The effects of RTP processing on recombination and electron transfer in Cz-Si wafers passivated with hydrogenated silicon-nitride thin films

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This study investigates the electronic passivation of p-type Czochralski silicon wafers using SiNx:H nitride layers treated by rapid thermal processing (RTP) at peak temperatures ranging from 600 to 900 °C. The impact of RTP process on reflectivity (R) and carrier lifetime (τ_{eff}) was analysed. The results show that SiNx:H passivation is the most effective at peak temperature of 700 °C. Additionally, exposing the wafers to a soaking step in hydrofluoric acid (HF) accelerated the degradation of τ_{eff} for samples treated at 700 °C. Further, raising the peak temperature above 700 °C had a negative impact on the quality of the SiNx:H layer, but was effective in increasing the volume passivation. The study highlights the importance of controlling temperature and processing and using hydrogenated silicon nitride films to reduce the thermal budget of RTP processing in the manufacture of silicon solar cells.

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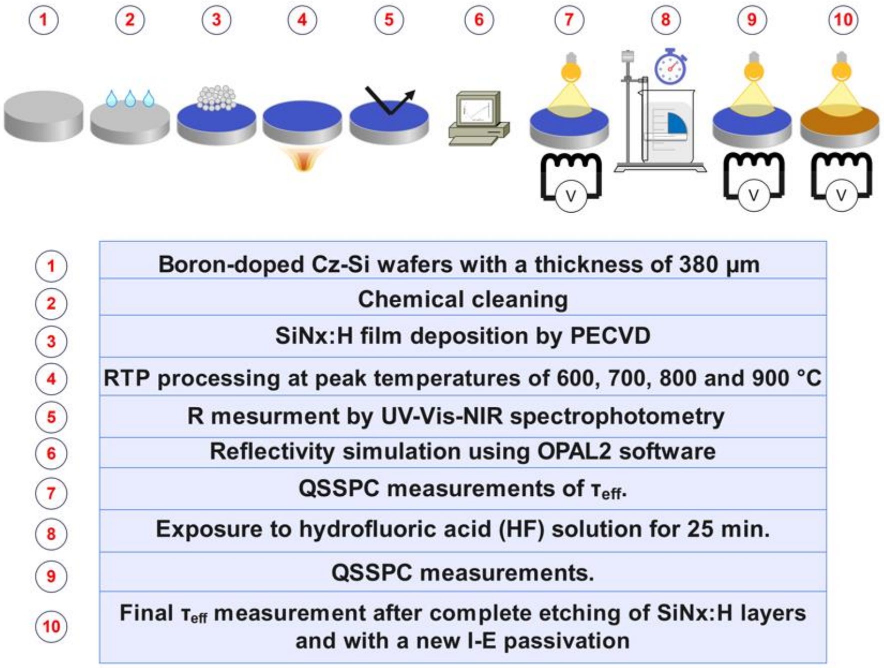
Keywords: Rapid thermal processing (RTP), Silicon nitride passivation, Carrier lifetime

1. Introduction

Rapid Thermal Processing (RTP) has emerged as an effective technique in manufacturing complex electronic components due to its ability to significantly reduce the time required for the manufacturing process [1-3]. This enables high levels of accuracy and repeatability in production. In particular, RTP finds new applications in the photovoltaic industry, where it is effective in reducing or eliminating the light and enhanced temperature-induced degradation (LeTID) phenomena that degrade the efficiency of solar cells during operation [4]. The performance of the RTP technique in this area depends on the process parameters and the structural composition of the solar cell. Because of its optical and electrical properties, the silicon nitride SiNx:H thin film is a key component used as an antireflective and passivation layer to reduce the surface recombination of charge carriers in solar cells [5,6]. Silicon nitride remains the subject of substantial research and development activities due to its attractive physical, chemical, electrical, and biological properties [7,8]. As a result, SiN_x thin films continues to be included in a multitude of traditional applications in the integrated circuitry (IC), photovoltaic, and optoelectronic fields. The usage of SiN_x is also being considered for a myriad of new technologies including quantum dots and nanocrystals, nonlinear telecommunication waveguides, tunable light-emitters for optical sensors and devices, and biological and biochemical materials for medical applications [9]. Therefore, understanding the underlying physics of the interactions between the SiNx:H layer and the silicon wafer is essential to optimize the RTP process and to eliminate defects in Si-based solar cells' fabrication. With this in mind, we have performed a microstructural-level investigation of as-deposited and annealed silicon c-Si wafers with an SiNx:H thin film to study changes in their optical-electrical properties as a function of annealing conditions. Our results show a strong dependence of the reflectance coefficient on the microstructural organization of the SiNx:H thin films after annealing. Additionally, we investigated the variation of the surface recombination velocity by exposing the samples to a hydrofluoric acid (HF) solution for 25 min, during which their carrier lifetime was monitored by QSSPC. Our results show that controlling the microstructure of the SiNx:H thin films by varying the annealing conditions can be used to improve the passivation layer and enhance the performance of the semiconductors, even when the initial bulk carrier lifetime is low.

