Influences of different oxidants on the characteristics of $HfAlO_x$ films deposited by atomic layer deposition*

Fan Ji-Bin(樊继斌)†, Liu Hong-Xia(刘红侠), Ma Fei(马 飞), Zhuo Qing-Qing(卓青青), and Hao Yue(郝 跃)

School of Microelectronics, Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an 710071, *China*

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A comparative study of two kinds of oxidants (H_2O and O_3) with the combinations of two metal precursors [trimethylaluminum (TMA) and tetrakis(ethylmethylamino) hafnium (TEMAH)] for atomic layer deposition (ALD) hafnium aluminum oxide ($HfAlO_x$) films is carried out. The effects of different oxidants on the physical properties and electrical characteristics of $HfAlO_x$ films are studied. The preliminary testing results indicate that the impurity level of $HfAlO_x$ films grown with both H_2O and O_3 used as oxidants can be well controlled, which has significant effects on the dielectric constant, valence band, electrical properties, and stability of $HfAlO_x$ film. Additional thermal annealing effects on the properties of $HfAlO_x$ films grown with different oxidants are also investigated.

Keywords: $HfAlO_x$, atomic layer deposition, oxidants, annealing

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1. Introduction

Recently, the metal–insulator–metal (MIM) capacitor has been widely used in silicon radio frequency (RF) for impedance matching and analog applications because of its high conductive electrode and low parasitic capacitance.[1–3] A high capacitance density is always required for an MIM capacitor in order to make its occupied area small, which can increase the circuit density, and further reduce the cost.[4] The adoption of high-κ dielectric constant material is a very efficient way to increase the capacitance density.[5] Among these high-κ dielectrics, the hafnium(Hf)-based dielectric has been most extensively investigated and used for the sub-45-nm complementary metal-oxide-semiconductor (CMOS) process because of its high dielectric constant, large band-gap, and good thermodynamic stability in contact with Si.[6,7] Furthermore, a very good performance HfO_2 MIM capacitor with a capacitance density of 3.0 fF/μm^2 has been demonstrated.[8] The further increase of the capacitance density can be implemented by scaling down the dielectric thickness, which may result in higher leakage current and voltage coefficient of capacitance.[9] However, one of the issues is that HfO_2 is susceptible to crystallization after high temperature processing.[10] It has also been reported that the electrical and thermal stability properties of HfO_2 film are significantly improved by adding the aluminum oxide into the hafnium film.[11,12]

In order to obtain low charge leakage, the defects and residual impurities in the high-κ film should be reduced as much as possible. In the atomic layer deposition (ALD) process, the oxidants have great influences on the defects and residual impurities in the high-κ film if the process conditions are optimized. However, the oxidant effects on the characteristics of hafnium aluminum oxide ($HfAlO_x$) have rarely been discussed. Therefore, in this paper, different oxidants (H_2O and O_3) are used to deposit $HfAlO_x$ films by ALD at 300 °C. The effects of the different combinations of the different oxidants with metal precursors on the physical properties and electrical characteristics of annealed $HfAlO_x$ films are investigated.

2. Experiment

The wafers are obtained after RCA cleaning and a 30-s dip in diluted Hf solution to remove the native oxide, which is followed by a 60-s rinse in deionized water. Liquid TEMAH is used as a hafnium precursor and TMA serves as an aluminum precursor. The container of the hafnium precursor is heated to 95 °C and the aluminum precursor is at room temperature, corresponding to a vapor pressure of 10 hPa to 15 hPa. When H_2O is used as an oxidant, the container is set at the room temperature, corresponding to a vapor pressure of 7 hPa. Used in the ozone generator is the ultra pure O_2 (99.999%) to obtain O_3, of which the concentration is 200 g/Nm^3. $HfAlO_x$ films are grown on p-type Si(100) wafers by a layer-by-layer deposition process using different metal processors (TMA and TEMAH) and oxidants (H_2O and O_3) at 300 °C. The sequence of sample A is

$$(\text{TEMAH}+H_2O/\text{TMA}+H_2O)_{25},$$

sample B is

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†Corresponding author. E-mail: jbfan@mail.xidian.edu.cn

