Impurity gettering by silicon nitride films: kinetics, mechanisms and simulation

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Introduction

Metallic impurities are both commonly encountered and harmful to the operation of silicon-based photovoltaic devices [1]. Gettering mitigates the harmful impacts of the metallic impurities on the performance of the devices [2].

It has been reported that plasma-enhanced chemical vapor deposited (PECVD) silicon nitride (SiN_x) films, which are commonly used as surface passivation layers and anti-reflection coatings in silicon (Si) solar cells, also induce impurity gettering effects at elevated temperatures [3]–[6]. To better estimate the gettering effect during cell fabrication and to optimise the gettering process, a better understanding of the gettering kinetics and mechanisms must be achieved.

It was reported by Liu et al. that a hydrogen-rich SiN_x film from a laboratory-scale PECVD reactor getters iron (Fe) impurities from the Si wafer bulk via a segregation mechanism, at least at high temperatures, where gettering takes place despite the solid solubility of Fe in Si exceeding the dissolved Fe concentration [4]. However, it is unclear whether segregation is the main gettering mechanism at low temperatures where metal impurities are supersaturated and precipitation is, in principle, possible as well. A uniformly distributed Fe within the bulk of the SiN_x films was previously observed and this supports the segregation gettering mechanism [4]. However later studies [5], [6] reported the aggregation of metals at the SiN_x/Si interface, which complicates the understanding of the gettering mechanism.

This study aims to investigate the mechanisms underlying the gettering of Fe by SiN_x films deposited from PECVD. The kinetics and activation energy of the gettering process will be studied.

Experimental details

Boron-doped float-zone (FZ) Si wafers with a resistivity of 2.5 Ωcm and thickness of 300±10 µm were used in this study. The wafers were intentionally contaminated with Fe introduced into the Si wafer bulk via ion implantation and annealing. The samples with bulk Fe concentrations of 1×10^{14} cm^{-3} and 6×10^{12} cm^{-3} were used in this study.

SiN_x films were deposited on both sides of the Si wafers. SiN_x was deposited using either a laboratory-scale static Roth&Rau AK-400 microwave-radiofrequency PECVD, or an industrial inline MAiA XS PECVD system from Meyer Burger.

The Fe-contaminated Si wafers with different SiN_x films were subjected to cumulative anneals to construct the bulk Fe-reduction kinetics. Effective minority carrier lifetime curves were measured by a photoconductance-based lifetime tester [7]. The interstitial iron (Fe_i) concentrations in the Si wafer bulk were determined from the effective lifetimes before and after Fe-B pair dissociation via strong illumination [8]. Error bars in Fe_i data were estimated by assuming a 5% uncertainty in lifetime measurements.

Results and Discussion

Figure 1 presents the Fe-reduction kinetics (i.e. gettering kinetics) of the samples with two different initial bulk Fe concentrations (10^{14} cm^{-3} and 6×10^{12} cm^{-3}) and with the same laboratory PECVD SiN_x films, annealed at 400°C. The figure clearly indicates that both samples yield very similar gettering kinetics, as can be seen from the parallel curves. Steady state is clearly observed after a sufficiently long annealing time. These results confirm that gettering at a low temperature (400°C) is mainly through a segregation mechanism.

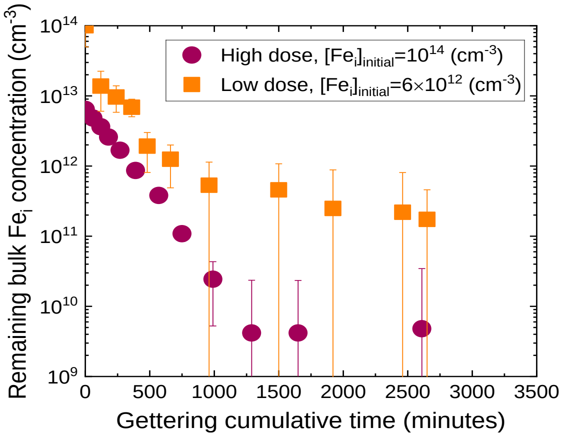

Figure 1. Fe-reduction kinetics at 400°C of samples with two different initial bulk Fe concentrations and the same SiN_x films (from a laboratory-PECVD).

Figure 2 shows the gettering kinetics of samples coated with either the laboratory-scale PECVD SiN_x films or the industrial-scale PECVD SiN_x. Similar shapes of the kinetics curves are observed, but with different gettering rates and steady state levels. The resemblance indicates that similar mechanisms are behind the gettering reaction of different silicon nitride films.

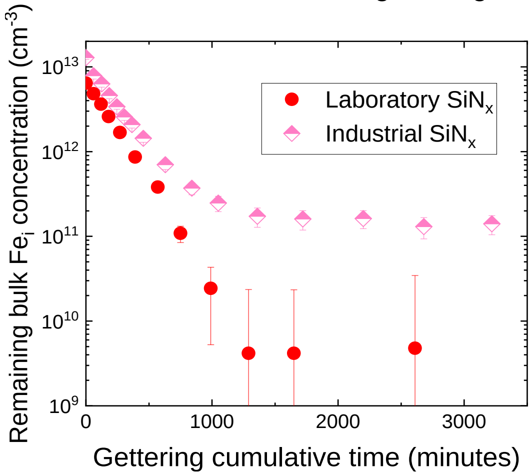

Figure 2. Fe-reduction kinetics at 400°C from two different SiN_x films (one from a laboratory-PECVD [red], and the other from an industrial-PECVD [pink]).

