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Plasma Information-Virtual Metrology (PI-VM) on Interlayer Formation of Plasma-Enhanced Atomic Layer Deposition

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Abstract

Plasma Information-Virtual Metrology (PI-VM) on Interlayer Formation of Plasma-Enhanced Atomic Layer Deposition

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In the deposition process, it is well known that the formation of the region where the deposition film and the substrate material coexist at the interface of deposition thin film and the substrate. In previous studies, this region was called an interlayer or interphase, and was used as an adhesive layer for bonding between heterogeneous materials. The Interlayer formation has been studied as a supplementary aspect to assist the properties of the deposited films and the effect of the physical properties of the interlayer on the process has been overlooked. For this reason, the plasma process monitoring which is widely used in
semiconductor manufacturing, the formation of the interface is not regarded as an object of management.

However, in semiconductor manufacturing industry, as the degree of integration of the device increases, the required film thickness and error margin of the thin film are reduced. In those sensitive processes, the formation of several nm scale interlayer can be affect the end-product characteristics. Recently, it has been observed that the interlayer formation influences the I-V characteristics of the CMOS gate oxide film, the reflectance fluctuation of the optical filter, and the moisture shielding property of the organic/inorganic multilayer structure film. In the above processes, a thicker interface is observed in plasma-assisted deposition process In other words, it can be understood that the management of the thin film deposition process of several tens of nm using the plasma should include the characteristics of the interface as well as the deposited thin film. Interlayer formation may affect the end-product characteristics, however, it is inefficient in terms of time and cost to directly measure all wafer states by using integrated metrology or offline metrology of nm scale measurement. In line with industry demands, the development of virtual metrology models based on phenomenological understanding is essential for heterogeneous thin film deposition processes on the order of tens of nm.

In this dissertation, the plasma enhanced atomic layer deposition (PEALD) was considered as the target process of virtual metrology development with considering interlayer formation. The PEALD is mainly used for deposition of thin, high-purity thin films of several tens of nano-meters. So, formation of few nm scale interlayer occupies the large portion in the process results. From the viewpoint of process monitoring, the precursor and the reactive gas are sequentially injected separately, and the adsorption amount of the precursor can be controlled as a factor independent of the plasma discharge step. Through this process control, the effect of plasma characteristics during the discharge step on deposition thin film growth
and interfacial formation could be evaluated separately.

Plasma-information variable (PI) and reactive atom diffusion model based variable were defined to monitor interlayer formation during plasma-enhanced atomic layer deposition. The PI variable is used to monitor the plasma characteristics during the plasma-on step. This PI variable is determined by using optical emission spectroscopy (OES) based on the excitation equilibria in plasma. Plasma temperature related information was evaluated by the emission intensity ratio of helium atoms having different excited states. The parameters based on the diffusion model were derived from the diffusion distance of reactive atom (thickness of the deposited film), the partial pressure of the reactive gas and the oxygen permeability of the deposited film.

PI-VM is applied to predict the deposited Al$_2$O$_3$ film growth and SiO$_2$ interlayer formation at different pressure and cycles. With consideration of PEALD character, which is difficult to acquire sufficient amount of data sets, partial least squares regression (PLSR) method was used to develop the PI-VM. From the evaluation results of PI-VM, the PEALD cycle shows the highest correlation with the Al$_2$O$_3$ films thickness. On the other hand, the plasma-on step pressure shows the highest correlation with the SiO$_2$ interlayer thickness. This result can be explained as the deposited film lattice vibration by incident ions flux and it enhanced the diffusion of reactive atoms. This interpretation is applicable to various deposition processes in which plasma irradiation is present such as plasma-enhanced chemical vapor deposition (PECVD), sputter etc. Especially, it will be useful for end-product management when plasma condition fluctuation is severe case.

The observation of interlayer formation and the virtual metrology by using the PI variable is important for the thin film deposition of several tens nm scale performed. As the required film thickness decreases or number of stacked layers increases, PI-VM considering interlayer formation will provides the key parameter for process management. Also, it can be contributes
to the develop advanced process control (APC) and fault detection and classification (FDC) for plasma-assisted processes

**Keywords:** interlayer formation, optical emission spectroscopy (OES), virtual metrology (VM), plasma-enhanced atomic layer deposition (PEALD), plasma process monitoring.

**Student ID:** 2012-30963
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Chapter 1
Introduction

1.1 Introduction of Atomic layer Deposition

The atomic layer deposition (ALD) is considered one deposition method with great potential for producing very thin, conformal films with control of the thickness and composition of the films possible at the atomic level [1-4]. This technic is considered a
subclass of chemical vapor deposition for thin film deposition. In contrast to chemical vapor deposition, the precursors and reactants are sequentially injected, non-overlapping pulses. A purge step is located between the precursor and the reactant injection step for an ideal reaction. In each of these pulses the precursor molecules react with the surface in a self-limiting way, so that the reaction terminates once all the reactive sites on the surface are consumed. Consequently, the maximum amount of material deposited on the surface after a single exposure to all of the precursors (so-called ALD cycle) is determined by the nature of the precursor-surface interaction [4]. By using this self-limited surface varying the number of cycles, it is possible to grow materials uniformly and with high precision on arbitrarily complex and large substrates.

Despite the excellent film properties, the commercial use of ALD is limited by the low deposition rate [5]. For that reason, commercialized ALD applications are those requiring a thickness of 20 to 30 nm or less, such as CMOS gate oxide deposition [6], self-aligned multiple patterning (SAxP) on Si wafer [7], moisture barrier film [8, 9] and polymer functionalization [10].
1.2 Importance of interlayer formation on plasma-enhanced deposition

![Diagram showing the relation between deposited film thickness, metrology difficulty, and interlayer portion.](image)

Figure 1-2 Relation between the deposited film thickness, metrology difficulty and interlayer portion.

In the previous researches about the chemical vapor deposition (CVD), the presence of the interlayer between the deposited film and the substrate is well known phenomena [11-13]. But, due to the large difference between the thickness of the deposited film and interlayer, interlayer usually considered as adhesive layer, not a target of process management. However, as the degree of integration of the device increases, required film thickness and error margin of the deposited film are reduced. As the required thin film thickness decreases from several hundred nanometers to tens of nanometers, the demand of ALD processes is increases. In a sensitive process such as ALD, the interlayer formation of several nm can be a problem for the process result management. In the following section, several examples about the effect of interlayer formation on process result are introduced.

1.2.1 Encapsulation process for flexible OLED devices

Organic light emitting diode (OLED) is considered promising candidates for thin and lightweight displays with high flexibility and high energy efficiency [1–4]. However, the
OLED easily reacts with oxygen or humidity and leads to form the dark spot. Because these materials are extremely vulnerable to moisture and oxygen, a barrier layer is essential and is required to be flexible, transparent and scalable. To achieve those requirements, organic-inorganic multilayer structure is adapted which is called Barix structure (4-5 dyads of organic-inorganic layer) [18]. The sandwich structure of organic-inorganic multilayer enhances the flexibility and suppresses the defects in inorganic layer [19, 20].

In the moisture barrier application, Al\textsubscript{2}O\textsubscript{3} has excellent moisture barrier performance, the tri-methyl-aluminum (TMA, Al(CH\textsubscript{3})\textsubscript{3}), which is a precursor used in Al\textsubscript{2}O\textsubscript{3} ALD, requires a high activation condition about 300-500 °C [21, 22]. In the organic-inorganic multilayered moisture barrier film deposition for flexible OLED encapsulation, the high process temperature causes stress due to the thermal expansion coefficient differences between the organic film and the inorganic film [23-25]. In the PEALD processes, the reactive O radical flux is provided on the deposition surface at low process temperature, and it is possible to deposit oxide thin film without organic substrate damage by high temperature [26]. However, reactive species from the plasma (radicals, energetic ions) causing various reactions on the organic substrate and this reactions are responsible for the formation of an interlayer. The interlayer is a region between the organic substrate and the inorganic film, with properties different from both the substrate and the bulk of the film [27]. The formation of the interlayer is necessary to improve the adhesion between the organic and inorganic layer. However, Al\textsubscript{2}O\textsubscript{3}-organic layer co-existed interlayer does not contribute significantly to the moisture barrier performance [28, 29]. From the A.P. Roberts et. al., carbon impurities inside the Al\textsubscript{2}O\textsubscript{3} lattice induce the nano-defect (< 1 nm) and Limit the WVTR of the Al\textsubscript{2}O\textsubscript{3} layer to < 10\textsuperscript{-2} g/m\textsuperscript{2}day [30]. For that reason, the interlayer formation between the organic-inorganic interphase can deteriorate the moisture barrier performance.
1.2.2 CMOS gate oxide deposition

![Diagram of CMOS gate oxide structure]

Figure 1-3 I-V characteristic of Al$_2$O$_3$ film deposited on Si wafer at different SiO$_2$ interlayer thickness.

The gate oxide thin films are essential components of many advanced structures and devices and are directly deposited on silicon substrates. In the gate oxide deposition, the thickness and dielectric constant of the oxide film are very important factors determining the I-V character of the device. In the high purity oxide PEALD about the 10-20 nm range, such as moisture barrier films and CMOS gate oxide deposition, the formation of un-intentional interlayer of several nm becomes a big issue [31, 32]. In the recent research about the growth of very thin (~10 nm) high dielectric constant (high-k) oxide films directly on Si has raised the question of the interlayer formation and its properties [9]. In particular, as the technology develops, the thickness of the single oxide film is decreasing, and the proportion of the interface in the entire thin film is expected to increase [32, 33].
1.3 Interlayer formation mechanism on thin film deposition

In the previous section, the effect of interfacial formation in PEALD on inorganic and organic substrates was introduced. In order to understand the interlayer formation process for various ALD applications, the physical differences of both organic and inorganic substrate will be introduced [34]. After that, suggested interlayer formation mechanism from previous study will be described [35-41].

The characteristics of each substrate are determined by the difference in bonding between organic-inorganic thin films used as a substrate in PEALD. The atoms in inorganic material have narrow interatomic distance by strong intrinsic bonds. However, the atoms in organic material are weakly bonded through the van der Waals force between the molecules, and they are vulnerable to temperature or easily broken off. Due to the difference between the organic film and the inorganic film, various interlayer formation mechanism have been studied such as thermal diffusion [35, 36], precursor infiltration [23, 37, 38], reactant penetration [39-41] and substrate ablation & re-deposition [27]. The effect of each mechanism on the interlayer formation varies depending on the process temperature of deposition process. However, in the

Figure 1-4 Characteristics of inorganic and organic substrates.
thin film deposition of several tens nm to several hundreds of nm in thickness, management of the interlayer formation is overlooked. For that reason, the effect of each mechanism on the interlayer formation with the change of PEALD cycle is insufficient. The following section provides a brief description of each interlayer formation mechanism.

1.3.1 Thermal diffusion

![Figure 1-5 Schematic diagram of interlayer formation by thermal diffusion.](image)

Thermal diffusion is a phenomenon in which oxygen atoms in the oxide film activated by the process temperature and diffuses through the oxide film. The oxygen concentration in the oxide layer at the gas-solid interface obeys the thermodynamic phase equilibria requirements. The diffusion of molecular oxygen occurs according to Fick’s law, with constant diffusivity [35, 36]. The convective contributions are completely neglected and the diffusion process is assumed to occur under pseudo-steady-state conditions. The chemical reaction takes place at the oxide-silicon interface according to first-order kinetics. Generally, it is the main interface formation mechanism when a high temperature process with a process temperature above 800 K is maintained for more than a few minutes [36]. This mechanism can contribute to all steps
1.3.2 Precursor infiltration

![Figure 1-6 Sequential schematic diagram of interlayer formation on organic substrate by precursor infiltration.](image)

The atomic layer deposition on hard surfaces proceeds through reactive sites available on the growth surface. However, for organic substrate, reactive sites may or may not be present, and many organic substrates are permeable to small molecules, allowing ALD precursors to move in and out of the near surface and bulk of the polymer substrate. For thermal ALD, Wilson et al [37, 38] suggested that Al₂O₃ grows on polymers via five steps: (a) diffusion of TMA molecules into polymer chains, (b) generation of Al₂O₃ clusters from the chemical reactions between TMA and H₂O, (c) growth and coalescence of Al₂O₃ clusters, (d) closure of vacant spaces between polymer chains by Al₂O₃ clusters, and (e) formation of a continuous Al₂O₃ film on the polymer surface. Once a continuous Al₂O₃ film is formed on the polymer...
surface, TMA molecules cannot penetrate further into the polymer substrate. From then on, pure Al₂O₃ film grows linearly with the number of PEALD cycles, just as in the case of the Al₂O₃ growth on the Si wafer.

1.3.3 Reactant penetration

![Diagram](image)

Figure 1-7 Schematic diagram of interlayer formation by reactant penetration.

