奈米世代 MOSFET 關鍵製程技術之研發(2/3)

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執行單位：交通大學電子工程研究所

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Abstract

Recently, MOSFETs with high-k gate dielectrics have been studied intensively and Al₂O₃ is a promising candidate because of its compatibility with the poly-Si gate process and relatively superior scalability. In the second year of this proposal, we utilized rapid thermal annealing technique to improve the quality of high-k film and reduce the thermal budget. Besides, a native oxide layer would easily formed at Si/Al₂O₃ interface during RTA process, resulting in significant increase of effective oxide thickness (EOT) and therefore we applied a NH₃ treatment at 800 degree C for 1 hr prior to Al₂O₃ deposition to suppress the growth of native oxide layer.

From the experimental data, it is obviously that O₂ penetration would induce the increase of the interfacial layer during RTA process. However, for samples with RTA in a N₂ ambient, the void-defect of sputtered Al₂O₃ film would be eliminated and the surface roughness after annealing also reduced. The dielectric reliability was enhanced with NH₃ pre-treatment. The conduction mechanism in Al₂O₃ thin film is dominated by Schottky conduction which occurred in the insulators with fewer defects and a more perfect metal-insulator interface. Samples after NH₃ treatment have higher barrier high to reduce the gate leakage current.

Besides, following the results of this proposal in the 1st year, we investigated the possible boron contamination from various HEPA and ULPA filters. Most commercial ULPA filters are made of glass-fiber, which may corrode in an acid vapor environment and release boron ions, resulting in the electrical property shifts of nano-devices. Through long term acceleration experiments and wafer exposure experiments in an bench with HF vapor, the increase of organic molecular and boron ions due to filter corrosion can be observed. The usage of PTFE ULPA filter can effectively prevent the boron contamination.
I. Introduction

Recently, MOSFETs with high-k gate dielectrics have been studied intensively and Al$_2$O$_3$ is a promising candidate because of its compatibility with the poly-silicon gate process and relatively superior scalability. As the dielectric constant of Al$_2$O$_3$ is higher than SiO$_2$, it will provide a significant increase in capacitance without scaling down the oxide thickness. Rapid thermal Annealing (RTA) is a short time processing technique that can contribute to reduce the thermal budget, low levels of surface roughness, and improve film qualities. Generally, there are many methods to passivate the Si surface such as surface nitridation, nitrogen-contained ambient annealing, or nitride deposition as the bottom layer. Nitridation of the Si surface using NH$_3$ treatment before the deposition of high-k materials has been shown to be effective in achieving the low EOT and preventing the boron penetration. However, this technique results in higher interface charges, which leads to higher hysteresis and reduced channel mobility. In this report, we studied the effect of suppressing interfacial layer growth by NH$_3$ surface treatments. The NH$_3$ treatment would nitridize the Si surface to form a silicon nitride layer. Silicon nitride is a superior barrier for H$_2$O and oxygen, and it can suppress oxygen to diffuse into Si substrate.

The cleanness of a clean room environment must be tightly controlled to achieve high-yield and high-performance ULSI manufacturing. Recently developed filters, such as HEPA and ULPA filters, effectively eliminate traditional contamination. However, the controllability of airborne molecular contamination (AMC) using present cleanroom technologies has not yet been validated because AMC is a kind of atomic or molecular level gas-phase contamination like organic and inorganic ones. In the near future, especially in the nanodevice era, contamination by organic compounds, inorganic ions and trace doping impurities in air in a cleanroom may dominate the characteristics, reliability, and even yield of devices. Acid vapor generated from the cleaning process is another important issue. Most commercial ULPA filters are made of glass-fiber, which may corroded in an acid vapor environment. Contaminants in a ULPA filter corroded by acid vapor will be released into the cleanroom air and adsorbed onto the surface of wafers, degrading the manufactured devices. Technologies for eliminating AMC from the manufacturing environment must be developed to solve these problems completely. Therefore, the development of a new filter material, which has minimal AMC and is resistant to acid vapor corrosion, is important to the fabrication of high-performance devices.