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$(\text{TEMAH+H}_2\text{O/TMA+O}_3)_{25}$,

sample C is

$(\text{TEMAH+O}_3\text{/TMA+H}_2\text{O})_{25}$,

and sample D is

$(\text{TEMAH+O}_3\text{/TMA+O}_3)_{25}$,

which are shown in Fig. 1. The subscript number (25) refers to the total deposition cycle. The metal precursor pulse time is kept the same, and a corresponding appropriate oxidant dose is used to make a saturated reaction. After all the films are annealed in the nitrogen at 600 °C for 60 s, the XPS and electrical measurements are carried out to characterize the different processed $HfAlO_x$ films.

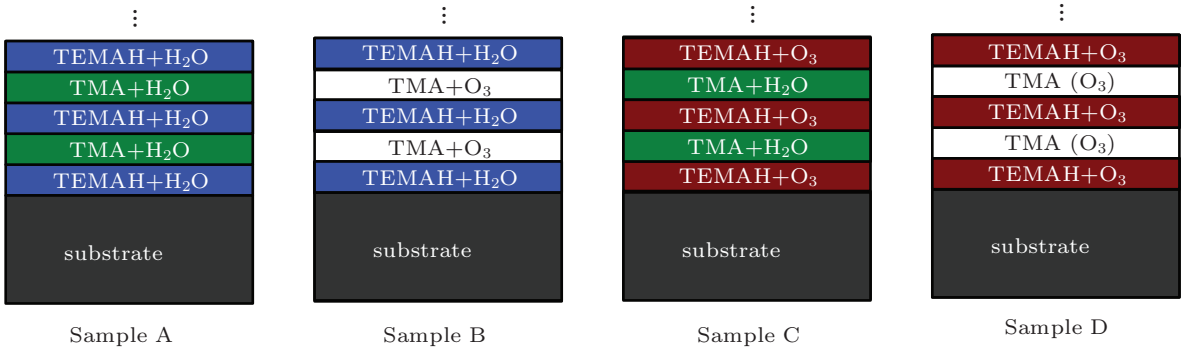


Fig. 1. (color online) Deposition sequences of $HfAlO_x$ films grown using different oxidants.

3. Results and discussion

Figure 2 shows the values of thickness and dielectric constant of the $HfAlO_x$ films. The thickness values of all samples are measured by Woollam M2000D Spectroscopic Ellipsometer. As shown in Fig. 2(a), sample A is thicker than sample D, indicating that the growth rate of the H_2O-based process is larger than that of the O_3-based process. This is due to the strong decomposition of O_3 in the direction of gas flow when the temperature is higher than 250 °C, and growth rate does not increase by increasing O_3 or TEMAH dose.[13] Furthermore, the thickness values of sample A and sample D change as much as 0.26 nm and 0.18 nm respectively, while negligible variations are observed for sample B and sample C. This can be explained by the densification of the films after thermal annealing. The extracted dielectric constant (ε) and equivalent oxide thickness (EOT) are shown in Fig. 2(b). The EOT and permittivity are determined as follows:

$$EOT_{\text{total}} = A\frac{\varepsilon_0\varepsilon_{\text{SiO}_2}}{C_{\text{OX}}}, \quad (1)$$

$$EOT_{\text{high-}k} = EOT_{\text{total}} - T_{\text{SiO}_x}, \quad (2)$$

$$\varepsilon_{\text{high-}k} = \frac{T_{\text{high-}k}}{EOT_{\text{high-}k}}\varepsilon_{\text{SiO}_2}, \quad (3)$$

where A is the area, C_{OX} is the accumulation capacitance of $HfAlO_x$ film, $\varepsilon_{\text{high-}k}$ and $\varepsilon_{\text{SiO}_2}$ are the permittivity values of $HfAlO_x$ and SiO_2 respectively. The results indicate that the as-deposited sample B and sample C have advantages in dielectric constant and equivalent oxide thickness compared with sample A and sample D. However, the dielectric constants of all $HfAlO_x$ films increase significantly after annealing, especially for those of sample A and sample D. Correspondingly, the EOT values of all samples decrease after annealing.