In PEALD, the reactant gas, H₂O is replaced by the O₂ plasma [42]. These O₂ plasmas produce reactive O radicals and energetic charged species abundantly, even at low process temperatures. Energetic charged species enhance the diffusivity of O radicals (atoms) through the Al₂O₃ film bulk, resulting in the formation of a SiO₂ layer between the Si wafer and the Al₂O₃ film. The SiO₂ interlayer is not observed for thermal ALD [39-41]. Energetic oxygen radical incidents on Al₂O₃ film surface and Al₂O₃ lattice vibration by ion bombardment increases oxygen diffusivity. Those hybrid phenomena form the interlayer during the plasma-assisted deposition.
1.3.4 Organic substrate ablation and re-deposition

In plasmas, energetic electrons and ions scissor chain networks, altering the bulk structure of polymers. Da Silva Sobrinho et. al. [27] explains the interlayer formation mechanism polymer substrate in terms of a fragmentation/re-deposition. Reactive species in plasma interact with the polymer surface and produce volatile organic species, which intermix with the reagent gas feed, thus giving rise to the observed carbon contained inorganic interlayer with gradually decreasing carbon content. Table 1-1 shows the summary of each interlayer formation mechanism.

Table 1-1 Brief information of interlayer formation mechanism.

<table>
<thead>
<tr>
<th>Formation mechanism</th>
<th>Observed processes</th>
<th>Reaction time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The reactive atoms present in the upper layer are thermally diffused and combined with the lower layer</td>
<td>TCVD, TALD, Anealling</td>
<td>min–hour</td>
</tr>
</tbody>
</table>
Precursor-infiltration

Precursors diffuse into the organic substrate and is oxidized to form a film

TALD PEALD

< 10 cycles

reactant penetration

The reactive atoms penetrate the upper layer and bonds with the lower layer

PECVD PEALD Sputtering

Depends on process conditions

Substrate ablation & re-deposition

In the reactive process, the weakly bonded lower layer forms an interface by repeating ablation and re-deposition

PECVD PEALD

Depends on process conditions

1.4 Development of virtual metrology for PEALD

As semiconductor and display devices are continuously miniaturized, the process margins have almost reached their limits [43]. For that reason, the process monitoring and diagnosis are more emphasized. In recent years, a phenomenological-based process diagnostic technique has been proposed that makes novel variables, named plasma-information (PI) variables to represent the state of the plasma assisted process [44]. In a plasma assisted process, the plasma directly contributes to the dissociation, adsorption and activation of the process gas. Therefore, the selection of the suitable plasma information parameter can greatly improve the accuracy of the process result prediction [45].

However, In the PEALD, the number of observation is not enough to apply statistical methods. Also, the effects of each interlayer formation mechanism on PEALD are not well understood. In this study, the main interface formation mechanism on PEALD was verified by using the plasma-chemistry monitoring. Also, the plasma effect on interlayer formation was studied by using the plasma-chemistry monitoring and deposited film analysis. Considering
the interlayer formation mechanism and the role of plasma, the virtual metrology for PEALD with considering the deposited film and the interlayer simultaneously was developed.

In this study, we propose a virtual metrology that simultaneously predicts deposited film and interlayer thickness using sensor variables monitored during the process for PEALD end-product management.
Chapter 2
Experimental Setup

2.1 Configuration of Plasma Assisted Deposition System

Commercial plasma deposition equipment (P-5000 Mark II, Applied Materials) was used for the experiment. It consisted of one load lock chamber and three plasma-enhanced chemical vapor deposition (PECVD) chambers. The control software and gas supply system of the equipment were modified in such a way that one PECVD chamber could be utilized for the SiO$_2$ PECVD and equipped multi-sensor (OES, VI-probe, hairpin-probe and electrical sensor), another chamber could be utilized for the plasma polymerization (PP) and the other for plasma-enhanced ALD (PEALD) processes.
The geometry of the PECVD, PP and PEALD chambers was the same. A capacitively-coupled plasma was produced between a shower-head powered electrode (top) and a solid grounded electrode (bottom). The gap between the powered and grounded electrodes was 8.65 mm. A 6 inch p-type Si wafer was placed on the bottom ground-electrode in the chamber, and the substrate temperature was adjusted with infrared lamps.
2.1.1 Operation window selection for ideal ALD reaction

To monitor the interlayer formation of PEALD on organic and inorganic substrate, Al2O3 PEALD was performed on the p-type silicon wafer and plasma polymerized polymer. Before the deposition, the bare Si wafer was cleaned in a buffered oxide etch solution to assure a hydrogen-terminated surface. One ALD cycle consisted of precursor dosing, purging, plasma-on, and purging steps. TMA [Al(CH3)3] and He/O2 were used as a precursor and a plasma gas, respectively. The PEALD operation window was selected for realizing the ideal ALD reaction on Si wafer. The precursor injection, purge and plasma-on step times were controlled and plasma-chemistry monitoring by OES and film analysis by XPS were conducted. For an ideal ALD reaction, the ligand should be completely removed during the plasma-on step after self-limited precursor adsorption. To confirm the complete ligand oxidation reaction, Ha signals observed in OES during the plasma-on step were observed. Figure 2-3 shows the temporal evolutions of Hα (656 nm) emission intensity at 1.0 Torr. At the beginning of the plasma step, significant amounts of H2O and COx are released from the –CH3 ligands, because the –CH3 ligands have been chemisorbed over the entire surface. As the –CH3 ligands are depleted on the surface, the production rate of H radicals is reduced. The Hα line intensity decreases more slowly in the latter half of the plasma step than in the former half. This phenomenon can be attributed to the non-uniform distribution of the –OH groups and –CH3 ligands on the surface. There are no plasmas with a perfectly uniform spatial distribution of charged species. More –OH surface groups can be formed at positions with a higher density of O radical, and the dissociation of –CH3 ligands is retarded at positions with a lower flux of charged species. At the end of the plasma step, the Hα emission intensity decays nearly to zero. This result implies that almost –CH3 ligands are removed on the surface during the plasma-on time.
The C and H contents in the $\text{Al}_2\text{O}_3$ film can be directly evaluated by analyzing the O1s spectrum obtained by using the XPS instrument. In Fig. 2-4, we analyzed the O1s spectra of the $\text{Al}_2\text{O}_3$ film deposited at different process temperature. According to the work of Haeberle et al. [46], the O1s spectrum consists of $\text{Al}–\text{O}$ (531.2 eV), $–\text{OH}$ (532.6 eV), and $–\text{COO}$ (532.7 eV) bonds; The O1s XPS spectrum consists of Al-O(531.2eV), $–\text{OH}$(532.6 eV), and $–\text{COO}$ (532.7 eV) bonds; the $–\text{OH}$ and $–\text{COO}$ bonds correspond to H– and C-containing impurities, respectively. Incomplete removal of $–\text{CH}_3$ ligands leaves the C– and H-containing impurities into the film; a lower content of these impurities yields a denser $\text{Al}_2\text{O}_3$ film. The substrate temperature only slightly influences the O1s spectral shape. The decreases of the -OH and -COO signals can be explained by the increase of the oxidation reactivity of $–\text{CH}_3$ ligand with increasing process temperature.
the –OH and –COO bonds overlap. It is confirmed that the spectral intensity for –OH and
Similar to Fig. 2-4, the O1s spectra of the Al₂O₃ film deposited at different pressure shows
in Fig. 2-5. The results in Fig. 2-5 reveal that an increasing the plasma-on step pressure leads
to an increase in removal rate of –CH₃ ligands. It can be explained that the sufficient oxygen
supplement by pressure increment enhance the –CH₃ oxidation rate.
Figure 2-5 O1s spectra of the Al₂O₃ films deposited in He/O₂ plasma for different pressures.

Table 2-1 shows the detailed process condition for Al₂O₃ PEALD for moisture barrier deposition.

Table 2-1 Details of Al₂O₃ PEALD recipe.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Al₂O₃ PEALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>TMA (Al(CH₃)₃)</td>
</tr>
<tr>
<td>Discharge gas</td>
<td>He or Ar</td>
</tr>
<tr>
<td>He/O₂/TMA flowrate (sccm)</td>
<td>200/100/30</td>
</tr>
<tr>
<td>Input power (W)</td>
<td>100</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>0.4-7.0</td>
</tr>
</tbody>
</table>
### Process Parameters

<table>
<thead>
<tr>
<th>Process temperature (°C)</th>
<th>100-250</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA dosing time (sec)</td>
<td>3</td>
</tr>
<tr>
<td>Plasma-on time (sec)</td>
<td>4</td>
</tr>
<tr>
<td>Purging time (sec)</td>
<td>10</td>
</tr>
</tbody>
</table>

### 2.1.2. Inorganic and organic substrate for PEALD

The 6inch p-type silicon wafer was used for the inorganic substrate. Before the Al2O3 PEALD, the native oxide layer was removed from the silicon surface. The silicon wafer was immersed in the buffer oxide etch (BOE) solution for at least 1 hour and then washed with the isopropyl alcohol for 5 min. From the above procedure, native oxide free silicon surface can be achieved (Fig. 2-6).

![Figure 2-6 TEM images of bare p-type silicon wafer after the buffer oxide etch (BOE) cleaning.](image)

In the organic substrate, it was hard to apply similar procedure on organic substrate due to the weak binding. Also, the organic substrate easily adsorbs the impurity particles when exposed to the outside. In this study, the organic film was grown by using plasma
polymerization for the capability of continuous process with PEALD Al₂O₃. The plasma polymerization chamber is connected with the PEALD chamber by the load-lock. In PEALD applications using organic substrates, flexible organic films are required. For organic films with higher flexibility, organic films with a low degree of crosslinking are required [47]. The organic layers (CₓHᵧ) were deposited by using n-C₄H₁₀ as a monomer which has longest aliphatic chain of gaseous monomer at room temperature. During the organic layer deposition, flow rates of n-C₄H₁₀ and He were kept at 50 and 100 sccm, respectively. The process temperature was kept at 100 °C. The input power was varied from 50 to 300 W for generation of plasma. The pressure during the deposition was varied from 0.3 to 3.0 torr (Table 2-2).

<table>
<thead>
<tr>
<th>Condition</th>
<th>CₓHᵧ plasma polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>n-butane (C₄H₁₀)</td>
</tr>
<tr>
<td>Discharge gas</td>
<td>He</td>
</tr>
<tr>
<td>He/C₄H₁₀ flowrate (sccm)</td>
<td>100/50</td>
</tr>
<tr>
<td>Input power (W)</td>
<td><strong>50-300</strong></td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td><strong>0.3-3.0</strong></td>
</tr>
<tr>
<td>Process temperature (°C)</td>
<td>80</td>
</tr>
<tr>
<td>Plasma-on time (sec)</td>
<td>600</td>
</tr>
</tbody>
</table>

The crosslinked hydrocarbon film was laminated by controlling applied power and pressure. As the applied power increased and the pressure decreased, the degree of crosslinking of the monomer was increased. At this time, the morphology of deposited films changed from oily film to dense film and finally particulate films was formed (Fig. 2-7).
The XPS results of the hydrocarbon films deposited at 1.5 torr, 200 W and 3 torr, 100 W, respectively, are shown in Fig 2-8. The C1s spectra consist of C=C (284 eV), C-C (284.8 eV) and C-H (285.2 eV) bonds [41]. In Fig. 2-8 (a), C1s spectra shows large portion of C=C and C-C bond, C=C:C-C:C-H = 2:5:3. However, in Fig. 2-8 (b), C1s spectra shift to C-H bond peak, C=C:C:C:C-H = 0:3:7. During the plasma polymerization, crosslinking of monomer occurred by series reaction of dissociation and activation of monomer. The dissociation of monomer required a higher energy electron (> 3.6 eV) than the activation (< 1 eV) [48]. For that reason, the increase of power and the decrease of pressure enhance the portion of high energy electron and lead the crosslinking of monomer. This relation well explains the different C1s spectra of Fig. 2-8. From this results, the organic layer deposition condition was chosen at 100 W, 3.0 torr.
Fig. 2-9 shows the composition of each hydrocarbon film on ternary phase diagram for various DLC films with respect to their sp3, sp2 type bonding and hydrogen content in the structure [49]. From the Fig. 2-9, the hydrocarbon film at 200 W, 1.5 Torr condition is almost DLC and the hydrocarbon film at 100 W, 3 torr is polymer-like case. In order to simulate the organic / inorganic moisture barrier deposition, Al₂O₃ PEALD was performed on the hydrocarbon film at 100 W, 3 torr.
2.2 Process monitoring tools

A multi-sensor was installed in the reactor to monitor deposited film and interlayer growth during plasma enhanced ALD. Using the hairpin probe, which can measure the plasma density with high accuracy, the diagnostic value of the non-intrusive sensor in the plasma-on step was validated. VI probe (Octive poly, Impedance Inc.) and electrical sensor (Prime Solution) were used for CCP reactor electrical characteristic monitoring. The OES (Maya 2000 pro, Ocean Optics Inc.) and SPOES (MPIA, PrimeSolution) were used for the main reaction by-product monitoring and plasma index derivation. Each of the multiple sensors was linked with the data integration toolbox to collect monitoring information in real time.
To find the effective sensor for plasma monitoring, commercial SiO$_2$ deposition recipe for AMAT-P5000 system was performed on 1 lot of 25 wafers. The sensor and observable variables which are effective for SiO$_2$ deposition thickness monitoring were selected and utilized as a main factor for the deposition thin film and interface formation monitoring during ALD process.

