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# The influence of nitrogen concentration gradients on the structural properties of silicon/silicon nitride passivation interfaces in solar cells

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The effects of an interface gradient in nitrogen concentration on a number of important properties of amorphous hydrogenated silicon nitride / crystalline silicon (a-SiN<sub>x</sub>:H/c-Si) interfaces in the context of solar cell devices are investigated using molecular dynamics simulations. We simulate interfaces with a gradient of nitrogen which goes from SiN<sub>1.2</sub> to Si over widths from 2–9 nm, in the presence of 10 at % hydrogen, to recreate the conditions present when SiN<sub>x</sub> layers are deposited onto c-Si by plasma enhanced vapour deposition. We examine how changing the width of the nitrogen gradient can affect a number of atomic level structural properties which influence the optical and electrical performance of solar cells. We examine the trajectories of our simulations to search for certain geometries which have previously been identified as being important at this interface. Silicon-silicon and silicon hydrogen bonds, which are help to determine the refractive index of the interface are shown to increase with increasing N gradient width. The fixed charge in the interface is also shown to increase with the width of the gradient. The results demonstrate how altering the width of the N layer can affect the efficiency of a-SiN<sub>x</sub>:H as both an anti-reflective coating and a passivation layer, and we suggest an optimal gradient width of, in the region of, 2 nm

## INTRODUCTION

The use of hydrogenated silicon nitride (SiN<sub>x</sub>:H) represents one of the most important technological advances in solar cell technology. This is due to its ability to fulfil the dual roles as an anti-reflective coating (ARC) and surface passivation layer for crystalline silicon (c-Si) [1]. These SiN<sub>x</sub>:H layers are deposited are commonly applied to c-Si surfaces using plasma enhanced chemical vapour deposition (PECVD) GONG2010 [2–4]. a-SiN<sub>x</sub>:H layers function as passivation layers by reducing the number of defective states at the c-Si surface, thus lowering the recombination rate at the surface. It is also important that the ARC absorbs as little of the incident light as possible, for this reason it is desirable that the SiN<sub>x</sub> layer contains as few Si-Si and Si-H bonds as possible, as these bonds can absorb light in the region of the spectrum in which the solar cell is active [4].

The electrical performance of a-SiN<sub>x</sub> passivation layers have been studied by means of deep-level-transient spectroscopy (DLTS) [5–7]. These studies reveal three different defect states (labeled A-C) which play a role at the Si-SiN<sub>x</sub> interface. Based on the DLTS measurements and theoretical analysis of the measured dependence of recombination rate on the excess carrier density it was established that the defect labelled C dominates the recombination rate [8]. This defect has been identified as a Si centre bound to three N atoms with one dangling bond, this centre has also been identified as an important defect state in bulk a-SiN<sub>x</sub> [9]. In accordance with

common practice this defect will be referred to herein as the K-centre, see inset on figure 1 for a graphical representation.

Another feature of the SiN<sub>x</sub> layer which affects the electrical performance of a device is the presence of a positive fixed charge in the layer. The fixed positive charge in the SiN<sub>x</sub> induces an inversion layer in the c-Si, which is highly conductive [10]. It has been demonstrated that high values of  $Q_f$  in SiN<sub>x</sub> result in improved effective surface recombination velocities [11, 12]. The major contribution to  $Q_f$  has been shown to be due to the presence of the K-centre [8]. Thus the K-centre has two contradictory roles in SiN<sub>x</sub> passivation layers in solar cells. Firstly it acts as a recombination centre, decreasing performance, secondly it acts as a centre for fixed charge increasing performance.

The nature of the Si/SiN<sub>x</sub> interface is very sensitive to the PECVD techniques and conditions used. For example it is possible to have either a gradual interface, where the concentration of N has a gradient to zero over a finite distance from the bulk SiN<sub>x</sub> to the c-Si, or a clean interface, where there is an abrupt change from SiN<sub>x</sub> to c-Si. In addition the width of the gradual interface can be controlled by the synthesis condition. Previously we have demonstrated how a graded Si/SiN<sub>x</sub> interface, in which the concentration of N reduces gradually from the bulk value to zero at the interface can result in a significant lowering of K-centre density at the interface [13]. We have also shown how it is possible to control the incorporation of N into c-Si surface by a process of nitridation [14], before deposition of the SiN<sub>x</sub>:H layer. This allows for the introduction of a N gradient in the device, giving control