II. Experiments

(A) Al$_2$O$_3$ Gate Dielectrics Using Rapid Thermal Annealing Technology

The 6-inch P-type Si (100) wafers are cleaned by the RCA cleaning process. The high-k material Al$_2$O$_3$ was then deposited by reactive sputtering in Ar/O ambient. After Al$_2$O$_3$ deposition, a high temperature post deposition annealing is performed at 750°C, 850°C and 950°C respectively for 30 sec by RTA Rapid Thermal Annealing (RTA). In our experiment, the gate electrode formations were used the Physical Vapor Deposition (PVD) systems. We deposit the TiN film (2000Å ) as the top gate electrode and the thermal evaporation system to deposit the Al film( 5000Å ) as the backside contact. The cross-sectional view and total experimental procedures of the structure were shown in Fig. 1. At last the Capacitance-Voltage (C-V) and Current-Voltage (I-V) characteristics were measured by HP-4284 and HP-4156C systems. The capacitance equivalent thickness (CET) was extracted from C-V curve.
(B) Al₂O₃ Gate Dielectrics using NH₃ Surface Nitridation Technology

First, the 6-inch P-type Si(100) wafers were cleaned with standard RCA clean. The samples were divided into two groups. One was without any surface treatment before Al₂O₃ deposition, and the other was with a NH₃ surface treatment before Al₂O₃ deposition. The NH₃-treatment is performed in high temperature furnace, 800°C for 1 hour. After NH₃-treatment, a SiNx layer (~10 Å) was deposited. Al₂O₃ dielectric was then deposited various thickness (30Å, 40Å, and 50Å) by reactive sputtering in the Ar/O (ratio = 24/1) ambient. After Al₂O₃ deposition, a high temperature post deposition annealing was performed at 900°C in the O₂ or N₂ ambient. Finally, the gate electrode formation was performed by the Physical Vapor Deposition (PVD) systems. We deposited the TiN film (2000Å) as the top gate electrode and the thermal evaporation system to deposit the Al film (5000Å) as the backside contact. The cross-sectional view and total process flow were shown in Fig. 10. The Capacitance-Voltage (C-V) and Current-Voltage (I-V) characteristics were measured by HP-4284 and HP-4156C systems, respectively. The capacitance equivalent thickness (CET) was extracted from C-V curve. In order to study the conduction mechanism in the Al₂O₃ film, the current-voltage characteristics with various temperature were measured at room temperature (RT), 50°C, 75°C, 100°C, and 125°C, respectively.

(C) Evaluation of AMC through Air Sampling

A specially controlled and fabricated clean bench (CB) was set up in a clean room of class 10k. Figure 19(a) schematically depicts the CB. Clean room air, from the air inlet of the CB, was initially filtered through a filter module that included inorganic and organic ion chemical filters, before flowing through the main filter, which was designed to be changeable. Two main filters were used, the NEUROFINE PTFE filter (PTFE) and the glass-fiber ULPA filter (GF). The air flow rate and turnover rate inside the CB were set to 0.4 m/s and 5 %, respectively. The exposure experiments were conducted in a 1ppm HF vapor environment.

Figure 19(b) presents the air sampling tools, Impinger and TENAX, which were equipped with a flow meter and a pump. The flow rate and sampling time of Impinger were 2 L/min and 24-72 hrs while those of TENAX were 100 mL/min and 5 hrs. Impingers collected mainly both metals and boron elements. These were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS). Organic substances were collected by a TENAX (a kind of absorbent) tube, and quantitatively analyzed by gas chromatograph mass spectrometer (GC-MS). The air in the CR was also analyzed for comparison. Table 2 summarizes the air sampling experimental conditions.

(D) Evaluation of AMC through Wafer Sampling

The AMC absorbed on the surfaces of actual 6” P-type (100) Si wafers was analyzed for each filter module. After standard RCA cleaning, wafers were divided into two parts, and exposed to the air in the CR and the CB for 24-72 hrs. The metal contaminants on these wafer surfaces were analyzed using total reflection X-ray fluorescence (TRXRF), while the organic contaminants were analyzed by thermal desorption system–atmospheric pressure ionized mass spectrum (TDS-APIMS). For comparison, the contamination of a wafer not exposed to any environment was evaluated as a control. Table 3 is the summary of wafer sampling experimental conditions.
III. Results and Discussion

