Modeling growth rate of HfO$_2$ thin films grown by metal–organic molecular beam epitaxy

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Received 30 December 2004; received in revised form 6 April 2005; accepted 12 April 2005
Available online 13 June 2005

Abstract

HfO$_2$ dielectric layers were grown on the p-type Si (100) substrate by metal–organic molecular beam epitaxy (MOMBE). Hafnium-tetra-butoxide, Hf(O-t-C$_4$H$_9$)$_4$ was used as a Hf precursor and Argon gas was used as a carrier gas. The thickness of the HfO$_2$ film and intermediate SiO$_2$ layer were measured by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The properties of the HfO$_2$ layers were evaluated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high frequency (HF) capacitance–voltage (C–V) measurement, and current–voltage (I–V) measurement. C–V and I–V measurements have shown that HfO$_2$ layer grown by MOMBE has a high dielectric constant ($k$) of 20–22 and a low-level of leakage current density. The growth rate is affected by various process variables such as substrate temperature, bubbler temperature, Ar and O$_2$ gas flows and growth time. Since the ratio of O$_2$ and Ar gas flows are closely correlated, the effect of variations in O$_2$/Ar flow ratio on growth rate is also investigated using statistical modeling methodology.

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Keywords: HfO$_2$; Gate dielectric; Thin film; Process modeling; MOMBE

1. Introduction

The rapid progress of complementary metal–oxide–semiconductor (CMOS) integrated circuit technology since the late 1980s resulted in the reduction of the gate oxide thickness. With the reduction of gate dielectric thickness to a few nanometers, higher dielectric constant material than the conventional SiO$_2$ (i.e. high-$k$ material) is needed to overcome the problem of an exponential increase in the leakage current level due to direct tunneling. Many researches for high-$k$ dielectric materials such as ZrO$_2$, Ta$_2$O$_5$, Al$_2$O$_3$, HfO$_2$, TiO$_2$, silicates (ZrSi$_x$O$_{y}$ and HfSi$_x$O$_{y}$), STO, and BST have been performed [1–5]. Among these candidates, HfO$_2$ is one of the most highlighted high-$k$ gate insulators because of its high dielectric constant (25–30), wide band-gap energy (5.68 eV), high breakdown field (15–20 MV/cm$^2$), and good thermal stability on Si substrate. The growth method of high-$k$ materials is also an important factor to determine the property of gate dielectric layer. In our experiments, we searched appropriate experimental conditions and examined the characteristics of HfO$_2$ films using metal–organic molecular beam epitaxy (MOMBE) system. MOMBE is one of the powerful techniques obtaining abrupt interface and controlled thickness of films, mainly due to source evaporation at a controlled rate under ultra high vacuum condition [6]. In this paper, the relationships between the growth rate of HfO$_2$ films grown by MOMBE and process variables of MOMBE systems are investigated. The electrical characteristics of HfO$_2$ films are investigated by high frequency (HF) capacitance–voltage (C–V) and current–voltage (I–V) measurements. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) were also performed to analyze the HfO$_2$ films grown by MOMBE systems.
2. Experiment

HfO₂ thin film was grown on a p-type Si (100) substrate, of which the native oxide was chemically eliminated by (50:1) H₂O/HF solution prior to growth by MOMBE. Hafnium-tetra-butoxide [Hf(O\textsubscript{t}-C\textsubscript{4}H\textsubscript{9})\textsubscript{4}] was chosen as the MO precursor because it has a appropriate vapor pressure and relatively low decomposition temperature. High-purity (99.999%) oxygen gas was used as the oxidant. Hf-t-butoxide was introduced into the main chamber using Ar as a carrier gas through a bubbling cylinder. The bubbler was maintained at a constant temperature to supply the constant vapor pressure of Hf-source. The apparatus of the system is schematically shown in Fig. 1. High-purity Ar carrier gas passed through the bubbler containing the Hf-source. The gas line from the bubbler to the nozzle was heated to the same temperature. The mixture of Ar and metal–organic gases heated at the tip of the nozzle flows into the main chamber. The introduced Hf-source decomposed into Hf and ligand parts when it reached a substrate maintained at high temperature and the Hf ion was combined with O\textsubscript{2} gas supplied from another nozzle. The base pressure and working pressure were \(\sim 10^{-9}\) and \(\sim 10^{-7}\) Torr, respectively. Annealing at 700 °C for 2 min was carried out following the growth of the films to diminish the density of the interfacial charged particles [7]. Detailed experimental conditions are listed in Table 1.

