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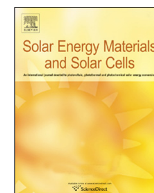

# Enhanced field effect passivation of c-Si surface via introduction of trap centers: Case of hafnium and aluminium oxide bilayer films deposited by thermal ALD

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ABSTRACT

Field effect passivation of crystalline silicon surface is controlled by tailoring the built-in charge in a bilayer dielectric system consisting of hafnium oxide ($HfO_2$) and aluminium oxide ($Al_2O_3$). The effective surface recombination velocity ($S_{eff,\ max}$) ~ 10 cm/s is achieved at intermediate bulk injection levels with thermal ALD deposited $HfO_2$ (top)/$Al_2O_3$ (bottom) bilayer system on n-type silicon with individual layer thickness between 3 and 7 nm. The best realized $S_{eff,max}$ value is lower by a factor of ~ 2.5 with respect to the single $Al_2O_3$ layer of similar thickness deposited under the same experimental conditions. The improved field effect passivation is quantified by enhanced effective charge density for the bilayer system in comparison with the corresponding value for single $Al_2O_3$ layer. The introduction of extra trap centers at the interface of the bilayer system is primarily responsible for the enriched field effect passivation, however, the sequence of the dielectric layers is important.

## 1. Introduction

Electronic passivation of a silicon (Si) surface refers to reduction of electronic states at the surface from $10^{15}$ $eV^{-1}$ $cm^{-2}$ (for bare Si) to levels below $10^{12}$ $ev^{-1}$ $cm^{-2}$ and the surface recombination velocity (SRV) is a measure of passivation quality. To enhance the performance of many semiconductor devices, the SRV is to be minimized. This can be realized by reducing the density of one type of charge carrier (electrons or holes) in the vicinity of the surface and the aerial density of interface states ($D_{it}$) is to be suppressed. The former can be achieved by electrostatically shielding one type of charge carriers by an electric field at the silicon surface. For example, in the case of silicon, an oxide layer over the silicon surface which contains intrinsic charges (commonly referred as "*Fixed*" charges due to their location) of a particular polarity is exploited. The fixed charges alter the density of one type of charges near the silicon interface that result in field effect passivation [1,2]. The latter can, generally, be achieved by deposition of a suitable dielectric/passivating film and/or attachment of a ligand such as atomic hydrogen with the unsaturated bonds at the surface. This is termed as chemical passivation [1,2]. For an efficient surface passivation of silicon solar cells, a high concentration of fixed charge in the deposited dielectric layer and a low density of interface states are required. For this, various dielectric layers such as silicon dioxide, silicon nitride, etc., are commonly used in solar cells [3,4].

During the last decade extensive research on $Al_2O_3$ particularly using atomic layer deposition (ALD) technique has been done and high level of passivation on moderately and heavily doped Si is achieved [5–12]. This has established $Al_2O_3$ as a superior material for passivation of wafer based c-Si solar cells [1–4] mainly because of its intrinsic charge. For example, ~ 23% efficiency solar cells on n-type [13] and ~ 22% on p-type Si [14] with $Al_2O_3$ as a passivation layer have been reported. Further cells exceeding 25% efficiency on n-Si have been realized with tunnel oxide passivated contacts [15]. The existence of charges in ALD deposited $Al_2O_3$ films [5–11] have been attributed to the native point defects on the basis of the first principle calculations [16–19]. In $Al_2O_3$, the oxide charge density depends on the process parameters during layer deposition and also on subsequent post deposition processing conditions [6–8]. Plasma-ALD deposition process, generally, produce higher fixed charge densities as compared to the thermal ALD, presumably due to the influence of highly reactive gas species in the plasma. Post-deposition annealing (at moderate temperatures within 300–450 °C) further enhances the charge density. ALD