(A) Al$_2$O$_3$ Gate Dielectrics Using Rapid Thermal Annealing Technology

After the Al$_2$O$_3$ deposition, the following processes may go through many high temperature treatments during the VLSI fabrication. Such high-temperature treatments are likely to change the morphology and properties of thin films. Fig. 2 and Fig. 3 shows the high frequency (100kHz) capacitance-voltage (C-V), and Fig. 4 shows the CET of Al$_2$O$_3$ samples (without surface treatment) after various post deposition annealing (PDA) temperature at 750°C, 850°C, 950°C in the O$_2$ or N$_2$ ambient. The capacitance of Al$_2$O$_3$ samples annealing in an O$_2$ ambient decreases with the increasing annealing temperature. Therefore, the CET increases after annealing in an O$_2$ ambient. This is because an O$_2$ penetration will induce the increasing of the interfacial layer at Al$_2$O$_3$/Si-substrate and higher annealing temperature increasing will speed up interface layer growth rate. On the contrary, the capacitance of Al$_2$O$_3$ samples annealing in a N$_2$ ambient is increasing when annealing temperature increases. Therefore, the CET decreases after annealing in a N$_2$ ambient. The void-defects generated after the sputtered Al$_2$O$_3$ formation and it could be densified followed a RTA process in a N$_2$ ambient. The current density (J) in the J-E curve was defined by $J = I / A$, where A is the area of capacitor. The CET determined by the C-V measurement.

Fig. 5 shows the J-E characteristics of Al$_2$O$_3$ film with RTA process in an O$_2$ ambient. It shows that the thicker Al$_2$O$_3$ film will resist large leakage current, and the lower leakage current was observed. However, the thicker dielectric thickness will reduce capacitance and the driving current. Fig. 6 shows the J-V characteristics of the fabricated Al$_2$O$_3$ film with RTA in a N$_2$ ambient. The capacitor can have a lower leakage current with thinner CET. This is due to RTA process in a N$_2$ ambient can improve Al$_2$O$_3$ film by eliminating void-defect. Fig. 7 shows J versus PDA temperature in the O$_2$ and N$_2$ ambient. Obviously, higher PDA temperature can reduce leakage for both annealing ambient. Consequentially, the sputtered Al$_2$O$_3$ film can be improved after a N$_2$ RTA process. If the leakage current density in the oxide ($J_{\text{ox}}$) is kept constant during the stress test (implying that the applied current is held constant), the stress time to breakdown becomes the variable. The length of stress time $t_{\text{BD}}$ elapsed until dielectric breakdown occurred. The time-to-breakdown behavior of a group of oxide samples under such test conditions is referred to as time-dependent dielectric breakdown (TDDB). The Weibull plot of charge to breakdown for Al$_2$O$_3$ samples with various PDA temperature in an O$_2$ ambient is shown in Fig. 8. Obviously, distribution of the samples with thinner CET is better than others. However, the level of the charge to breakdown is lower than we expect. Fig. 9 shows the Weibull plot of charge to breakdown for Al$_2$O$_3$ samples with various PDA temperature in a N$_2$ ambient. For various PDA temperatures, their distribution and charge to breakdown are almost the same and they are not dependent on Al$_2$O$_3$ thickness. This means that the interfacial layer determines the breakdown of the whole stack.

(B) Al$_2$O$_3$ Gate Dielectrics Using NH$_3$ Surface Nitridation Technology

Figure 11 shows the comparisons of the C-V curves of the samples with and without surface treatment after PDA 900°C in an O$_2$ ambient. It is clear that samples with a NH$_3$ treatment had higher capacitance at strong accumulation than samples without a NH$_3$ treatment. The CET of Al$_2$O$_3$ film is effectively reduced after NH$_3$ nitridation since NH$_3$ surface can suppress the growth
of interfacial layer. In Fig. 11, we can also found the C-V curves shift negatively after NH3 nitridation can be observed due to the nitridation-induced fixed positive charges. Since positive fixed charges in conventional NH3 nitridation film is due to N–H bonds at the interface. Fig. 12 shows the comparisons of the C-V curves of the samples with or without surface treatment after PDA 900°C in a N2 ambient. We still can find that the CET of Al2O3 film is effectively reduced after NH3 treatment. However, the amount of the C-V curves shift negatively after NH3 nitridation is decreasing. The reason is due to that PDA in a N2 ambient will enhance the magnitude of fixed charge in Al2O3 film. Fig. 13 shows the variation of deposited thickness (measured by ellipsometer) versus CET after PDA 900°C in an O2 ambient. The NH3 treatment can effectively reduce the CET despite the initial oxide thickness, which shows the excellent CET scalability of this nitridation process. Because the presence of Si3N4 layer can effectively suppress the diffusion of oxygen species into the high-k/Si substrate interface. Without surface nitridation, Al and O atoms are easier to react with Si and are likely to form additional silicon dioxide and/or aluminum silicate layer with relatively lower k value. Fig. 14 shows the variation of Al2O3 thickness versus capacitance equivalent thickness (CET) after PDA 900°C in a N2 ambient. We can see almost the same result in an O2 ambient as in a N2 ambient, except in a N2 ambient with higher k value. Figure 15 (a) and (b) show the relationship of gate leakage current versus gate bias after PDA 900°C in the O2 and N2 ambient, respectively. The NH3-treatment samples show lower leakage current even with thinner CET. It is postulated that the NH3-treatment can improve the quality of interface between high-k and silicon substrate and effectively reduce the leakage current. Fig. 16 shows the curve of Current density versus CET curves at Vg = -1V with NH3 treatment and without NH3 treatment. It is clear that NH3 treatment can effectively reduce leakage current. Fig. 17(a) and (b) show the Weibull plots of the charge to breakdown (QBD) of Al2O3 samples with nearly the same CET after PDA 900°C in the O2 and N2 ambient, respectively. The samples with NH3 treatment shows more charge to breakdown (QBD). Thus, we suspect that surface nitridation may effectively reduce the concentration of oxygen vacancies during PDA due to its capability to suppress oxygen diffusion. On the other hand, the stronger Si-N bonds bring a stronger interface layer. When part of voltage drop across the Si3N4 interfacial layer in samples, the voltage drop across the Al2O3 film is lower than expectation and the influence of the electric field stress is not as severe as the un-NH3 treatment Al2O3 samples. As the result, it will enhance the QBD for NH3 treated Al2O3 samples.

