Study of Hafnium Silicate Treated with NO Gas Annealing

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The physical and the electrical properties of nitrided hafnium-silicate films treated with NO gas annealing were investigated using high-resolution transmission electron microscopy, X-ray photo-electron spectroscopy, near-edge X-ray absorption fine structure and capacitance-voltage measurements. We confirmed that nitrogen incorporation during the NO gas annealing treatment enhanced the thermal stability of Hf silicate. The suppression of phase separation was observed in hafnium-silicate films with high nitrogen contents. Moreover, small hysteresis changes were observed in the C-V curves. The negative shift of the threshold voltage was caused by the incorporation of nitrogen in the hafnium silicate films.

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I. INTRODUCTION

High-k gate dielectrics, such as HfO₂, ZrO₂, rare earth oxides and their silicates, have been regarded as potential gate dielectric materials for replacing conventional SiO₂/SiON gate insulators because they can reduce the leakage current and improve the reliability [1, 2]. Among high-k materials, hafnium-silicate (Hf-silicate) is one of the most promising materials for complementary metal-oxide semiconductor (CMOS) applications because of its relatively high dielectric constant, large band gap and good thermal stability on silicon [3–5]. However, it was reported that Hf-silicate systems show a phase separation to SiO₂ and HfO₂ after annealing at temperatures above 800 °C due to the positive enthalpy of the mixed state of SiO₂ and HfO₂ [6]. The phase separation leads to a degradation of the thermal stability and of the dielectric and electrical properties [16]. Several researchers demonstrated that incorporated nitrogen could improve thermal stability. Akbar et al. showed that NH₃ post-deposition annealing improved the electrical properties of Hf-silicate [7]. Quevedo-Lopez et al. reported the enhanced thermal stability of plasma-nitrided Hf-silicate films by using a Fourier transform infrared (FTIR) spectroscopy analysis [8]. However, the reasons for and mechanisms of that improvement were not fully understood. The reported data showed that the nitridation process using NH₃ gas and plasma had some problems: i.e., the threshold voltage shifts in the NH₃ annealing case and generation of N₂ molecular states in plasma nitridation [9]. Moreover, during the nitridation process using a plasma, complex binding states are generated in nitrides, indicating that Hf-silicate films have many trap charge states, resulting in a V₉₀ shift [10]. However, Hf-silicate films annealed in NO gas show a stable and simple binding state in the film. Oxygen in the NO gas can react with defects, which causes a charge state, decreasing the charge state in the film. The application of nitridation using NO gas to Hf-silicate films is the very promising process to control the interface state. In this research, we investigate the effect of nitrogen incorporated during NO gas treatment on the suppression of phase separation and the improvement of thermal stability in Hf-silicate system.

II. EXPERIMENT

A p-type Si (100) substrate was cleaned chemically using the Radio Corporation of America (RCA) method and the native oxide was removed with a dilute HF solution. The Hf-silicate films were grown by using an
HR-TEM images of (HfO\textsubscript{2})\textsubscript{0.7}(SiO\textsubscript{2})\textsubscript{0.3} and (HfO\textsubscript{2})\textsubscript{0.3}(SiO\textsubscript{2})\textsubscript{0.7} samples annealed in ambient NO gas at 900 °C and 1000 °C are shown in Figure 1. The thickness of the Hf-silicate films is calculated by using the distance of the silicon fringe. The thickness of the interfacial layer increased to ~4 nm at 900 °C and to ~6 nm at 1000 °C in both samples. The oxygen atoms in the NO gas diffuse into the Hf-silicate films and react with the Si substrate, which in turn causes an increase in the thickness of the interfacial layer between the silicon substrate and the Hf-silicate film. Both samples partly crystallized during 900 °C NO gas annealing. However, they exhibited different trends at 1000 °C: In particular, the (HfO\textsubscript{2})\textsubscript{0.7}(SiO\textsubscript{2})\textsubscript{0.3} sample separated into SiO\textsubscript{2} and HfO\textsubscript{2} phases and had rough surfaces while the (HfO\textsubscript{2})\textsubscript{0.3}(SiO\textsubscript{2})\textsubscript{0.7} sample had a relatively flat surface and did not fully separate. This suppression of phase separation was caused by diffusion of nitrogen atoms in the NO gas. In spite of the phase separation in the (HfO\textsubscript{2})\textsubscript{0.3}(SiO\textsubscript{2})\textsubscript{0.7} sample at 1000 °C, the film was not fully crystallized because of the nitrogen in the NO gas. This phenomenon appears in the NEXAFS spectra (Figure 4).

The bindings of nitrogen and oxygen were analyzed by using XPS to investigate the suppression of phase separation. The XPS spectra in Figure 2 show the N 1s spectra of hafnium-silicate films. The intensity of the N
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Fig. 2. XPS spectra of hafnium-silicate films annealed in an ambient of NO gas in a temperature range from 800 °C to 1000 °C for 1 minute: N 1s spectra of (a) \( \text{HfO}_2 \text{SiO}_2 \) and (b) \( \text{HfO}_2 \text{SiO}_2 \).

Fig. 3. XPS spectra of hafnium-silicate films annealed in an ambient of NO gas in a temperature range from 800 °C to 1000 °C for 1 minute: O 1s spectra of (a) \( \text{HfO}_2 \text{SiO}_2 \) and (b) \( \text{HfO}_2 \text{SiO}_2 \).

