A study of Plasma Atomic layer deposited hafnium oxide thin film for silicon surface passivation: Effect of annealing in hydrogen ambient

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Abstract

In this study, wehave investigated the silicon surface passivation property of Plasma Atomic Layer Deposited (PALD) hafnium oxide (HfOx) thin films. Our results demonstrate that as-deposited HfOx film exhibit poor passivation quality that can be improved by performing post-deposition annealing at 450℃ in hydrogen ambient. Hafnium oxide film (100 ALD cycle) is annealed for different durations in steps of 15 minutes. Measured effective lifetime improves with annealing and capacitance-voltage characteristics provide insight into the change in oxide charges and interface defect density as a function of annealing time. The fixed charges present in the film are ~1012 cm-2 andtherefore field effect passivation is found to be an important passivation mechanism in plasma ALD deposited HfOx films. Dit reduction with annealing in hydrogen ambient shows the importance of annealing in hydrogen which facilitates the attachment of hydrogen atoms to the defect sites present at the silicon surface.

Keywords: Hafnium oxide, Silicon, Plasma Atomic Layer Deposition, Surface passivation

1.Introduction

One of the main focus areas for efficiency gains and cost reductions in industrial crystalline silicon solar cells is the decrease of recombination losses at the crystalline silicon (c-Si) surface. A c-Si solar cell's efficiency is greatly affected by the recombination of photogenerated charge carriers on its surface, particularly when the thickness is less than that of an industrial cell (<180 μm) [1]. Both at the silicon wafer's surface and in the bulk, the recombination of the photogenerated charge carriers is taken into account by the recombination losses. "Surface passivation" refers to the decrease in charge carrier recombination that takes place at the c-Si surface. The surface recombination rate (Us) can be defined as a function of the interface state defect using the Shockley–Read–Hall (SRH) formalism.

Essentially, there are two methods for lowering surface recombination. The S_{n0} and S_{p0} parameters collectively indicate the first step, chemical passivation, which is lowering the rate at which interface states absorb electrons and holes by having fewer states or lower capture probability. Changing their ratio at the surface, ps/ns, will reduce the number of one type of carriers, n_s or p_s, available at the surface. By applying chemical species like hydrogen or laying a dielectric layer, unsaturated or dangling bonds at the c-Si surface are

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saturated, resulting in chemical passivation. Two different methods are used to achieve the second type of passivation. The first is accomplished by introducing an electric field into the semiconductor surface, which changes the concentration of surface carriers. As it isan electric field that permeates the semiconductor surface and alters the surface carrier concentration is responsible for the first. This is known as the surface passivation's field-effect component. A constant charge density in the dielectric film creates the electric field. The second tactic involves the high-concentration in-diffusion of dopants—either carrier type—near the surface. This results in the creation of a near-surface charge carrier gradient [1-3]. For many years, dielectric layers—like thermally generated SiOx, a-Si:H, SiNx, etc.—have been the subject of intensive research and use in silicon surface passivation [2,4]. The atomic layer deposition (ALD) technique has shown great promise in recent years for the deposition of aluminum oxide films and their use as an efficient passivation layer in industrial silicon solar cells [5-7]. For silicon surface passivation, numerous new ALD produced dielectric layers, including TiO_2 [8,9], AZO [10,11], HfO_x, and their stacks [12–14], are also being investigated. In the current work, the plasma ALD process is used to deposit hafnium oxide thin films under ideal film growth conditions. After annealing the hafnium oxide film in a hydrogen atmosphere, an increase in its measured lifetime is seen. With respect to bare wafer circumstances, injection level dependence demonstrates an enhanced minority carrier lifespan. The existence of negative fixed charges is indicated by C-V measurements which may be adjusted by altering the annealing conditions, and the films are suitable for use in silicon solar cells.