2.2.1 Hairpin probe

The hairpin probe was used as a reference diagnostic tool for the non-intrusive measurement tools such as VI-probe and OES. Fig. 2-10 shows the installment of hairpin probe. The hairpin probe is the kind of electrodynamic probes that rely on the physics of propagation of electromagnetic waves through plasma [50, 51]. It is a simplest form the probe is a U-shaped structure that is inductively coupled to a swept microwave source. This structure, known as a hairpin probe, has a resonance whose quarter-wavelength is equal to the length of the probe. When placed in the plasma, the refractive index of the medium around the probe changes, and the resulting change in the resonant frequency of the probe can be directly related to the electron density in the vicinity of the probe [52]. It is known that the uncertainty of the plasma density measurement by the above method is theoretically 1% or less at low pressure. This is superior to the Langmuir probe's uncertainty > 30%, which is widely used in the past under low pressure conditions. Using a hairpin probe with high reliability, the measurement results of the non-intrusive diagnostic system, such as VI probe, OES, etc., were verified. The fundamental resonance frequency of a hairpin probe in a uniform medium of dielectric constant is given by equation (2.1).

$$f = \frac{c}{4L\sqrt{\varepsilon}}$$  \hspace{1cm} (2.1)

Where $L$ is the length of the probe, and $c$ is the speed of light. When the probe is immersed in a vacuum, $\varepsilon = 1$, while for the case of a weakly magnetized low-pressure plasma,
" is given by equation (2.2).

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \] (2.2)

Where \( \omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}} \) is a (angular) plasma frequency, and \( \omega \) is a induced frequency from the network analyzer. Because the dielectric constant in the plasma is smaller than in vacuum, the hairpin resonance frequency in the presence of plasma has a higher frequency than for the vacuum case. By measuring this frequency shift and using the equations above it is possible to determine the electron density of the plasma surrounding the probe tip [50].

Figure 2-10 Figures of hairpin probe installment.
Fig. 2-11 shows the resonance signal obtained in vacuum. The variation of resonance frequency shifting by the dielectric constant variation in plasma-on step means the plasma density (Fig 2-12).

![Resonance signal obtained in vacuum.](image)

Substituting the time varying resonance frequency shifting results on the equation (2-3), plasma density evolution during the plasma-on step was measured (Fig. 2-13).

\[ n_e \left( 10^{10} \text{ cm}^{-3} \right) = 1 - \frac{f_r^2}{f_0^2} \]  \hspace{1cm} (2.3)

Where \( f_0 \) is the resonance frequency in vacuum and \( f_r \) is the resonance frequency after plasma-turn on.
2.2.2 OES

The optical emission spectroscopy (OES) is non-invasive, easy to implement and measurements are fast. By detecting light from the electronic transitions of atoms and molecules it is possible to identify and monitor the chemical species in plasma [53]. The plasma characteristics and plasma chemistry were monitored using the emission line of Helium and oxygen used in the PEALD plasma-on step.
2.2.2.1 He emission lines selection

The He emission lines were used to diagnose the equilibrium state of the plasma, excluding the chemical reaction. To measure the excitation state of the He atom from the emission signal, the emission signals which have simple electron transition path and sufficient emission intensity should be selected. Also, to minimize the error from the sensitivity differences of spectrometer, it is better to select the emission line pair with similar wavelength. Fig. 2-13 shows the He atom energy level diagram. To simplify the transition path for plasma equilibrium state measurement, He 388 nm and 587 nm signals passing through the metastable state of the transition was excluded from the emission line selection.

![Figure 2-14 Example of a He atom energy level diagram [54].](image)

Table 2-3 shows the main transition lines observed in optical emission spectra of He
plasma. He emission line pair which has the similar wavelength and branching ratio of the emitted light signal and sufficient signal to noise ratio was selected. From Table 2-3, the He 443 nm-412 nm pair, He 504 nm-471 nm pair, and the He 728 nm-706 nm can be a candidate for the selecting the pair with similar branching ratio.

<table>
<thead>
<tr>
<th>Transition</th>
<th>λ (nm)</th>
<th>$A_{ji} \times 10^8$ s$^{-1}$</th>
<th>$B_{ji}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5^1S \rightarrow 2^1P$</td>
<td>443.8</td>
<td>0.0330</td>
<td>0.482</td>
</tr>
<tr>
<td>$4^1S \rightarrow 2^1P$</td>
<td>504.8</td>
<td>0.0675</td>
<td>0.596</td>
</tr>
<tr>
<td>$3^1S \rightarrow 2^1P$</td>
<td>728.1</td>
<td>0.1829</td>
<td>1.000</td>
</tr>
<tr>
<td>$5^3S \rightarrow 2^3P$</td>
<td>412.0</td>
<td>0.0444</td>
<td>0.475</td>
</tr>
<tr>
<td>$4^3S \rightarrow 2^3P$</td>
<td>471.3</td>
<td>0.0955</td>
<td>0.596</td>
</tr>
<tr>
<td>$3^3S \rightarrow 2^3P$</td>
<td>706.5</td>
<td>0.2790</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Fig. 2-14 shows the full spectrum data of He/O$_2$ plasma during the plasma-on step at different pressure. In the He emission line pair candidate, He 728 nm-706 nm shows high emission intensity at all plasma-on step pressure conditions. For that reason He 706.5 nm and 728.1 nm pair was selected for plasma equilibrium condition (temperature) measurement.
2.2.2.2 CO and O emission lines selection

The CO and O emission lines were selected based on plasma-chemistry during the plasma-on step. Fig. 2-16 shows the possible reaction during the plasma-on step. Based on the previous study about the interlayer formation during the plasma-assisted process, Reactive O radical can react with self-limited and infiltrated precursor. At the beginning of the process, the reaction between the O radical and the substrate is expected.
In the Fig. 2-16, CO 483 nm, the by-product of the reaction, and the O 777 nm signal, the reactant, were selected. The Time-resolved CO 483 nm and O 777 nm intensities for the Si wafer at the single plasma-on step are shown in Fig. 2-18.
2.2.2.3 IR Background Subtraction

Optical emission spectroscopy (OES) is used to identify chemical species and monitor the changes of process results during the plasma process. However, plasma process monitoring or fault detection by using emission signal variation monitoring is vulnerable to background signal fluctuations. When using an infrared heater for high temperature uniformity and fast response, the emitted infrared can react as a background signal of the spectrometer. Unlike the electrical background noise of spectrometer, the infrared background signal shows a large variation with the process step change. Fig. 2-19 shows the full spectrum of He/O\textsubscript{2} plasma during the plasma-on step with the IR and electrical background signal. The atomic emission signal and the infrared background signal were separated using the different tendency according to the wavelength change.

Figure 2-19 Full spectrum of He/O\textsubscript{2} plasma during the plasma-on step with the IR and electrical background signal.

To subtract the IR background signal from the observed spectrum, observed spectrum region was separated as Fig. 2-20.
Figure 2-20 Segmentation of emission spectrum for infrared background signal subtraction from the emission signal of by-product molecules.

$S_1$ denotes the atomic emission signal with considering the emission line broadening. $S_2$ is the sum of the infrared background signal and the electrical noise of the spectrometer. At this time, assuming that the distance between $\lambda_2$ and $\lambda_3$ is close and the slope of the infrared background signal is not large, a linear assumption is possible. Therefore, when a region satisfying $\lambda_3 - \lambda_2 = \lambda_2 - \lambda_1 + \lambda_4 - \lambda_3$ is selected, $S_2 \approx S_3 + S_4$ is valid. In conclusion, atomic emission signal intensity $S_1$ is equal to the area integral value of the wavelength range of $\lambda_2$ and $\lambda_3$ and subtracts the $S_3$ and $S_4$ area as equation (2.5).

\[
\int_{\lambda_2}^{\lambda_3} I \, d\lambda = S_1 + S_2 \tag{2.4}
\]

$S_1 = \text{emission intensity, } S_2 = \text{background noise}$

\[\therefore S_1 = \int_{\lambda_2}^{\lambda_3} I \, d\lambda - (\int_{\lambda_1}^{\lambda_2} I \, d\lambda + \int_{\lambda_3}^{\lambda_4} I \, d\lambda) \tag{2.5}\]

This relation was embedded in the tool box used in the experiment and the infrared background signal was subtracted from the emission optical signal in real time. Fig. 2-21 shows the Time resolved He 706 nm intensity during the PEALD cycles before and after IR background subtraction. Figure 2-21 shows that the IR background is well subtracted.
Figure 2-21 Time resolved He 706 nm intensity during the PEALD cycles (a) before and (b) after IR background subtraction.

The signal to noise ratio of the He 706 nm signal during the PEALD initial 3 cycle is calculated by equation (2.6).

\[ SNR = \frac{\text{mean}(S_1)}{\text{stdev}(S_1)} \]  \hspace{1cm} (2.6)

Table 2-4 shows the signal to noise ratio of He 706 nm signal at different process temperature before and after IR subtraction.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>SNR: w/o IR subtraction.</th>
<th>SNR: w IR subtraction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>99.0491</td>
<td>30.4276</td>
</tr>
<tr>
<td>150</td>
<td>15.4291</td>
<td>31.2489</td>
</tr>
<tr>
<td>200</td>
<td>11.7625</td>
<td>23.0581</td>
</tr>
<tr>
<td>250</td>
<td>13.8215</td>
<td>25.0042</td>
</tr>
</tbody>
</table>
Applying the same procedure to the O 777 nm signal is shown in Fig 2-22 and Table 2-5. From those results, we confirmed that the SNR of the OES signal is improved by the IR background subtraction. In the following chapter, whole OES data is the result of removing the IR signal by the above method.

![Figure 2-22 Time resolved O 777 nm intensity during the PEALD cycles (a) before and (b) after IR background subtraction.](image)

### Table 2-5 Signal to noise ratio of O 777 nm intensity (a) before and (b) after IR background subtraction.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>SNR: w/o IR subtraction.</th>
<th>SNR: w IR subtraction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>15.5798</td>
<td>11.9675</td>
</tr>
<tr>
<td>150</td>
<td>22.6388</td>
<td>40.7027</td>
</tr>
<tr>
<td>200</td>
<td>25.8686</td>
<td>34.9003</td>
</tr>
<tr>
<td>250</td>
<td>18.7442</td>
<td>25.0125</td>
</tr>
</tbody>
</table>
2.2.3 VI probe

Voltage sensors were built in RF matchers to observe the peak-to-peak RF voltage for each frequency. Forward/reflected power and the load/tune capacitor position of the matcher for each frequency were also monitored [56].

Electrons and ions present in the plasma show different dynamic depending on the applied voltage and frequency. Though its electrical characteristics, plasma can be regarded as a single electric element, which is called an equivalent circuit model. In the equivalent circuit model, the power dissipation due to collisions in bulk plasma is similar to the resistance component. The inertia of the bulk plasma for a high frequency electric field is similar to the inductance component, and the charge charged on the electrode surface plays a role of capacitance. An equivalent circuit model of a typical CCP reactor is shown in Fig. 2-24 [57].
In the equivalent circuit model, each component is expressed as Equation (2.7)-(2.9). Where, \( \nu_m \) is an electron-neutral collision frequency, \( v_e \) is an electron thermal velocity, \( l_p \) is the length of the plasma bulk, \( L_p \) is a plasma inductance, \( \omega_{pe} \) is a plasma frequency, \( A \) is a chamber electrode area, \( n_e \) is a plasma density, \( d_{sheath} \) is a plasma sheath thickness, and \( \varepsilon_0 \) is a permittivity, \( 8.85 \times 10^{-12} \text{ F/m} \) [58].

\[
R_p = \left( \nu_m + \frac{v_e}{l_p} \right) l_p
\]  
(2.7)

\[
L_p = \frac{1}{\left( \frac{\omega_{pe}^2 \varepsilon_0}{\omega_{pe}^2 \varepsilon_0} \right)} = \frac{m l_p}{A n_e \varepsilon_0^2}
\]  
(2.8)

\[
C_{sheath} = \frac{\varepsilon_0 A}{d_{sheath}} = \frac{e n_e \omega \varepsilon_0 A^2}{2 l_{rms}}
\]  
(2.9)

Plasma density, temperature, and chamber geometry were substituted into equation (2.7)-(2.9) to calculate the plasma resistance, inductance and capacitance. From the calculation result, it is confirmed that most of the measured reactance components were came from the capacitance. From this relation, plasma density can be evaluated by the equation (2.10).

\[
X_c = \frac{1}{\omega C_s} = \frac{2 l_{rms}}{e n_e \omega \varepsilon_0 A^2} = 2.45 \times 10^{19} \frac{l_{rms}}{n_e}
\]  
(2.10)

To verify the validity of the plasma density derived from the VI probe, measured plasma density was cross-validated by the hairpin probe result. Fig. 2-25 shows the schematic
diagram for cross-validation test of VI-probe and hairpin probe. The VI-probe was installed between the matcher and the powered-electrode, and the hairpin probe was inserted into the CCP chamber.

Figure 2-25 Schematic diagram for cross-validation system for VI-probe and hairpin probe.

In Fig. 2-25 system, applied power was increase as stepwise function for plasma density control. At this time, the pressure and gas flow rate were fixed. Fig. 2-26 shows the stepwise increase of input power for cross-validation test of VI-probe and hairpin probe. Fig. 2-27 shows the measured plasma density from hairpin probe and VI-probe at stepwise input power variation. From the Fig. 2-27, it was confirmed that plasma density trend monitoring was possible by using VI-probe.
Figure 2-26 Stepwise input power variation for cross-validation test of VI-probe and hairpin probe.