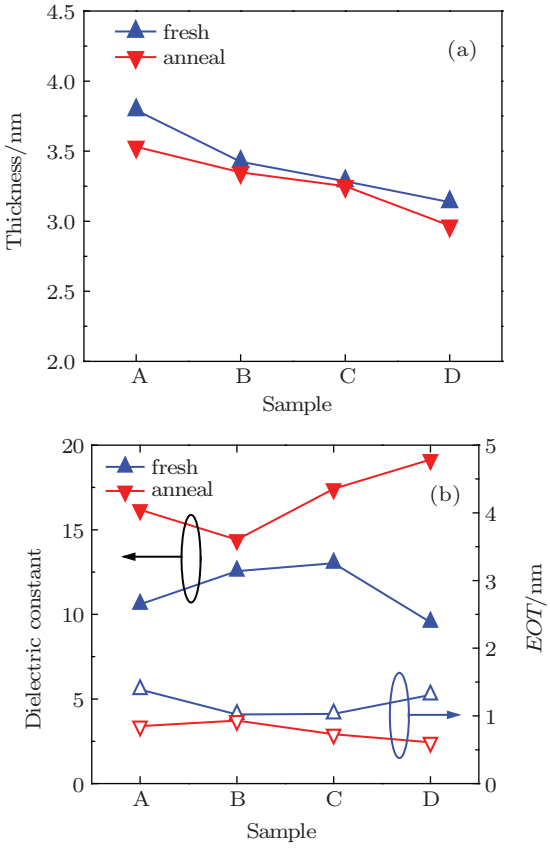


Fig. 2. (color online) Values of thickness and dielectric constant of the $HfAlO_x$ films before and after annealing.

Figure 3 shows the XPS spectra of the $HfAlO_x$ films before and after annealing. The main peaks are from Hf, Al, and O, subordinate peaks are from C and N. The remaining peaks are mainly attributed to the Si substrate and oxygen Auger

peaks. An obvious change is observed in the spectrum of sample A after annealing, whereas almost no changes are observed for the rest of the samples. The difference may be explained by the fact that H_2O tends to be physisorbed on the surface strongly, which contributes to forming high-concentration hydroxyl/hydrogen groups in the films although the purge time is sufficiently long.[14] The residue of hydroxyl/hydrogen groups will generate a lot of dangling bonds or defects during the deposition, which increases the impurity residuals in the films. However, O_3 is easy to purge and no oxidant by-products reside in the films compared with H_2O. During the annealing, the intermixing reaction between the HfO_2 layer and the AlO_x layer occurs, which is accompanied with the decomposition and re-composition of unstable bonds or groups residing in the films. Therefore, the obvious change is observed in the XPS spectrum after annealing.