2.**Experimental Details**

In the present study, phosphorous doped FZ silicon wafers (100), with resistivity (5±0.2) Ω-cm and thickness (325±25) µm are used. Substrate is cleaned using ultrasonic treatment in deionized water (DI) followed by standard cleaning procedure 'Radio Corporation of America (RCA) standard clean (SC-I and SC-II)' [15]. Afterward, the substrate is rinsed with DI water and then dipped in a 5% HF solution for 2 minutes. The cleaned silicon wafer is loaded into the ALD reaction chamber. Depositions are carried out using a remote plasma ALD system (M/s Picosun Model R200) operating at a temperature of 200°C. For hafnium oxide film deposition, Tetrakis-ethyl methylamino hafnium (TEMAHf,Sigma Aldrich, vapor pressure: 0.01 hPa at 78°C) and oxygen plasma are used as metal precursor and oxidant, respectively. Herein, we have used $25kW$ plasma power for oxygen plasma generation. Due to the low vapor pressure of the TEMAHf precursor, it needs to be heated to realize sufficient vapor pressure for the effective delivery of TEMAHf vapors into the reaction chamber [16].The HfO_x thin films are deposited by repeating ALD cycle 100 times. After the deposition of HfO_x film, post-deposition annealing is carried out in a tubular furnace using a hydrogen generator system (> 99.999% purity, Model: H2PEM-510, M/s Parker Filtration and Separation) in a vertical tube furnace at 450^oC temperatures for different time durations. Here annealing is carried out in steps of 15 min followed by cooling, measurement and further anneal of 15 min is applied. SRV values are derived from the measurement of the minority carrier lifetime using the photo-conductance decay method (Model: WCT-120, Sinton lifetime tester), which allows for the assessment of surface passivation's efficacy. Symmetrically passivated samples are made by depositing the same thickness of hafnium oxide films on both sides of the substrates in order to perform τ_{eff} measurements. The flat band voltage (V_{FB}), fixed charges (Q_F), and interface trap (D_{it}) density are determined through C-V measurements. Metal-insulator-semiconductor (MOS) structures are created by utilizing an e-beam evaporation system to deposit aluminum.

Annealing is done before metal contacts formation, and MIS structure is utilized for C-V measurements by applying an Al polka dot pattern to the film. Here, a potentiostat (Model: Reference 600 Potentiostat/ Galvanostat/ ZRA, M/s Gamry Instruments, Inc., USA) is used to perform C-V measurements on a MOS structure at 1MHz. To meet the small-signal requirement for oxide capacitors, an ac voltage signal of 10 mV is applied in addition to the dc voltage.

