responsible for the removal of HfN bonds and enable ALD on low temperature substrates. Atomic force microscopy showed that the root mean square roughness in the high Ar dilution sample was 0.093 nm, indicating high flatness.

1. Introduction

In the field of microelectronics, a high dielectric constant (high-k) thin film such as HfO₂ or HfSiON is in use as a gate insulating film of a thin film transistor [1–8]. These high-k films are used to reduce the leakage current while maintaining the drive current by quasi-maintaining the scaling law [9–11]. In recent years, research on ReRAM devices utilizing HfO₂ has also made progress [12, 13].

Atomic layer deposition (ALD) is used as a technique for forming these nanoscale thin films. ALD is a technique for forming a film by repeating a deposition process for each adatom layer mainly by alternately supplying a metal-organic precursor and an oxidizing agent or a nitriding agent [14–17]. ALD has been spreading as an indispensable technology for the formation of three-dimensional devices typified by recent FinFETs [18, 19], and 3D-NANDs [20, 21], and its application has been extended to coating not only semiconductors but also organic materials [22–24] and nanoparticles [25, 26].

During the thermal ALD process, precursor semi-atomic layer deposition requires surface activation by thermal energy, and the film quality and deposition rate generally depend on the substrate temperature [27, 28]. The fact affects applications requiring low-temperature processes such as the coating on organic polymer substrates [29–32]. In contrast to thermal ALD, in which the reaction depends on thermal energy, plasma-enhanced ALD (PEALD) makes it possible to lower the processing temperature by utilizing active species from plasma for the reaction [33–35]. PEALD is also used for HfO₂ film formation [36–38] achieving a dielectric constant higher than thermal ALD [39].

The role of reactive oxygen species in the ALD process of HfO₂ has been studied theoretically. Jeon et al [40] used density functional theory to calculate the oxidation reaction pathway of Hf(OH)₃NH₂ for metastable...
oxygen molecule $\text{O}_2(a^1\Delta_g)$, ground state oxygen molecule $\text{O}_2(X^3\Sigma_g^−)$, metastable oxygen atom $\text{O}(^1\text{D})$ and ground state oxygen atom $\text{O}(^3\text{P})$. $\text{Hf(OH)}_2\text{NH}_2$ simulates the adsorption state of a precursor with H atoms. The results show a process leading to the desorption of $^1\text{HNO}$ via the singlet transition state $^1\text{[Hf(OH)}_2\text{NH}_2 \cdot \text{O}_2]$ for all but the ground state oxygen molecules. The high reactivity of the excited atoms is not shown. However, an important assumption for this calculation is that the chemisorption on the substrate is complete. The oxidation of the HfN bond in the case of incomplete chemisorption between the substrate and Hf has not been fully studied.

Among atomic oxygen, metastable oxygen atom O ($^1\text{D}$) is predicted to utilize the internal energy of 1.97 eV for the oxidation reaction. Regarding the utilization of O ($^1\text{D}$) for surface reaction, improved SiO$_2$ film quality by rare gas diluted oxygen plasma was proposed [41, 42]. We have elucidated the mechanism by which rare gas (Ar, Kr) excited atoms generate O ($^1\text{D}$) by dissociative excitation of oxygen molecules, and the rare gas dilution environment enables flux enhancement to the substrate surface [43, 44]. The principle has been demonstrated for the formation of high-quality SiO$_2$ films [44, 45].

The large supply of metastable oxygen atoms by rare gas diluted oxygen plasma can contribute to the improvement of low-temperature ALD film quality. The precursor physically adsorbed on the substrate requires the supply of activation energy to shift to the chemisorption state at a low substrate temperature. Although the ground state O ($^3\text{P}$) can oxidize HfNH$_2$, it has not been clearly shown whether the reaction can proceed at the interface of the physisorbed state Hf precursor. If O ($^3\text{P}$) is not sufficiently reactive, then O ($^1\text{D}$), which possesses high internal energy, is proposed to play a major role. The concept of the reaction scheme is summarized in figure 1. The model is based on the supply of metastable oxygen atoms or their internal energies to the interface between the low-temperature substrate and the physically adsorbed Hf precursor, resulting in the dissociation and oxidation of the HfN bond and the release of HNO to the gas phase. The metastable oxygen atoms are believed to compensate for the lack of activation energy for the interfacial reaction due to the low temperature substrate.