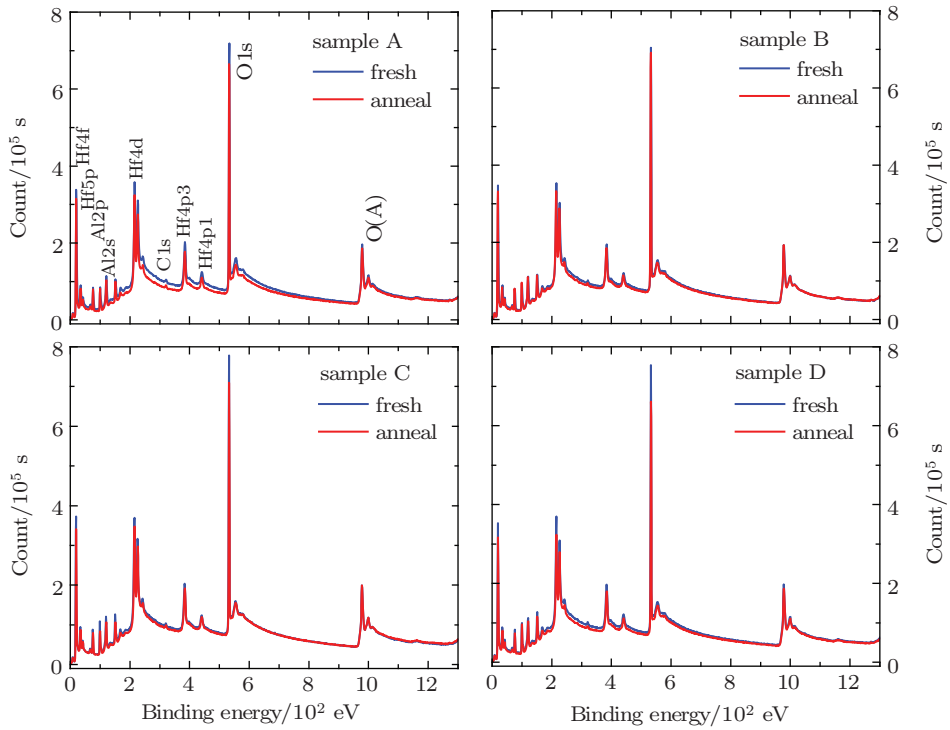


Fig. 3. (color online) XPS spectra of $HfAlO_x$ films grown using different oxidants before and after annealing.

In order to confirm the above discussion, the percentage compositions of C and N impurities for $HfAlO_x$ films are shown in Fig. 4. As shown in Fig. 4(a), the as-deposited sample A has a high C impurity level compared with the other as-deposited samples. After annealing, the percentage composition of C impurity for sample A decreases significantly, while those of the other samples only change a bit due to their low initial concentrations. The residual C impurity mainly comes from the residues of metal precursors or C containing groups attached to the metal atoms for the as-deposited samples. The results indicate that the oxidant O_3 is more likely to achieve the saturate surface reaction compared with H_2O, and has an advantage in controlling the C impurity level. However, the percentage compositions of the N impurity for as-deposited $HfAlO_x$ samples are almost the same except sample D, which is shown in Fig. 4(b). Due to the strong oxidization and lability of O_3, O_3 can split the N–C bonds and C–H bonds of by-products and ligands that still attach to Hf in the deposition process.[13] It leads to the formation of the unstable Hf–N or Hf–O–N bonds in the films.[15,16] Since the residue of N impurity comes only from TEMAH precursors, the N impurity concentration of sample D is higher than those of the other samples. These unstable bonds can decompose and the nitrogen diffuses to the Hf silicate in the annealing process, and the N concentration decreases.[17]

In summary, the $HfAlO_x$ film grown with O_3 as the oxidant generates lower C impurity level and higher N impurity level than the films grown using H_2O. Thermal annealing reduces the C and N impurity concentrations and improves the characteristics of $HfAlO_x$ films, especially the refractive indexes and the dielectric constants. This is consistent with the variation of the dielectric constant shown in Fig. 2(b). Furthermore, the XPS quantitative analysis is performed to determine the chemical composition of the film, and the results are shown in Table 1. The atomic composition ratios of Hf to Al to O are very close to 1:2:6 for all the samples before and after annealing. The result indicates that the oxidants each have a small influence on the stoichiometry of $HfAlO_x$ film, except the C

and N impurities.

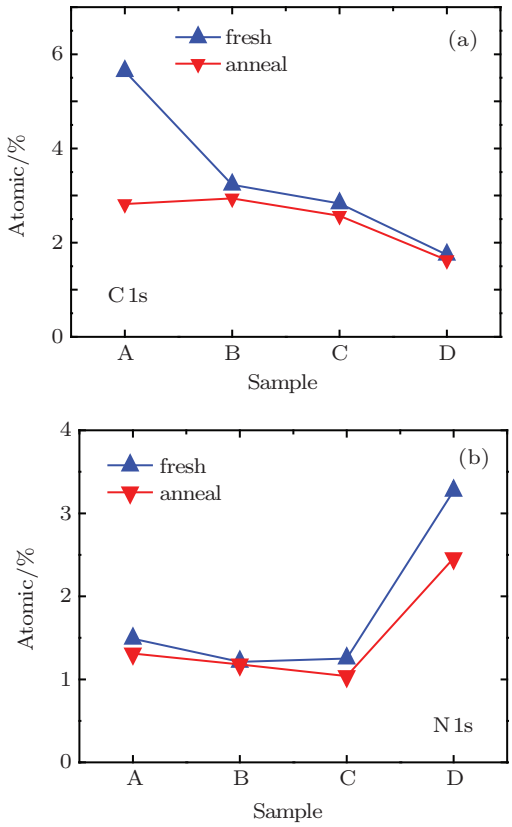


Fig. 4. (color online) Percentage compositions of C and N atoms in $HfAlO_x$ films before and after annealing.