Figure 2-27 Plasma density from hairpin probe and VI-probe at stepwise input power variation.
2.2.4 XPS depth profile

![Figure 2-28 Schematic diagram of XPS measurement.](image)

The TEM images of Al\(_2\)O\(_3\)-organic layer show uncertain interlayer that couldn’t evaluate the pure Al\(_2\)O\(_3\) thickness and carbon-contained Al\(_2\)O\(_3\) interlayer thickness. Also, the organic layers are too vulnerable and are easily damaged during TEM specimen manufacturing using FIB. Considering the carbon fragment generated in the FIB process and the resolution of EDS, the interface analysis using TEM-EDS is limited. The XPS measures the photoelectron signal emitted from each element by incident X-ray. The elements present in the incident x-ray path are consumed as much energy as the binding energy and then released into the photoelectron. The emitted photoelectrons collide with the atoms in the upper film and the intensity decreases until reaching the detector. In this procedure, a careful interpretation is required for the XPS
depth profiling data owing to three limitations. First, the sputter rate depends on the material; although Al₂O₃, Si, and CₓHᵧ are sputtered for the same amount of time, their sputtered depths are different [59]. Second, the depth resolution is reduced with increased sputtering time because the Ar ion beam damages the surface that is being probed; an increase in sputtering time increases the roughness of the probing surface, resulting in a decrease in depth resolution [60]. The third limitation is associated with the sampling depth. The atoms beneath the probing surface contribute to the spectrum signal, although their influence is exponentially attenuated with the depth [61, 62]. The number of photoelectrons that reach the detecting surface per unit time, Is, can be expressed as Iₛ = I₀exp(−d/λ), where I₀ is the number of photoelectrons generated per unit time at a depth d, and λ is the electron mean free path in the film. The sampling depth is defined by the distance (from the surface) at which 95% of photoelectrons do not reach the probing surface. It equals 3λ, whose value depends on the electron kinetic energy and the sputtered atomic species. The emitted photoelectrons have different sampling depth depending on their respective energies, which are in the nm range. By using the nm range sampling depth, XPS can be diagnosed the chemical composition variation of Al₂O₃-CₓHᵧ interlayer at a few nm above and can prevent the damage on interphase or additional impurity contamination in the Al₂O film. The depth profile of the sample in terms of XPS quantities can be obtained by combining a sequence of ion gun etch cycles interleaved with XPS measurements from the current surface. An ion gun is used to etch the material for a period of time before being turned off whilst XPS spectra are acquired. Each ion gun etch cycle exposes a new surface and the XPS spectra provide the averaged atomic composition of a few nm depth region from the surface. The XPS depth profile for Al₂O₃-CₓHᵧ hybrid layer or Al₂O₃-Si wafer, stoichiometric equivalent Al₂O₃ will be measured, but carbon or silicon signal will be detected when the residual thickness of sputtered Al₂O₃ film becomes thinner than the sampling depth of carbon or silicon. Assume the substrate
material detected time is $t_1$, Al$_2$O$_3$ sputtering rate by Ar sputtering is $v_{Al2O3}$ and the sampling depth of substrate material is $\lambda$, the thickness of pure Al$_2$O$_3$ layer is given by equation (2.11).

$$\text{Pure Al}_2\text{O}_3 \text{ thickness} = V_{Al2O3} \times t_1 + 3\lambda$$ (2.11)

From the previous research, the sampling depths for Si and C atoms can be presumed to be 7.2 and 4.8 nm, respectively, based on the work of Ebel et. al., [59] and Penn et. al., [60]. In the evaluation of pure Al$_2$O$_3$ and interlayer thickness by using XPS depth profiling, a careful interpretation is required for the Ar ion beam damages the surface that is being probed; an increase in sputtering time increases the roughness of the probing surface, resulting in a decrease in depth resolution [61]. In order to minimize the surface roughing effect, photoelectron accepting area is minimized [62]. The Ar sputtering area was set to 2000 x 2000 μm and the diameter was set to 100 μm, which is narrower than the sputtered surface curvature, in order to obtain sufficient resolution in the prediction of pure Al$_2$O$_3$ film and interface thickness using the XPS depth profile.

The Al$_2$O$_3$ film sputtering rate by Ar sputtering is measured by XPS depth profiling on
known Al$_2$O$_3$ film (100 nm thickness) on Si wafer. Fig. 2-30 shows the XPS depth profiles for the 100 nm thick Al$_2$O$_3$ film deposited on the Si wafer. When the Al$_2$O$_3$ film is completely sputtered, the Al concentration is zero (926 nm). At this time, the concentration of O remains slightly due to the SiO$_2$ interface. The Al$_2$O$_3$ sputtering rate by Ar is about 0.108 nm/sec.

![Figure 2-30 XPS depth profiles for the 100 nm thick Al$_2$O$_3$ film deposited on the Si wafer as a function of sputtering time (number of PEALD cycles = 100 and sputter time resolution = 30 s).](image)

Fig. 2-31 shows the XPS depth profile of Al$_2$O$_3$ film on Si wafer. It shows the trend of the changes in atomic concentrations of a film as a function of the depth. The concentrations for Al, O, and Si were quantified as a function of sputtering time from the spectrum signals of Al2p, O1s, and Si2p, respectively, by using the spectrum analysis software embedded in the XPS instrument.
Figure 2-31 XPS depth profiles for the Al$_2$O$_3$ film deposited on the Si wafer as a function of sputtering time (number of PEALD cycles = 100 and sputter time resolution = 15 s).

The substrate material, Si was observed between the 60 sec region. Substituting the Si observed time and the sampling depth into equation (2.11), the thickness is expected to be 13.72 nm. This result is similar to the Al$_2$O$_3$ thickness observed at TEM, 13.5 nm. This interlayer thickness measurement method using XPS depth profile, was also applied to the Al$_2$O$_3$ on C$_x$H$_y$ layer.

2.2.5 Virtual metrology

Although the statistical VM methodology has many advantages, there may be a limitation if the number of observation is not enough [63, 64]. On the other hand, partial Least Squares (PLS) regression technique is useful when the number of independent variables is greater than or equal to the number of samples, and there are other factors that affect the correlation between the variables [65, 66]. In the PEALD, generally lack the number of data set than CVD. For that reason, deposited film and interlayer thickness were predicted by PLS. In addition, plasma information (PI) variable, which is known to be useful for predicting plasma
processes, was used to compensate for errors from insufficient data sets [67]. Fig. 2-32 shows
the flow chart for developing procedures of phenomenology-based VM model. This
methodology applies PI variables and interlayer formation parameter on the following
conventional VM development procedures [68, 69].

The detailed descriptions for each step in Fig. 2-32 are as follows. First, the dimensionality
of input data obtained during process can be diminished by introducing domain knowledge in
data preprocessing step. Especially for OES data, the line intensities including information
about specific chemical species can be extracted by using the excitation kinetics in plasma.
Surface reaction mechanism for TMA oxidation and interlayer formation by oxygen radical
are as follows; 1) self-limited adsorption of precursor occurred during the precursor injection
step, 2) reactive oxygen radical induced on the precursor-adsorbed surface and oxidized the
precursor, and 3) induced ion bombardment enhanced the oxygen radical diffusion on the
substrate and formatted interlayer [40, 70]. The wavelengths related to these chemical species are found from NIST atomic spectroscopy databases. Total number of selected wavelengths is 5 from 1200 OES data. The total 11 records are partitioned to training dataset and validation dataset. Training set was used to build up the VM model, and validation set was used to evaluate prediction accuracy of the trained model. The number of training dataset was 5 and that of validation dataset was others. The data was separated randomly and repeated 1000 times to eliminate dependency of models on training and validation set.

The prediction accuracy of the VM models was evaluated in validation dataset as mean absolute percentage error (MAPE). MAPE is very adapted to measure regression quality when the target variable is positive and remains quite far away from zero [71]. The formula of MAPE is shown as

$$MAPE = \frac{\sum_{i=\text{validation}} \left| \frac{(y_i - \hat{y}_i)}{y_i} \right|}{N_{\text{validation}}} \times 100$$

Where $y_i$ is the measurement value of i-th output variable, $\hat{y}_i$ is the expected value of i-th output variable, and $N_{\text{validation}}$ is the number of records in validation dataset. The performance of VM model becomes better when MAPE becomes closer to zero.
Chapter 3
Plasma Monitoring Sensor and Observable Variable Selection

3.1 Plasma sensor selection for plasma assisted process monitoring

Effective plasma monitoring sensors and observable variables were derived for the plasma assisted oxide film deposition process. Spectrometer (Maya 2000 pro, Ocean Optics Inc.), SPOES (MPIA, PrimeSolution Ltd.), VI-probe (Octive poly, Impedance Inc.) and electrical sensor (PrimeSolution Ltd.) were installed on the well-known capacitively-coupled plasma chamber, AMAT-P5000 system. For the 25 wafers, the SiO₂ deposition was performed, and the equipment variables and observable variables from each sensor were collected during the deposition step of each wafer.

3.1.1 SiO₂ plasma enhanced chemical vapor deposition

In order to find a suitable sensor for plasma assisted process monitoring, a commercially well-known SiO₂ PECVD process was performed in AMAT-P5000 system. The commercial SiO₂ PECVD uses a precursor containing a hydrocarbon ligand similar to the Al₂O₃ PEALD and a plasma process is performed in a few Torr regime. Through the SiO₂ process monitoring, Effective sensors and observable variables for the monitoring of hydrocarbon precursors the oxidation process were confirmed. Figure 3-1 shows a commercial SiO₂
deposition recipe. This recipe consists of a cleaning step using He, O₂, NF₃, and a SiO₂ deposition step using He, O₂, and TEOS. 580 W and 190 W are applied to the cleaning step and the deposition step, respectively. Table 3-1 shows detail recipe of commercial SiO₂ deposition recipe.

![Figure 3-1 Process sequence of SiO₂ PECVD and gas flow rate for each step.](image)

**Table 3-1 Details of SiO₂ PECVD and cleaning recipe.**

<table>
<thead>
<tr>
<th>Condition</th>
<th>SiO₂ PECVD</th>
<th>Cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>TEOS (Si(OC₂H₅)₄)</td>
<td>None</td>
</tr>
<tr>
<td>Discharge gas</td>
<td>He/O₂</td>
<td>He/O₂/NF₃</td>
</tr>
<tr>
<td>He/O₂/TEOS/He-carrier flowrate (sccm)</td>
<td>460/460/</td>
<td>460/460</td>
</tr>
<tr>
<td>Input power (W)</td>
<td>190</td>
<td>580</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>Process temperature (°C)</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Plasma-on time (sec)</td>
<td>63</td>
<td>90 x 2</td>
</tr>
</tbody>
</table>

The deposited SiO₂ film thickness of each wafer was measured at 9 points by ellipsometer.
(M2000D, Woollam Inc.). Detailed position of 9 points was shown in Figure 3-2. Wafer center (0,0), 4 points 33 mm depart from the center (±22.3, ±22.3) and the 4 points 65 mm depart from the center (±65.0, ±65.0).

![Figure 3-2 Measurement position of SiO$_2$ film thickness by using ellipsometry.](image)

Figure 3-3 shows the Psi and Delta function of SiO$_2$ deposited film. An ellipsometer measures the angles Psi and Delta as a function of incident angle and wavelength. These measured parameters are defined as equation (3-1).

$$\tan(\Psi)e^{i\Delta} = \frac{R_P}{R_S}$$

(3-1)

Where $R_P$ and $R_S$ are the Fresnel reflection coefficients of the sample [72], p and s mean the parallel and perpendicular direction of the incident plane. Substituting the measured $\Psi$ and $\Delta$ on equation (3-1), the refraction index ($n$), extinction coefficient ($k$), and film thickness can be determined using a model fit. First, an initial model of the sample is created which includes the sample's layers and substrate and a guess at their respective thicknesses. Using a nonlinear regression technique, the model parameters are varied to fit the experimental data until the best fit between the model and experimental data is achieved.
Fig. 3-4 shows the wafer-to-wafer deposited SiO$_2$ film thickness distributions. The SiO$_2$ film thickness of each wafer shows parabolic distribution. The SiO$_2$ thickness of the central region was about 5% thicker than the edge region. The averaged SiO$_2$ thickness of each wafer is shown in Fig. 3-5.
Fig. 3-5 shows the deposited SiO$_2$ thickness variation for 25 wafers. As the PECVD process stabilized, the deposited film thickness increased from 1896 Å to 2161 Å. This drift phenomenon is explained by the thermal and chemical equilibrium between the reactor inner wall and plasma. To find a suitable sensor for the plasma-assisted deposition process monitoring, multi-sensor (OES, SPOES, VI-probe, etc) data was acquired during the deposition step of each wafer. Fig. 3-6 shows the W2W variation of each plasma monitoring sensor such as equipment sensor (matcher tune position), VI-probe (phase), OES, SPOES, and electrical sensor.
Figure 3-6 W2W variation of each plasma monitoring sensor (a) EES (matcher tune position), (b) VI-probe (phase), (c) OES (CO 483 nm), (d) SPOES (CO 483 nm) and (e) electrical sensor.