The purpose of this study is to utilize the supply of metastable oxygen atoms by highly diluted O$_2$ (1%)/Ar plasma to the formation of HfO$_2$ thin film by PEALD in low temperature region, and to promote the interfacial reaction between precursor and substrate. Optical emission spectroscopy (OES), probe measurement, x-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM) were used as experimental methods.
2. Experimental

Figure 2 shows the PEALD equipment used in the study. The reactor is a cylindrical stainless-steel chamber with an inner diameter of 110 mm and a height of 250 mm. It has a plasma source at the top, a sample exchange door at the front, and an exhaust port at the back. The sample is placed on the center axis of the chamber, 160 mm below the plasma source connection. A downstream type configuration is adopted. A resistive heater heats the sample and the chamber, and the temperature in this study is set to 150 °C. The sample is a 1 mm thick SiO₂/Si(100) wafer cut in 10 × 10 mm², and its surface is covered with a 1.0 nm thick SiO₂ film formed in nitric acid at 110 °C. The standard Omicron SPM sample plate of stainless steel is used as the sample holder. A combination of a turbo-molecular pump (Pfeiffer, 150 l s⁻¹) and a rotary pump (Adixen, 250 l min⁻¹) evacuates the reactor through a diaphragm valve. The base pressure is 3 × 10⁻⁵ Pa, and the pressure in all regions is monitored by a crystal/cold cathode gauge (Tokyo Electronics, CC-10).

The plasma source is an inductively coupled plasma (ICP) in a stainless-steel tube having an inner diameter of 34 mm and a length of 120 mm. A 10-turn stainless steel wire is used as a coil and connected to a VHF power supply (manufactured by Tokyo High Power, 70 MHz, 100 W) via a matching circuit. The plasma gas is Ar and O₂ supplied by a mass flow controller (Stec, SEC-400). Gas is introduced from the side of the plasma source.

In order to investigate the characteristics of the plasma, OES and ion saturation current measurements are performed while changing the gas composition and pressure. A viewport is installed in the lower part of the chamber, and an axial line integral of optical emission is obtained by a spectroscopic including a lens, an optical fiber, and a multi-channel spectrometer (Oceanphotonics, HR-4000). O I (615.60 nm, 615.68 nm, 615.82 nm) [46] was selected for the spectroscopic object. The emission reflects the excited atom density of the O 4d(⁵D) level (12.7 eV) generated by electron collision with oxygen atoms. An ion current probe made of stainless steel 30 × 30 mm² in size is placed at the sample position from the lower part of the chamber via an introduction terminal, and an ion saturation current is measured by applying a bias voltage of −15 V.

Tetrakis EthylMethylAmino Hafnium (TEMAH) is used as the hafnium precursor, and during the loading process, the vapor is diffused from the cylinder heated to 130 °C and filled in the reactor. After adsorbing TEMAH to the sample, N₂ gas flow is used to purge excess TEMAH in the reactor. An oxygen filter is installed in the N₂ introduction path to remove the impurity oxidant in N₂. Figure 3 shows a specific PEALD procedure. When supplying TEMAH, the exhaust valve is closed, and the reactor is filled with TEMAH vapor for 20 s. The
pressure of TEMAH in the chamber is around 10 Pa. After the evacuation of TEMAH, N₂ flows at a flow rate of 50 c.c. min⁻¹ at a pressure of 100 Pa for 60 s for scavenging. After the evacuation of N₂, plasma gas flows at a total flow rate of 100 c.c. min⁻¹ to generate inductively coupled plasma for 60 s and then the reactor is evacuated.