2. Experimental

For this study, boron-doped Cz-Si wafers with a thickness of 380 μm and resistivity in the range of 1.5 to 3 Ω.cm with an interstitial oxygen concentration of $6 \cdot 10^{17} cm^{-3}$ were used. To remove any saw damage, they were etched with a NaOH solution, resulting in a thickness of ~ 250 μm, and then cleaned with a standard RCA solution. An 80 nm layer of silicon nitride (SiNx:H) was deposited on both sides of the wafers using a PECVD system (SEMCO). The samples were cycled at a selection of temperatures in an RTP furnace (AccuThermo AW610). Subsequently, the reflectivity (R) and carrier lifetime (τ_{eff}) were measured by UV-Vis-NIR spectrophotometry (Cary 500) and quasi-steady-state photoconductivity QSSPC (Sinton-120), respectively. Finally, the samples were exposed to a 5% hydrofluoric acid (HF) solution for 25 minutes and the carrier lifetime was monitored with QSSPC. The general processing steps and measurements used in this study are summarized in Fig. 1.



① Boron-doped Cz-Si wafers with a thickness of 380 µm

② Chemical cleaning

③ SiNx:H film deposition by PECVD

④ RTP processing at peak temperatures of 600, 700, 800 and 900 °C

⑤ R mesurment by UV-Vis-NIR spectrophotometry

⑥ Reflectivity simulation using OPAL2 software

⑦ QSSPC measurements of τ_{eff}.

⑧ Exposure to hydrofluoric acid (HF) solution for 25 min.

⑨ QSSPC measurements.

⑩ Final τ_{eff} measurement after complete etching of SiNx:H layers and with a new I-E passivation

Fig. 1. The process flow chart (color online)

3. Results and discussions

The reflectance of silicon wafers with silicon nitride (SiNx:H) layers after a rapid thermal processing (RTP) step can be altered by the temperature of the RTP. It is well-known that the reflectance of SiNx:H is contingent on the processing conditions and temperature [10,11]. In the region of 600 °C, the reflectivity of SiNx:H may remain relatively low since it has not gone through major structural alterations. With an increase in temperature, the reflectivity of SiNx:H may become more intense due to shifts in optical qualities such as the refractive index, absorption coefficient and scattering coefficient [10–12]. These shifts may be caused by a range of variables such as modifications to the SiNx:H density and microstructure [13,14], the formation of flaws or other optical irregularities [15]. To obtain more information, OPAL2 software [16] was used to simulate the reflectivity of the silicon wafer and match it with the experimental data (Fig. 2). Compared to conventional modelling software, the OPAL2 calculator offers a simplified approach to the calculation of reflection, absorption and transmission (RAT). In standard software, RAT is calculated for each ray using Fresnel's equations at each interaction, resulting in extended calculation times. In contrast, OPAL 2 is based on the principle that all rays share a common path and reflect from identical facets at identical angles, resulting in a uniform RAT [17]. By grouping rays according to their paths, the program reduces the resolution of Fresnel's equations to those for each path, significantly accelerating the simulation time. The OPAL 2 approach integrates three key components: ray tracing, thin film optics, and equivalent current calculations.

