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Interface state density and barrier height improvement in ammonium sulfide treated Al₂O₃/Si interfaces

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ABSTRACT

The HF treatment removes the native oxide and lays behind the dangling bonds over the Si surface which causes the increment in density of interface traps (D_{it}) through the direct deposition of high-k dielectric on Si. Here, we propose the facile method for reduction of interface traps and improvement in barrier height with the $(NH_4)_2S$ treatment on Al_2O_3/Si interfaces, which can be used as the base for the non-volatile memory device. The AFM was used to optimize the treatment time and surface properties, while XPS measurements were carried out to study the interface and extract the barrier height (Φ_B). The short period of 20 s treatment shows the improvement in the barrier height (1.02 eV), while the one order reduction in the D_{it} ($0.84 \times 10^{12} \text{ cm}^2/\text{eV}$) of sulfur passivated $Al/Al_2O_3/Si$ MOS device. The results indicate the favorable passivation of the dangling bonds over the Si surfaces covered by sulfur atoms.

1. Introduction

The non-volatile memories (NVM) are the device which does not require external voltage for storing or erasing the bit while the electronic states were used to store or erase the data [1]. Among the different types of NVM, the charge trapping flash type memory devices are the one where the carriers (holes/electrons) are stored in the discrete traps of the storage layer. The basic device is composed of thin tunneling layer, charge trapping layer (storage layer), and blocking layer. The charges are stored after applying the voltage to the gate terminal tunnel through the Si channel into the storage layer. The stored charges cause the shift in the threshold voltage of devices termed as programming or erasing based on the positive or negative applied gate voltage [2-5]. The preliminary devices were composed of the metal-oxide-nitride-oxide-semiconductor (MONOS) structure. However, further scaling of nitride layer limited as it directs towards an increase in the leakage current [6,7]. Therefore, replacement of nitride layer with high-k dielectric were proposed by several researchers which retain a higher physical thickness [8–10] with reduction in the leakage current.

Among several high-k dielectrics, Al_2O_3 is probably served as blocking and tunneling layer in the MONOS type of NVM devices due to

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its higher band gap of ~6.6–8 eV [11,12]. However, the direct deposition of high-k dielectrics over the Si leads to the charge loss due to de-trapping of electrons and holes [13,14]. The possible reason behind this de-trapping is the contamination, oxide/interface defect density, mobile ions, or the dangling bonds present over the surface [15]. Therefore, the pretreatments of the Si surface or intentional passivation layer formation could be solution to overcome these issues. In this context, sulfur passivation of Si surfaces was proposed by simple treatment of aqueous ammonium sulfide ((NH₄)₂S) solution to reduce the density of interface traps.

Literature showed sulfur solution treatment mainly utilized over the Ge and compound semiconductors based MOS devices as their interfaces/native oxides are not stable [16,17]. However, few reports were utilized the ((NH₄)₂S) solution for the Si surface passivation [18,19]. The insight of the surface treatment for the reduction of D_{it} in blocking layer is not understood well. Therefore, we are investigating the surface and interface properties by atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS). The solution treatment time was mainly optimized by the atomic force microscopy. The results show the 20 s ((NH₄)₂S) treatment is enough and beneficial to remove the dangling bonds and forming the single layer of the sulfur. Furthermore,

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the 20 s $((NH_4)_2S)$ treatment improves the Schottky barrier height which is extracted from the core level spectra of the Si and valence band edge.

2. Materials and methods

2.1. Materials

Aqueous 5–6% ammonium sulfide solution was purchased from Xilong Scientific Co., Ltd. The chemical was used as received; no further purification was performed. The n-type (100) oriented Si substrate having resistivity of 1–10 Ω -cm was used to fabricate the devices. The substrates were precleaned with standard RCA-I and RCA-II cleaning method. To remove the native oxide, 2% Hydrofluoric acid (49%) was dipped in for 30 s followed by a rinse in distilled water. Finally, the substrates were blown with dry N₂ (99.99% purity).

2.2. Device fabrication

Two type of devices was fabricated. One was without passivated named as pristine and another was sulfur passivated as shown in Fig. 1. In start, to optimize the process time, the precleaned Si substrates immersed into the aqueous solution of ammonium sulfide for different time (5 s - 15 min) followed by the DI rinse. The untreated and treated samples were immediately loaded into the reaction chamber of thermal ALD (NCD Lucida 1000-flow type reactor). The 10 nm Al₂O₃ was deposited on the sulfur passivated Si substrates at substrate temperature of 250 °C. The total 110 cycles of ALD process were performed having the near about ~1 Å growth rate per cycle. The details of precursor and recipe parameters are given in Table 1. The 200 nm Al metal electrode was deposited by thermal evaporator through shadow mask having the circular diameter 200 μ m.