The chemical analysis of the sample is performed by XPS (Physical Electronics, PHI 1600 ESCA) outside the PEALD chamber. The excitation x-ray is a 400 W Mg K-α ray. The escape angle of photoelectrons is 45°. Multipak software from Physical Electronics is used for data analysis. In order to focus on the process evaluation, the HfO₂ film made by PEALD is evaluated without annealing.

A non-contact mode AFM evaluates the roughness of the HfO₂ film surface. The sample is introduced into an ultra-high vacuum AFM (Omicron, VT-AFM) [47, 48], and the sub-nanometer range morphology of the surface is imaged by a cantilever (Nanosensors, SSS-NCH) with a tip curvature of 2 nm. For data evaluation, SPIP software from Image Metrology is used.

3. Results and discussion

3.1. Plasma characteristics

Figure 4(a) shows the relation of O I intensity and ion saturation current density. Details of the OES and ion saturation current measurement are shown in the supplemental is available online at stacks.iop.org/JPCO/4/095013/mmedia. Here, O I intensity is the integral of the three O atom emission lines from 615.2 nm to 616.2 nm, excluding the background signal. In O₂, the maxima marked at 10 Pa in O I intensity and ion saturation current density, and both decrease with increasing pressure. In O₂ (1%)/Ar, the ion saturation current density decreases with increasing pressure while the O I intensity increases. Figure 4(b) shows the pressure dependence of the ratio of O I intensity to ion saturation current density (OI/Ji), which is a parameter that indicates the relative intensity of O to the ions among the active particles supplied by the plasma. OI/Ji increases with gas pressure in the O₂(1%)/Ar plasma. On the other hand, OI/Ji peaks at 50 Pa in the O₂ plasma, and decreases with increasing pressure in the pressure range above 50 Pa, where HfO₂ deposition was possible in this study. The pressure dependence of OI/Ji shows the exact opposite trend depending on the presence or absence of Ar dilution. This feature indicates that the use of O₂ (1%)/Ar plasma has the potential to reduce film damage due to ion bombardment and activate the surface reaction due to O radicals simultaneously.

3.2. Effect of Ar dilution on HfO₂/SiO₂ interface

Due to the stability of the SiO₂ substrate surface, the surface reactivity of TEMAH in pure O₂ plasma ALD at low substrate temperature is insufficient, and the film quality in the first 10 ALD cycles is low. (The ALD cycle dependence of the HfO₂ film quality is shown in the supplemental) Therefore, the effect of Ar dilution on the film quality is verified for the 10 ALD cycle sample.

Figures 5(a)–(d) show the XPS spectra of Hf 4f, O 1s, N 1s, and C 1s after the 10 PEALD cycles with 300 Pa O₂ (1%)/Ar plasma and 50 Pa pure O₂ plasma half-cycle. Ion saturation currents of 50 Pa pure O₂ plasma and 300 Pa O₂ (1%)/Ar plasma are 6.7 × 10⁻⁸ A cm⁻² and 1.1 × 10⁻⁷ A cm⁻², the two are equivalent. This means that the effects of ion injection on film growth are similar in the two cases. For Hf 4f in figure 5(a), the peak of HfO₂ is evident in the case of O₂ (1%)/Ar plasma, and the peak shift due to the Hf silicide [39, 49] is observed in the sample with O₂ plasma half-cycle. In O 1s of figure 5(b), a peak shift to 532 eV due to Si–O–Hf can be confirmed in the case of O₂ (1%)/Ar plasma. This reflects the presence of hafnium silicate at the SiO₂/HfO₂ interface. In the case of pure O₂ plasma, the peak of Si–O–Si is strong, and the formation of hafnium silicate is not clear.

Angle-resolved XPS measurements of each sample were performed over a take-off angle of 20–75°, and the HfO₂ film thickness was derived with Multipak software. The HfO₂ film thickness was 0.7 nm for O₂ (1%)/Ar plasma. Therefore, the growth per cycle (GPC) is 0.07 nm.

![Figure 3. Procedure of PEALD for HfO₂ deposition.](image)
Figure 5(c) shows the XPS spectrum of N 1s. In the case of O2 (1%)/Ar plasma, the C–N–H [50] and Hf–N–H [51] signals are small compared to the pure O2 plasma.