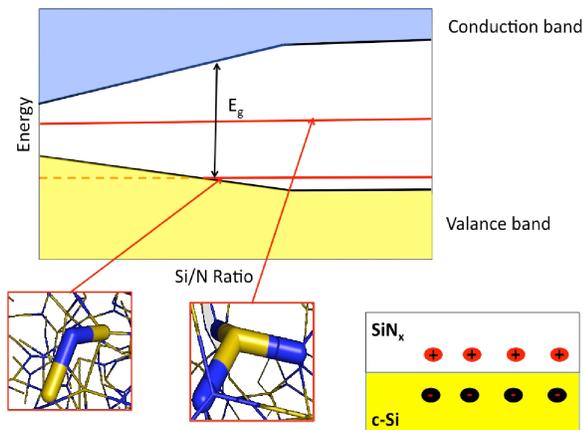


FIG. 1. (Colour online). Upper, schematic representation of the  $\text{SiN}_x$  band structure as a function of the Si/N ratio. The red lines represent defect energy levels due to K- and N- defects. Lower left, the structure of the N-defect one N atom (blue), bonded to 2 Si atoms (yellow), with one dangling bond. Lower, centre K-defect, one Si atom bonded to 3 N atoms with one dangling bond. Lower right, representation of the formation of an inversion layer of negative charge in c-Si, due to fixed positive charge in the  $\text{SiN}_x$  layer.

of the  $Q_f$  and interface trap density, independent of the  $\text{SiN}_x$ :H layer.

In this paper we provide a model for how the level of nitridation affects the important features of the ARC in a solar cell. We use a topological analysis of molecular dynamics (MD) simulations to investigate the effect of the gradient layer introduced by nitridation on the density of Si-Si and Si-H bonds, responsible for light absorption in the ARC. We then estimate the fixed charge in the ARC, by calculating the density of K centres. Finally we combine our model for defect distributions with Shockley-Reed-Hall (SRH) recombination statistics[15, 16] to provide a model for how the carrier trapping rate is affected by width of the N gradient layer introduced by nitridation.

## NUMERICAL METHODS

In order to represent the interaction between the atoms in our system we have used the Tersoff potential, as parametrised by de Brito Mota *et al.* [17, 18] for hydrogenated silicon nitride. To generate amorphous  $\text{SiN}_x$ :H structures we used a melt and quench methodology which we have verified previously[13]. Starting from a random configuration of atoms in a simulation cell with a dimensions chosen to match the experimental density of  $\text{SiN}_{1.2}$ , 3.10 g/cc. The random configuration is then run, using a timestep of 0.2 fs, for 0.5 ns at 2500 K in the canonical (NVT) ensemble until to achieve a well equilibrated system. The system is then quenched to 350 K at a rate of

$3 \times 10^{11}$  K/s.

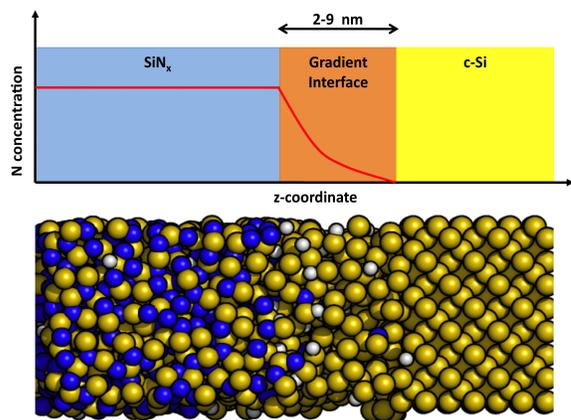


FIG. 2. (Colour online). System composition in our simulations. A layer of  $\text{SiN}_{1.2}$  is on the left hand side of the system, this is linked to a layer of pure crystalline Si through a layer with a gradually reducing value of  $x$  in  $\text{SiN}_x$ . The width of the gradient interface layer is varied from 2-9nm.