3. Result and discussion

The metal-oxide-semiconductor (MOS) capacitor structure Au/HfO\textsubscript{2}/p-type Si was fabricated to measure its electrical characteristics. The high frequency (1 MHz) C–V curve and I–V curve of HfO₂ films grown by MOMBE are shown in Fig. 2. From measured capacitance and physical thickness, the dielectric constant and the equivalent oxide thickness can be obtained. Actually, the total capacitance must be calculated as series connection of HfO₂ layer capacitance and SiO₂ layer capacitance because an unexpected SiO₂ layer between HfO₂ and p-Si substrate shown in Fig. 3 affects the total capacitance strongly [8]. The thickness of SiO₂ layers was measured by HRTEM and had a value of 10–20 Å with experimental conditions. It can be identified by TEM images that the formation of SiO₂ was affected by experimental conditions such as the growth time [9], O₂/Ar gas ratio, and substrate temperature (not shown in here). The formation of SiO₂ layer is attributed to the excess oxygen during the film growth and should be eliminated or minimized because of its low dielectric constant. In addition, HfO₂ samples grown at substrate temperature of 400 °C showed an amorphous nature in Fig. 3(a). However, when the substrate temperature was at 450 °C, a large portion of the HfO₂ film was crystallized and some of the grain boundaries were observed in Fig. 3 (b). Ignoring the depletion region effect, the dielectric constant \(k=20–22\) can be calculated. This relative low dielectric constant

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>300–600 °C</td>
</tr>
<tr>
<td>Bubbler temperature</td>
<td>70–130 °C</td>
</tr>
<tr>
<td>Nozzle temperature</td>
<td>270 °C (Fixed)</td>
</tr>
<tr>
<td>Base pressure</td>
<td>(10^{-9}) Torr</td>
</tr>
<tr>
<td>Working pressure</td>
<td>(10^{-7}) Torr</td>
</tr>
<tr>
<td>Gas flow (Ar)</td>
<td>2–6 sccm</td>
</tr>
<tr>
<td>Gas flow (O₂)</td>
<td>1–8 sccm</td>
</tr>
<tr>
<td>Growth time</td>
<td>20, 30, 40, 50, 60 min</td>
</tr>
<tr>
<td>Rapid thermal annealing temp.</td>
<td>700 °C (2 min in N\textsubscript{2} ambient)</td>
</tr>
</tbody>
</table>
compared with the bulk HfO$_2$ dielectric constant ($k = 25–30$) may be due to the polycrystalline nature of the grown HfO$_2$ films and Hf–silicate interfacial layer (not identified in HRTEM image but other research showed that HfO$_2$/SiO$_2$ interface are marginally unstable with respect to formation of silicates [10]) that has lower dielectric constant compared with the bulk HfO$_2$. Generally, the thickness resulted from C–V curve is slightly higher than that from SEM. This may be due to two major quantum effects: (i) additional band bending because of surface electrons (or holes) above the edge of conduction band and (ii) presence of charge centroid [7]. Fixed oxide charge density ($\sim 8 \times 10^{11}$/cm$^2$) and interface state density ($\sim 1 \times 10^{12}$ eV$^{-1}$cm$^{-2}$), attributing to the interface trap density in the oxide layer, were calculated using the flat-band voltage shift [11], and Lehovec’s equation [12]. The level of leakage current densities of HfO$_2$ film at positive gate bias (0–2 V) and at negative gate bias (0–2 V) is approximately $10^{-9}$ A/cm$^2$ and $10^{-7}$ A/cm$^2$, respectively, which are relatively low levels compared with that of the conventional SiO$_2$.