It is important to study the conduction mechanisms of leakage current in Al2O3 film to improve its electrical and dielectric properties. Typically, two possible effects are in the metal-insulator interface, one is Schottky effect, the other is Frenkel-Poole effect. The Schottky-Richardson emission generated by the thermionic effect is caused by the electron transport across the potential energy barrier via field-assisted lowering at a metal-insulator interface. The leakage current equation is:

\[ J = A^* T^2 \exp \left( \frac{\beta_i \sqrt{v}}{k_B T} - \phi_s \right) \]

where \( \beta_i = (e^3 / 4\pi\varepsilon_0\varepsilon)^{1/2} \), \( A^* \) effective Richardson constant, \( \phi_s \) the contact potential barrier. We
can find the slope of the leakage current equation.

\[
\ln J = \frac{\beta_s}{k_BT} \sqrt{\frac{E}{T}} + \left[ \ln \left( A'T^2 \right) - \frac{\phi_s}{k_BT} \right]
\]

\[
slope = \frac{\beta_s}{k_BT}
\]

The Frenkel-Poole (F-P) emission is due to field-enhanced thermal excitation of trapped electrons in the insulator into the conduction band. The leakage current equation is:

\[
J = J_0 \exp \left( \frac{\beta_{FP} E^{1/2} - \phi_{PF}}{k_BT} \right)
\]

where \( J_0 = \sigma_0 E \) is the low-field current density, \( \sigma_0 \) the low-field conductivity, \( \beta_{FP} = \left( \frac{e^3}{\pi \epsilon_0 \epsilon} \right)^{1/2} \), \( e \) the electronic charge, \( \epsilon_0 \) the permittivity of free space, \( \epsilon \) the high frequency relative dielectric constant, \( T \) absolute temperature, \( E \) the applied electric field, \( K_B \) the Boltzmann constant, \( \phi_{PF} \) the contact potential barrier. We can find the slope of the leakage current equation.

\[
\ln J = \frac{\beta_{FP}}{k_BT} \sqrt{\frac{E}{T}} + \left[ \ln \left( J_0 \right) - \frac{\phi_{PF}}{k_BT} \right]
\]

\[
slope = \frac{\beta_{FP}}{k_BT}
\]

