Effect of DC Bias on the Plasma Properties in Remote Plasma Atomic Layer Deposition and Its Application to HfO$_2$ Thin Films

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Direct current biased remote plasma atomic layer deposition (RPALD) was developed and applied to deposit HfO$_2$ films, and these results were compared with those of RPALD. DC biased RPALD system exhibits effective features that allow the plasma density to be controlled by dc bias. When dc bias was applied to the radio frequency (RF) plasma, the amount of free radicals and ions were increased. The electrical properties of HfO$_2$, such as the effective oxide thickness (EOT) and the breakdown voltage, were improved by dc bias when compared to those of RPALD. This is due to the relatively high amount of free radicals controlled by the plasma density.

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Various thin film deposition methods have been studied to deposit high quality dielectric materials, including reactive sputtering, chemical vapor deposition, and atomic layer deposition (ALD), with ALD being the most promising method. Since the ALD process utilizes a self-limiting reaction method, it has the ability to grow thin films with excellent conformality and compositional control of atomic scale dimensions. Plasma-enhanced atomic layer deposition (PEALD) has been proposed and applied as an alternative method to thermal ALD. PEALD commonly produces better film quality at lower growth temperatures than the thermal ALD. This is a result of the required activation energy being provided by the plasma source. In plasma deposition as well as other plasma surface modification processes, a critical role is played by the ionized and dissociated fragments incident at the surface. The radicals, typically generated with a plasma discharge, are of a highly reactive type which are widely used in thin film deposition processes. Additionally, ions, which can be accelerated or decelerated using an electric field, are being extensively employed in the deposition of thin film. The influence of the plasma parameters on film formation ranges from simple substrate cleaning, resulting in enhanced adhesion, to morphological changes. Therefore, the control of the amount of free radicals and ions in plasma are both very important in the chemical reaction for the determination of the material properties.

Several methods to control the ion energy and the plasma density have been suggested, and we have developed a new dc biased RPALD system. In RPALD, plasma is generated remotely, outside of the chamber, by using Ar gas, oxygen plasma, and ionized dissociated fragments incident at the surface. The radicals, typically generated with a plasma discharge, are of a highly reactive type which are widely used in thin film deposition processes. Additionally, ions, which can be accelerated or decelerated using an electric field, are being extensively employed in the deposition of thin film. The influence of the plasma parameters on film formation ranges from simple substrate cleaning, resulting in enhanced adhesion, to morphological changes. Therefore, the control of the amount of free radicals and ions in plasma are both very important in the chemical reaction for the determination of the material properties.

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Experimental

Figure 1 shows the experimental setup of the dc biased RPALD system. It consists of a capacitively coupled plasma (CCP) produced at a frequency of 13.56 MHz with dc power. This system has an effective feature that allows the plasma density to be controlled by the RF power and the dc bias, respectively. The RF electrode is connected to an RF power source (13.56 MHz) through a matching box. The dc power (HUITTINGER Electronic, Freiburg, Germany, PMP-1) is applied by a negative voltage pulse to the grid. Pulsed dc power is being adopted for its significant advantage in arc suppression over constant dc power. The aluminum grid is anodized so that metallic impurities from the grid can be suppressed.

The HfO$_2$ films were deposited at 300°C on a SiO$_2$ (3 nm)/Si substrate structure using Tetakis(ethylenediamino)hafnium (TEMAHf, Hf[N(C$_2$H$_4$)(CH$_3$)$_2$]) as the Hf precursor with O$_2$ plasma as a reactant. The SiO$_2$ layer of 3 nm was grown on a Si (100) substrate by rapid thermal anneals. The SiO$_2$ surface was pretreated in situ with N$_2$ plasma prior to HfO$_2$ deposition. The basic process of HfO$_2$ deposition consists of the following four steps: (i) Hf precursor exposure, (ii) purging of the residual precursors and by-products from the chamber by using Ar gas, (iii) exposure of the oxygen plasma, and (iv) purging of the reactants and by-products from the chamber by using Ar gas. The RF plasma power was applied, from 100 to 300 W, to generate CCP plasma. To investigate the re-sputtering of deposited HfO$_2$ film and the film thickness, the film thicknesses were measured by ellipsometry and TEM. Various dc powers were tested, which affected the amount of free radicals and ions. The ions impinging on the substrate were estimated from the saturation current density of ions flowing to a probe connected to a picoammeter; the probe was positioned on the Si substrate. XPS using Mg K$_x$ X-ray source was employed to investigate the impurity in HfO$_2$ films. To investigate the electrical properties of the HfO$_2$ films, metal-oxide semiconductor capacitors, with a 100 nm thick Pt electrode, were fabricated. Pt electrode was deposited by E-beam evaporator at room temperature through a shadow mask. After Pt deposition, forming gas annealing was carried out in a 95% N$_2$/5% H$_2$ ambient at 450°C for 30 min. Capacitance-voltage ($C$–$V$) and current-voltage ($I$–$V$) measurements of the HfO$_2$ films were obtained by using the Agilent B1500A semiconductor device analyzer.

