Suppression of the thermal quenching of photoluminescence in irradiated silicon heterojunction solar cells

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We report on the decrease in photoluminescence (PL) intensity with the increase of the sample temperature (thermal quenching) in crystalline silicon and its suppression after ion irradiation. The crystalline silicon surface was passivated with intrinsic and doped hydrogenated amorphous silicon (a-Si:H) layer stacks as for making silicon heterojunction solar cell precursors. Low energy argon ion irradiation, in the range between 5 and 17 keV, was used for controlled defect formation either in the thin a-Si:H top layer or at the interface with the crystalline silicon beneath. The irradiation defects introduce radiative recombination centers in the a-Si:H as can be measured from PL at low temperature. Moreover, the irradiation and annealing result in a strong modification of the thermal quenching of the PL intensity up to 500 K, showing evidence for the strong reduction of thermally activated non-radiative recombinations at the amorphous-crystalline interface. This result can have implications in the field of crystalline silicon surface passivation.

1 Introduction Silicon heterojunction (SHJ) solar cell technology holds great promise for high-efficiency solar cell production on an industrial scale. So-called HIT (Heterojunction with Intrinsic Thin layer) solar cells have reached record conversion efficiencies of 25.6% in interdigitated back contact geometry [1], and show above 20% energy conversion efficiency at the industrial production level. The appropriate combination of crystalline silicon with intrinsic and doped hydrogenated amorphous silicon (a-Si:H) thin layers (typical thickness ~10 nm) leads to a photovoltaic device with a rich physical behavior. In particular, the record values for the open-circuit voltage ($V_{oc}$) up to 750 mV are related to the excellent crystalline silicon surface passivation by hydrogenation of the silicon dangling bonds, leading to a reduction of the interface defect density. Several groups have shown that interface passivation represents a challenge for SHJ solar cell improvement and may be addressed using hydrogen plasma treatment for example [2–4]. Also, one critical aspect regarding surface passivation, in the frame of silicon heterojunction solar cells, is its degradation with annealing at temperatures above 200 °C [5, 6]. Here we use ion irradiation to modify the a-Si:H thin layer and its interface with the crystalline silicon substrate. The competition between radiative and non-radiative recombination processes is probed using photoluminescence spectroscopy. Photoluminescence from amorphous silicon/crystalline silicon heterostructures has been proven to be an efficient tool for estimating wafer surface defects and interface recombinations [7, 8]. We have previously shown that a fine tuning of ion irradiation parameters at low energy (10–17 keV) and low fluences ($10^{10}$–$10^{14}$ cm$^{-2}$) may lead to controlled degradation of the solar cell where one can correlate lifetime and PL intensity decrease with a given interface defect density [9]. We study here the PL as a function of the temperature, and provide evidence for a strong modification of the photoluminescence thermal quenching after ion irradiation and annealing of the a-Si:H thin film.

2 Experimental We used high quality float zone phosphorus-doped c-Si(100) wafers, about 280 µm thick, as a substrate for thin film deposition. The 4th wafers were first
cleaned for 30 s in a solution of 5% diluted hydrofluoric (HF) acid, which allows for native oxide removal. The wafers were then loaded into a plasma-enhanced chemical vapor deposition (PECVD) reactor operating at a RF frequency of 13.36 MHz. The samples were maintained at a temperature ~200 °C during deposition. Intrinsic hydrogenated amorphous silicon layers (i) a-Si:H were coated on both faces of the wafer (21 nm on top face and 45 nm on back face). Top faces were further coated with either n type or p type hydrogenated amorphous silicon. For such thickness of the i-layer, the PL emission does not depend on the doping type of the top amorphous silicon layer. Thin film thicknesses were determined by modeling the spectroscopic ellipsometry measurements performed on the samples. After a-Si:H deposition, the samples were cut into four pieces for implantation at CSNSM using the IRMA implanter [10]. Argon ion irradiation was performed with an energy in the range of 5–17 keV and fluences between 10^{12} and 10^{15} cm^{-2}. The implantations were performed at room temperature with ion currents below 2 μA cm^{-2} over a typical swept surface of 28 cm² (homogeneous implantation of one fourth of wafer). After irradiation, the samples were annealed for 30 min in N₂–H₂ gas mixtures. Effective carrier lifetimes were measured before and after irradiation by using a Sinton Consulting WCT-120 tester in transient mode. The photoluminescence was measured in reflection geometry at 45° using an argon laser (λ = 488 nm) at a power of 20 mW as an excitation source, and a spectrometer TRIAX320 from Horiba equipped with a liquid nitrogen cooled InGaAs photodiode detector. For these measurements, samples of 10 × 5 mm² were glued with silver paste in an optical closed-cycle cryostat from ARS Instruments equipped with two quartz windows. The PL data were corrected from the instrument response function as measured using a halogen lamp with a known spectrum corrected from the instrument response function as obtained from the SRIM simulation.