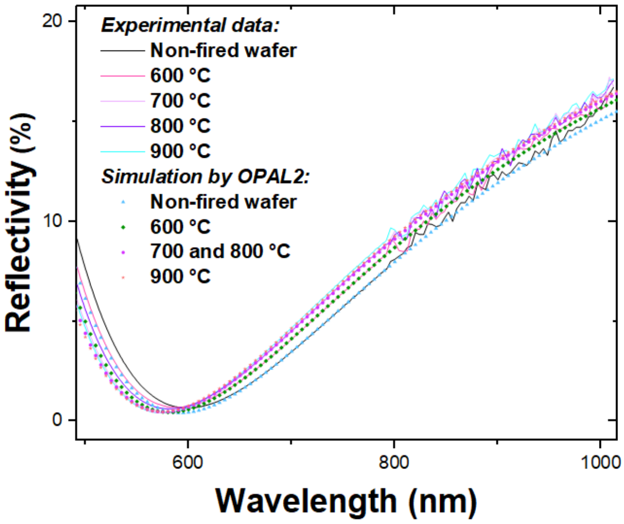


Fig. 2. The reflectivity results after (RTP) process at different peak temperatures: the lines represent the experimental results and discontinued lines are the simulations obtained using the OPAL2 software (color online)

The thicknesses of SiNx:H layers used in the different R-curves were taken from the simulation and displayed in Fig. 3, verifying the effect of the RTP process on the SiNx:H passivation layer.

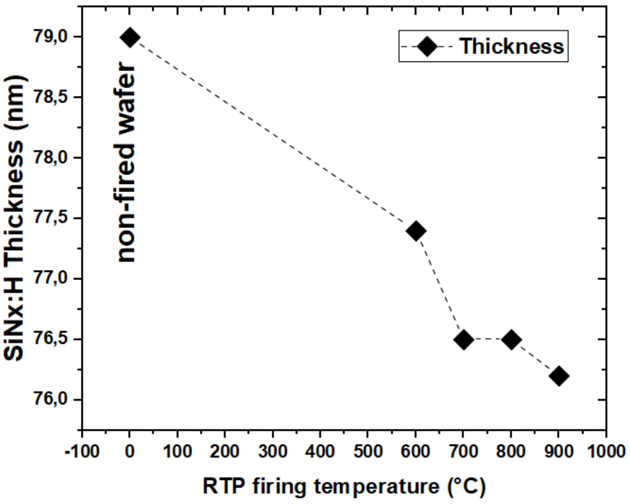


Fig. 3. The variation of SiNx:H thickness with RTP firing temperature

According to Fig. 4, the highest value of the carrier lifetime was found to be around 700 °C. This implies that RTP is the most efficient at this temperature to achieve the greatest surface lifetime. Additionally, at 700 °C, the SiNx:H films have reached a balance between the densification that enhances its passivation performance and the low activation energy formation of harmful defects, which can impair its performance. Furthermore, the results align with the thickness shredding as a function of temperature attained by the OPAL2 software. Moreover, when the temperature increases to 800 °C, the carrier lifetime diminishes to 160 µs, showing that the RTP procedure could initiate the formation of negative defects in the SiNx:H layer. Additionally, for temperatures higher than 800 °C, the carrier lifetime decreases drastically, signifying that the SiNx:H layer is severely damaged at high temperatures due to factors like hydrogen exodiffusion or cracks formation in the SiNx:H layers [15].

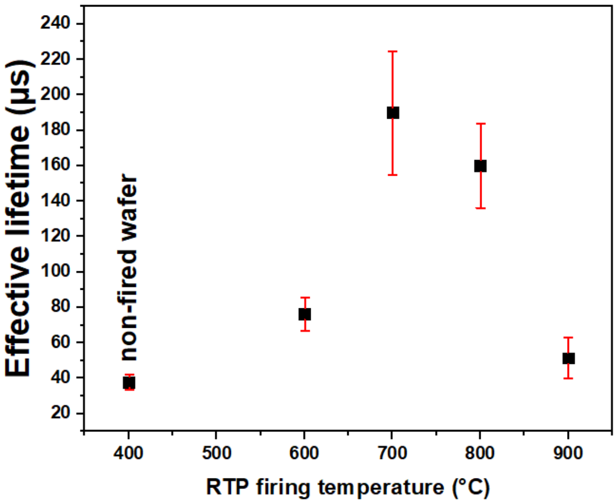


Fig. 4. Variation of carrier lifetime with RTP firing temperature

Fig. 5 provides an insight into the behaviour of the SiNx:H layers with respect to temperature variations.