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deposited $HfO_2$ is widely used in microelectronics, due to its excellent electrical and optical properties, but its application as a passivation layer has been reported only recently [20–24]. Both positive [20–23] as well as negative [24] fixed charges are observed in $HfO_2$. These charges originate from the native point defects which are energetically stable in their charged state [25–28]. Apart from the defects that create fixed charge density, there are other energetically favourable point defects which are capable of trapping electrons and consequently get charged under external stimuli. These trap centers also contribute to the total oxide charge density and thus in the field effect passivation of silicon surface. It is possible to engineer these native point defects in a dielectric layer adjacent to Si surface [29]. Thus improvement in passivation can be made by manipulating the charge by employing bi- or multi-layer dielectric systems. Recently, introduction of extra trap centers [29–33] or formation of dipole layers at the interface of two dielectric layers have also been reported [34–37]. For example, Jordan et al. [30] have shown enhanced charge density in ALD deposited Si/$Al_2O_3$/$SiO_2$/$Al_2O_3$/Al and Si/$Al_2O_3$/$HfO_2$/$Al_2O_3$/Al structures due to the presence of fixed and trapped charges where capacitance-voltage (C-V) profiling and trap spectroscopy by charge injection and sensing (TSCIS) are used to determine the two types of charge densities. Charge-tailoring and the possibility of a virtually zero-charge passivation layer for Si have been reported for a stack layout of $Al_2O_3$ and interfacial $HfO_2$ or $SiO_2$ layers [31]. Töfflinger et al. [32] have reported charge trapping in plasma enhanced chemical vapour deposited Si/$Al_2O_3$/$SiN_x$/Al structures using constant voltage stress C-V measurement and the hysteresis observed in the data is exploited to determine the charge densities.

Although single layer ALD $Al_2O_3$ can provide a good quality silicon surface passivation, the level of passivation is commonly dependent on the thickness of the oxide layer. For thermal ALD $Al_2O_3$, good passivation is, generally, realized with film thickness more than 10 nm. In the case of multilayers (say with two dielectric layers system), a suitable mechanism can be found for the introduction of right kind of point defects into the band gap of a dielectric layer which would act as trap centers as discussed in [38]. These centers are capable of capturing charges particularly under the influence of external stimuli such as light, temperature and electrical bias, thereby the total oxide charge density is enhanced. Consequently, the passivation quality can be improved while keeping the thickness of dielectric layers within 10 nm. This motivated us to explore the possibility of trap center introduction in a bilayer system consisting of $Al_2O_3$ and $HfO_2$ while the total oxide thickness remains ~ 10 nm. The investigation shows improved surface passivation with an ultrathin (3–7 nm) $HfO_2$ layer (top layer) deposited over (7–3 nm) $Al_2O_3$ (layer adjacent to Si) on n-type Si as compared to the single layer $Al_2O_3$/n-Si. However, the quality of surface passivation is strongly dependent on the stack layout. During the study, flat band voltage ($V_{fb}$), effective oxide charge ($Q_{eff}$) and interface states density ($D_{it}$), are determined by the capacitance-conductance-voltage (C-G-V) measurements carried out under normal (un-stressed) and stressed (electrical bias-stress) conditions. The results under stressed condition provided a clear insight into the trapping phenomena. The quality of field effect passivation of Si surface is estimated by measuring injection level dependent effective minority carrier lifetime ($\tau_{eff}$) from which the surface recombination velocity ($S_{eff}$) is determined.

## 2. Experimental

Single layer of $Al_2O_3$ or $HfO_2$ and bilayers of $HfO_2$/$Al_2O_3$ and $Al_2O_3$/$HfO_2$ are deposited on single crystalline silicon by thermal atomic layer deposition (ALD, Model: R200, M/s Picosun, Finland) at $T_{dep}$ = 300 °C. The choice of $T_{dep}$ is based on our previous studies related with surface passivation using single layer $HfO_2$ or $Al_2O_3$. The films are deposited on 2.5 Ω-cm chemically mechanically polished (100) FZ n-Si (325 ± 10 µm). Tri-methyl aluminium (TMA) and tetrakis ethyl methyl amino hafnium (TEMAHf) are the precursors used for $Al_2O_3$ and $HfO_2$ layers respectively with $H_2O$ as an oxidant. The wafers are cleaned in piranha solution followed by 5% HF dip, quick rinse in DI water and finally $N_2$ blow drying prior to the loading into the ALD deposition chamber. A typical ALD cycle composition is given in Table 1 and the sample details are given in Table 2. After the film deposition, annealing ($T_{anl}$) is done at 400 ± 2 °C in $N_2$ ambient for 105 s and 600 s in a rapid thermal processing system (RTP Model: AS-one 150, M/s Annealsys, France).