Is increases in both films as the annealing temperature increases, which indicates that the NO gas is more active at high than at low temperatures. Table 1 reports the nitrogen quantities inferred using XPS spectra. The nitrogen content of the \( \text{HfO}_2 \text{SiO}_2 \) sample was higher than that of the \( \text{HfO}_2 \text{SiO}_2 \) sample. The above TEM images and XPS data show that phase separation were suppressed as the nitrogen content increases.

Figure 3 shows the O 1s spectra. The O 1s spectra can be deconvoluted into three energy states, HfO2, SiO2 and Hf-silicate [11]. The intensity of the SiO2 increases as Hf composition decreases. A more important finding is that the incorporated N is strongly affected by the composition of SiO2 in the silicate films: i.e., Si-O binding shifted.
Table 1. Composition of nitrogen by using XPS spectra.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Nitrogen Composition (at.%)</th>
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<tbody>
<tr>
<td></td>
<td>(HfO$<em>2$)$</em>{0.7}$(SiO$<em>2$)$</em>{0.3}$</td>
</tr>
<tr>
<td>As-deposited</td>
<td>0.0</td>
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<tr>
<td>800 °C</td>
<td>0.0</td>
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<tr>
<td>900 °C</td>
<td>0.0</td>
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<tr>
<td>1000 °C</td>
<td>1.8</td>
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Fig. 4. NEXAFS spectra of the O K edge for hafnium-silicate films annealed in an ambient of NO gas; (a) (HfO$_2$)$_{0.7}$(SiO$_2$)$_{0.3}$, (b) (HfO$_2$)$_{0.3}$(SiO$_2$)$_{0.7}$.

Fig. 5. NEXAFS spectra of the N K edge for hafnium-silicate films annealed in an ambient of NO gas.

Figure 4 shows the NEXAFS spectra of the O K edge for Hf-silicate films as a function of the annealing temperature. The NEXAFS analysis is a sensitive method for detecting bonding changes that might be associated with phase separation. The O K edge of Hf-silicate films can be represented as an overlap of features due to SiO$_2$ and HfO$_2$ [6]. If the SiO$_2$ and HfO$_2$ phases are separated, the O K edge of the Hf-silicate films would change. The peak P2 coincides with the energy position of the main peak in amorphous SiO$_2$ (Si 3sp state), resulting in an overlap of the second d-state peak (P2) from HfO$_2$ with the main peak of SiO$_2$ [13]. Moreover, the O K-edge spectra depend on the incorporated nitrogen content. The film with a high HfO$_2$ content (such as (HfO$_2$)$_{0.7}$(SiO$_2$)$_{0.3}$) contains a small quantity of nitrogen. In this case, the peaks are separated into four peaks representing the typical features related to the O K edge of HfO$_2$. As the nitrogen content incorporated into the film with a high SiO$_2$ portion is increased, the peaks flatten. This illustrates that the incorporation of N during the NO gas annealing treatment suppresses the phase separation of Hf-silicate films. This agrees with the XPS spectra, as mentioned.

The chemical structure of the N incorporated into films during the annealing treatment with NO gas was obtained from the spectra of the N K edge (Figure 5).
cause of the composition of HfO$_2$, though phase separation occurred in the (HfO$_2$:0.7(SiO$_2$):0.3 sample. The change in the flat band voltage of hafnium silicate films annealed at high temperature exhibited a negative shift, indicating an increase in positive trap charge compared with as-deposited films [9]: The nitrogen incorporated into the hafnium-silicate films has a dominant influence on the nitridation of SiO$_2$ in the silicate film, inducing that shift. The threshold voltage shifted little in the (HfO$_2$:0.3(SiO$_2$):0.7 sample annealed at 800 °C, even when it had 2.4 at. % nitrogen. The probability of a $V_{th}$ shift increases with the incorporation of nitrogen. The amount of trapped charge can be small if the number of unstable nitrogen bonds is small. Thus, the nitrogen content can increase the probability of the $V_{th}$-shift, but that is not a necessary condition for the shift. In the case of the (HfO$_2$:0.3(SiO$_2$):0.7 sample annealed at 800 °C, the shift in $V_{th}$ was small, despite the 2.4 at. % nitrogen content, because most of the nitrogen bindings were stable. In the case of the (HfO$_2$:0.7(SiO$_2$):0.3 sample, as seen in the TEM image, despite the large degree of phase separation, the hysteresis exhibited a (considerable) 0.1 volt gap. The reason for these two incompatible results is still unclear and requires more study.

### IV. CONCLUSION

The structural characteristics of hafnium-silicate films were investigated, including those with nitrogen incorporated by NO annealing. The quantity of incorporated nitrogen increases with NO annealing temperature and Si content. The intensity of Si-O bonding was greater in films with greater nitrogen content. This tendency implies that the nitrogen incorporation by NO annealing is strongly related to the Si and O bonding, such as SiON. As the temperature of the NO gas annealing increases, the suppression in the phase separation of Hf-silicate films is enhanced by the incorporation of nitrogen. The changes in the capacitance-voltage characteristic indicate that the quantity of the positive trap charge depends on the incorporation of nitrogen. The Hf-silicate films annealed in NO gas exhibit desirable properties, even though they contain only a small amount of incorporated nitrogen. Moreover, our Hf-silicate film has desirable electrical properties, such as hysteresis and a threshold voltage shift.

### REFERENCES