The amorphous sample generated is then placed in contact with the (111) surface of a slab of c-Si. To generate the gradient interface we re-run the system again at 2500 K for 0.5 ns and quench to 350 K at the same rate. During this simulation part of the c-Si and a- $\text{SiN}_{1.2}$ :H layers are held in a fixed position, in each case the portion of the atoms allowed to move during the molecular dynamics is half of the desired gradient interface width on each of the c-Si and a- $\text{SiN}_{1.2}$ :H side of the interface. The interdiffusion of Si and N which takes place during this step results in a N gradient across the desired width, represented schematically in figure 2, which re-creates the effects of nitridation before application of the a- $\text{SiN}_{1.2}$ :H by PECVD experimentally. The final compositions of the simulation cells used in this study are presented in table I.

Sample #	# Si	# N	# H	Volume / $\text{\AA}^3$
2nm	406	487	99	9435.17
3nm	507	609	124	11793.96
4nm	609	730	149	14152.75
5nm	710	852	174	16511.54
6nm	811	974	198	18870.33
7nm	1095	913	223	21229.13
8nm	1014	1217	248	23587.92
9nm	1116	1339	273	25946.71

TABLE I. Compositions of the cells used to create samples of a- $\text{SiN}_x$ :H for the different interface widths, showing number of Si, N and H atoms and the volume of the cell.

In order to search for defects in our system we have used the RINGS software package[19] to analyse the tra-

jectory of our equilibrium MD simulations of the interfaces. Within this analysis the coordination of an atomic centre is defined by the number of neighbouring atoms which are said to be “bonded” to that atom. The bonding is defined as the inter-atomic separation being within the first peak of the pair correlation function of the two atoms defined for a-SiN<sub>x</sub>. Having thus defined the coordination of each atom it is a simple task to count and map the defective centres in the simulation.

## RESULTS AND DISCUSSION

### Optical properties

The optical performance of SiN<sub>x</sub>:H coated solar cells is affected adversely by light absorption in the ARC. In the case of SiN<sub>x</sub>:H coatings it is known that either Si-Si or Si-H bonds can be responsible for absorption. It is difficult to distinguish which is responsible for more light absorption. In figure 6 we plot the dependence of both densities on the width of the N gradient at the c-Si interface. It is clear that wider nitridation gradients result in higher densities of Si-Si and Si-H bonds in the ARC. So when considering parasitic light absorption it is clear that a narrower nitridation layer is favourable. In addition, the refractive index ( $n$ ) of SiN<sub>x</sub>:H on c-Si is known to be related to either the concentration of Si-H or Si-Si bonds. Whilst it is again difficult to determine which of the bond densities is more important, since our analysis reveals that they are correlated to one another and also to the gradient width, optimization of  $n$  could, in principle, be achieved tuning the gradient width. We will now consider other properties of the SiN<sub>x</sub>:H layer which are more related to the electronic properties of the cell.

### Fixed charge

As we described in the introduction, the presence of a fixed charge ( $Q_f$ ) in the SiN<sub>x</sub>:H layer is desirable as it reduces the minority carrier density in the c-Si interface region, thus reducing the recombination rate and increasing the majority carrier lifetime. In the following section we will consider how the nitridation profile affects the fixed charge.

The fixed charge in Si-SiN<sub>x</sub> interfaces has been shown to consist of a constant contribution from oxygen correlated states and an operating condition dependent contribution due to K<sup>+</sup> centres[1, 8]. In this study we are considering the effects of different levels of nitridation, therefore we consider only the latter contribution to  $Q_f$ . We analyse the trajectories of our MD simulations to identify K centres, which are defined as under coordinated Si centres bonded to three N atoms. We define

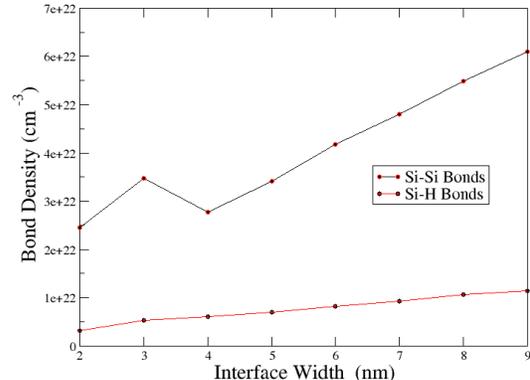


FIG. 3. (Colour online). Density of silicon-silicon and silicon hydrogen bonds and percentage of silicon centres which have the geometry corresponding to the K-centre defect, as a function of the width of the N density gradient at the a-SiN<sub>x</sub>:H/c-Si interface.

