

Light-induced degradation of native silicon oxide–silicon nitride bilayer passivated silicon

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This article reports on the effects of aging and light induced degradation of the passivation quality of the interface formed by the crystalline silicon surface and facile grown oxide—SiN_x bilayer. Stable passivation quality against aging and light soaking require thicker oxide layers grown at room temperature, suggesting that thicker oxide layers mitigate the migration of hydrogen from the interface and hence the defect density under light soaking. In addition, the stoichiometry of the PECVD SiN_x influences the stability of the passivation quality. Specifically, the rate of degradation in passivation quality is observed to correlate with the optical absorption properties of SiN_x; the higher the optical absorption the greater the degradation in passivation. This result is attributed to neutralization of the K⁺ centers in SiN_x. Passivation layers with SiN_x deposited with 5% silane in nitrogen to ammonia gas ratio of 7 and facile grown native oxide thickness of ~1 nm resulted in the most stable passivation scheme within the scope of the reported experiments. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933037>]

Low temperature processed passivation schemes for the crystalline silicon (cSi) surface have received significant research attention owing to their potential applicability for various high-efficiency low-cost ultra-thin silicon photovoltaic cell concepts. In this context, passivation materials exhibiting low optical absorption losses and stability against solar illumination are of particular interest *vis-à-vis* attaining time-stable high photo-current densities.

Plasma enhanced chemical vapour deposited (PECVD) SiN_x, by itself or in combination with other dielectric or semiconductor layers, has been reported as a potential low temperature passivation layer for the crystalline silicon surface.¹ Stoichiometry of PECVD SiN_x can be controlled during the deposition process by changing the precursor gas mixture composition in order to take advantage of optical and physical properties of the dielectric.² Silicon-rich silicon nitride has been reported to provide better passivation quality than nitrogen-rich silicon nitride. Contrarily, high values of fixed positive charge density at the cSi-SiN_x interface for such SiN_x layers due to its high trapped charge density can lead to parasitic shunting that reduces the short circuit photocurrent density.³ A thin layer of thermally grown SiO₂⁴ or low temperature PECVD silicon oxide⁵ layer has been deposited between the cSi surface and SiN_x layer in order to reduce or remove this parasitic shunting effect.

A low-temperature passivation scheme comprising facile grown native oxide (aSiO_x) and PECVD silicon nitride (SiN_x) bilayer has recently been reported to provide high quality surface passivation of crystalline silicon.⁶ The native oxide based passivation scheme has also been used to fabricate Back Amorphous-Crystalline silicon Heterojunction

(BACH) solar cell⁷ and Laterally Inherently Thin (LIT) heterojunction solar cell.⁸

Photostability and, in particular, light-induced degradation (LID) is of importance in the operation of silicon heterojunction photovoltaic cell. Metastability of hydrogenated amorphous silicon (aSi:H) due to the Staebler-Wronski effect⁹ degrades the passivation quality by as much as 40% in terms of the effective minority carrier lifetime for intrinsic aSi:H (*i*-aSi:H) passivated cSi surfaces. However, *n* and *p* doped aSi:H used in silicon heterojunction cells have been reported to prevent degradation of the passivation quality,¹⁰ which in turn precludes any deterioration in the performance of the aSi:H-cSi heterojunction solar cell.¹¹ Stable cell performance of aSi:H and PECVD SiN_x dual layer passivated silicon heterojunction cells has also been reported¹² albeit the effect of light soaking on the passivation quality of the dual layer passivation scheme have not been examined.

This article reports on the effect of light soaking on the passivation quality of the native silicon oxide-PECVD silicon nitride (aSiO_x-SiN_x)–crystalline silicon interface. More importantly, the role of the thin native oxide layer (~1 nm thick) in maintaining the passivation quality is investigated in this study. Changes in trapped charge density, *Q*_S, and surface defect density, *N*_S, at the cSi and aSiO_x-SiN_x bilayer interface as a result of light soaking are analyzed to reveal the importance of the thin native oxide layer. Further, the article examines the influence of the PECVD SiN_x film stoichiometry on light-induced degradation of the interface. An optimum stoichiometry is proposed from a LID perspective.