Figure 5(d) show the XPS spectrum of C 1s. The C 1s spectrum is decomposed in the C–C [52], C–O [53], C–N [54], C=O [55], and O–C=O [55] components. The C–C component is recognized as an organic molecule adsorbed during transport. The C–O, C–N, C=O, and O–C=O components originate from organic molecules mixed into the HfO2 film during the PEALD process. In the case of O2 (1%)/Ar plasma, C–N and C=O were reduced, and no O–C=O was generated in comparison to the pure O2 plasma.

Figure 6 shows the C 1s and N 1s signal intensities with respect to the Hf 4f signal intensity for different gas pressure. The Hf 4f signal is assumed to be proportional to the thickness of the deposited HfO2 film. The amount of C and N highly depends on the thickness of the HfO2 film, and the film thickness changes non-monotonically with the gas pressure. Plotting C and N against Hf gives a clearer trend of the amount of impurities against the film thicknesses. Here, the intensities are derived by the integral for the binding energy (Hf 4f: 14 to 24 eV, N 1s: 396 to 405 eV) for Hf 4f and N 1s. For C 1s, integral is performed for the components of C–C, C–N, and C–O in the film. Since the origin of carbon impurities has variety, such as the organic molecules adsorbed in the chamber, it may not completely reflect the purity of the film formation process. In contrast, it is reasonable to judge that the source of nitrogen impurities is TEMAH. In the case of O2 (1%)/Ar plasma, the N 1s intensity shows the lowest relative to the Hf 4f intensity at the pressure of 300 Pa. Under that condition, typical ALD growth is observed. As an overall trend, the HfO2 film thickness increases in the conditions with high impurity content, as indicated by the C 1s and N 1s intensities. At Hf 4f/ 3000 cps, high growth are seen to be caused by impurities. Impurity concentration and growth per cycle (GPC) are not monotonic with respect to pressure changes. This will be discussed later with the OI/ J parameters.

Figure 7 shows the relation between the intensity ratio of N 1s to Hf 4f/(N 1s/Hf 4f) and the Hf 4f/intensity and GPC. Here, GPC is the average value over 10 cycles. At O2 (1%)/Ar 300 Pa, N 1s/Hf 4f is lowest and the GPCs is moderate. Here, typical ALD behavior is seen. Equally high GPCs were observed for samples with high N 1s/Hf 4f (O2 50, 200 Pa and O2(1%)/Ar 50 Pa). It can be imagined that the film with more impurities has a
higher deposition rate due to the large number of surface adsorption sites derived from the impurities. The GPC is lower (0.04 nm) at O$_2$ (1%)/Ar 100 Pa. In the O$_2$ 10 Pa sample, the GPC is low and the growth seems to have stopped in one atomic layer. The low growth is probably due to precursor desorption by ion sputtering.

Figure 8(a) shows the Hf 4f intensity and GPC with OI/J$_i$ on the horizontal axis. Figure 8(b) shows the intensity ratios of C 1s to Hf 4f (C 1s/Hf 4f) and N 1s to Hf 4f (N 1s/Hf 4f) with OI/J$_i$ on the horizontal axis. C 1s/Hf 4f and N 1s/Hf 4f are parameters that indicate the concentration of C and N impurities in the film, respectively. At 10 Pa of O$_2$, where OI/J$_i$ is extremely low, the GPC is low because the incident particles are mainly ions and sputtering may be prominent. The high impurity concentration is considered to reflect the
residue of alkyl groups at the time of sputtering. In the range of moderate OI/Ji values, the GPC is not stable and high growth due to impurities occurs. The solid and dashed lines in figure 8(b) show the trend of N 1s/Hf 4f for O2 and O2(1%)/Ar. In the case of O2, where O(3P) is the major component, the nitrogen impurity increases as OI/Ji increases. On the other hand, in the case of O2(1%)/Ar, where O(1D) can be expected to act, the nitrogen impurity decreases together with the carbon impurity as OI/Ji increases. The difference in impurity removal between O(3P) and O(1D) is considered to be the source of the difference in film quality.