**Table 1**
Atomic layer deposition parameters for $Al_2O_3$ and $HfO_2$ film deposition used in the present study.

| Parameter | $Al_2O_3$ | $HfO_2$ |
|---|---|---|
| TMA/TEMAH pulse | 0.1 s | 1.6 s |
| $N_2$ Purge | 6 s | 10 s |
| $H_2O$ Pulse | 0.1 s | 0.1 s |
| $N_2$ Purge | 10 s | 10 s |

**Table 2**
Sample details including the layer(s) structure, their individual ($d_{HfO2}$, $d_{Al2O3}$) and the total ($d_{total}$ = $d_{HfO2}$ + $d_{Al2O3}$) thickness along with number of ALD cycles.

| Sample | Layer structure | ALD cycles | $d_{HfO2}$, $d_{Al2O3}$ (nm) | $d_{total}$ (± 0.2 nm) |
|---|---|---|---|---|
| S1 | $Al_2O_3$/Si | 100 | 0, 11.2 | 11.2 |
| S2 | $HfO_2$/$Al_2O_3$/Si | 30, 70 | 2.8, 7.4 | 10.2 |
| S3 | $HfO_2$/$Al_2O_3$/Si | 50, 50 | 4.8, 5.5 | 10.3 |
| S4 | $HfO_2$/$Al_2O_3$/Si | 70, 30 | 6.4, 3.1 | 9.5 |
| S5 | $HfO_2$/Si | 100 | 9.2, 0 | 9.2 |

Single side oxide deposited samples are used for capacitance-voltage (C-V) and conductance-voltage (G-V) measurements where MIS structure (Al/Oxide(s)/n-Si/Al) is fabricated by depositing 300 nm thick circular aluminium dots of 1 mm diameter over the oxide layer(s) at a pressure of $10^{-6}$ Torr using e-beam evaporation through a shadow mask while covering the entire back silicon surface with 300 nm aluminium layer. For minority carrier lifetime measurements symmetrically passivated samples (oxide(s)/n-Si/oxide(s) without metal contacts) are made with the same oxide thickness on both sides covering the entire surface area.

The oxide layer thickness ($d_{ox}$, where ox = $Al_2O_3$, $HfO_2$ or $Al_2O_3$ +$HfO_2$) is measured using a spectroscopic ellipsometer (Model: M2000U, M/s J.A. Wollam Co. Inc., USA) in rotating compensator configuration. Variable angle spectroscopic ellipsometry (VASE) measurement in the wavelength range of 240–1000 nm is performed on as-deposited and annealed samples. Si-jaw, Cody-Lorentz (C-L) and Tauc-Lorentz (T-L) oscillator functions are used to model Si substrate, $Al_2O_3$ and $HfO_2$ films respectively [M/s J.A. Woollam Software Data Library]. The extracted layer thicknesses are given in Table 2. High frequency capacitance-voltage (C-V) and conductance-voltage (G-V) measurements are performed in parallel mode using impedance/gain phase analyser (Model: 1260, M/s Solartron, UK). The C-V measurements are made in 10 kHz to 1 MHz frequency range with voltage sweep to traverse from inversion to accumulation mode and back where the ac signal is kept at 20 mV to meet the small signal requirement for oxide capacitors. The parameters $V_{fb}$ and $Q_{eff}$ are determined from high frequency C-V data whereas $D_{it}$ is estimated from C-V and G-V curves measured at an intermediate frequency (= 50 kHz). The same parameters are also determined from the C-V data obtained under stressed (electrical bias-stress) conditions where the positive voltage ($V_{stress}$) in + 1 to + 3 V range is applied for different time durations (0–400 s). The minority carrier lifetime is measured by a photo-conductance decay method using Sinton's lifetime tester (Model: WCT-120, M/s Sinton Inc, USA) in the transient mode. The compositional analysis of dielectric layers is done using Rutherford Backscattering Spectroscopy (RBS) which in the case of aluminium oxide revealed 40 and 60 at% of Al and

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