3 Results and discussion

3.1 Defect profile due to ion irradiation
The profile of displaced atoms has been calculated using the SRIM simulation program [11]. The mean projected range for the argon ions is 11.6, 15.5, and 23.2 nm for ion implantation energies of 5, 10, and 17 keV, respectively, while straggles also increases with energy from 5 to 10 nm. The depth distribution of displaced atoms was determined using the detailed calculation with full damage cascade in the SRIM program. As can be seen in Fig. 1, at 5 keV ion energy, damages are located in the top amorphous layer. At this energy, the estimated sputtering yield is about 0.87 atoms·ion^{-1}, resulting in a negligible sputtering of only one monolayer at the highest fluence used here \(10^{15} \text{cm}^{-2}\). At 10 keV, as can be seen from Fig. 1, the damages are located in the amorphous layer down to a depth of about 40 nm. The defect concentration per ion at the amorphous/crystalline interface is about 100 times less with 10 keV as what is obtained at an energy of 17 keV, so that we reach a comparable level of interface defects for an irradiation with a fluence 100 times higher, i.e., 10 keV and \(10^{14} \text{ions} \cdot \text{cm}^{-2}\) and 17 keV and \(10^{15} \text{ions} \cdot \text{cm}^{-2}\) introduce about the same defect concentration at the a/c interface. At an energy of 10 keV and a fluence of \(10^{14} \text{cm}^{-2}\) the concentration of displaced atoms is about \(1.2 \times 10^{22} \text{cm}^{-3}\) (about 25 at.%) at the profile maximum, i.e., at a depth of about 10 nm. The vacancy concentration at the amorphous-crystalline interface, which corresponds to the argon ions end-of-range, is estimated to be about \(3 \times 10^{14} \text{cm}^{-2}\) as compared to the initial interface state density usually considered at about some \(10^{16} \text{cm}^{-2}\). As presented in Defresne et al. [9], such an irradiation lowers the effective carrier lifetime from about 4 ms down to 100 μs for an injection corresponding to an excess carrier density of \(10^{15} \text{cm}^{-3}\). Interestingly, when the irradiation is performed at 5 keV and \(10^{15} \text{ions} \cdot \text{cm}^{-2}\) the effective carrier lifetime is not changed, as only the top a-Si:H layer is affected by the irradiation. In that case, every atom is moved twice at the profile maximum, corresponding to 2 dpa (displacement per atom) and the amorphous/crystalline interface is not reached by the ions.

3.2 Low temperature photoluminescence
The irradiation introduces defect levels in the band gap of amorphous silicon that give rise to radiative recombination mechanisms. We observe two broad contributions (at 1.2 and 1.4 eV) at low temperature (10 K), as shown in Fig. 2. These contributions are quenched when the temperature rises above 100 K. They indicate two main recombination paths that may be associated to different defect configurations. As the energies involved (1.2 and 1.4 eV) are rather high, one can attribute these emissions to tail-to-tail recombinations due to structural disorder introduced by the ion irradiation, instead of dangling bonds, expected at low energy (about 0.8 eV) [12]. Such a low energy region was not explored in the present measurements because the InGaAs detector did not allow accessing this energy range. After annealing at 300 °C (573 K), the higher energy PL contribution vanishes, indicating that we have annealed out the corresponding defects, while the PL at ~1.2 eV
decreases but is still present, which is rather unexpected for such a metastable structure as a-Si:H.