Results and Discussion

First, we examined OES to clarify the dominant reactive species of both the RF plasma and the dc biased RF plasma. Figure 2a shows the intensity of OES peaks in the wavelength range of 200–1100 nm for the O$_2$ plasma process from 100 to 300 W, under a pressure of 0.5 Torr. The most significant oxygen lines in this
experimental condition were at 777.4 and 844.6 nm. These lines correspond to the transition of the oxygen atom in the state 5P to 5S. Following are the two main processes that could produce emissions from 777.4 and 844.6 nm: dissociative excitation and direct impact excitation of oxygen atoms. The dissociative excitation is the dominant mechanism for 777.4 nm emissions, while the direct electron impact excitation is more important for the 844.6 nm emission, where excitations are predicted by the following reactions: $e + O_2 \rightarrow e + O^+ + O$ and $e + O \rightarrow e + O$. The intensities of both spectral lines at 777.4 and 844.6 nm increase with increasing RF power. The OES emission intensity is roughly proportional to the plasma density. By increasing the RF power, the electron-neutral collision is increased due to the increase in electron density; therefore, it results in an increase of the electron-neutral impact excitation rate. When dc power of 30 W was applied to the grid, the intensities of both spectral lines in plasma are increased. In capacitatedly coupled plasma, the sheath drop voltage accelerates ions. These ions bombard a chamber wall and generate the secondary electrons. These secondary electrons are accelerated in the plasma sheath and ionize neutral gas atoms. The dc bias makes the sheath drop voltage much higher. These high energy ions generate more secondary electrons. The secondary electron contributes to generate plasma more efficiently due to the dc bias.15,16 Figure 2b shows a total impinging charge on the substrate as a function of RF power and dc bias. The plasma consists of neutral atoms or molecules, and of both positive and negative charges. We consider an oxygen plasma in which only three charged species are considered: $O_2^+$, created by electron impact ionization, $O^-$, created by dissociative attachment, and electrons. Negative ions are trapped within the plasma by the positive potential of the plasma and are assumed to be lost only by recombination with positive ions in the plasma. Most of the electrons are lost to the wall. Therefore, only positive ions reach the surface of substrate. The current, resulting from the ions impinging on the surface, was measured by a picammeter. As shown in Fig. 2b, as RF power is increased from 50 to 200 W, the current also increases due to an increase in the amount of ion. When the dc bias was applied to the RF plasma, the impinging charges on the substrate increased as compared to the RF plasma. As dc power is increased from 20 to 40 W, the current increases due to an increase in the amount of ion. Thus, the number of ions can be easily controlled by varying the dc bias.

The self-limiting process was confirmed by the measurements of film thickness, depending on the number of both RPALD and dc biased RPALD cycle. Figure 3 shows the HfO₂ film thickness deposited by RPALD and dc biased RPALD versus the number of cycle. As shown in Fig. 3, the HfO₂ film thickness is directly proportional to the number of cycle. The constant growth rate of 0.73 Å/cycle was achieved for both RPALD and dc biased RPALD. This result implies that the HfO₂ films were deposited under self-limiting process without resputtering of deposited films for both RPALD and dc biased RPALD.

The chemical bonding state and impurity in the HfO₂ films deposited by RPALD and dc biased RPALD were studied by XPS. To increase the XPS sensitivity, the XPS survey spectra were measured at takeoff angles of 90° and the analyzer pass energy was set to be 100 eV. Figure 4 shows the XPS survey and Hf 4f spectrum for the 7 nm thick HfO₂ film both deposited by RPALD and dc biased RPALD at 300°C. As shown in Fig. 4a, the HfO₂ films showed well-defined Hf, O, and C peaks with no evidence of Al or other metal impurities. Carbon peak was observed on the surface when the films were exposed to air. This means that there is no possibility of sputtering of dc grid during both the RPALD and dc biased RPALD.

Figure 1. (Color online) DC biased remote plasma ALD system.

Figure 2. (a) Dependence of emission intensity on RF power. Solid and open circles correspond to the intensity of 777.4 nm lines with and without dc bias, respectively. Solid and open triangles correspond to the intensity of 844.6 nm lines with and without dc bias, respectively. (b) Plot of RF power versus current with and without dc bias.
processes. Figure 4b is Hf 4f core level spectrum of 7 nm HfO₂ films. For Hf 4f, the spin-orbit doublet peaks of Hf 4f⁷/₂ and Hf 4f⁵/₂ are set at an area ratio of 4:3 with a spin-orbit splitting of 1.6 eV. As shown in Fig. 4b, one set of doublet peaks located at 17.0 and 18.6 eV fit well for the XPS curve. There was no difference in the binding energy shift between RPALD and dc-biased RPALD, which represented the fully oxidized HfO₂. These results indicate that dc bias does not affect the chemical bond of HfO₂.