Double-side polished *n*-type (100) FZ wafers with resistivity of 1–5 Ω-cm were used in this passivation study. Standard RCA cleaned¹³ wafers were kept in a cleanroom environment to grow native oxide at room temperature, and subsequently, silicon nitride layer was deposited using the Oxford PlasmaLab 100 direct rf PECVD system. The details of the native oxide growth and PECVD deposition conditions

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have been reported elsewhere.⁶ The duration of the growth of facile grown native oxide layers prior to the deposition of SiN_x was varied from 20 min to 80×10^3 min in order to study the effect of oxide thickness. Precursor gases for silicon nitride depositions consisted of NH_3 , which was held constant at a flow rate of 50 sccm, and 5% silane in nitrogen, the flow rate of which was varied from 200 sccm to 650 sccm. We define the precursor gas ratio (GR) as the quotient of $(\text{SiH}_4 + \text{N}_2)$ to NH_3 flow rates following Schmidt and Kerr.² The effect of varying the GR from 4 to 13 was explored for samples where the facile grown native oxide growth time (OGT) was 80×10^3 min.

Thicknesses and dielectric properties, namely, refractive indices and extinction coefficients of the SiN_x films, were measured using a SOPRA *GES5E* spectroscopic ellipsometer. The excess carrier density (ECD) dependent effective minority carrier lifetime, τ_{eff} , was measured using a Sinton Silicon Lifetime Tester WCT-120 system. Transient methods were used to measure injection-dependent τ_{eff} of the sample. Oxide thicknesses, measured using Parallel Angle Resolved X-ray Photoelectron spectroscopy (PARXPS), as a function of oxide growth time have been reported previously.⁶

The surface charge density, Q_S , and defect density, N_S , are inferred from the ECD dependent S_{eff} and simple closed form (SCF) dangling bond interface recombination model.^{14,15} The inferred Q_S and N_S values provide a systematic measure for the study reported herein.

Light-induced degradation experiments were carried out on a SiO_x and PECVD SiN_x passivated crystalline silicon samples two years after the samples were originally prepared. During this time, the samples were stored at typical room ambient conditions. Delayed light soaking experiments allowed investigation of the aging effect on the passivation quality of the a SiO_x - SiN_x passivation scheme. The light-induced degradation study was carried out by exposing the samples under one sun AM 1.5 solar irradiation. The surface passivation quality, determined via the minority carrier lifetime, was monitored as a function of the cumulative exposure time for each side, i.e., a cumulative time of t indicates that each side (front and back) was exposed to AM 1.5 light for t . Initially, both sides of a given sample were exposed to 1 sun irradiation alternatively over 10^3 min time steps up to a cumulative light exposure of 5×10^3 min per side. Then,

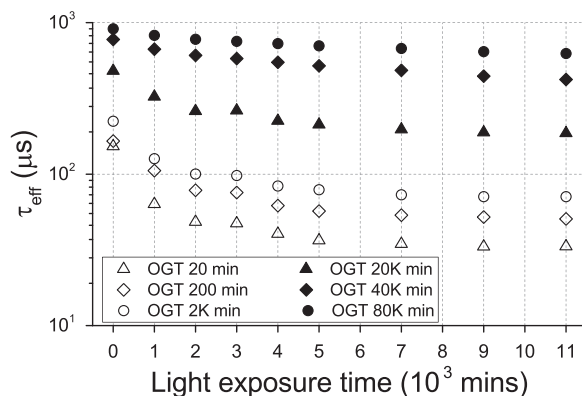


FIG. 1. τ_{eff} of the a SiO_x -PECVD SiN_x bilayer passivated cSi samples as a function of cumulative exposure to AM 1.5 light.

the time step was increased to 2×10^3 min per side. The total cumulative light exposure was 11×10^3 min per side.

