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

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Abstract—The mechanisms behind the gettering effect of silicon nitride films for removing iron impurities in silicon are investigated in this study. The silicon nitride films are from plasma-enhanced chemical vapor deposition (PECVD). By monitoring the iron reduction kinetics in the silicon wafer bulk during cumulative anneals, it is found that silicon nitride gettering takes place mainly via a segregation mechanism with an activation energy of 0.9±0.1 eV for the investigated PECVD silicon nitride film.

Keywords—gettering, iron, segregation, silicon nitride, activation energy.

I. 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 (SiNx) 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 SiNx 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 SiNx films was previously observed and this supports the segregation gettering mechanism [4]. However later studies [5], [6] reported the aggregation of metals at the SiNx/Si interface, which complicates the understanding of the gettering mechanism.

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

II. 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 $10^{14}$ cm$^{-3}$ and $6\times10^{12}$ cm$^{-3}$ were used in this study.

SiNx films were deposited on both sides of the Si wafers. SiNx 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 SiNx 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.

III. RESULTS AND DISCUSSION

A. Gettering mechanism

Fig 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 $6\times10^{12}$ cm$^{-3}$) and with the same laboratory PECVD SiNx 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.

![Fig. 1. Fe-reduction kinetics at 400°C of samples with two different initial bulk Fe concentrations and the same SiNx films from a laboratory-PECVD.](image-url)
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. A detailed discussion and modelling of the different gettering kinetics can be found in an upcoming journal publication.

![Graph showing Fe-reduction kinetics at 400°C from two different SiN films](image)

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

### B. Steady state and activation energy for segregation

As can be seen from Figs 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 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 Fig 3 for a laboratory PECVD SiN film. The Arrhenius fit estimates an activation energy $E_a$ of $0.9 \pm 0.1$ eV for the studied laboratory-PECVD SiN.

![Graph showing Arrhenius plot with a line for Ea=0.9±0.1 eV](image)

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

### IV. 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 $0.9\pm0.1$ eV for the studied PECVD SiN$_x$ film.

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