3.3 Thermal quenching of photoluminescence

Let us focus on the PL from the crystalline silicon wafer. Firstly, we present in Fig. 3 the temperature dependence of the PL from the as-deposited sample in the range 10–250 K (a) and 300–500 K (b). At the lowest temperature (10 K), we observe in the PL spectrum a main sharp peak centered at 1.1 eV related to the free exciton recombination assisted with transverse optical phonon. At this temperature the energy gap is about 1.165 eV. We observe in the spectrum, with a much smaller intensity, the transverse acoustic assisted free exciton recombination at about 1.14 eV, as well as other multi-phonon assisted recombinations at lower energy (about 1.04 eV). As the temperature increases, the main peak shifts to lower energies and broadens as the band gap narrows and the density of states for electrons and holes broadens. The PL intensity can be described through the spontaneous radiative recombination rate per energy interval \( d_r^{sp}(\hbar\nu) \) of electrons and holes via band–band transitions by

\[
d_r^{sp}(\hbar\nu, T) = B(\hbar\nu, T)n_en_h(d(\hbar\nu)),
\]

with \( n_e \) and \( n_h \) the electron and hole concentrations, and \( B(\hbar\nu, T) \) the spectral radiative recombination coefficient as a function of the photon energy \( \hbar\nu \) and of temperature \( T \) [13]. The rate of spontaneous emission in excited crystalline silicon is also described by the generalized Kirchhoff’s law that allows to model the PL spectra and obtain an estimation of quasi-Fermi level splitting [14] as well as interface defect densities [8].

The temperature dependence of the PL from crystalline silicon was measured and analyzed in detail by Trupke et al. [13] in the range 77–300 K, where the absorption coefficient of c-Si was inferred from the PL data over more than 20 decades and where the radiative recombination coefficient \( B(T) \) (in Eq. (1)) was found to strongly decrease with increasing temperature.

Considering the irradiated samples, we studied the temperature dependence of the PL after annealing at 300 °C (573 K) under \( N_2–H_2 \) gas, in order to separate the effect of annealing and PL quenching. To begin with, let us first consider the PL intensity at room temperature. As, we have shown in Defresne et al. [9], the irradiation at high enough energy lowers the PL intensity together with the effective carrier lifetime. Indeed when the argon ions used for the irradiation reach the amorphous–crystalline interface, we can observe a strong PL intensity decrease. For instance after irradiation at 10 keV with a fluence of \( 10^{14} \) ions cm\(^{-2} \) or 17 keV with a fluence of \( 10^{15} \) ions cm\(^{-2} \), we observed that the PL intensity is decreased by a factor about 100 while the carrier lifetime is decreased at the same time from about 4 ms down to 100 \( \mu \)s. However, after annealing at 300 °C we recover a PL intensity on the same order of magnitude as the initial sample together with a good lifetime (manuscript under preparation). The irradiation at lower energy (5 keV \( 10^{15} \) ions cm\(^{-2} \)), at which the argon ions do not reach the crystal, shows only little effect on the PL intensity which stays on the same order of magnitude. We show now in Fig. 4 the temperature dependence of the PL from the sample irradiated at 10 keV and \( 10^{14} \) ions cm\(^{-2} \).
and annealed at 300°C. The temperature dependence of the spectra is presented in the range 8–200 K (a) and 300–500 K (b). In the low temperature range (a), the broadening and shift to lower energy of the spectra agrees with the observation on the non-irradiated sample. However, in the high temperature range 300–500 K (b) the sample shows a clear modification of the PL evolution.