Fig. 1 shows the crystalline silicon surface passivation quality in terms of the effective minority carrier lifetime, τ_{eff} , as a function of the cumulative light exposure for samples with varying native oxide layer growth times. SiN_x layers for these samples were deposited at a gas ratio of 7. Crystalline silicon samples with oxide layers grown for longer periods of time not only exhibit better initial surface passivation quality (higher values of τ_{eff}) but are also more stable against light soaking. Fig. 2 shows τ_{eff} as a function of cumulative light exposure for samples with SiN_x deposited at different gas ratios; this set of samples have native oxide layers with a high OGT of 80×10^3 min. Passivation quality is more stable for samples having nitrogen-rich SiN_x , which were deposited using lower values of gas ratio, compared to samples with silicon-rich SiN_x , which were deposited at high gas ratios. For silicon rich SiN_x samples, passivation quality is observed to degrade significantly with light soaking. Further, the rate of degradation in the passivation quality (τ_{eff}) becomes more severe with increased gas ratio. Close observation of the τ_{eff} profiles indicates that during the early period of light soaking the rate of LID is greater than that during the later period of light soaking; this is clearly illustrated in the inset.

Fig. 3 summarizes the effect of aging and light induced degradation on the passivation quality for oxide layers grown with different OGT and with SiN_x layers deposited at GR of 7. All samples exhibit a slight drop in τ_{eff} values following two years of aging and samples with lower OGTs generally show the largest drop in the effective minority carrier lifetime. The light soaked samples exhibit a much greater degradation in τ_{eff} albeit the trends are similar. That is, thicker oxides layers (longer OGTs) appear to preserve the surface passivation quality more effectively under light soaking; this is clearly seen in the inset which shows the relative change in τ_{eff} due to light soaking as a function of the OGT.

Estimated interfacial trapped charge density, Q_S , and dangling bond density, N_S , were inferred from the interface recombination model using the excess carrier dependent

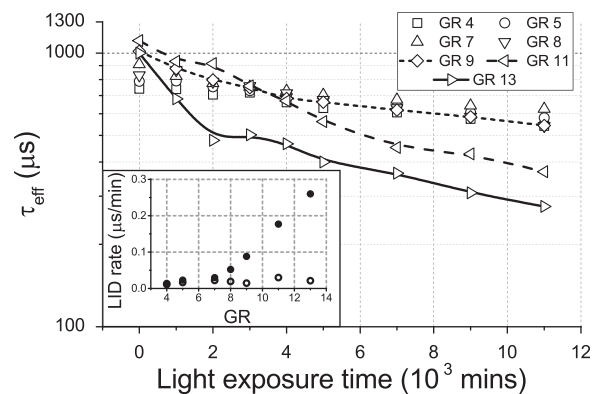


FIG. 2. τ_{eff} of the a SiO_x -PECVD SiN_x bilayer passivated cSi samples as a function of cumulative exposure to AM 1.5 light. Oxide growth time of the native a SiO_x was 80×10^3 min followed by the deposition of PECVD SiN_x layers which were deposited at gas ratios varying from 4 to 13. The inset shows the fast degradation rate (\bullet) which occurs during the early period ($0-3 \times 10^3$ min) of light exposure and the slow degradation rate (\circ) which occurs in the later period ($5 \times 10^3-11 \times 10^3$ min) of light exposure.

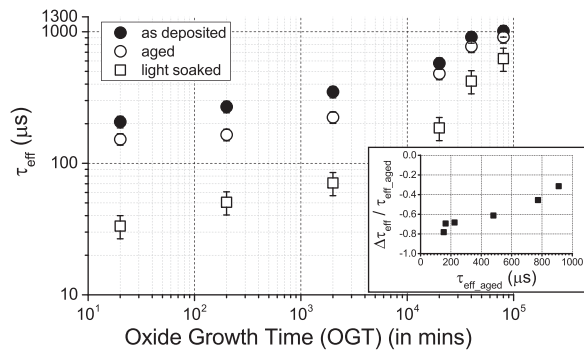


FIG. 3. τ_{eff} as a function of OGT time for the aSiO_x layers during different stages of the study, i.e., as deposited, aged, and light soaked. The inset shows the relative change in τ_{eff} due to light soaking as a function of the oxide growth time.