2.3. Characterization

The treated samples were analyzed by means of the atomic force microscopy (AFM: Park XE-100). The X-ray photoelectron spectroscopy (XPS) characterization was performed by using Phi Model at the energy of 1.48 KeV, while the high-resolution transmission electron microscopy (TEM) were performed to know the interface property and thickness wisely. The electrical measurements like capacitance voltage (C–V) and conductance voltage (G-V) were performed by using 4219A impedance analyzer. Minimum five device were tested for each case and the extracted electrical parameter were the average of all those measured values.

Table 1

ALD	process	parameters	during	the A	l_2O_3	deposition	on	pristine	and	treated	l Si
surfa	aces.										

Step Name	TMA ^a Pulse	Purging	H ₂ O Pulse	Purging
N ₂ Gas Flow ^b	50 sccm			
TMA Pulse time	0.2 s	-	-	-
H ₂ O Pulse time	-	-	0.2 s	_
Purging	-	15 s	-	30 s
Substrate Temperature	250 °C			

^a TMA: Trimethyl Aluminum.

^b Total Purge N_2 gas flow = 200 sccm.

3. Results

3.1. Atomic force microscopy

The surface properties of ALD-Al2O3 films deposited on sulfur passivated Si surfaces with different treatment time were characterized by AFM. Fig. 2 (a)-(f) shows the AFM micrographs of the Si surfaces treated for different time starting from pristine to 15 min with aqueous ammonium sulfide solution. The images clearly show the physicochemical damage of the surface for the treatment time over 1 min. The number of voids was observed to be increased with increase in treatment time. Fig. 2 (g) shows the root mean square roughness of the samples versus the treatment time in sec. The lowest RMS roughness was observed for the 20 s treatment time. While RMS roughness increased significantly as the aqueous ammonium sulfide treatment time over 5 min, which reflected that the sulfur treatment creates the serious defects over the Si surface. It means the 20 s treatment time is beneficial for sulfur passivation of the Si surface. The possible reason behind this increase in surface roughness is the depletion of sulfur atoms over the Si surface which decreases the conductivity of the surface and increases the number of fixed oxide charges at the interface [20,21]. Further, this amount of roughness is may observed different for different concentration of the solution, here, only 5-6% sulfur containing solution was used.

3.2. X-ray photoelectron spectroscopy

Fig. 3 (a) shows the Si 2p core level spectrum of the sulfur passivated Si surface treated for 20 s. The deconvoluted peak centered at 99.36 $(Si2p_{3/2})$ corresponds to the bulk Si representing Si–Si bonding [22], while peak around 100.06 eV representing the Si–C $(Si2p_{1/2})$ bonding with small shift [23]. As no other peak is observed; it specifies the removal of native oxide which founds near about 103. 2 eV. The inset of



Fig. 1. Schematic of Pristine and (NH₄)₂S treated Al/Al₂O₃/Si MOS device, inset shoes the dangling bonds replaced by the Sulfur atom (blue) passivates the Si surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. Atomic Force Microscopy images of the (NH₄)₂S treated Si surfaces with different time (a) Pristine (b) 20 s (c) 30 s (d) 5 min (e) 10 min (f) 15 min (g) RMS roughness as a function of treatment time.

Fig. 3 (a) shows the sulfur 2p core level spectra in which broad peak at 168.24 eV shows the formation of sulfates or Poly-sulphide over the surface [18]. The observed results are comparable to the XPS results reported by Aibin et al. for the sulfur passivated Si surfaces in their work [24]. Furthermore, the S2p detection proves the removal of dangling bond over the surface and replacement O–H bond with the O–S shows the formation of sulfates.