As can be seen from Figures 1 and 2, gettering steady state is achieved over a sufficiently long anneal time. The final gettered Fe concentration at steady state to the initial bulk Fe concentration reflects the gettering capability of the SiN_x films. An Arrhenius plot of this steady-state Fe concentration ratio as a function of temperature enables an estimation of the activation energy for the segregation gettering process. An example is shown in Figure 3 for a laboratory PECVD SiN_x film. The Arrhenius fit estimates an activation energy E_a of 0.9±0.1 eV for the studied laboratory-PECVD SiN_x.

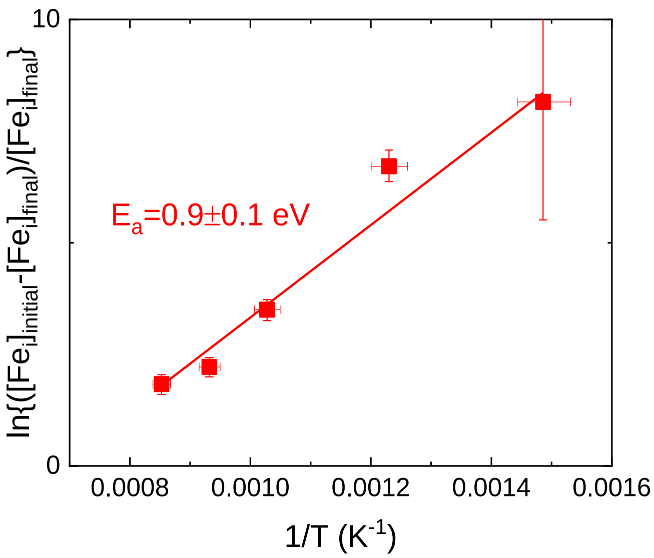

Figure 3. Fe concentration ratios at segregation steady state as a function of temperature for the studied laboratory-PECVD SiN_x film.

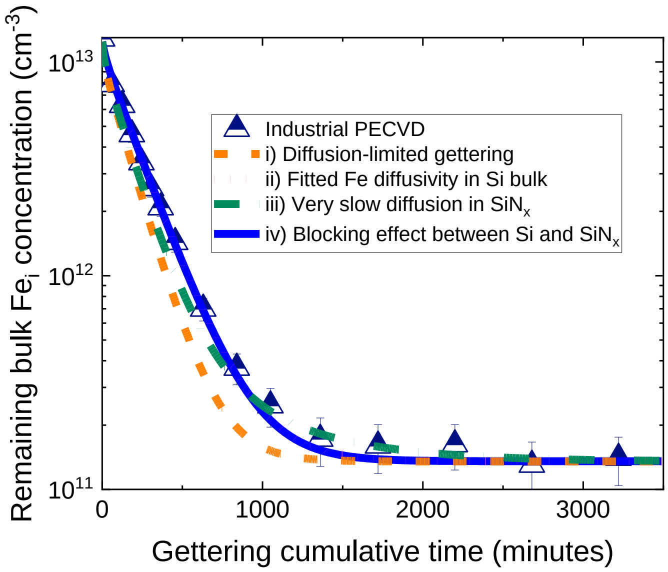

Figure 4. Experimental and simulated gettering kinetics of an industrial PECVD SiN_x film, with different simulation assumptions.

As can be observed in Figure 3, different SiN_x films have different gettering kinetics. Simulation was carried out to model the segregation gettering kinetics, based on different assumptions about the impurity transport in the silicon wafer bulk, through the Si/SiN_x interface, and in the SiN_x films. A numerical algorithm to solve the diffusion equations was used [9],[10]. The following assumptions were proposed: i) Fe diffuses in the silicon wafer bulk according to the reported diffusivity in Si, and the diffusivity in SiN_x is reduced by the same factor as the segregation coefficient of SiN_x (the same approach as was used in modelling phosphorus diffusion gettering); ii) the diffusivity of Fe in the silicon bulk was varied to fit the experimental data; iii) Fe diffuses very slowly in SiN_x, with a diffusivity that is even smaller than the one reduced by the segregation coefficient (as is used in Assumption i); and iv) there is a blocking layer between silicon and the silicon nitride gettering layer.
It can be seen from Figure 4 that the industrial PECVD SiN_x kinetics differs from the diffusion-limited case (i). As a result, the fitted diffusivity of Fe in Si (ii) needs to be much smaller than the reported values. Although this assumption (ii) produces a good fitting to the data, it requires varying the Fe diffusivity in Si at the same temperature (400°C) in order to fit the experimental kinetics of different SiN_x films, which seems less likely.

As shown in Figure 4, assuming a much reduced diffusivity of Fe in SiN_x (iii) results in a gettering kinetics that is initially fast (diffusion-limited gettering) and then slows down due to slow impurity diffusion in SiN_x. This obviously does not fit the experimental data. The gettering kinetics of different SiN_x films can also be well described by introducing a blocking layer between Si and SiN_x, which hinders the transport of Fe into SiN_x (iv), as shown in Figure 4. This blocking layer may arise from unintentional oxidation of the silicon surfaces prior to SiN_x deposition, or the growth of a SiN_x layer that is of a different composition to the bulk of the SiN_x film. This seems to be a more reasonable explanation than varying the Fe diffusivity in Si at the same temperature for different samples.

Conclusion

By studying the SiN_x gettering kinetics of Fe-contaminated Si wafers at 400°C, gettering of Fe by SiN_x films is confirmed to occur through a segregation mechanism at low temperatures. This conclusion, coupled with the finding from a previous study [4], suggests that Fe is gettered by SiN_x films via a segregation mechanism over a wide temperature range of 400°C–900°C. The activation energy of the segregation gettering process is estimated to be 0.9±0.1 eV for the studied PECVD SiN_x film. Simulation of the gettering kinetics suggests that there may be a blocking effect for the transport of iron impurity from the silicon wafer bulk to the silicon nitride gettering layer.

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