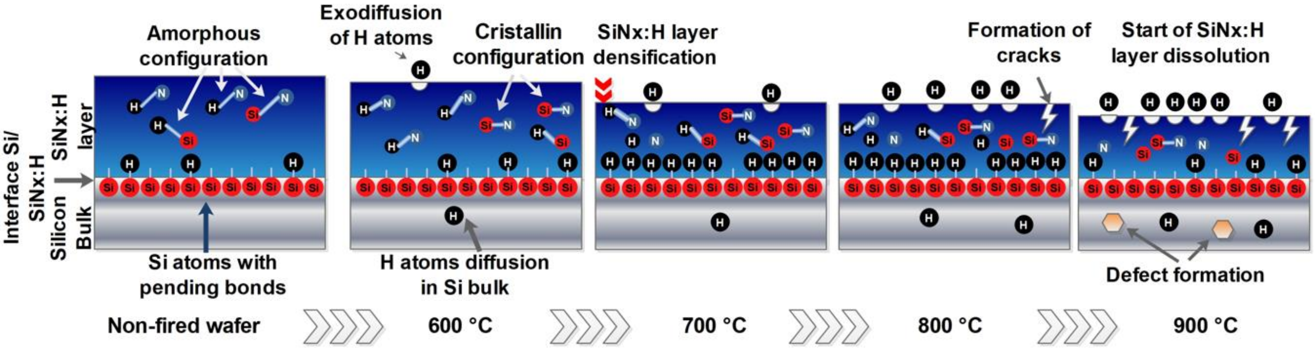


Fig. 5. Diagram showing the RTP temperature peak's effect on the behaviour of SiNx:H films deposited on silicon wafers (color online)

The Rapid Thermal Processing (RTP) technique is a critical determinant with a significant impact on the surface and bulk lifetime of semiconductor wafers. To ensure the highest quality of semiconductor products, it is imperative to thoroughly investigate this issue. In this context, a rigorous experiment was conducted to monitor the carrier lifetime of samples (τ_{eff}) exposed to a 5% hydrofluoric acid (HF) solution for 25 minutes using QSSPC. Dekkers et al [18] have presented a similar method to investigate the degradation of the open circuit voltage (V_{oc}) with the etching time of an HF-deposited layer on mc-Si solar cells. However, in our approach, we directly measure the variation of τ_{eff} with the time of immersion in HF. Also, τ_{eff} depends on directly to surface passivation quality [19,20]. Additionally, we deliberately chose wafers instead of complete solar cells, since the latter include more layers and parameters that could affect the silicon substrate. Fig. 6 presents the changes in the carrier lifetime resulting from exposure to hydrofluoric acid (HF) solution, which vary depending on the level of exposure and the RTP temperature peaks. The samples treated at peaks of temperature 600 and 700 °C show a total degradation after 600 s in HF solution, while those treated with temperature peaks of 800 and 900 °C exhibited complete degradation after 1200 seconds. These results can be attributed to the densification of the passivation layers at 800 and 900 °C and hydrogen diffusion in a silicon substrate and enhance the bulk passivation [21], which effectively prevents surface passivation degradation at these temperatures. Another possibility is the gettering effect of the SiNx:H layer optimization with firing temperature [22,23].