In Fig. 3-6, the I-V phase from VI-probe and the CO 483 nm (by-product of precursor oxidation) signal from OES/SPOES show a high correlation with deposited thin film thickness. On the other hand, EES (matcher tune position) and electrical sensor show low correlation. To confirm the effectiveness of plasma information variable based VM in
previous research [67], the reaction rate of precursor oxidation reaction was expressed by PI variables (3.1).

\[ K = c_0 n_e e^{-\frac{E_A}{T_e}} \] (3.1)

Where \( c_0 \) is constant, \( n_e \) is a plasma density, \( T_e \) is a plasma temperature, and \( E_A \) is the activation energy of the precursor (TEOS) [73]. The plasma temperature in equation (3-1) was obtained from the He emission line intensity ratio by OES and the plasma density was obtained from the measured capacitance by VI-probe. Figure 3-7 shows the W2W variation of obtained plasma temperature from OES, plasma density from VI-probe (phase), and the calculated TEOS oxidation reaction rate from equation (3.1).

![Graphs showing W2W variation of plasma temperature, plasma density, and TEOS oxidation reaction rate.](image)

Figure 3-7 W2W variation of (a) plasma temperature from OES, (b) plasma density from VI-probe (phase) and (c) TEOS oxidation reaction rate.
The variation of the SiO$_2$ film thickness of each wafer and the observables variables of the each sensor are shown in Fig. 3-8. The SiO$_2$ thin film thickness and observable variables are linearly normalized to the maximum value of 1 and the minimum value of 0.5. In Fig. 3-8, the VI-probe, OES, and plasma information parameters well follow the deposition rate variation.

![Figure 3-8 Normalized SiO$_2$ thickness and observable variables of multi-sensor.](image)

In order to quantify the monitoring accuracy of each observable variable, the linearity with the thickness of the thin film is shown as $R^2$ in Fig. 3-9. Fig. 3-9 demonstrated the utility of VI-probes and OES, which are widely used for process monitoring. Also, the effectiveness of domain-knowledge based plasma information variables on process monitoring was reaffirmed.
Figure 3-9 $R^2$ of each observable variables for SiO$_2$ PECVD process monitoring.
Chapter 4
Interlayer Formation Characteristics of PEALD

A better understanding of the phenomena occurring at the organic/inorganic or inorganic/inorganic interface is essential not only for the expanding the application areas of hybrid films. The goal of the present study is to understand the growth mechanism of an Al$_2$O$_3$ layer on silicon wafer and organic layer during PEALD. We compared the physical and chemical properties of the Al$_2$O$_3$ films that were deposited on a Si wafer and on a C$_x$H$_y$ organic layer. The thickness and interlayer morphology of the deposited Al$_2$O$_3$ films were examined closely. The chemical elements contained in the Al$_2$O$_3$ films were analyzed as a function of the depth, with a special focus on the carbon impurity concentration. Time-resolved optical emission intensities for CO molecule were compared for different PEALD cycles with or without injecting TMA. Finally, the growth mechanism of Al$_2$O$_3$ on an organic layer was inferred from the comparison of the experimental results for the Si wafer and the C$_x$H$_y$ substrate.

4.1 Interlayer formation on inorganic substrate

In PEALD, one Al$_2$O$_3$ deposition cycle consists of four steps: TMA dosing, purging, O$_2$ plasma-on, and purging. In the TMA dosing step, Al(CH$_3$)$_3$ is chemisorbed to –OH surface groups and CH$_4$ is generated as a byproduct: Al–OH$^*$ + Al(CH$_3$)$_3$(g) → AlO–Al (CH$_3$)$_2$ + CH$_4$(g), where the asterisk designates the surface species [74–76]. The surface reaction between Al(CH$_3$)$_3$ and –OH occurs via ligand exchange; hence, it stops as a result of the steric
hindrance of –CH₃ ligands. In the O₂ plasma-on step, the Al atoms are oxidized to Al₂O₃ by removing –CH₃ ligands, and –OH surface groups are newly generated: AlO–AlCH₃ + 4O(g) → AlOAl–OH* + H₂O(g) + COₓ(g). Purging steps exhaust the residual gases from the TMA dosing step [CH₄ and Al(CH₃)] and the plasma-on step (O, O₂, H₂O, and COₓ). The O₂ plasmas produce O radicals and charged species abundantly, so that O atoms penetrate through the Al₂O₃ film; and a SiO₂ layer grows on the Si wafer surface: Si* + 2O(g) → SiO₂ [77]. The SiO₂ growth stops when the diffusivity of the O atoms through the SiO₂ layer and Al₂O₃ film approaches zero. Fig. 4-1 shows a TEM image of the Al₂O₃ film deposited on the Si wafer (number of cycles = 150). In the Figure 4-1, the deposited film is sharply divided into an Al₂O₃ film and the SiO₂ interlayer.

Figure 4-1 TEM images of Al₂O₃ film deposited on the Si wafer, for different numbers of PEALD cycles.
The deposited film and interlayer thickness of each cycle condition are plotted in Fig. 4-2. The \( \text{Al}_2\text{O}_3 \) grows continuously with the number of ALD cycles, whereas the \( \text{SiO}_2 \) growth almost stops within 50 PEALD cycles. From the linear increase of the deposited film thickness, it was confirmed that the ideal ALD reaction occurred. On the other hand, the mechanism related to the interlayer formation is inefficient after the initial several tens of cycles.

![Figure 4-2 Measured \( \text{Al}_2\text{O}_3 \) film and \( \text{SiO}_2 \) interlayer thickness for different numbers of cycles (1.0 Torr).](image)

To evaluate dominant mechanism for interlayer formation during the PEALD on silicon wafer, process temperature, cycle, and plasma-on step pressure were controlled. To observe the effect of thermal diffusion on interlayer formation, the process temperature was varied from 100 to 250 °C, the common \( \text{Al}_2\text{O}_3 \) PEALD process range. Fig. 4-3 shows TEM images of the film for different process temperatures, deposited in He/O\(_2\) plasmas (number of cycles = 50). The deposited film and interlayer thickness of each cycle condition are plotted in Fig. 4-4. The \( \text{Al}_2\text{O}_3 \) thickness slightly decreases by the process temperature...
increment. But the SiO$_2$ interlayer thickness is hardly influenced by the process temperature. This result implies that the process temperature range in 100 to 250 °C slightly affects the diffusivity of O atoms in the Al$_2$O$_3$ film and SiO$_2$ interlayer formation. In previous studies, the interface formation by thermal diffusion is generally considered in process temperature above 800 °C. Based on this background, Fig. 4-4 result can be considered a reasonable result.

![TEM images of Al$_2$O$_3$ film and SiO$_2$ interlayer deposited in He/O$_2$ plasma for different substrate temperatures (number of deposition cycles= 50).](image-url)
To observe the effect of reactant penetration on interlayer formation, the plasma-on step pressure was varied from 0.4 to 7 Torr. Fig. 4-5 shows TEM images of the film for different plasma-on step pressures, deposited in He/O$_2$ plasmas (process temperature = 250 °C). The deposited film and interlayer thickness of each cycle condition are plotted in Fig. 4-6. The Al$_2$O$_3$ thickness is hardly influenced by the plasma-on step pressure. These results indicate that the ideal ALD reaction occurred regardless of the plasma-on-step pressure change. This result is consistent with the XPS results of Fig. 2-5. On the other hand, the SiO$_2$ interlayer thickness is drastically decreased by the plasma-on step pressure. Although the reactant (oxygen) partial pressure in the chamber increased linearly by the plasma-on step pressure increment, the interlayer thickness decreased. This result means that the pressure-dependent factor contributes to the reactant (oxygen) diffusion rate through the Al$_2$O$_3$ film.
Figure 4-5 TEM images of Al₂O₃ film deposited on the Si wafer, for different plasma-on step pressure.

Figure 4-6 Thicknesses of the Al₂O₃ film and SiO₂ interlayer for different plasma-on step pressure, estimated from the TEM images in Figure 4-5.

To sum up Fig. 4-2, 4-4, and 4-6, interlayer formation on Si wafer is 1) growth occurs
mainly in the initial cycle, 2) Less affected by process temperature, and 3) strongly influenced by plasma-on step condition. In summary, the main mechanism of interlayer formation on silicon wafer is sub-surface oxidation by incident O flux during the plasma-on step (known as reactant penetration [39-42]). Following the reactant penetration model, the incident O atom must pass through the Al$_2$O$_3$ deposited film and SiO$_2$ interlayer to react with the Si wafer. This process can be assumed as diffusion of a neutral O atom (Fig. 4-7).

Incident oxygen flux on the substrate is neutralized by three-body collision with the Al$_2$O$_3$ deposited film and then diffused into the Al$_2$O$_3$ layer. From Fig. 2-3, sufficient oxygen flux was supplied to the deposited film surface to form stoichiometric Al$_2$O$_3$ film. So, the oxygen consumption during the diffusion of Al$_2$O$_3$ layer can be neglected. In this case, the oxygen atom diffusion flux through the Al$_2$O$_3$ and SiO$_2$ layers can be assumed equal and the diffusion flux of O atoms in Al$_2$O$_3$ is explained by Fick's law. The diffusion of O atoms per each PEALD cycle can be expressed as equation (4.1).

$$\Gamma_{atom} = D_{Al2O3} \frac{P_1(t) - P_2(t)}{L_{Al2O3}(t)} = D_{SiO2} \frac{P_2(t) - P_3(t)}{L_{SiO2}(t)}$$  \hspace{0.5cm} (4.1)$$

Where the $\Gamma_{atom}$ is oxygen atom diffusion flux, $D_{Al2O3}(t)$ is an oxygen diffusion coefficient of Al$_2$O$_3$ layer at specific cycle $t$, $D_{SiO2}(t)$ is an oxygen diffusion coefficient of SiO$_2$ interlayer at specific cycle $t$, $L_{Al2O3}(t)$ and $L_{SiO2}(t)$ is film thickness of Al$_2$O$_3$ layer and SiO$_2$. 

![Figure 4-7 Schematic diagram of oxygen diffusion for interlayer formation in PEALD on Si wafer.](image-url)
interlayer, \( P_1(t), P_2(t) \) and \( P_3(t) \) means the oxygen pressure or concentration of each position in Fig. 4-8.

![Oxygen pressure distribution model of Al\(_2\)O\(_3\)/SiO\(_2\) interlayer/Si wafer system.](image)

The equation (4.1) can be simplified by using the relationship between the Al\(_2\)O\(_3\) layer and SiO\(_2\) interlayer properties. In the concept of oxygen diffusion, Al\(_2\)O\(_3\) shows lower oxygen diffusion coefficient than SiO\(_2\) (\( D_{Al2O3} < D_{SiO2} \)). In the concept of diffusion length, deposited film (Al\(_2\)O\(_3\)) shows higher growth rate than interlayer (SiO\(_2\)) (\( L_{Al2O3}(t) > L_{SiO2}(t) \)). By using the above relationship, the pressure of each layer can be simplified as equation (4-2).

\[
P_1(t) - P_2(t) \gg P_2(t) - P_3(t) \approx P_1(t) \quad (4.2)
\]

When the equation (4.2) is substituted into the equation (4.1), the oxygen diffusion rate is simply summarized as in (4.3).

\[
\Gamma_{atom} = \left( D_0 \exp \left( - \frac{E_{diff}}{kT_{Al2O3}} \right) \right) \frac{P_{atom}(t)}{L_{Al2O3}(t)} \quad (4.3)
\]

The thickness of the interlayer formed during the entire PEALD cycle is equal to the total amount of oxygen diffused during the whole PEALD cycle. So, the thickness of SiO\(_2\) interlayer formed after the PEALD can be expressed as equation (4.4).
In equation (4.4), the interlayer growing per rate is inversely proportional to the thickness of Al₂O₃ film grown at specific cycle. Following this explanation, decrease of interlayer growth rate with increasing PEALD cycle can be explained. However, it can’t explain the constant interlayer growth rate with increasing process temperature. Also, in Fig. 4-6, The decrease in plasma-on step pressure means a decrease in oxygen partial pressure in the reactor. Despite the decrease in oxygen partial pressure, the interlayer thickness increased. This result is the opposite of equation (4.4). From the unexplained results of Fig. 4-4, it can be expected that the factors determining the Al₂O₃ film temperature (T_{Al₂O₃}) is not a process tempeature. From the Fig. 4-6, it can be expect that the Al₂O₃ film temperature (T_{Al₂O₃}) is a function of the plasma-on time pressure.

The Al₂O₃ film heating mechanism associated with plasma-on-step pressure is considered ion bombardment. The atomic distance of ideal Al₂O₃ film is about 0.17 nm, which is smaller than the size of oxygen molecules (Fig. 4-9). At this time, the ion existing in the plasma is accelerated by the potential differences between the substrate and the plasma, and is incident. The incident ions collide with the atoms of the top layer in substrate. The atoms colliding with the ion couldn’t reach the thermal equilibrium state and is thermally vibrated. Thermally vibrated atoms repeat the increase and decrease of the lattice spacing and it enhances the oxygen permeability deposited film. From the H. B. Profijt et. al., incident ion energy on grounded-substrate shows several eV on sub-torr order plasma-on step pressure condition [78]. The energy of the incident ion is defined as a function of the plasma temperature as in equation (4.5). The temperature of the Al₂O₃ layer in the ion energy dissipation length will be proportional to the incident ion energy.

\[
Q_{\text{Ion}} \propto (eV_{sh} + \frac{kT_e}{2}) \propto T_{Al₂O₃} \tag{4.5}
\]
Figure 4-9 Plasma roles on interlayer formation in PEALD on Si wafer.