3.Results and Discussion

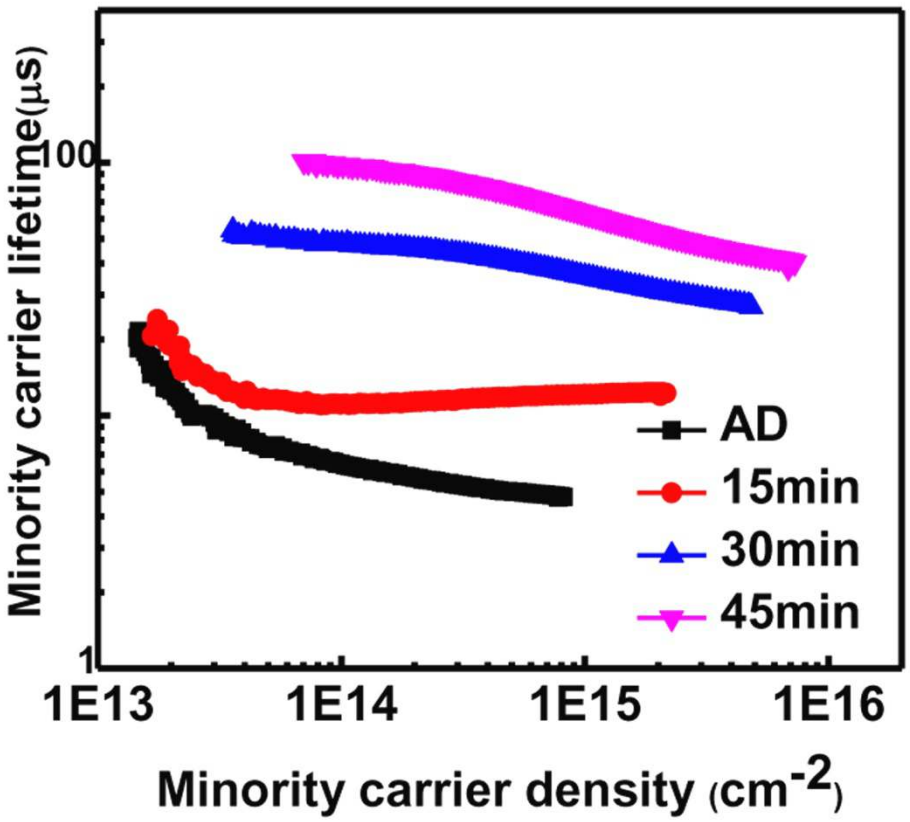

Fig. 1:Change in effective minority carrier lifetime w.r.t. excess minority carrier density s for the sample prepared at 200°C substrate temperature after repeating 100 ALD cycles.

The minority carrier lifetime (τ_{eff}) for as-deposited (AD) and annealed film is plotted against injection level in Fig. 1. The data shows that the passivation quality improves with annealing and lifetime values increased from 6 μs to 81 μs with 45 postdeposition annealing (t_{anl}) at a fixed annealing temperature (T_{anl}=450ºC) in steps of 15 min. Minority carrier lifetime, $\tau_{eff,}$values are given in table 1. The samples are subjected to post deposition annealing (PDA) in hydrogen ambient and their τ_{eff} values as a function of injection level shows an overall improvement in lifetime values over the whole injection level range (Fig. 1).

Table1: Measured parameters of as deposited and annealed samples

Sample	Lifetime value (μs)	D_{it} (x10^{12}) (eV^{-1} cm^{-2})	Q_{eff} (x10^{12}) (cm^{-2})	V_{fb} (V)	ΔV_H (V)
Bare	11.965	-	-	-	-
As-Deposited	6.41	0.123	4.42	2.099	0.831
15 min	14.72	0.0487	0.526	1.729	1.112
30min	52.345	0.062	0.127	0.326	1.631
45min	81.57	2.96	0.989	0.273	1.871

Poor surface passivation quality is achieved for as-deposited films as τ_{eff}<10 μs is achieved. This may be attributed to increased surface roughness originating from the interaction between plasma species and the surface sites as is evident from approximation 2 folds decrease (12 μs to 6 μs at 1E15 cm^{-3}) in the τ_{eff} values with reference to the bare wafer. However, the bare wafer condition is recovered, i.e., the τ_{eff} is regained to the similar level after performing a 15min PDA. Annealing the samples for another 15min improved the τ_{eff} values to approximation 9 folds with respect to AD films. This improvement may be attributed to reduction in SRH recombination losses. The next 15min of annealing further improves the lifetime values to ~13 folds w.r.t. as deposited films.

To understand the passivation mechanism responsible for improved lifetime results, CV and GV measurements were carried out on the prepared MOS structures. Capacitance–voltage (C-V) measurement is commonly used to quantify the quality of the deposited dielectric layer, as well as its interface with the substrate. Figure 2(a) shows the high frequency (1MHz) C–V curves of as-deposited and annealed samples. The C-V sweep is carried from the state of strong inversion to strong accumulation (IA) and back (AI), in order to measure the voltage hysteresis (ΔV_H). The voltage hysteresis i.e., the difference between flat-band voltages corresponding to the forward (IA) and backward (AI) sweeps, marks the presence of mobile charges and charge trapping in the oxide. For AD sample, the CV curves lie in the positive voltage region indicating the presence of negative oxide charges in the pristine films. Furthermore, the voltage hysteresis increases with increase in the annealing time. Performing a post deposition annealing in H_2 ambient causes a significant shift in the C-V curves towards negative voltage direction for all samples.

Additionally, the decrease in the density of negative oxide charges is indicated by the shift in the IA curves towards the negative voltage region as the annealing duration increases. This could be explained by a decrease in the density of point defects that cause negative charge, such as hafnium vacancies and oxygen interstitials [14]. Reverse sweep generation causes hysteresis to form in the curves, suggesting that trap charges are present in the film structure. When charged electrostatically, trap states or defect states shield the charges of the opposite polarity and lessen surface recombination losses. The acceptor type of trap charges is implied by the direction of hysteresis. The density of trap charges rises with increasing annealing duration due to an increase in hysteresis. An increase in the oxide capacitance in the annealed samples indicates that the film quality has improved.