Through screening experiments at different experimental conditions, it was identified that the growth rate of HfO$_2$ films grown by MOMBE system was affected by many process variables. Among these process variables, the substrate temperature, bubbler temperature, growth time, Ar and O$_2$ gas flow were chosen as main process variables to determine the properties and the growth rate of HfO$_2$ films.

It is shown the relationship between the growth rate and the substrate temperature in Fig. 4. Through experiments in various conditions, we have found that there were two regions showing a different trend in growth rate (region a and region b). At below 300 °C, there has been found almost no growth of HfO$_2$ layer. When the substrate temperature reached at 450 °C, the growth rate had a maximum value, and decreased with increasing substrate temperature until at 600 °C. To investigate the region a, SEM images of HfO$_2$ films grown by MOMBE at different substrate temperature (300°C–450°C) were shown in Fig. 5. As shown in Fig. 5(a), it was found that HfO$_2$ film was not grown under the temperature of 300°C because Hf source was not effectively decomposed. At the temperature of 350 °C, HfO$_2$ films began to grow, and the crystallization of HfO$_2$ films were enhanced as the substrate temperature increased, shown in Fig. 5(b)–(d). In our MOMBE system, HfO$_2$ films
grown at 450 °C of the substrate temperature showed the thick film thickness (i.e. large growth rate) and fully crystallized structure. In order to examine the region b, XRD spectra of HfO₂ films grown at 450 and 550 °C of the substrate temperature are shown in Fig. 6. HfO₂ films have been found to exist in monoclinic phase, tetragonal phase, cubic phase, and amorphous structure [13–16]. This crystal structure depends on the growth method and experimental condition of HfO₂ films. It was found that there were monoclinic (m) and tetragonal (t) phase in our HfO₂ films grown by MOMBE system, and monoclinic phase (m) was dominant. Through XRD spectra, it was shown that the crystal structure of HfO₂ films was changed with the substrate temperature. At 450 °C, various crystal phase and crystal direction were shown in XRD spectrum. However, at 550 °C, the overall XRD spectrum became simple and some peaks disappeared. So, it can be assumed that the excess thermal energy from higher substrate temperature does not contribute to the growth of films but only change the crystal structure of HfO₂ films. Another explanation for region b is related to the small crystallite size at higher substrate temperature. From each XRD spectrum, the crystallite size of HfO₂ films in different substrate temperature was obtained. Using Scherrer’s formula [17], the calculated crystallite size is approximately 7.2 nm at 450 °C and 4.6 nm at 550 °C, respectively. It shows that the substrate temperature beyond a certain level limits the growth of crystallite size. In other research related to ZrO₂ film [18], it was shown that the incorporation of the hydrocarbon-rich environments limits the crystallite size. The decomposition rate of Hf-t-butoxide source increases with increasing substrate temperature. Fully decomposed source due to the high substrate temperature makes a chamber of MOMBE the hydrocarbon-rich circumstances. The incorporation of the hydrocarbon-rich circumstances limits the crystallite size, and finally limits the growth rate. If we remind that HfO₂ and ZrO₂ is II–VI compound which have similar properties, this explanation can be persuasive. In addition, the observed XRD peak locations are not shifted to any particular direction, so it is possible to suppose
that there is no uniform tensile or compressive stress in the film [17].

The relationship between the growth rate and the bubbler temperature is shown in Fig. 7. It shows that the growth rate of HfO\textsubscript{2} films is a linear function of the bubbler temperature. If we remind of the fact that the bubbler temperature in MOMBE process is the major control parameter of transferred volume of Hf precursor, this phenomenon can be easily understood.