lifetime values corresponding to the samples presented in Fig. 3. The inferred Q_S and N_S values as a function of the native oxide thickness for the as-deposited, aged, and light-soaked samples are shown in Fig. 4. In all instances [as-deposited, aged (2 years), and light-soaked (11×10^3 min each side)], the samples exhibit increased interfacial trapped charge density and decreased interfacial defect density such that the smallest changes in Q_S and N_S are observed for the thickest native oxide layer. Both the decrease in Q_S and the increase in N_S contribute to the decrease in the observed effective minority carrier lifetime with OGT or native oxide thickness presented earlier. The progressive reduction in the decrease in Q_S with increasing native oxide layer thickness indicates the corresponding decrease in tunneling of carriers from the bulk silicon to the PECVD SiN_x layers, thus signifying the thicker native oxide layers ability to more effectively preserve the trapped positive charges in the silicon nitride dielectric layer. It is interesting to observe that the Q_S values are essentially constant for native oxide layer thicknesses of up to approximately 5 Å, suggesting that the oxide layer becomes a progressively better tunneling barrier for thicknesses exceeding this value. With regard to changes in N_S , the progressive reduction in the increase in N_S with increasing native oxide layer thickness indicate the corresponding increase in the stability of the interface against defect formation—both during aging and light soaking. Given the passivation role of hydrogen at the native oxide—silicon interface, the thicker oxide layers serve to reduce the probability of hydrogen migration from the silicon-oxide interface notwithstanding the production of photogenerated carriers in silicon, and thus mitigate the increase in interfacial defect density with light soaking.¹⁶ Mahtani *et al.*¹⁰ have

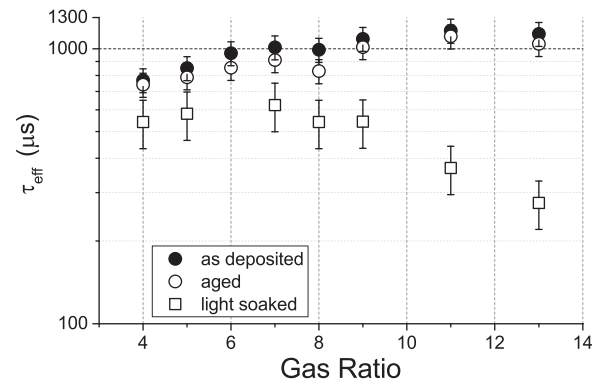


FIG. 5. τ_{eff} as a function of GR used for the PECVD SiN_x layer deposition for as-deposited, aged, and light soaked samples. Oxide growth time for the native oxide was 80×10^3 min for these samples.

reported similar observations of metastability at the amorphous-crystalline silicon heterojunction interface.

The influence of the composition of the SiN_x films as determined by the varying gas ratio, GR, on passivation quality is shown in Fig. 5. The native oxide layers for all these samples were grown for 80×10^3 min. For the as-deposited samples τ_{eff} is higher for SiN_x deposited at higher values of GR. A small to negligible degradation in passivation quality is observed due to aging for 2 years, and the change in τ_{eff} appears to be independent of the GR used for the PECVD SiN_x deposition. In contrast, light soaking affects the passivation quality markedly. Further, samples with SiN_x films above GR of 8 show significantly larger degradation in passivation quality than those below GR of 8. Films grown with large gas ratios have silicon rich SiN_x composition while films grown with small gas ratios have nitrogen rich SiN_x composition. To better understand the effect of light soaking and the film composition, the optical properties of the SiN_x films were measured, and the optical absorption, in terms of percentage of the radiant intensity of AM1.5 illumination, is plotted as a function of the GR in Fig. 6. The silicon rich SiN_x films exhibit up to four-fold greater absorption than nitrogen rich SiN_x films. The higher optical absorption correlates with the overall observed degradation in passivation quality, and, in particular, to the increase in N_S and decrease in Q_S . Previously reported values of optical bandgap and refractive indices at different stoichiometric composition of SiN_x also indicate low absorption for nitrogen-rich SiN_x.¹⁷

With regard to the differences in the observed rates of degradation in passivation quality under illumination, we note that photo-generation of carriers due to optical