The barrier height was extracted for the sulfur untreated and treated Si surface from the valence band edge spectrum shown in Fig. 3(b), which can be calculated form the following relation [25]:

$$\begin{split} q \mathcal{D}_n &= E_g - E_V^i + \left(E_{core}^i - E_{core}^G \right) \\ &= E_g - \left(E_{core}^G - E_{VC} \right) \end{split} \tag{1}$$

where, E_g is the band gap energy of the Si that is 1.12 eV, E_{VC} is the binding energy of Si core level peak specifies the difference between Si2p_{3/2} peak and the valence band maxima with reference to the fermi energy of the Si edge extracted from the low energy Si core level spectrum. For core Si, the E_{VC} is equal to the ~99 eV [25]. While E_{core}^G is the spectrum extracted in similar way as E_{VC} for the surface treated with the aqueous (NH₄)₂S. Here, the valence band maxima for the sulfur treated sample is 0.26 eV reflected from Fig. 3(b), while the deconvoluted Si2p_{3/2} is located at 99.36 eV. Therefore, the extracted Schottky height is equal to the 1.02 eV which is higher than the pristine untreated Al₂O₃/Si interface (supporting information Figure S1 and S2) core level spectra (0.32 eV).



Fig. 3. (a) The deconvoluted Si 2p Core level spectrum, inset shows the S2p core level spectrum. (b) valence band edge of sulfur passivated Si surface.

3.3. Electrical characteristics of $Al/Al_2O_3/Si$ metal oxide semiconductor device

The main objective of this work was to reduce the density of interface traps between tunneling layer and Si interface. The direct deposition of high-k dielectric causes the formation of unintentional interface between Al_2O_3 and Si, which tends to the charge loss due to oxide defects and contamination. Therefore, the density of interface traps was investigated from the metal-oxide-semiconductor structure, fabricated by depositing Al electrode over the Si/Al₂O₃ pristine and various time treated samples.

Fig. 4 shows the typical high frequency (1 MHz) capacitance voltage (C–V) curves of the pristine and different time treated $Al/Al_2O_3/Si$ MOS device. The curve shows three different distinctive regions namely accumulation, depletion, and inversion. Wherein, the accumulation capacitance was observed to be varied as the function of treatment time. The possible reason behind this change is the formation of sulfur passivation interfacial layer which decreases the conductivity of the surface and forms the fixed number of charges as discussed before.



Fig. 4. Typical C–V spectra of the $Al/Al_2O_3/Si$ MOS device treated for the different time. The average thickness of 10 nm for Al_2O_3 were considered for all samples at the time of measurement.

Further, it also increases the Schottky barrier height as reported by Aibin et al. [24]. However, the further reasons are not clear as not much more work has been reported on this kind of work. Fig. 5(a) and (b) shows the high-resolution cross sectional TEM images of the pristine and 20 s treated samples, where the clear interface formation of ~0.95 nm was seen for the treated sample. The overall of thickness of Al₂O₃ layer is near about ~10.5 \pm 0.2 nm. While no interface is observed in the untreated sample. However, after 30 s it may start to generate defects and causes physicochemical damage to the Si surfaces as confirmed from the AFM images. The density of interface (D_{it}) traps was extracted from the high frequency conductance method by using equation (2) [26].

$$D_{it} = \frac{2.5}{Aq} \left(\frac{G_p}{\omega}\right)_{peak} \tag{2}$$

Where,

$$\frac{G_p}{\omega} = \frac{\omega G_m C_{\alpha x}^2}{G_m^2 + \omega^2 (C_{\alpha x} - C_m)^2}$$
(3)

Here, $\omega = 2\pi f$, C_{ox} is the oxide capacitance calculated in accumulation region from the linear extrapolation method explained by Seo et al. [27], G_m and C_m are the measured conductance and capacitance taken at voltage where capacitance reaches to its maximum value in accumulation region, respectively. Further, A is the electrode area, while q is the electronic charge. The $(Gp/\omega)_{peak}$ represents the highest value of Gp/ω versus frequency graph. Fig. 6 shows the extracted D_{it} as the function of treatment time. The lowest D_{it} of 0.84×10^{12} cm²/eV was observed for the device treated for 20 s. Further, as discussed in the AFM results, the sulfur contents reduce the conductivity of the surface and increases the trap density which shows similar behavior for D_{it} with increase in the treatment time as depicted in Fig. 6.

4. Discussion

It is well known that the HF acid removes the native oxide over the silicon surface while it leaves behind the Si–H bonds over the surface of cleaned sample, which may again react with the oxygen in the air and can form the oxide layer over a long-time exposure during the transfer of sample to ALD chamber [28]. Therefore, the immediate transfer is preferable after cleaning of sample to the next process step. Further, the direct deposition of Al_2O_3 on Si surface creates the negative surface states, which acts as the trapping centers in the non-volatile memory and leads to the charge loss [8,13]. In addition, possibilities of the V_n-H defect cannot be avoided as the H atoms lead to the change in the trap levels and result in the trap centers near the interface [29]. Also, the H



Fig. 5. The high resolution cross sectional TEM images of Al₂O₃/Si interface a) Pristine b) treated for 20 s. The treated sample shows the clear interface of 0.95 nm in between Si and Al₂O₃.