From the equations as shown above, leakage current behaviors of insulate films can be investigated further on the leakage current density (\( J \))-electric field (\( E \)) characteristics such as \( \ln J \) vs. \( E^{1/2} \) plots. The plot of the nature log of leakage current density versus the square root of the applied electric field was observed. It is found that the leakage current density is linearly related to square root of the applied electric field. The linear variations of the current correspond either to Schottky emission or to Frenkel-Poole conduction mechanism. For trap states with Coulomb potentials, the expression is virtually identical to that of the Schottky emission. The barrier height, however, is the depth of the trap potential well, and the quantity \( \beta_{FP} \) is larger than in the case of Schottky emission by a factor of 2. Distinction between the two processes can be done by comparing the theoretical value of \( \beta \) with the experimental one obtained by calculating the slope of the curve \( \ln J-E^{1/2} \). The dielectric constant of Al \(_2\)O\(_3\) is 7.63 at PDA O\(_2\) ambient and 8.29 at PDA N\(_2\) ambient extracted by Fig. 20, the theory \( \beta \) values are 4.40\times10^{-23} for Frenkel-Poole and 2.20\times10^{-23} for Schottky after PDA in an O\(_2\) ambient and the theory \( \beta \) values are 4.22\times10^{-23} for Frenkel-Poole and 2.11\times10^{-23} for Schottky after PDA in a N\(_2\) ambient. Table 1 (a) and (b) shown the experimental \( \beta \) and Schottky barrier high of Al\(_2\)O\(_3\) samples with NH\(_3\) and without NH\(_3\) treatment after PDA 900°C in an O\(_2\) ambient and after PDA 900°C in a N\(_2\) ambient, respectively. Fig. 18 (a) and (b) show the conduction mechanism fitting of Al\(_2\)O\(_3\) samples with NH\(_3\) and w/o NH\(_3\) treatment after PDA 900°C in an O\(_2\) ambient and after PDA 900°C in a N\(_2\) ambient, respectively. We find the conduction mechanism in Al\(_2\)O\(_3\) thin film is dominated by Schottky
(C) Pre- and Post-corroded Fiber Structure in HF Vapor Environment

Figure 20 shows the fiber structure of PTFE-fiber and glass-fiber after the HF vapor corrosion. The pre- and post-corroded fiber structure of PTFE did not reveal any difference and this meant the PTFE-fiber was resistive for HF vapor. On the contrary, the fiber structure of glass-fiber shown in Fig. 20(b) displayed the serious degradation in HF vapor environment. The glass-fiber was inevitable to be corroded due to the strong reduction of HF to glass. It is worthy to notice that the corrosion of glass-fiber may release the boron and organic contaminants contained in glass-fiber ULPA filter, thus causing the degradation of device characteristics. Therefore, the PTFE ULPA filter is suitable to be used in acid vapor environment.

(D) Air Sampling Results in HF Vapor Environment

Figure 21 is the ICP-MS analysis results of metals and boron for different filter modules in HF vapor environment. The PTFE and the glass-fiber ULPA filter can effectively filter the metals including Na, K, Ca, Mg and Al. The CB with the PTFE and the GF ULPA filter, however, showed higher concentration of Fe ions than CR. It was suggested that the steel construction of clean bench corroded by HF vapor, releasing the Fe ions to air. Besides, the CB with GF filter showed large concentration of boron than the CB with PTFE filter. This may due to the corrosion of glass-fiber in HF vapor, releasing the boron atoms contained in glass-fiber as mentioned above. The detail analysis results of ICP-MS are listed in Table 4.

The organic compounds were considered to be another contamination the glass-fiber will release in HF vapor. Figure 22 shows the analysis results of GC/MS. It was found that all the organic contaminants were removed in the CB with PTFE filter. But for the CB with GF filter, high concentration of organic contaminants appeared. According to our study in Chapter 2, these organic contaminants may come from the binder in GF ULPA filter. In HF vapor environment, the degradation of glass-fiber will release more organic contaminants as show in Fig. 22. Table 5 shows the detail analysis results of GC/MS.

IV. Conclusion

In this thesis, characteristics and reliability of Al₂O₃ gate dielectrics with pre-deposition NH₃ treatment and rapid thermal annealing in O₂ and N₂ ambient have been investigated. Several important phenomena were observed and summarized as follows. PDA can effectively reduce leakage current. For the samples with PDA at O₂ ambient, the interfacial layer increases with the higher PDA temperature. It is obviously that O₂ penetration will induce the increasing of the interfacial layer at Al₂O₃/Si-substrate and higher annealing temperature will speed up interface layer growth rate. For samples with PDA in a N₂ ambient, the void–defect of sputtered Al₂O₃ film will be eliminated. The as deposited Al₂O₃ film shows larger roughness, and after PDA it will become smoother. However, with higher PDA temperature, surface rough will slightly increase.

The surface NH₃ treatment can lower the CET value and reduce the leakage current. In addition, the dielectric reliability was enhanced with NH₃ treatment. The low Weibull slope of Al₂O₃ film may result from sputter-induced defects causing weak spots. Significant process improvements are necessary to enhance dielectric quality, such as MOCVD, ALCVD. The conduction mechanism in Al₂O₃ film was investigated by the various temperature measurement...
and fitting. The conduction mechanism in Al₂O₃ thin film is dominated by Schottky conduction which occurred for insulators with fewer defects and a more perfect metal-insulator interface. Samples after NH₃ treatment will have higher barrier high to reduce the leakage current.