Figure 4-10 Ion energy distributions (IEDs) for the Ar plasma in a CCP configuration measured at (a) the grounded electrode and (b) at the powered electrode [78].
Fig. 4-11, the oxygen diffusion coefficient of the Al₂O₃ film shows an exponential correlation with the temperature between 1500 and 2000 °C [79].

![Graph showing oxygen diffusion coefficient of Al₂O₃ layer for different temperatures](image)

**Figure 4-11** Oxygen diffusion coefficient of Al₂O₃ layer for different temperature [79].

From the model about the plasma roles on interlayer formation during PEALD (Fig. 4-9) and
the detailed data in previous researches [78, 79], it is possible to explain the SiO$_2$ interlayer formation increase with decreasing plasma-on step pressure. As the plasma-on step pressure decreases, the partial pressure of oxygen in the reactor decreases linearly. But it is considered that the decrease of plasma-on step pressure leads the increase of ion bombardment and it makes the Al$_2$O$_3$ film temperature and oxygen diffusivity increases. The validity of the above model was evaluated by virtual metrology in Chapter 5.

4.2 Interlayer formation on organic substrate

Similar to the interlayer formation study for Si wafers, the interlayer formation on organic substrate during the PEALD was observed. Fig. 4-12 shows TEM images of the Al$_2$O$_3$ film deposited on the C$_x$H$_y$ layer, for different numbers of PEALD cycles. It has been known for thermal ALD that a continuous Al$_2$O$_3$ film is formed on polymer materials at least above 15–20 ALD cycles. But in Fig. 4-12, the continuous Al$_2$O$_3$ film didn’t appear on the C$_x$H$_y$ even at 20 ALD cycles. The image contrast in Fig. 4-12, caused by infiltration of TMA molecules and O atoms into the C$_x$H$_y$ substrate, is observed at the Al$_2$O$_3$/C$_x$H$_y$ interface. Also, the penetration depths of Al$_2$O$_3$ into the C$_x$H$_y$ layer are uneven. This may be associated with the non-uniformity of the C$_x$H$_y$ layer, such as the surface roughness and degree of cross-linking in the backbone. The above results indicate that the ideal ALD reaction does not occur even after 20 cycles of PEALD.

For the Si wafer, the Al$_2$O$_3$ thickness increases linearly with the number of PEALD cycles; the growth per cycle (GPC) is ~0.148 nm. For the C$_x$H$_y$ layer, the Al$_2$O$_3$ thickness increases rapidly during the initial 20 PEALD cycles. With a further increase in the number of PEALD cycles, the GPC of Al$_2$O$_3$ saturates to the same value as that on the Si wafer. Consequently, the
thickness is slightly larger for $\text{Al}_2\text{O}_3$ on the $\text{C}_x\text{H}_y$ than for $\text{Al}_2\text{O}_3$ on the Si. At the same number of PEALD 100 cycles, the $\text{Al}_2\text{O}_3$ thickness (not including the $\text{Al}_2\text{O}_3/\text{C}_x\text{H}_y$ interface) on the $\text{C}_x\text{H}_y$ is 18.68 nm, which is 5.48 nm thicker than the $\text{Al}_2\text{O}_3$ thickness on the Si (13.2 nm). Initially, there are no $-\text{OH}$ groups on the $\text{C}_x\text{H}_y$ surface or inside the $\text{C}_x\text{H}_y$ bulk. During the TMA dosing step for the first ALD cycle, TMA molecules easily penetrate through the $\text{C}_x\text{H}_y$ surface via diffusion. Since the diffusion is not self-limited, a large number of TMA molecules would be trapped in the $\text{C}_x\text{H}_y$ bulk near the surface region. At the subsequent plasma-on step, the trapped TMA molecules react with O radicals (atoms), producing the $\text{Al}_2\text{O}_3$ nucleation clusters. In $\text{O}_2$ plasmas, the density of O radicals is high enough for $-\text{OH}$ groups to be formed abundantly on the $\text{C}_x\text{H}_y$ surface. Electrons and ions are accelerated over the sheath region, enhancing the surface reactivity, and thus further activating the formation of $-\text{OH}$ groups on the surface. Accordingly, the $\text{C}_x\text{H}_y$ surface would be changed to be rich in $-\text{OH}$ groups within the first few PEALD cycles. Before the surface is entirely covered with $-\text{OH}$ groups, infiltration of TMA molecules into the $\text{C}_x\text{H}_y$ bulk occurs together with the surface reaction between $-\text{CH}_3$ ligands and $-\text{OH}$ groups. During this period, plasma oxidation reactions proceed in the $\text{C}_x\text{H}_y$ bulk near the surface as well as on the $\text{C}_x\text{H}_y$ surface, resulting in the non-uniform growth of particle-like $\text{Al}_2\text{O}_3$ clusters. As the number of PEALD cycles increases, small $\text{Al}_2\text{O}_3$ clusters grow to large $\text{Al}_2\text{O}_3$ clusters that coalesce and eventually close the vacant spaces in the $\text{C}_x\text{H}_y$ backbone. Abundant O radicals and energetic charged species in plasmas allow a continuous $\text{Al}_2\text{O}_3$ film to be formed at after fewer cycles than in the case of thermal ALD.
Figure 4-12 TEM images of Al$_2$O$_3$ film deposited on the Si wafer and C$_x$H$_y$, for different numbers of PEALD cycles.

Figure 4-13 Al$_2$O$_3$ film thickness on the Si wafer and C$_x$H$_y$ layer for different numbers of PEALD cycles.
Fig. 4-14 (a)–(c) show the C1s, Al2p, and O1s spectra, respectively, obtained from XPS depth profiling for the Al2O3 film on the CxHy layer (PEALD cycles = 100). The C1s spectrum consists of C–C (sp2: 284.0 eV and sp3: 284.8 eV), C–O (286.0 eV), and C=O (289.0 eV) bonds; the Al2p spectrum has a peak at the binding energy of 74.6 eV; the O1s spectrum consists of Al–O (531.2 eV) and C–O (532.7 eV) bonds [46, 81]. The XPS probing position gets closer to the CxHy layer with increased sputtering time; an increase in sputtering time results in an increase in the C1s intensity and a decrease in the Al2p and O1s intensities. In all the spectra, the binding energy that has the peak intensity shifts toward a lower or a higher energy direction, with increased sputtering time. This energy shift indicates that the chemical compositions of the Al2O3 film changes along the depth.
Figure 4-14 XPS spectra of (a) C1s, (b) Al2p, and (c) O1s for the Al$_2$O$_3$ film on the C$_x$H$_y$ layer, obtained by varying the sputter time (number of PEALD cycles = 100).

The results for the Al$_2$O$_3$ film on the Si wafer and the C$_x$H$_y$ layer at 100 PEALD cycles are plotted in Fig. 4-15 (a) and (b), respectively. For Al$_2$O$_3$ on the Si, the Al concentration decays to zero at a sputtering time of 270 s. The O concentration decays to zero later than the Al concentration because of the SiO$_2$ interlayer. The sampling depth of the Si is 7.2 nm; the Si
concentration begins to increase before the Al concentration decays to zero. The C concentration increases only slightly with the sputtering time, and it always remains below 2.0%. In fact, the Al₂O₃, SiO₂, and Si regions are clearly separated, as shown in Fig. 4-1. However, the Al, O, and Si concentrations presented in Fig. 4-15 shows significant mixing for sputtering times greater than 200 sec. This demonstrates the limitation of XPS depth profiling. For Al₂O₃ on the CₓHᵧ, the C concentration rises, starting at a sputtering time of 90 sec, and continuously increases with the sputtering time. The Al and O concentrations decay to zero later than those for the Si wafer. This is probably attributable to a smaller sputtering rate for the CₓHᵧ than for the Si.
Figure 4-15 XPS depth profiles for the Al$_2$O$_3$ film deposited on the (a) Si wafer and (b) C$_x$H$_y$ layer as a function of sputtering time (number of PEALD cycles = 100 and sputter time resolution = 15 s).

The XPS depth profile of Fig. 4-15 was converted to the density variation according to the physical distance using the sampling depth difference of Si and C described in Chapter 2. In Fig. 4-16, in the case of Al$_2$O$_3$ deposited on the Si wafer, the Al$_2$O$_3$ film thickness without carbon impurity was measured about 13.5 nm. However, in the case of Al$_2$O$_3$ deposited on C$_x$H$_y$ layer, the Al$_2$O$_3$ film thickness without carbon impurity was measured only 6 to 7 nm. This result indicates that there is a continuous influx of carbon impurities during the PEALD initial cycles.
To find the reason for the thick carbon impurity contained film deposition in PEALD, XPS depth profile were proceeded for the Al\textsubscript{2}O\textsubscript{3} deposited film of different PEALD cycles. Fig. 4-17 shows the XPS depth profiles for the Al\textsubscript{2}O\textsubscript{3} film deposited on the C\textsubscript{x}H\textsubscript{y} layer with different PEALD cycles (number of PEALD cycles = 30, 50, 100, 150 and sputter time resolution = 15 s) Fig. 4-17, the interlayer thickness is a region where Al and C coexistence region. In the same Ar sputtering conditions, the coexistence of Al-C during long sputtering time implies the thick interlayer formation. For easier viewing of the results in Fig. 4-17, differentiating the C1s intensity by sputtering time is shown in Fig. 4-18. As the thick interlayer formed, the C1s signal gradually increases by the sputtering time, and the differential value decreases. In Fig. 4-18, Al-C interlayer film growths during the initial 30 cycles. After that only Al\textsubscript{2}O\textsubscript{3} deposited film was growths without interlayer formation.
Figure 4-17 XPS depth profiles for the Al$_2$O$_3$ film deposited on the C$_x$H$_y$ layer as a function of sputtering time with different PEALD cycles (number of PEALD cycles = 30, 50, 100, 150 and sputter time resolution = 15 s).
In TALD, the interlayer formation by precursor infiltration is observed less than 20 cycles. But in Fig. 4-18, interfacial formation was also observed in more cycles in PEALD. Interlayer formation over a longer cycle than TALD can be expected as a plasma effect. To observe the role of plasma on interlayer formation, plasma-chemistry monitoring by using OES was performed. The expected chemical reaction path for Al$_2$O$_3$ PEALD in organic substrate is shown in Fig. 2-16. To observe the reaction path characteristics during a single plasma-on step, discharge conditions were classified as shown in Fig. 4-19 (a) - (c). The Fig. 4-19 (a): PEALD on Si wafer condition that is expected to react only with self-limited precursor and plasma, Fig. 4-19 (b): PEALD on C$_x$H$_y$ layer without precursor injection condition which is expected to react only with organic substrate and plasma, and Fig. 4-19 (c): PEALD on C$_x$H$_y$ layer with precursor injection condition which is expected to all reaction will occurred.

\[ \text{Figure 4-18 1st derivation of C1s intensity as a function of sputtering time with different PEALD cycles.} \]
In the Fig. 2-16 and 2-17, CO molecular spectrum of CO (483 nm) and the line spectrum of H\(_\beta\) (486 nm) are also observed during the PEALD plasma-on step. The peak intensity is slightly higher for the H\(_\beta\) line spectrum than for the CO molecule spectrum, whereas the spectral range is much wider for the CO spectrum than for the H\(_\beta\) spectrum. For this reason, we utilized the CO 483 nm emission spectrum as an indicator of the oxidation rate of C atoms. In Fig. 4-19, The CO 483 nm emission intensity shows a different time variation trend depending on the PEALD condition. Fig. 4-19 (a) shows the temporal evolution of the CO
483 nm emission intensity for the Si wafer during the plasma-on step at the initial PEALD cycle. For the Si with TMA injection, the –CH₃ ligands have covered the entire surface via the TMA dosing step. When the plasma is turned on, a large number of CO and CO₂ molecules are generated from the surface oxidation reactions, leading to a sharp increase in CO intensity. The production rate of COₓ molecules is reduced as the –CH₃ ligands are removed from the surface. As a result, the CO intensity slowly decreases with the plasma-on time, and it decays nearly to zero at the end of the plasma-on step. Fig. 4-19 (b) shows the temporal evolution of the CO emission intensity for the CₓHᵧ during the plasma-on step at TMA-off case. For the TMA-off case (without TMA injection), CO and CO₂ are generated from the oxidization of the C atoms on the CₓHᵧ surface. This oxidation reaction is not self-limited. Consequently, it proceeds during the entire plasma-on step. Energetic electrons and ions enhance the surface reactivity with time, resulting in a continuous increase in CO 483 nm intensity. In Fig. 4-19 (c), the TMA-on case (with TMA injection), CO and CO₂ are generated by oxidizing not only the C atoms on the CₓHᵧ surface but also the –CH₃ ligands trapped in the CₓHᵧ backbone. As a result, the CO intensity is stronger for the TMA-on case than for the TMA-off. Figure 4-20 shows the CO 483 nm signals of Fig. 4-19 (a) - (c) at the first cycle. Compares the temporal evolution of the CO emission intensity for the Si wafer and the CₓHᵧ layer. The CO intensity is stronger for the CₓHᵧ without TMA injection than for the Si with TMA injection. This means that the oxidation reaction occurs more actively with the CₓHᵧ surface than with the –CH₃ ligands. For the CₓHᵧ with TMA injection, the CO intensity decreases with the plasma-on time, similar to the CO intensity profile for the Si. However, it remains at a highly-positive value even at the end of the plasma-on step. This is because the oxidation reaction on the CₓHᵧ surface is not self-limited. The CO intensity is maximal at the first PEALD cycle. The portion of the CₓHᵧ surface area covered with Al₂O₃ expands with the increasing number of PEALD cycles. This hinders O radicals from reacting with the CₓHᵧ surface, resulting in a decrease in
CO intensity as the number of PEALD cycles increases.