The relationships between the growth rate and gas flows are shown in Figs. 8 and 9. It is shown that the growth rate of HfO\textsubscript{2} films increases with increasing gas flow of carrier gas (Ar). They also showed that the growth rate of HfO\textsubscript{2} films increases with increasing gas flow of oxidant (O\textsubscript{2}). But the tendency of increasing growth rate is not linear, and the effects of O\textsubscript{2}/Ar gas flow ratio must be also taken into account [19,20]. As the O\textsubscript{2}/Ar ratio was varied, an ionic species that dominate the deposition process can be also varied, and it can affect characteristics of HfO\textsubscript{2} films such as dielectric constant, surface morphology, fixed charge concentration and the growth rate. To investigate the effect of O\textsubscript{2}/Ar gas ratio more, XPS analysis was performed. Fig. 10(a) shows the XPS spectra for Hf 4f level that were calibrated from C 1s peak at 284.5 eV. It was shown each spectrum at different O\textsubscript{2} gas flow (2–8 sccm and Ar gas flow was fixed at 2 sccm). As shown in Fig. 10(a), the Hf 4f\textsubscript{5/2} and Hf 4f\textsubscript{7/2} peaks, which have binding energies of 16.05 eV and 17.76 eV, respectively, related to Hf–O bonding in HfO\textsubscript{2}, shifted to the higher binding energy with increasing of O\textsubscript{2} gas flow. The origins of binding energy shift are
suggested as a number of factors such as charge transfer effect, presence of electric field, environmental charge density, and hybridization. Among these, charge transfer is regarded as a dominant mechanism causing a binding energy shift. According to the charge transfer mechanism, removing an electron from the valence orbital generates increase in core electron’s potential and finally leads a chemical binding energy shift [21]. Therefore, it is considered that the Hf 4f_{5/2} and Hf 4f_{7/2} peaks shift (ΔBE=0.6 eV) originated from the enhanced charge transfer with increasing O₂ gas flow, i.e. the larger portion of Hf atoms was fully oxidized with increasing O₂ gas flow. Fig. 10(b) shows the O 1s core level peaks also demonstrated binding energy shift with changing of O₂ gas flow. Each peak can be split into two sub-peaks by Gaussian fitting which represent the Hf–O bonding at ~531 eV and O–C or O–Si bonding at ~532.5 eV [22,23]. The relative quantities of Hf and O elements incorporated in the layer can be obtained by comparing the areas of Hf 4f peak and O 1s sub-peak for Hf–O bonding.

The relationship between growth time and growth rate is shown in Fig. 11. Growth time is critical and direct factor to determine the growth rate. Through the Fig. 11, it can be identified that the growth rate increases with increasing growth time. It shows that growth rate and growth time have the linear relationship over 20 min of growth time. However, there were no experimental results about the growth rate below the 20 min of growth time. Considering other research related with the growth rate of thin films, it can be assumed that the growth rate has a logarithm function of growth time, and more experiments for the growth rate below 20 min of the growth time will be
needed to fully understand the relationship between the growth rate and the growth time. XRD spectra and SEM images of HfO₂ films grown at different growth time are shown in Figs. 11 and 12. It can be also identified that the growth time affects the crystal structure of HfO₂ films (Fig. 13).

The growth rate in the deposition process is one of the important factors, which can determine optical and electrical characteristics. Therefore, the statistical modeling methodology is used to predict the response factor and analyze the relationship between input factors to reduce the time and the cost for the manufacturing process. Prior to the modeling, the experimental design matrix is generated by using factorial design to reduce the runs of the experiment and then add to the additional points, center point and star point, to cover the weak ranges for the predicted model [24]. Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problem in which a response is influenced by several variables and the objective is to optimize the response [25]. Response surface models may be represented as the full quadratic model:

\[ y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} b_{ij} X_i X_j + \sum_{i=1}^{n} b_{i} X_i^2 \]

where \( y \) is the response variable, \( n \) is the number of independent process factor, \( b \) are model coefficient, and \( X_i \) are process factor values. The order in which experiments were performed has been randomized to avoid statistically the effect of irrelevant factors, which may be present, but not considered in this paper. The residual plot describes the difference between the predicted value and the measured value. One of the assumptions of this analysis is that the residuals are both normally and randomly distributed with zero mean and unit variance. The predicted model based on the statistical methodology can characterize the certain process factors without many experiments and identify the accuracy and validity of our model.