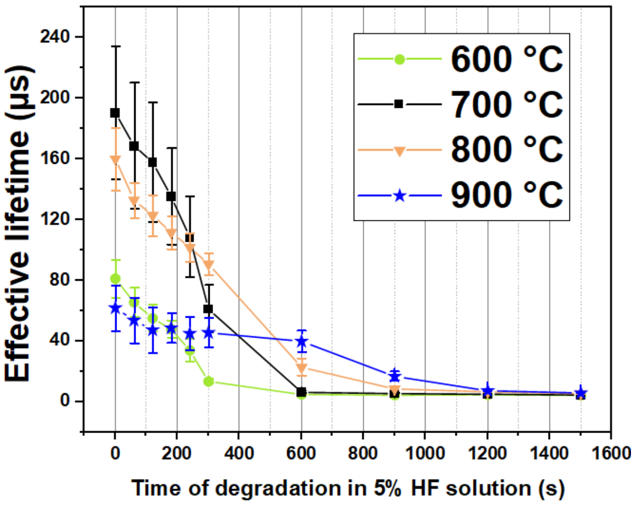


Fig. 6. Carrier lifetime variations as a function of exposure to hydrofluoric acid (HF) solution for different RTP temperature peaks (color online)

After complete removal of the SiNx:H layer, the samples were subjected to quasi-steady-state photoconductivity (QSSPC) testing to determine their carrier lifetimes (Fig. 7). Additionally, a passivation process using iodine ethanol was performed to eliminate surface recombination effects and to mitigate any electrical variations in wafer volume resulting from the RTP process. The results of the experiment showed that the carrier lifetime values were lowest for the samples treated at 600 °C and 700 °C. In contrast, the samples treated at 800 °C exhibited higher carrier lifetimes compared to those treated at 700 °C. These observations could be attributed to the hydrogen passivation effect of SiNx:H on the volume of silicon wafers, which is enhanced by annealing in the RTP furnace, and visible even at a high temperature peak of 900 °C.

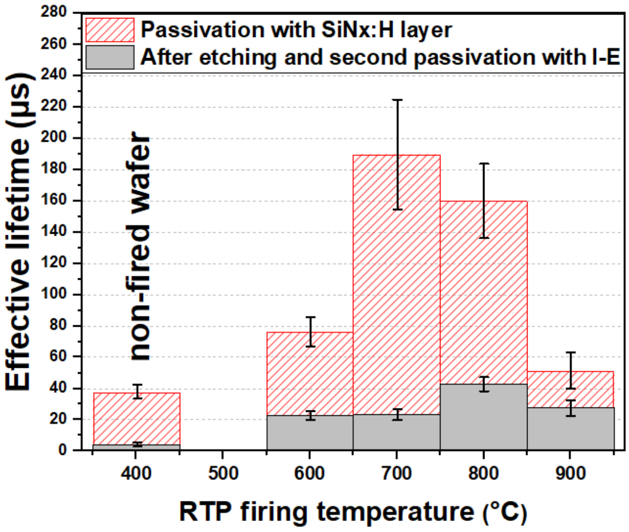


Fig. 7. Comparison of effective lifetime immediately after RTP annealing and following complete removal of the SiNx:H layer (color online)

4. Conclusions

This study has investigated the effects of rapid thermal processing (RTP) on the reflectivity and carrier lifetime of silicon wafers coated with a silicon nitride (SiNx:H) layer. Our results indicate that the reflectivity of the SiNx:H layer depends on the temperature and processing conditions used during the RTP process. At temperatures below 600 °C, the SiNx:H layer exhibits low reflectivity. However, as the temperature increases, the reflectivity of the SiNx:H layer increases due to changes in its optical properties. The carrier lifetime of the silicon wafer is also significantly affected by the RTP process. The optimum temperature for achieving maximum surface lifetime has been found to be around 700 °C. At very high temperatures, the carrier lifetime decreases significantly due to several factors, including hydrogen exodiffusion from the SiNx:H layer and acceleration of the defect formation rate in the silicon bulk [24]. The complete removal of the SiNx:H layers form the samples treated at peaks 800 and 900 °C revealed clearly the bulk passivation effect. Finally, the RTP temperature process is a key factor that has a significant impact on both the surface and bulk lifetime of silicon wafers. Therefore, rigorous investigation and optimization of the RTP and SiNx:H process is essential to ensure the production of high-quality solar cells.

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