The qualitative and quantitative analyses of AMC in the CB with different filter module in HF vapor environment were investigated. The experimental results showed that the GF ULPA filter will release boron and organic contaminants in HF vapor environment, while the PTFE ULPA filter still maintained low concentration of contaminants. The effects of the materials from which air filters are made on device characteristics were also investigated. The glass-fiber ULPA filter released AMC when exposed in an HF vapor environment. These contaminants included organic compounds and boron trace dopants and degraded the device characteristics. In contrast, the HF vapor did not affect the PTFE ULPA filter. These results suggested that the PTFE fiber can be a good ULPA filter material for providing a very clean environment.

計畫成果自評
本計畫為三年期計畫，依原訂計畫第二年目標，本計畫完成了奈米級閘極介電層關鍵製程技術之研發以及奈米級微污染分析防治，相關論文仍在投稿當中。在奈米級閘極介電層關鍵製程技術之研發方面，開發出未來奈米元件用之高介電常數 Al₂O₃ 閘極介電層，並研究其特性及最佳化條件，此高介電氧化鋁薄膜經過 NH₃ 的前處理及 N₂ RTA 製程退火處理，可獲得最佳電性，適用於未來的奈米元件製程；最後在奈米級微污染分析防治方面，我們以氫氟酸加速實驗檢驗了目前無塵室空氣濾網的適用性，並採用新開發之 PTFE 濾網來控制無塵室中之硼微污染跟有機污染。本計畫未來一年將以前兩年為基礎，繼續進行氧化鋁和臭氧水製程之奈米閘極絕緣層跟無塵室微污染對於奈米元件之影響等相關研究。
1. RCA clean and LOCOS

2. Al₂O₃ deposition (60Å) by Reactive Sputter

3. RTA treatment N₂/5 slm/30 sec or O₂/5 slm/30 sec 750°C, 850°C, 950°C

4. Top electrode formation TiN-2000 Å & Backside contact formation Al -5000Å

Fig.1 Process flows of experimental samples
Capacitance area = $10^{-4}$ cm$^2$

Fig. 2 The C-V curves of Al$_2$O$_3$ samples annealing in an O$_2$ ambient

Fig. 3 The C-V curves of Al$_2$O$_3$ samples annealing in a N$_2$ ambient
Fig. 4 The CET of Al$_2$O$_3$ samples after various post annealing temperature 750°C, 850°C, 950°C

Fig. 5 The J-E curves of Al$_2$O$_3$ samples with various PDA temperature in an O$_2$ ambient.
Fig. 6 The J-E curves of Al₂O₃ samples with various PDA temperature in a N₂ ambient.

Fig. 7 The J at Vg = -1 V of Al₂O₃ samples with various PDA temperature
Fig. 8 The Weibull plot versus the charge to breakdown $Q$ (C/cm$^2$) of Al$_2$O$_3$ samples with various PDA temperature in an O$_2$ ambient.

Fig. 9 The Weibull plot shows the charge to breakdown $Q$ (C/cm$^2$) of Al$_2$O$_3$ samples with various PDA temperature in a N$_2$ ambient.
1. RCA clean
2. Without treatment
3. Al₂O₃ deposition (30, 40, 50 Å)
4. RTA treatment N₂/5 slm/30 sec or
5. Top electrode formation TiN -2000 Å pattern contact

Fig.10  Process flows of experimental samples
Fig. 11: C-V curve of Al₂O₃ sample with surface treatment compare to Al₂O₃ sample without surface treatment after PDA 900°C in an O₂ ambient.

Fig. 12: C-V curve of Al₂O₃ sample with surface treatment compare to Al₂O₃ sample without surface treatment after PDA 900°C in a N₂ ambient.
Fig. 13: CET versus Optical thickness of Al₂O₃ sample with surface treatment compare to Al₂O₃ sample without surface treatment after PDA 900°C in an O₂ ambient

Fig. 14: CET versus Optical thickness of Al₂O₃ sample with surface treatment compare to Al₂O₃ sample without surface treatment after PDA 900°C in an N₂ ambient
Fig. 15(a): The gate leakage current density ($J$) versus electric field ($E$) curves for NH$_3$ nitrided and w/o NH$_3$ nitrided after PDA 900°C in an O$_2$ ambient.