Fig. 6. The D_{it} versus treatment time curve for the Al/Al₂O₃/Si MOS devices. The minimum number of samples was 5–8 for each case.

atoms possess higher formation energy resulted in unstable Si–H bonds over the surface [30]. Therefore, it is important to passivate these dangling bonds over the Si surfaces.

The ammonium sulfide is the redox molecule in which the two sulfur atoms are attached to the single ammonia molecule with weak bonding. This easily loses the sulfur atom when reacted with O–H bonds present over the Si surface and forms the single atomic layer of the sulfur over the surface. The possible mechanisms for this sulfur formation are [18]:

$$S^{2-} + H^+ \to HS^- \tag{4}$$

$$2HS^{-} + 2O_2 \rightarrow S_2 O_3^{2-} + H_2 O \tag{5}$$

The sulfide and hydro-sulfide ions in aqueous $(NH_4)_2S$ solution reacts with the oxygen atom over the surface and effectively passivates the dangling bond present over the Si surfaces by forming the sulfide layer (see Fig. 1). The previous studies reported the addition of ammonium hydroxide into the $(NH_4)_2S$ make it dilute with higher sulfur concentration and reported that the sulfur concentration does not change the oxidation states and provides the clean surface control. However, higher concentrated sulfide solution leads to the etching of Si surfaces even at shorter treatment time.

The positive side of this redox molecule is its simplicity and easy

detachment with ammonia. The sulfur contains 2⁻ charge over it. This charge formation increases the barrier height over the Si surfaces, and this is the main cause behind the reducing the accumulation charge after the sulfur treatment time of 20 s. In inversion mode of the MOS device, the carriers from surface states diffused into the bulk states of the Si, the empty surface states again get filled at the higher applied voltage as shown in Fig. 7 (a). The formation of large barrier prohibits easy injection of the carriers towards the bulk side. In addition, the sulfur treatment reduces the density of interface traps at the Al_2O_3/Si interfaces. This could lead to the charge loss prevention when utilized as the tunnel layer in charge trap type NVM device. The expected band diagrams after 20 s sulfur treatment of MOS device is shown in Fig. 7 (b).

In operation of NVM capacitors, the flat band voltage plays an important role as the memory window was defined by means of the shift in the flat band voltage upon the applied bias. The flat band voltage shift is occurred due to the charges captured in the traps of the trapping layer. The overall voltage shift is the component of the traps at interface between blocking, trapping, and tunneling layer (equation (6)) [31]. Therefore, to achieve higher traps at the interface of trapping and tunneling oxide, it is useful to minimize the interface traps at the semiconductor and tunnel oxide interface.

$$\Delta V_{FB} = \sum \frac{T_{respective \ layer} N_{respective \ layer} \epsilon_{layer}}{\varepsilon_{respective \ Layer} \varepsilon_o}$$
(6)

where, the respective layer could be trapping layer, blocking layer of tunnel layer. Therefore, the ammonium sulfide treated Al_2O_3/Si interfaces could be facile tool to improve the memory window in the charge trap memory device with Al_2O_3 tunnel layer.

5. Conclusion

In summary, the surface and interface properties of the pristine and sulfur passivated Al₂O₃/Si interface were investigated by means of the AFM and XPS measurements in this study. The AFM images reflects the physiochemical damage of Si surfaces with aqueous (NH₄)₂S treatment over 30 s. Therefore, short time treatment is enough to passivate the dangling bonds over the surface. The barrier height found to be improved as extracted from the core level spectra of the Si2p as compare to the pristine sample. The lowest D_{it} of 0.84 × 10¹² cm²/eV traps was extracted from the C–V curves of Al/Al₂O₃/Si MOS devices treated for 20 s with ammonium sulfide. The observed results are beneficial for the use of sulfur passivated Al₂O₃/Si interfaces as the blocking layer in charge trap type NVM devices.



Before Treatment

After Sulphur Treatment

Fig. 7. The Band diagram of Al/Al₂O₃/Si MOS device (a) before treatment (b) after treatment of 20 s with ammonium sulfide. The horizontal black lines define the surface states, while red arrow indicates the diffusion/refilling of the states near interface at higher voltages. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cap.2021.03.019.

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