Fig. 4-21 shows the temporal evolution of the CO emission intensity during the first 40 PEALD cycles. The CO intensity profile for the Si is not influenced by the number of PEALD cycles, although it fluctuates slightly because of the noisy background signals. The CO intensity for the C₅H₈ layer decreases rapidly during the first six PEALD cycles; thereafter, it fluctuates slightly with the PEALD cycles. It should be noted that the CO intensity is always higher for the C₅H₈ than for the Si. Wilson et al [37] and George [74] investigated the growth mechanism of Al₂O₃ on various polymer materials in thermal ALD by using in situ Fourier transform infrared spectroscopy (FTIR) and QCM. Their FTIR and QCM results showed that TMA molecules moved in and out of the polymer bulk whereas the H₂O reactant did not adsorb into the polymer bulk. The diffusion of TMA molecules in and out of the polymer bulk proceeded until a continuous Al₂O₃ film was formed. In PEALD, O atoms can diffuse into the C₅H₈ backbone even after formation of a continuous Al₂O₃ film. In my previous paper [70], the SiO₂ interlayer grew until the number of deposition cycles reached the range of 40–50.
The stronger CO spectrum for the $\text{C}_x\text{H}_y$ compared to that for the Si after 6 PEALD cycles originates from the chemical interaction of O radicals with the $\text{C}_x\text{H}_y$ bulk. Chemical reactions between O radicals and the $\text{C}_x\text{H}_y$ surface actively occur until the $\text{C}_x\text{H}_y$ surface is entirely covered with a continuous $\text{Al}_2\text{O}_3$ film. During this period, not only CH$_4$, CO, and CO$_2$ but also C atoms are possibly generated. Ion bombardment can break $\text{C}_x\text{H}_y$ chain networks, producing C atoms as well. Organic materials are permeable to small molecules, so that C atoms readily move out of the $\text{C}_x\text{H}_y$ bulk. During this process, a portion of the C atoms would be trapped in the $\text{Al}_2\text{O}_3$ film. The trapped C atoms survive during the subsequent TMA dosing step, because they do not react with TMA molecules. However, they do react with O atoms in the plasma-on step, leading to a stronger CO emission intensity for the $\text{C}_x\text{H}_y$ than for the Si. In PEALD, O atoms can diffuse through the $\text{Al}_2\text{O}_3$ bulk and reach the $\text{C}_x\text{H}_y$ backbone. The high diffusivity of O atoms enables a stronger CO intensity for the $\text{C}_x\text{H}_y$ than for the Si, even after the formation of a continuous $\text{Al}_2\text{O}_3$ film (>10 ALD cycles). The trapped C atoms in $\text{Al}_2\text{O}_3$ do not fully react with O atoms, and the remaining C atoms are incorporated into the $\text{Al}_2\text{O}_3$ film. This results in a higher C concentration for $\text{Al}_2\text{O}_3$ on the $\text{C}_x\text{H}_y$ than for $\text{Al}_2\text{O}_3$ on the Si. A further increase in the number of PEALD cycles increasingly hinders the diffusion of O atoms through the $\text{Al}_2\text{O}_3$ film, and finally prevents any trapping of C atoms in the $\text{Al}_2\text{O}_3$ film; at that point, carbon-free $\text{Al}_2\text{O}_3$ is formed.
Figure 4-21 CO 483 nm emission signals during the initial PEALD 40 cycles on Si wafer and CₓHᵧ layer.
Chapter 5
Development of Virtual Metrology

5.1 Domain-knowledge based variable selection for PEALD VM

In Chapter 4, main mechanism of the interlayer formation process for PEALD on Si wafer and CₓHᵧ layer was studied. In PEALD on Si wafer, deposited film lattice vibration by ion bombardment and reactant penetration enhancement are the main mechanism for interlayer formation. In the PEALD on CₓHᵧ, organic substrate ablation & re-deposition by reaction between the reactive o radical and organic substrate are the main mechanism for interlayer formation. Although the interlayer is formed by different mechanisms on Si wafer and CₓHᵧ layer, it has a similarity that the mechanism is activated by the reactivity of the plasma. For the high prediction accuracy of the virtual metrology, the plasma temperature representing the reactivity of the plasma was selected as the plasma information variable.

The plasma information variable (≈ plasma temperature) was derived from the He excitation state emission line ratio selected in Chapter 2.2. Before the OES spectrum analysis, plasm equilibrium state was determined by hairpin probe. For the low temperature plasma, the corona equilibrium can be applied to analyze the emission intensity of OES, which has been developed with the assumption of the energy loss from the radiative recombination equaled to the energy gain from the excitation of atoms or ions. Condition for application of corona model is given by Griem criteria, equation (5.1) [80].
\[ n_e < 1.4 \times 10^{14} z^7 \left( \frac{kT_e}{z^4 E_{iz}} \right)^4 \]  

(5.1)

Where \( n_e \) is the electron density, \( z \) is the atomic charge number, \( E_{iz} \) is the ionization energy, and \( kT_e \) is the plasma temperature with Boltzmann constant \( k \). Hairpin probe was used to observe plasma equilibrium status during the plasma-on step in Chapter 4 condition. Through a network analyzer connected to the hairpin probe, the transmittance of electromagnetic waves between 1.73 GHz and 1.78 GHz was measured. The electromagnetic wave frequency was increased by 0.001 GHz. The variation of the resonance frequency was observed at 0.1 second intervals during the plasma-on step (4 sec). Fig. 5-1 shows the time resolved plasma density at different plasma-on step pressure. In Fig. 5-1, plasma reached equilibrium state after 0.25 seconds after the RF power induced. As the plasma-on step pressure increased from 0.4 to 7 Torr, the plasma density in the equilibrium state increased from 1.44 to 6.23 \( \times 10^{14}/m^3 \).

![Figure 5-1 Time resolved plasma density at different plasma-on step pressure.](image)

Hairpin probe was used to observe plasma equilibrium status during the plasma-on step in Chapter 4 condition. Through a network analyzer connected to the hairpin probe, the
transmittance of electromagnetic waves between 1.73 GHz and 1.78 GHz was measured. The electromagnetic wave frequency was increased by 0.001 GHz. The variation of the resonance frequency was observed at 0.1 sec intervals during the plasma-on step (4 sec). Fig. 5-1 shows the time resolved plasma density at different plasma-on step pressure. In Fig. 5-1, plasma reached equilibrium state, after 0.25 sec RF power induced. As the plasma-on step pressure increased from 0.4 to 7 Torr, the plasma density in the equilibrium state increased from 1.44 to 6.23 x10^{14} #/m^3. Plasma density measured by hairpin probe was plotted on the Fig. 5-2, operating region of the thermodynamic equilibrium model. The x-axis range in Fig. 5-2 shows the conventional plasma temperature region for CCP plasma. From 0.4 to 7 Torr, the plasma density is less than 10^{15} #/m^3. In this pressure range, the plasma equilibrium state can be assumed to be in the corona equilibrium.

![Figure 5-2 Operating region of the thermodynamic equilibrium model in terms of n_e and T_e.](image)

In plasmas to which the CE model is applicable, especially the excitation of ground-state helium atoms requires inelastic collisions with high-energy electrons at energies above 22 eV because the excitation threshold energy levels (2p states) of neutral helium are located near 22
eV. In plasma information variable derivation by using corona equilibrium, 2p state He emission line pair was selected with large threshold energy differences, similar emission line wavelength, and sufficient signal to noise ratio. From the definition of corona equilibrium, the downward transition by electron collision can be neglect and it means that upward transition rate is equal to the downward transition by radiation decay. So, the emission line intensity ratio of the selected He emission line pair is equal to the ratio of excite state population: equation (5.2).

\[
\frac{I_1}{I_2} = \frac{n_e n_g \sigma_{\text{exc}}^1}{n_e n_g \sigma_{\text{exc}}^2} = \frac{\int_{E_{\text{th},1}}^{\infty} \sigma_1 f(E) dE}{\int_{E_{\text{th},2}}^{\infty} \sigma_2 f(E) dE}
\]  

(5.2)

Where \( I_1, I_2 \) are the emission line intensity of each He emission line, \( n_g \) is the He atomic concentration in the discharge volume, \( Q_{\text{exc}} \) is the excitation rate of each He emission line, and \( \sigma \) is the excitation cross section of each He emission line. In the left side of equation (5.2) is a measured He emission line intensity ratio and the right side is the product of cross-section and electron energy distribution function (EEDF). The excitation cross-section of the emission line is a physically given value. So, measured intensity ratio of He emission line pair can be expressed as a function of plasma temperature.

Figure 5-3 Selected He 2p emission line excitation cross-section.
Figure 5-4 Calculated He 2p emission line ratio–plasma temperature relation.

5.2 Al$_2$O$_3$ and interlayer thickness monitoring by virtual metrology

In Chapter 4, the interlayer formation mechanism on PEALD was observed. Based on this mechanism, domain-knowledge based variables were introduced to manage the PEALD process results. By using the derived variables, the PEALD process results, deposited film (Al$_2$O$_3$) and interlayer (SiO$_2$) thickness were predicted. PLSR was used for virtual metrology. From the VIP analysis from the PLSR, the effect of the derived variables on PEALD VM was evaluated. Table 5-1 shows the data set used for the prediction of PEALD. Table 5-1 consisted of a data set of cycle number and plasma-on step pressure variation. For each data, the process results (predicted variables) are Al$_2$O$_3$ and SiO$_2$ thickness. Observable variables consisted of process conditions (cycle number, pressure), sensor data (selected OES emission signal, VI-probe data) and derived variables (PI information and diffusion model based variables).
### Table 5-1 PEALD VM data set.

<table>
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<tr>
<th>Discharge Number</th>
<th>pressure</th>
<th>cycle</th>
<th>$\text{Al}_2\text{O}_3_\text{thk.}$</th>
<th>Interlayer_thk.</th>
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<td>150</td>
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<td>6.0</td>
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<td>1</td>
<td>100</td>
<td>13.2</td>
<td>5.8</td>
</tr>
<tr>
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<td>1</td>
<td>50</td>
<td>7.8</td>
<td>5.4</td>
</tr>
<tr>
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<td>1</td>
<td>40</td>
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</tr>
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<td>7</td>
<td>100</td>
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<td>3.5</td>
</tr>
</tbody>
</table>

The PEALD process results were predicted as the algorithm in 5-5. The domain-knowledge based PI variable and diffusion model based variables were added to the general virtual metrology algorithm (Fig. 2-31).
Figure 5.5 Flow chart of VM development procedure. There are 2 kinds of parameters are added on the selected feature; addition of the PI variables and the diffusion model based parameter.

First, observable variables (process conditions, sensor data) were pre-processed as noise subtraction and variable selection. Selected variables (features) were normalized. Training set was used to build up the VM model, and validation set was used to evaluate prediction accuracy of the trained model. The number of training dataset was 5 and that of validation dataset was others. The data was separated randomly and repeated 1000 times to eliminate dependency of models on training and validation set. The diffusion model based variable derived from the result of Al₂O₃ thickness VM and PI variable were used for SiO₂ interlayer thickness VM. The training and validation set was configured with the same configuration as the Al₂O₃ VM.
5.2.1 VM for Al₂O₃ deposited film

11 data sets of cycle number and plasma-on step pressure variation were used for Al₂O₃ VM. Fig. 5-6 shows the measured Al₂O₃ thickness (black square points) and predicted value for PLSR with different variable data set. The black line is the measured Al₂O₃ thickness of each data set. The red, blue, and magenta lines are the predicted Al₂O₃ thicknesses by the VM. The red line is the case where both the cycle number and the plasma-on-step pressure variation set were used. The blue line is the case where the cycle number variation set was used. The magenta line is the case where the plasma-on step pressure variation set was used. At each condition, MAPE of the VM between measured Al₂O₃ and predicted value is 24.54%, 45.404%, and 384.35 %. The large MAPE difference in the blue and magenta cases, where the number of data used is similar, implies a VM's low accuracy for pressure changes and high accuracy for cycle variation.

Figure 5-6 Measured Al₂O₃ thickness (black square points) and predicted value for PLSR with different variable data set.
The VIP analysis (Fig. 5-7) shows similar trend to Fig. 5-6. Each bar in Fig. 5-7 represents the correlation between process conditions and sensor data to Al₂O₃ thickness. The PEALD cycle has the highest correlation with Al₂O₃ thickness among various parameters. This result implies that the deposited thickness depends only on the cycle in the case of the ideal ALD operation window.