This change in the PL spectra with temperature is emphasized in Fig. 5 where the spectra measured at 300 and 500 K on both, irradiated and non-irradiated samples, are plotted together. One can observe a strong decrease (quenching) of the PL for the non-irradiated sample when the temperature is increased from 300 to 500 K. On the contrary, the PL spectra of the irradiated sample shows almost no quenching, but a shift of the spectra.

Figure 6 shows the temperature dependence of the integrated PL for the irradiated samples (5, 10, and 17 keV) together with the non-irradiated one. The integrated PL intensities were normalized to 1 at the maximum value at 50 K. The non-irradiated sample shows two regions, between 50 and 200 K and for temperatures above 200 K, where the intensity drops with different slopes. Interestingly, this result was not reported before and shows a different behavior as that observed with an oxide passivation layer [15]. Indeed, the temperature dependence of the integrated PL intensity was discussed by Trupke et al. [15], showing a maximum at $T = 130$ K due to a competition between enhanced surface recombination (decreased lifetime) and increased radiative recombination coefficient at low temperature. This maximum has been shown to occur between 150 and 200 K in the frame of efficient silicon light-emitting diodes [16]. In our study, the samples have a different passivation, with hydrogenated amorphous silicon instead of silicon dioxide, which may explain the shift of the integral PL maximum to lower temperature (50 K). This temperature where the PL intensity is maximum is not affected by irradiation. However, the two-step behavior is more pronounced after irradiation and annealing where the integral PL intensity is seen to decrease between 50 and 200 K as for the non-irradiated sample, while it stays...
constant or even shows a slight increase when the temperature rises above 200 K. In that case the surface passivation has been modified in such a way that the PL quenching has been suppressed in the range 200–500 K. In this range, and following Trupke et al. [13], the radiative recombination coefficient \( B(T) \) decreases with temperature, which should lead to the lowering of the PL intensity, as observed with the non irradiated sample. Thus, some other mechanism, as increased surface passivation, should act to the benefit of PL emission to explain such a modified behavior. We could gain some deeper understanding of the phenomena with the measurement of the temperature dependence of carrier lifetime in the range 200–500 K, for instance with modulated PL [17, 18]. We also reported in Fig. 6 the integral PL temperature dependence for the sample irradiated at 5 keV and \( 10^{15} \) ions \( \cdot \) cm\(^{-2} \). As mentioned, in that case the ions do not reach the amorphous/ crystalline interface. We do not observe the suppression of PL quenching, indicating that the ions must reach the interface for inducing the beneficial structural reorganisation. Also, this sample was not annealed, which will be further studied to exclude any possible annealing effect over the PL quenching behavior.

4 Conclusions Argon ion irradiation of heterojunction solar cell precursors introduces structural disorder in a-Si:H leading to tail-to-tail radiative recombinations as observed with low-temperature PL. The radiative recombination through irradiation induced defect levels in a-Si:H was still present even after annealing at 300 °C. Moreover, the PL intensity quenching between 200 and 500 K was shown to be cancelled by the irradiation and annealing of the top hydrogenated amorphous silicon passivating layer, for irradiation conditions where the ions reach the amorphous-crystalline interface. The lowering of the radiative recombination coefficient must be compensated by some other mechanism to explain this result. We assume that this compensating mechanism is intimately related to surface passivation as the carrier lifetime is dominated by thermally activated non-radiative recombinations at the amorphous-crystalline interface. Interestingly, the irradiation and annealing process allows to stabilize the PL intensity. We can conclude that the absence of thermal quenching for the PL in the irradiated and annealed samples, associated with a similar level of passivation as in the initial samples (similar PL intensity at room temperature), indicates that the passivation itself must be more robust for temperatures higher than room temperature, at least up to 500 K. As a matter of perspective, it would be interesting to have access to the carrier lifetime as a function of temperature for the different samples to confirm this indication of increased robustness. These results are relevant in the field of silicon heterojunction photovoltaic solar cells where some improvements may be related to better tuning of interface passivation. Ion irradiation appears to be an interesting option for near-surface modification and improved passivation of amorphous hydrogenated silicon/crystalline silicon interfaces.

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