Two images of Fig. 5 show cross-sectional TEM of the 10 nm thick HfO₂ films deposited on the 3 nm thick SiO₂ buffer layer at 300°C. Figures 5a and b show HfO₂ films deposited by RPALD and dc-biased RPALD, respectively. The SiO₂ buffer layers were grown by RTA in O₂ ambient. As shown in Fig. 5, the SiO₂ buffer layer was slightly increased after 10 nm HfO₂ deposition by RPALD and dc-biased RPALD. This slight increase in the SiO₂ buffer layer is considered due to the oxygen plasma impact on the SiO₂ layer. And interlayer between HfO₂ and SiO₂ is not observed. Therefore, the oxygen plasma in RPALD and dc-biased RPALD may not have enough energy to incorporate the Hf atom into the SiO₂ buffer.

Figure 6 shows C–V curves of 10 nm HfO₂ films deposited by RPALD and dc-biased RPALD at 150, 250, and 300 W, measured at 100 kHz using a Pt electrode. Forming gas annealing was performed at 450°C for 30 s in N₂/H₂ ambient. Quantum-mechanical correction was applied for analyzing EOT. The EOT values of the HfO₂ films deposited at 150, 250, and 300 W with RPALD were 2.58, 2.36, and 2.15 nm, respectively. In the case of the dc-biased RPALD HfO₂ films with the same RF powers, the EOT values were 2.42, 2.07, and 2.09 nm, respectively. The dielectric constants were calculated by the C–V data of Fig. 3 with physical cross-sectional TEM measurements. The dielectric constant of the 10 nm HfO₂ films with dc-biased RPALD is higher than that of RPALD. In addition, the dielectric constant is nearly proportional to the density of the HfO₂/SiO₂ stack. Therefore, the dc bias application to RF power resulted in the improvement of the film quality due to the relatively high ion energy and current under the same RF power. The flatband voltage, VFB, can be extracted from the C–V results according to the flatband capacitance (Cfb). The flatband voltage shift depends on the fixed oxide trap charge in the interfacial layer between the metal oxide and SiO₂. For positive charge, the flatband voltage shifts to a more negative gate voltage with respect to the ideal flatband voltage. In this case, it is clearly shown that the ideal flatband voltage is about 0.73 V. The properties of the interfacial layer which are critical in determining the flatband voltage are affected by the plasma. The flatband voltage shift of 0.07 V to positive direction was observed as RF power was increased. This means that the effective positive oxide charges are reduced with high RF power due to an increase in the amount of ion and radical. The flatband voltages of HfO₂ films with dc-biased RPALD were shifted in the negative direction about 0.07 V as compared to HfO₂ films with RPALD under RF powers of 150 and 250 W. This means that the effective positive charges of RPALD film are less than that of dc-biased RPALD films. While the flatband voltage of dc-biased RPALD HfO₂ film at 300 W was shifted in the positive direction as compared to RPALD. This means that the effective positive charge of dc-biased RPALD films are more than that of RPALD films. This result shows
that the flatband voltage shift is dependent on changing the RF and dc power, which could thereby control the plasma parameters.

$\text{I-V}$ characteristics of the HfO$_2$ films are shown in Fig. 7, which displays the effects of RF power and dc bias on the leakage current. The leakage current densities for the 10 nm HfO$_2$ films deposited by both RPALD and dc biased RPALD were measured to be approximately $1.13 \times 10^{-5}$ A/cm$^2$ at $-0.5$ MV. The similar leakage current densities may be attributed to the deposition of HfO$_2$ on the SiO$_2$ buffer layer, which has a low defect density, and to the similar intrinsic defects in the HfO$_2$ films. The breakdown voltage of the RPALD HfO$_2$ films was proportional to the RF power. When the RF power was increased from 150 to 300 W, the breakdown voltage was increased to about 0.3 MV/cm. In the case of the DC biased RPALD HfO$_2$ films, the breakdown voltage was increased when compared to the RPALD HfO$_2$ films. The results indicate that HfO$_2$ films with dc biased RPALD have high film density which causes an increase in the breakdown voltage.

**Conclusion**

The dc bias is applied to the grid in the RPALD system to control the plasma density. When dc bias was applied to the RF plasma, the amount of radicals and ions increased. Thus, the amount of ions and radicals can be easily controlled by varying the dc bias. XPS results show that there is no possibility of sputtering of dc grid during RPALD and dc biased RPALD processes. The dielectric constant and the breakdown voltage of the HfO$_2$/SiO$_2$ films with dc biased RPALD exhibit better values than those with RPALD under the same RF power. Therefore, the HfO$_2$ films with dc biased RPALD exhibited improved electrical properties.

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