Fig. 15(b): The gate leakage current density ($J$) versus electric field ($E$) curves for NH$_3$ nitrided and w/o NH$_3$ nitrided after PDA 900°C in a N$_2$ ambient.
Current density (A/cm$^2$) at $V_g = -1$ V

Fig. 16 Current density at $V_g = -1$ V versus CET curves for NH$_3$ treatment and without NH$_3$ treatment.

Fig. 17 (a) The weibull plot shows charge to breakdown for Al$_2$O$_3$ samples with NH$_3$ and w/o NH$_3$ treatment at PDA after PDA 900°C in an O$_2$ ambient.
Fig. 17 (b) The Weibull plot shows charge to breakdown for Al₂O₃ samples with NH₃ and w/o NH₃ treatment at PDA after PDA 900°C in a N₂ ambient.

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<td>2.59*10⁻²³</td>
<td>0.74 ev</td>
</tr>
<tr>
<td>125°C</td>
<td>2.71*10⁻²³</td>
<td>0.70 ev</td>
</tr>
</tbody>
</table>

Table. 1(a) The experimental β and Schottky barrier high of Al₂O₃ samples with NH₃ and w/o NH₃ treatment after PDA 900°C in a O₂ ambient

<table>
<thead>
<tr>
<th>Temperature</th>
<th>w/o NH₃ treatment</th>
<th>With NH₃ treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>βexp</td>
<td>Schottky barrier high</td>
</tr>
<tr>
<td>25°C</td>
<td>1.93*10⁻²³</td>
<td>0.73 ev</td>
</tr>
<tr>
<td>50°C</td>
<td>1.83*10⁻²³</td>
<td>0.65 ev</td>
</tr>
<tr>
<td>75°C</td>
<td>2.04*10⁻²³</td>
<td>0.69 ev</td>
</tr>
<tr>
<td>100°C</td>
<td>2.13*10⁻²³</td>
<td>0.72 ev</td>
</tr>
<tr>
<td>125°C</td>
<td>2.01*10⁻²³</td>
<td>0.77 ev</td>
</tr>
</tbody>
</table>

Table. 1(b) The experimental β and Schottky barrier high of Al₂O₃ samples with NH₃ and w/o NH₃ treatment after PDA 900°C in a N₂ ambient
Fig. 18(a) The conduction mechanism fitting of Al₂O₃ samples with NH₃ and w/o NH₃ treatment after PDA 900 ℃ in an O₂ ambient.

Fig. 18(b) The conduction mechanism fitting of Al₂O₃ samples with NH₃ and w/o NH₃ treatment after PDA 900 ℃ in a N₂ ambient.
## TABLE 2
Summary of Air Sampling Experimental Conditions

<table>
<thead>
<tr>
<th>Contamination Type</th>
<th>Sampling Equipments</th>
<th>Flow Rate</th>
<th>Sampling Time</th>
<th>Analysis Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Compounds</td>
<td>TENAX Tube</td>
<td>100 mL/min.</td>
<td>5 hrs</td>
<td>GC/MS (Gas Chromatograph Mass Spectrometer)</td>
</tr>
<tr>
<td>Metals &amp; Boron</td>
<td>Impinger</td>
<td>2 L/min.</td>
<td>72 hrs</td>
<td>ICP-MS (Inductively Coupled Plasma Mass Spectrometer)</td>
</tr>
</tbody>
</table>

**Bench Condition**
- Filter module: 1. PTFE ULPA filter + Chemical filter  
  2. Glass-Fiber ULPA filter + Chemical filter
- Air flow rate: 0.4 m/s
- Turnover rate: 5%
- Temperature: 23 °C
- 1ppm HF Vapor

## TABLE 3
Summary of Wafer Sampling Experimental Conditions

<table>
<thead>
<tr>
<th>Contamination Type</th>
<th>Exposing Location</th>
<th>Exposing Time</th>
<th>Analysis Method</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Compounds</td>
<td>CR and CB</td>
<td>24 hrs, 72 hrs</td>
<td>TDS-APIMS (Thermal Desorption System – Atmospheric Pressure Ionized Mass Spectrum)</td>
<td>D3, D4, D5, D6, DEP, DBP, TEP, TBP, BHT</td>
</tr>
<tr>
<td>Metals</td>
<td></td>
<td></td>
<td>TRXRF (Total Reflection X-Ray Fluorescence)</td>
<td>Na, K, Ca, Mg, Fe, Ti, V, Cr, Mn, Co, Ni, Cu, Zn</td>
</tr>
</tbody>
</table>