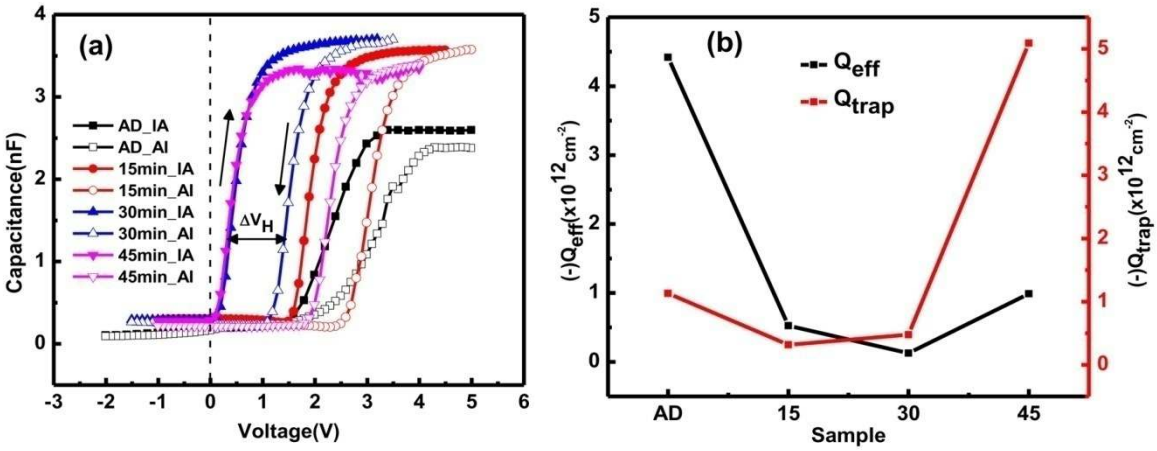

Fig. 2: *(a)High frequency (1MHz)capacitance–voltage curves for as deposited and annealed, films. (b) Effective fixed charges (Q_{eff}) and trap charge density (Q_{trap}) for as-deposited as well as annealed samples.*

This is consistent with our lifetime outcomes. Acceptor (0/-) type trap states are demonstrated to exist in n-Si samples in Fig. 2(a). Fig. 2(b) depicts the effective oxide charge density (Q_{eff}) and the trap charge density (Q_{trap}) for as-deposited and annealed samples. Negative Q_{eff} ($\sim 10^{12} cm^{-2}$)are found to be present in all the samples. As the annealing time increases, D_{it} values also decreases. The interface defect density for HfO_x/n-Si samples was found to be ~ 2 x 10^{12} eV^{-1} cm^{-2}. It is evident from C-V measurements that the field-effect passivation has good contribution in the overall passivation performance of the film. D_{it} values decreases with initial annealing conditions which indicates towards improved chemical passivation [16,17]. D_{it} improvement may be associated with unsaturated dangling bonds reduction by attachment of H-atom at the oxide/silicon interface. 45 min annealing shows sudden increase in D_{it} values and increase in Q_{eff} values also. However there is overall improvement at 45 min annealing conditions reflected in measured effective lifetime values (~13 fold w.r.t. as deposited film). It suggests that field effect and chemical passivation coexist and cooperate in Al_2O_3 surface passivation. Surface passivation quality is a trade-off between chemical and field effect, with the optimal passivation (maximum τeff or minimum SRV) potentially achieved when the two quantizing parameters, Q_F and D_{it}, reach their highest and lowest values, respectively. These films can be appropriately tailored by managing the annealing conditions and process, which will aid in the activation of the right kind of fixed and trap charges that are present at the silicon/film interface. These films hold significant promise for use in silicon solar cells and other sophisticated solar cell configurations.

4.Conclusion

The study presents the investigation of surface passivation property of Plasma Atomic Layer deposited (PALD) hafnium oxide (HfO_x) thin film. These films are important for realizing good quality surface passivation in silicon solar cells devices.Thesurface passivation is realised by post-deposition annealing of hafnium oxide films (100 ALD cycles) in hydrogen ambient. CV investigation gives an insight towards the improved passivation behaviour under annealing in hydrogen ambient in terms of Q_{eff} and D_{it} values representing the field and chemical passivation component respectively.

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