Table 1. Percentage compositions of atomic atoms in $HfAlO_x$ films.

		Hf_{4f}/at%	Al_{2p}/at%	O_{1s}/at%	C_{1s}/at%	N_{1s}/at%
Sample A	fresh	11.86	21.27	59.74	5.64	1.49
	anneal	11.86	22.08	61.93	2.82	1.31
Sample B	fresh	12.23	22.95	60.38	3.23	1.21
	anneal	11.99	21.70	62.19	2.94	1.18
Sample C	fresh	12.02	23.36	60.54	2.83	1.25
	anneal	12.14	23.39	60.86	2.57	1.04
Sample D	fresh	12.10	23.71	59.18	1.74	3.27
	anneal	12.29	23.30	60.32	1.63	2.46

Figure 5 shows the XPS valence band spectra of $HfAlO_x$ films before and after annealing. Each of the valence bands shows a sharp rise at ~ 5 eV associated with the metal-oxide valence band minimum. The valence band maximum (VBM) of each sample is determined by extrapolating the leading edge of the valence band spectrum to the base line from its specific spectrum.[18] The VBM values of as-deposited sample A, sample B, sample C, and sample D are 3.80 eV, 4.02 eV, 4.05 eV, and 4.07 eV, respectively. The VBM reductions of sample A and sample D are attributed to the high concentration of C or N impurity. After annealing, the VBM values of sample A and sample D increase to 4.65 eV and 4.47 eV respectively, whereas those of sample B and sample C change negligibly. This trend is consistent with that of C or N impurity variation after annealing discussed above.

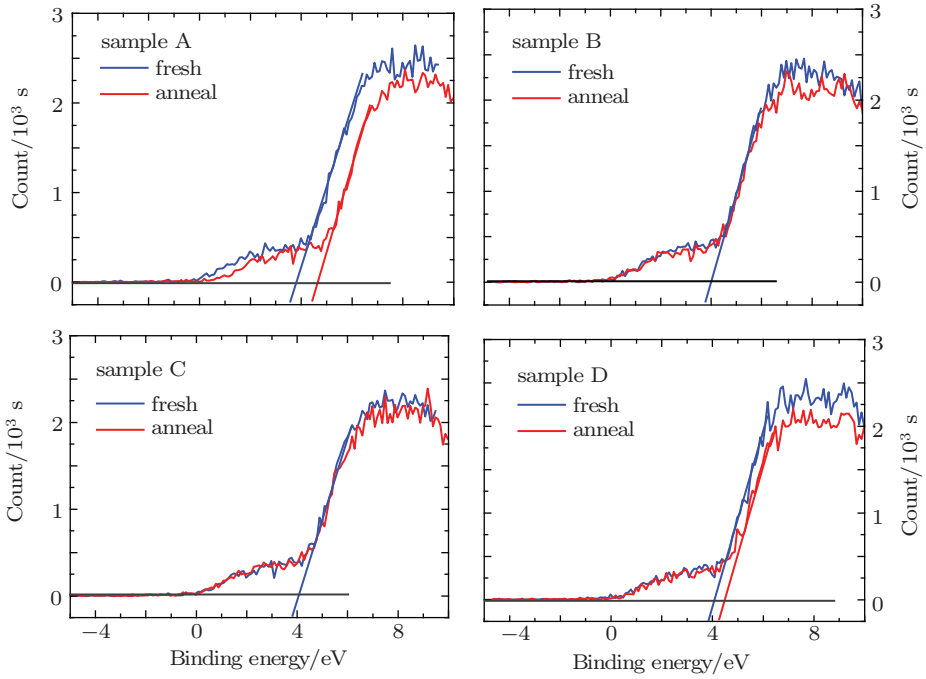


Fig. 5. (color online) Valence band spectra of $HfAlO_x$ films before and after annealing.