In our paper, we performed the statistical modeling about the growth rate in different O₂/Ar gas ratio to verify the effect of gas flows on growth rate. The design matrix using the 2-factor factorial method and additional one center point and two star points is summarized in Table 2. At first, we performed the analysis of variance (ANOVA) to calculate the \( P \)-values that indicate whether the process variables are statistically significant on the response. Based in the results

Table 2
Design of experiment for the effect of O₂/Ar ratio

<table>
<thead>
<tr>
<th>Run</th>
<th>O₂ flow rate</th>
<th>Ar flow rate</th>
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<tbody>
<tr>
<td>1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>2</td>
<td>−1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>−1</td>
</tr>
</tbody>
</table>

*P*-value of the simple regression model

Table 3
Results of experimental design

<table>
<thead>
<tr>
<th>Factor</th>
<th>Statistical significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate</td>
<td></td>
</tr>
<tr>
<td>O₂ gas flow</td>
<td>0.0027</td>
</tr>
<tr>
<td>Ar gas flow</td>
<td>0.0185</td>
</tr>
</tbody>
</table>
shown in Table 3, it is verified that O$_2$ and Ar gas flows are statistically significant on the growth rate. In addition, we calculated the regression coefficients by means of the least square estimation method. In this way, we could extract the simple linear regression model for O$_2$/Ar ratio effect on the growth rate of HfO$_2$ film. Fig. 14 shows that the plot of residual versus fitted value. We assumed that the residuals are both normally and randomly distributed. It is observed that for randomized run orders, the residuals are scattered about zero and there is no special features or patterns in residuals. The contour plot of response surface is shown in Fig. 15. The plot shows that when the one of gases (Ar or O$_2$) is insufficient compared to the other, the growth rate is restricted, and when both gas flows are sufficient, the growth rate has a high level. Also we could identify that Ar gas flow and O$_2$ gas flow are closely correlated. When O$_2$/Ar ratio is about unity, the growth rate had a tendency to increase steeply.

4. Conclusion

The characteristics of the HfO$_2$ dielectric layer on the p-type Si substrate by MOMBE process were investigated. HfO$_2$ films grown by MOMBE had a high dielectric constant ($k=20–22$). It was identified that there existed the fixed oxide charge ($\sim 8 \times 10^{11} \text{ cm}^{-2}$) and interface state density ($\sim 1 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$) in the HfO$_2$ layer. Leakage current density of HfO$_2$ film grown by MOMBE is about $10^{-9}–10^{-7} \text{ A/cm}^2$ in $–2$ to $2 \text{ V}$ gate voltage. It is observed that the growth rate of HfO$_2$ film was affected by the substrate temperature due to changing of growth direction, crystal structure, and crystallite size. It was also revealed that the HfO$_2$ film grown by MOMBE had monoclinic and tetragonal phase and there was no uniform strain. The growth rate increased with increasing the bubbler temperature. The effects of gas flows on the growth rate were also investigated by SEM and XPS. It is observed that the low level of gas flows limited the growth of films. In addition, it was founded that the growth time greatly affected the growth rate of HfO$_2$ films. Using the statistical modeling methodology, it can be concluded that the low level of gas flows limited the growth rate, and the growth rate was appeared to be increased when O$_2$ gas flow rate is almost comparable to Ar gas flow rate with sufficient flow rate.
Acknowledgements

This research was supported by the MIC (Ministry of Information and Communication), Korea, under the ITRC (Information Technology Research Center) support program supervised by the IITA (Institute of Information Technology Assessment).

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