O2(1Δg) is a radical species that contributes to the oxidation of precursors [40]. Although the highest effect is expected at high pressure of O2 200 Pa, it does not seem to have a positive effect on the realization of low-temperature ALD with few impurities in the current experiment.

As shown above, the increase of the oxygen active species in O2 (1%)/Ar plasma under the low ion flux contributes to the promotion of the precursor oxidation reaction in the initial stage of ALD growth at low substrate temperature. The appearance of Si–O–Hf bonding and the decrease of residual N atoms represent the enhancement of the precursor oxidation. Although the density measurement of metastable oxygen atoms in the deposition reactor is not performed, an increase in the flux of the metastable O(1D) is expected in the rare gas diluted plasma. It is believed that the enhanced reaction corresponds to the increase in the O(1D) flux that activates the reaction of the substrate and the absorbed TEMAH. Insufficiently chemisorbed TEMAH has excess alkyl groups in the interface with SiO2 surface. The internal energy of metastable O(1D) can supply excess energy.
to the breakage of the bonding in the interfacial layer. The process compensates for the lack of thermal energy required for the reaction of TEMAH and the substrate.

### 3.3. Effect of Ar dilution on film uniformity

Regarding HfO$_2$ thin films deposited up to 10 ALD cycles, the effect of Ar dilution on the film surface morphology investigated by AFM is shown in figures 9 (a)–(c). Figures 9 (a) and (b) show the 2D surface height in a plane having a width of 500 nm. In the sample with 50 Pa of pure O$_2$ plasma, unevenness with a width of about 100 nm can be confirmed. The shortening of the width can be confirmed in the sample of 300 Pa O$_2$ (1%)/Ar. Figure 9 (c) shows the cross-sectional height along the lines (A1) and (B1) across the relatively flat areas in the samples. The amplitude of the unevenness decreases under the condition of Ar dilution. The root mean square roughness in each line are (A1) 0.267 nm and (B1) 0.093 nm.

The reduction of surface roughness with the high Ar dilution condition may correspond to the reduction of impurities in the PEALD HfO$_2$ film. In the case of pure O$_2$, the incomplete oxidation of the adsorbed TEMAH molecule results in the remaining N atoms and alkyl groups. The remaining alkyl groups reside between the atomic layers, which is imagined to have resulted in pit formation and increased surface roughness.

### 4. Summary and conclusions

In the PEALD of HfO$_2$ on SiO$_2$/Si(100) substrate at 150 °C, the effect of introducing metastable oxygen atoms with high oxidizing ability on the reaction between precursor and substrate was investigated. Metastable oxygen atoms can be introduced by changing the plasma gas from pure oxygen to high Ar diluted oxygen. Emission spectroscopy and ion current measurements were used to evaluate plasma characteristics, and XPS and AFM were used to evaluate deposited films.

The metastable oxygen atoms is believed to have enhanced the oxidation of the incomplete chemisorption state of the precursor at low temperature of 150 °C, succeeded to form Hf silicate interface, and decreased the impurity nitrogen atoms in the HfO$_2$ film compared to the pure oxygen plasma ALD. Atomic force microscopy showed that the root mean square roughness in the high Ar dilution was 0.093 nm, indicating high flatness. Plasma emission spectroscopy and ion saturation current measurement show that highly Ar diluted oxygen plasma can maintain a high oxygen atom generation rate at the pressure above 100 Pa where the ion flux decreases. The highly Ar diluted O$_2$ plasma is believed to have reduced the ion irradiation damage and enhanced
the reaction between TEMAH and the substrate in the initial stage of the HfO₂ film growth by supplying the metastable oxygen atoms.

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Figure 9. Surface morphologies of PEALD-grown HfO₂ films measured by noncontact AFM. Images of the samples with plasma half-cycle of (a) pure O₂ at 50 Pa and (b) O₂ (1%)/Ar at 300 Pa are shown. Cross-sectional height change (c) is plotted along the lines (A1 and B1) across the flat area.
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