**Filter module:**
- 1. PTFE ULPA filter + Chemical filter  
- 2. Glass-Fiber ULPA filter + Chemical filter
- Air flow rate: 0.4 m/s
- Turnover rate: 5%
- Temperature: 23 °C
- 1ppm HF Vapor
### TABLE 4
Air Sampling Results of Metals and Boron in HF Vapor Environment

<table>
<thead>
<tr>
<th>Metals &amp; Boron (µg/m³)</th>
<th>CR Detection Limit</th>
<th>CB_PTFE Detection Limit</th>
<th>CB_GF Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Filter - Chemical Filter</td>
<td>-</td>
<td>Chemical Filter</td>
<td>Chemical Filter</td>
</tr>
<tr>
<td>Main Filter - PTFE Filter</td>
<td>-</td>
<td>PTFE Filter</td>
<td>Glass-Fiber Filter</td>
</tr>
<tr>
<td>Na</td>
<td>0.25 0.002 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
<td>&lt;0.002 0.002 0.002</td>
</tr>
<tr>
<td>K</td>
<td>0.006 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
</tr>
<tr>
<td>Ca</td>
<td>0.004 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.004 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
<td>&lt;0.004 0.004 0.004</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.004 0.004 0.004</td>
<td>0.008 0.004 0.004</td>
<td>0.05 0.004 0.004</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.004 0.004 0.004</td>
<td>0.0036 0.0008 0.0008</td>
<td>0.062 0.0009 0.0009</td>
</tr>
<tr>
<td>B</td>
<td>0.024 0.0008</td>
<td>0.0036 0.0008</td>
<td>0.062 0.0009</td>
</tr>
</tbody>
</table>

### TABLE 5
Air Sampling Results of Organic Compounds in HF Vapor Environment

<table>
<thead>
<tr>
<th>Organic Compounds (µg/m³)</th>
<th>CR Detection Limit</th>
<th>CB_PTFE Detection Limit</th>
<th>CB_GF Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Filter - Chemical Filter</td>
<td>-</td>
<td>Chemical Filter</td>
<td>Chemical Filter</td>
</tr>
<tr>
<td>Main Filter - PTFE Filter</td>
<td>-</td>
<td>PTFE Filter</td>
<td>Glass-Fiber Filter</td>
</tr>
<tr>
<td>D3:C₆H₁₈O₃Si₃</td>
<td>2.1 0.03</td>
<td>&lt;0.03 0.03</td>
<td>*1 0.03</td>
</tr>
<tr>
<td>D₄:C₈H₂₄O₄Si₄</td>
<td>&lt;0.07 0.07</td>
<td>&lt;0.07 0.07</td>
<td>0.11 0.07</td>
</tr>
<tr>
<td>D₅:C₁₀H₃₀O₅Si₅</td>
<td>0.34 0.03</td>
<td>&lt;0.03 0.03</td>
<td>0.14 0.03</td>
</tr>
<tr>
<td>D₆:C₁₂H₃₆O₆Si₆</td>
<td>0.04 0.03</td>
<td>&lt;0.03 0.03</td>
<td>0.14 0.03</td>
</tr>
<tr>
<td>DEP:C₁₂H₁₄O₄</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
<td>0.27 0.03</td>
</tr>
<tr>
<td>DBP:C₁₆H₂₂O₄</td>
<td>0.27 0.22</td>
<td>&lt;0.22 0.22</td>
<td>1.4 0.22</td>
</tr>
<tr>
<td>TEP:C₆H₁₅O₄P</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
</tr>
<tr>
<td>TBP:C₁₃H₂₇O₄P</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
</tr>
<tr>
<td>BHT:C₁₅H₂₄O</td>
<td>&lt;0.03 0.03</td>
<td>&lt;0.03 0.03</td>
<td>0.04 0.03</td>
</tr>
</tbody>
</table>

*1: Can not separate organic compounds peaks
Fig. 19(a) Schematic diagram of specially designed clean bench with the HF vapor.

Fig. 19(b) Air sampling equipments used for the evaluation of metals and organic contaminations.
Fig. 20 The SEM photographs of (a) PTFE-fiber and (b) Glass-fiber structures.
Fig. 21 Air sampling results of metals and boron in HF vapor environment.

Fig. 22 Air sampling results of organic compounds in HF vapor environment.