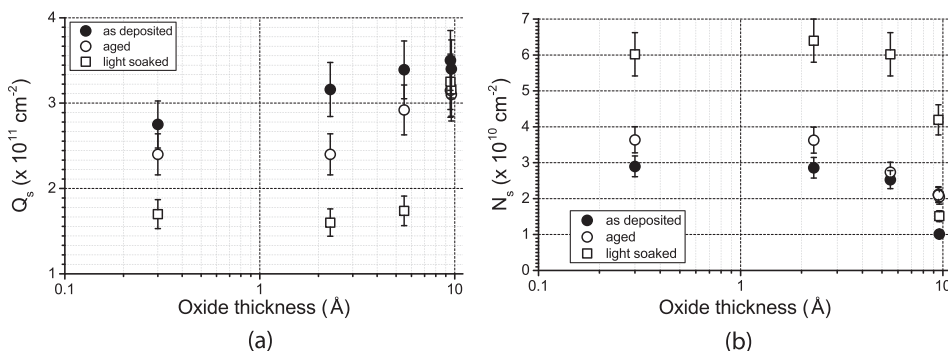


FIG. 4. (a) Inferred interfacial trapped charge density, Q_S and (b) inferred interfacial defect density, N_S , as a function of native SiO_x thickness during different stages of the study, i.e., as deposited, aged, and light soaked. PECVD SiN_x layers for these samples were deposited at a gas ratio of 7.

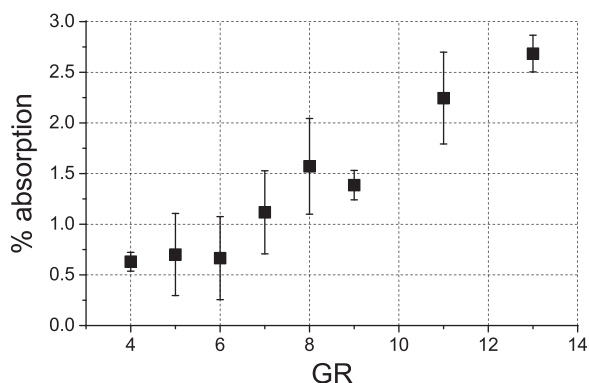


FIG. 6. Absorption in the top PECVD SiN_x layers as a function of the gas ratio, GR, used for the deposition of the SiN_x film.

absorption in the n -type silicon absorber can lead to injection of majority electrons into the SiN_x by way of tunneling through the native oxide. The injected electrons will recombine with the trapped charges in the SiN_x and thus neutralize the K^+ -centers. This in turn leads to a reduction in the trapped charge density in SiN_x and hence a reduction in the field-effect passivation with exposure time. The presence of optical absorption in silicon rich SiN_x , in contrast to nitrogen rich SiN_x , gives rise to a fast rate of degradation in passivation initially and thereafter a slow rate of degradation in passivation. We attribute the fast rate of degradation to the photogeneration within SiN_x , which leads to additional neutralization of the K^+ -centers. Further, it is worth noting that tunneling of carriers and diffusion of hydrogen through the oxide layer will proceed at room temperature^{18,19} albeit at a much slower rate and accordingly some degradation in passivation quality due to aging is deemed viable.

In summary, this article reports on the influence of facile grown native oxide thickness on light induced degradation of the crystalline silicon surface passivated using the aSiO_x - SiN_x dual layers. Thicker native oxide layers exhibit higher passivation quality and greater stability against aging and light soaking. The composition of PECVD SiN_x films also influences the passivation quality and stability against light degradation. Silicon rich SiN_x films, while exhibiting better passivation quality in as-deposited bilayer films, suffer the greatest level of light-induced degradation, which correlates with increased light absorption in these films (compared to nitrogen rich SiN_x films). Native oxide-silicon nitride passivation layers with PECVD SiN_x films deposited at a gas ratio of 7 and native oxide thickness of 1 nm exhibit the most stable passivation scheme within the scope of this study. The results of this study suggest thicker native oxide layers, for example, grown at room temperature using an ozone ambient, has the potential to yield a more stable interface passivation against light soaking.

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