Figure 6 shows the C–V characteristics of $HfAlO_x$ before and after annealing ($f = 100$ kHz). The gate voltage (V_G) is swept from accumulation to inversion and then swept back. Due to the densification of $HfAlO_x$ film and decrease of the impurity concentration, the capacitance value of each of the $HfAlO_x$ films in the C–V curves increases after annealing. Furthermore, the width step appears in each of the C–V curves of the as-deposited $HfAlO_x$ films grown by O_3, and it disappears

after thermal annealing process. The width step is caused by the trapped holes injected from the $HfAlO_x$ layer into the depletion layer. The width of the depletion layer in the Si substrate grows with V_G increasing, which reduces the total capacitance of the capacitor. However, if all the trapped holes in the $HfAlO_x/SiO_2$ layer are injected into the depletion layer, the growth of the depletion layer stops and the capacitance becomes constant. Due to the thermal annealing supplying enough thermal energy for the traps or defects decomposition and re-composition, the traps or defects decrease and the width step disappears after annealing.

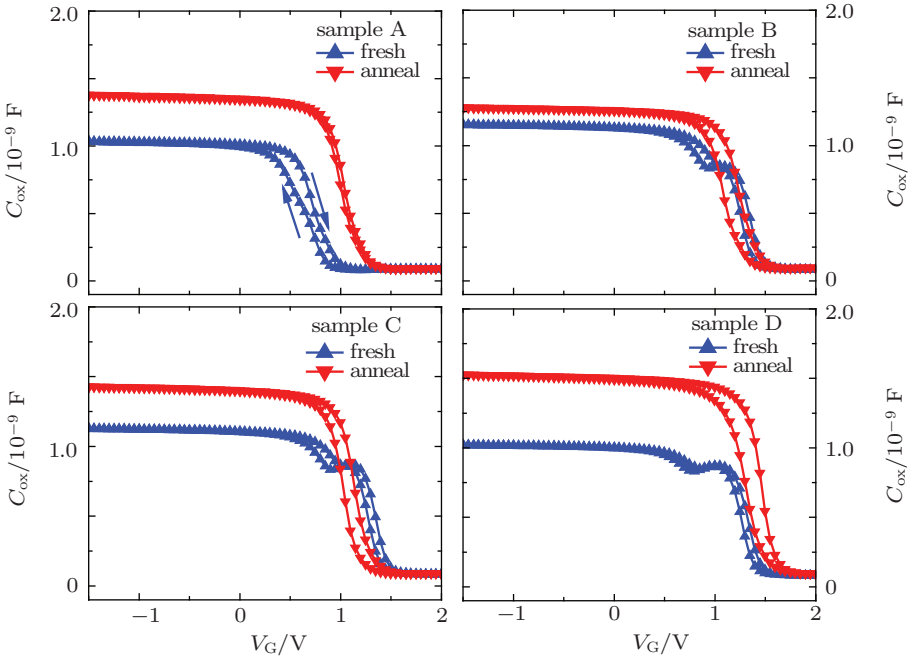


Fig. 6. (color online) The C–V characteristics of $HfAlO_x$ before and after annealing ($f = 100$ kHz).

4. Conclusions

Preliminary results in the development of ALD-grown $HfAlO_x$ films serving as MIM capacitance are presented. The oxidants (H_2O and O_3) effects on the physical properties and electrical characteristics of $HfAlO_x$ films are investigated. Except for the C and N impurity levels, ALD $HfAlO_x$ films display comparatively small changes in composition for different oxidants. Due to the relatively low contamination levels, $HfAlO_x$ films grown with both H_2O and O_3 used as oxidants have many advantages compared with only one oxidant used. Further, the oxidant effects on the dielectric constant, valence band, electrical properties, and stability of ALD $HfAlO_x$ films are evaluated. In addition, the post annealing process reduces the impurity level and improves the electrical characteristics of the $HfAlO_x$ films, thereby making them become a suitable insulator in MIM capacitor devices.

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