![Graph showing Variable Importance in Projection for VM models using PLSR for Al₂O₃ thickness with different variable data set.](image)

Figure 5-7 Variable Importance in Projection (VIP) for VM models using PLSR for Al₂O₃ thickness with different variable data set.

From the Fig. 5-7, it can be confirm that the Al₂O₃ thickness used as the observable variable of the SiO₂ interlayer VM is a direct function of the cycle.

5.2.2 VM for SiO₂ interlayer

The VM was developed for the SiO₂ interlayer formation during the PEALD. 7 data sets of plasma-on step pressure variation were used for SiO₂ VM. Fig. 5-8 shows the measured Al₂O₃ thickness (black square points) and predicted value for PLSR with the case of different
observable variable selection. The black line is the measured SiO$_2$ interlayer thickness. The red, blue, magenta, and cyan lines are the predicted SiO$_2$ interlayer thicknesses by the VM. The red line is the case where process condition and selected OES emission signals were used for the VM. The blue line is the case where process condition and VI-probe signals were used for the VM. The magenta line is the case where process condition, selected OES emission signals and VI-probe signals were used for the VM. The cyan line is the case where the PI variable was added on the observable with process condition, OES and VI-probe signals for the VM. At each condition, MAPE of the VM between measured SiO$_2$ interlayer thickness and predicted value is 80.31%, 104.86%, 109.85%, and 19.66%. The large MAPE difference in the cyan and other cases implies a derived PI variable has high correlation with SiO$_2$ interlayer formation.

The VM was developed for the SiO$_2$ interlayer formation during the PEALD. 7 data sets of plasma-on step pressure variation were used for SiO$_2$ VM. Fig. 5-8 shows the measured

![Figure 5-8 Interlayer thickness of measured (black square points) and predicted value for PLSR with different plasma-on step pressure.](image)

The VM was developed for the SiO$_2$ interlayer formation during the PEALD. 7 data sets of plasma-on step pressure variation were used for SiO$_2$ VM. Fig. 5-8 shows the measured
Al₂O₃ thickness (black square points) and predicted value for PLSR with the case of different observable variable selection. The black line is the measured SiO₂ interlayer thickness. The red, blue, and magenta lines are the predicted SiO₂ interlayer thicknesses by the VM. The red line is the case where process condition and selected OES emission signals were used for the VM. The blue line is the case where process condition and VI-probe signals were used for the VM. The magenta line is the case where process condition, selected OES emission signals and VI-probe signals were used for the VM. The cyan line is the case where the PI variable was added on the observable with process condition, OES and VI-probe signals for the VM. At each condition, MAPE of the VM between measured SiO₂ interlayer thickness and predicted value is 80.31%, 104.86%, 109.85%, and 19.66 %. The large MAPE difference in the cyan and other cases implies a derived PI variable has high correlation with SiO₂ interlayer formation.

In chapter 4.1, the interlayer formation during the PEALD on Si wafer, the lattice vibration by incident ion is the main mechanism for reactant gas diffusion. Based on this mechanism, \( \exp(T_e) \) was derived as the plasma information variable from OES measurement. Fig. 5-9 shows the correlation between the SiO₂ interlayer thickness and derived PI variable, \( \exp(T_e) \). The Fig. 5-9 implies that domain-knowledge based PI variables are important for predicting process results. The VIP analysis (Fig. 5-9) shows similar trend to Fig. 5-7 and 5-8. Each bar in Fig. 5-9 represents the correlation between observable variables to SiO₂ interlayer thickness. The PI has the highest correlation with SiO₂ interlayer thickness among various observable variables. The process condition, plasma-on step pressure shows the 2\(^{nd}\) highest correlation with SiO₂ interlayer thickness. This result implies that the decreases of plasma-on step lead the plasma temperature and incident ion energy increases. Finally, enhanced reactive gas diffusion makes the thick interlayer during the PEALD.
Figure 5-9 Correlation between the SiO$_2$ interlayer thickness and derived PI variable, exp(T$_e$).

Figure 5-10 Variable Importance in Projection (VIP) for VM models using PLSR for interlayer thickness with different plasma-on time pressure.

The VM was developed for cycle variation data set. 6 data sets of PEALD cycle variation were used for SiO$_2$ VM. Fig. 5-10 shows the measured Al$_2$O$_3$ thickness (black square points)
and predicted value for PLSR with the case of different observable variable selection. The black line is the measured SiO\textsubscript{2} interlayer thickness. The red, blue, and magenta lines are the predicted SiO\textsubscript{2} interlayer thicknesses by the VM. The red line is the case where selected OES emission signals and VI-probe signal were used for the VM. The red line is the case where selected OES emission signals and VI-probe signal were used for the VM. The blue line is the case where process condition (cycle) is add on the OES and VI-probe signals. The magenta line is the case where process condition, diffusion model based variable (\(1/\sum Al_2O_3\) thickness) is add on the OES and VI-probe signals. At each condition, MAPE of the VM between measured SiO\textsubscript{2} interlayer thickness and predicted value is 56.95\%, 41.98\%, and 25.02\%. The large MAPE difference in the magenta and other cases implies a derived diffusion model based variable has high correlation with SiO\textsubscript{2} interlayer formation.

Figure 5-11 Interlayer thickness of measured (black square points) and predicted value for PLSR with different PEALD cycles.

The VIP analysis (Fig. 5-12) shows similar trend to Fig. 5-11. Each bar in Fig. 5-12 represents the correlation between process conditions and sensor data to SiO\textsubscript{2} interlayer
thickness. The diffusion model based variable \((1/\sum Al_2O_3 \text{ thickness})\) has the highest correlation with SiO\(_2\) interlayer thickness among various parameters. This result implies that the reactive gas diffusion model in Chapter 4.2 well explain the interlayer formation during the PEALD.

![Figure 5-12 Variable Importance in Projection for VM models using PLSR for interlayer thickness with different PEALD cycles.](image)
Chapter 6

Conclusion

In PEALD on organic and inorganic substrates, it was observed that the interlayer is an important factor for end-product property management in the case of deposited film thickness under the tens of nm scale. In PEALD on inorganic substrate, deposited film lattice vibration by ion bombardment and reactant penetration enhancement are the main mechanism for interlayer formation. In this case, the interlayer is grown toward the substrate direction from the deposited film/substrate interface. The interlayer forms a distinct boundary with the deposited film and grows to 3-10 nm according to the plasma-on step recipe. On the other hand, in the PEALD on organic substrate, the ablation & re-deposition of organic substrate by the reactive o radical are the main mechanism for interlayer formation. In this case, the interlayer is grown toward the deposited film direction from the deposited film/substrate interface. The interlayer forms an obscure boundary with the deposited film and grows to reduce the thickness of the pure deposited film.

Considering the plasma roles and main mechanisms on interlayer formation, plasma-information (PI) variable and diffusion model based variable are introduced. By using the virtual metrology with those domain-knowledge based variables, Al₂O₃ film and interlayer thicknesses were predicted by observable variables measured under various PEALD conditions. It is confirmed that PI-VM improves the prediction reliability at high values for wide PEALD operation window. From the Variable Importance in Projection (VIP) values derived from partial least squares regression (PLSR) re-affirmed that the PI and diffusion model based variables are important for process results prediction. This PI-VM for PEALD enables the fault detection and classification (FDC) for nanometer scale thin film deposition by backtracking of the plasma-chemistry. In addition the validity of the algorithm in which the
deposited film thickness, which is a prediction variable of common VM, acts as an observable variable of another VM for interlayer formation. This means that even if the deposited film growth rate is affected by the plasma condition, such as PECVD, it can be interpreted by the PI variable and iterative VM algorithm. PEALD on organic conditions, where plasma ablation and re-deposition occurs, may be analyzed by the domain knowledge-based observable variable introduction about re-deposition phenomena.
Reference


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초 록

증착 공정에서 증착 박막과 기판 사이에 두 영역의 물질이 공존하는 영역의 형성은 잘 알려진 현상이다. 많은 선행 연구들에서 증착 박막과 기판 물질이 공존하는 영역을 계면 (interlayer) 또는 혼성층 (interphase) 등으로 불리며, 이중 물질 간의 접합을 위한 접합층 (adhesive layer)로 활용되었다. 이에 따라 공정 중 계면 형성 과정보다 형성 결과에 따른 접합력 상승에 연구 초점이 맞춰졌으며, 후열처리 (annealing)을 통해 의도적인 계면 형성이 연구되었다. 계면의 형성은 증착된 박막의 성질을 돕는 보조적인 측면의 활용이 주로 연구되어, 여러 산업현장에서 활용되고 있는 공정 모니터링의 관리에 대상으로 여겨지지 않았다.

그러나 최근 반도체 생산 공정의 집적도가 증가함에 따라 요구되는 박막의 두께와 공정의 마진이 줄어들고 있다. 높은 정밀도가 요구되는 공정에서 수 nm의 계면 형성이 전체 박막에 미치는 영향이 늘어나고 있다. 최근 선행 연구에서 공정 중 형성된 계면이 CMOS 게이트 산화막의 I-V 특성, 광학 필터의 반사를 변동과 유기박막과 유-무기막 구조의 수분 방지막의 수분 차폐 특성 등에 영향을 미치는 것이 확인되었다. 위 연구들에서 계면 형성 메커니즘이 연구되고 있으며, 플라즈마를 활용한 공정에서 보다 두꺼운 계면이 관찰되고 있다. 즉, 플라즈마를 활용한 수십 nm scale의 이중 박막 증착 공정의 관리는 증착 박막뿐 아니라 계면의 특성 역시 포함되어야 함을 알 수 있다. 수 nm scale의 계면 형성이 공정 결과에 영향을 미칠 수 있으나, nm scale의 전단을 통해 공정 결과를 전수조사를 수행하는 것은 비용적으로 큰 부담이 된다. 산업계 수요에 맞춰볼 때, 현상학적 이해에 기반한 가장 계측 모델의 개발은 수십 nm scale의 이중 박막 증착 공정에 필수적인 요소이다.
본 학위 논문에서, 계면 형성을 고려한 공정 가상 계측 방법론의 적용 대상으로 플라즈마 원자 증착법을 선정하였다. 플라즈마 원자 증착법은 수십 nm 스크일의 은은 고순도 박막의 증착 공정에 주로 활용되어, 수 nm의 계면 형성이 공정 결과 중 차지하는 분율이 크다. 또한 선행 연구에서 두꺼운 계면이 관찰됨으로 플라즈마의 계면 기여 해석에 적합하다. 공정 모니터링 측면에서도 전구체와 반응성 기체가 순차적으로 구별되어 주입되어, 전구체의 흡착량을 플라즈마 방전 스텝에 독립적인 인자로 제어할 수 있다. 이러한 공정 제어를 통해, 플라즈마 방전 스텝이 증착 박막 성장 및 계면 형성에 미치는 영향을 분리하여 관찰할 수 있었다.

플라즈마 원자 증착 중 계면 형성을 모니터링하기 위해 플라즈마 인자 (plasma-information variable, PI)과 반응성 원자확산 모델에 기반한 인자를 정의하였다. PI 인자는 플라즈마 방전 스텝 상태를 모니터링하기 위해 사용되었다. 플라즈마 방전 스텝 중 PI 인자는 광학적 분광법 (optical emission spectroscopy, OES) 에 기반한 플라즈마 여기 상태 관찰을 통해 도출하였다. 이 때, 다른 여기 상태를 가지는 헬륨 원자의 방출 신호의 비율을 코로나 모델에 대입하여 플라즈마 온도 정보를 산출하였다. 확산 모델에 기반한 인자는 각 사이클 별 확산 거리 (증착 박막의 두께), 반응성 기체의 분압과 증착 박막의 산소 투과도를 통해 도출하였다.

각기 다른 플라즈마 방전 스텝 압력과 사이클에 대한 Al₂O₃ 박막 성장과 SiO₂ 계면 형성을 PI-VM을 활용하여 예측하였다. 다수의 데이터 세트 확보에 어려움이 있는 플라즈마 원자 증착 공정의 특성을 고려하여, 부분최소제곱회귀 (partial least squares regression, PLSR) 방법을 사용하였다. PI-VM을 통해 평가된 결과에서 Al₂O₃ 박막의 성장은 사이클에 가장 높은 상관도가 관찰되었다. 반면, SiO₂ 계면은 플라즈마 방전 스텝의 압력에 가장 큰 상관도를 보였다. 매 사이클의 압력과의 상관도는 사이클이 증가함에 따라 순차적으로 감소하였다. 위 경향은 플라즈마
마방전스텝중, 증착박막표면으로입사하는이온에의한증착박막결정의진동과그에따른반응성원자의확산도증가로설명가능하였다.위현상은플라즈마화학기상증착법(plasma-enhancedchemicalvapordeposition,PECVD)등에서도높은증착률을위해플라즈마온도를증가시킨조건등에적용가능할것이다.

본연구에서수행된수십nm스케일의박막증착중계면형성의관찰과PI인자를활용한가상계측방법은다층박막및단일박막의요구두께가감소함에따라보다주요하게작용할것이다.연구된계면형성의주요인자와VM모델은계면형성을고려한고급프로세스제어(advancedprocesscontrol,APC)등의활용이기대된다.

주요어:계면형성,광방출분석법(OES),가상계측방법론(VM)(PEALD),플라즈마원자층박막증착(PEALD),플라즈마공정모니터링
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