Si-N and Si-Si bonds based on the first peak of the pair correlation functions, as described in a previous study[13]. The region in which the fixed charge of the SiN<sub>x</sub>:H layer is important has been shown to be around 20nm[1]. In our samples the bulk region of SiN<sub>x</sub>1.2:H will have the same density of fixed charge in each system, thus any differences will be due to different levels of fixed charge in the gradient region. For this reason we consider only the first 9nm of the SiN<sub>x</sub>:H layer in all of our samples in this analysis, since the remainder of the SiN<sub>x</sub>:H will be the same from the point of view of  $Q_f$  concentration. The results are presented in figure 4.

We can see from figure 4, that there is a peak in the number of K centres at an interface width of between 2 and 3 nm. We note that not all K centres will be positively charged and contributing to the fixed charge in the SiN<sub>x</sub> layer, therefore our analysis does not provide an absolute value for the value of  $Q_f$ , however, we think that it is reasonable to assume that the greater the number of K centres the higher the fixed charge will be under otherwise identical circumstances, thus the comparison of the number of K centres in the various systems gives an indication of how much they will contribute relatively to the fixed charge. Our simulations show that too heavy nitridation resulting in an interface width of greater than 3 nm would be expected to reduce the fixed charge

### Trap density

We now consider how the distribution of defects is affected by the gradient at the interface. Figure 4 shows how the distribution of two important defects in the a-SiN<sub>x</sub>:H layer depend on the width of the layer if a-

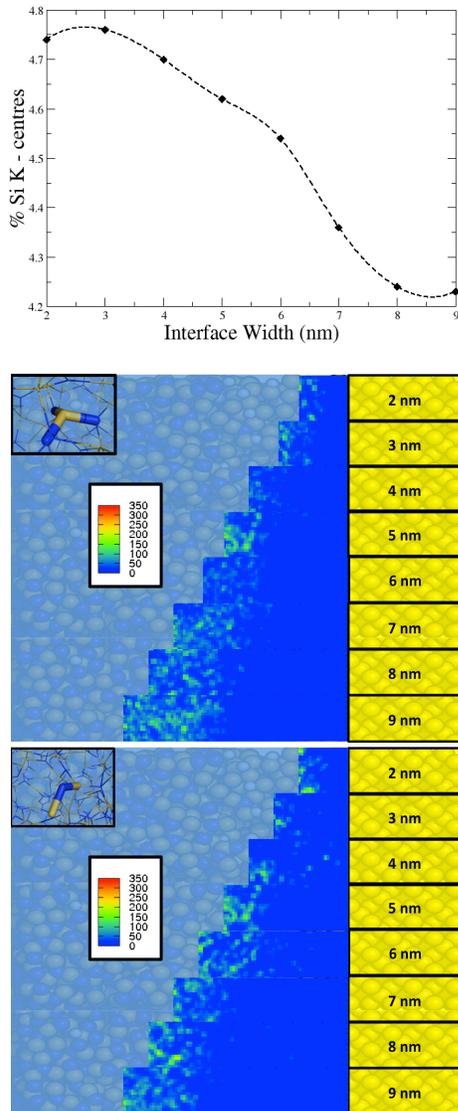


FIG. 4. (Colour online). Plots of the density of important geometrical defects across the gradient layer in the a-SiN<sub>x</sub>:H/c-Si interface. From top to bottom on each graph ranging between 2nm 9nm wide gradients with x=1.2 on to the left of the plots and x=0 at the interface with c-Si. Left plot shows K-centre density, right plot shows N-centre density. Insets on each plot show a graphical representation of the defect in question.

SiN<sub>x</sub>:H. It has been shown [4] that increased trap state densities ( $D_{it}$ ) at the semiconductor/insulator interface results in reduced carrier lifetimes. Thus it is desirable to minimise  $D_{it}$  at the interface in order to improve device performance. Figure 4 a plots the density of K-centre defects mentioned previously across the various interfaces. Clearly from this figure the wider interface gradients lead to a reduction of the K centre density at the interface. Figure 4 b plots the density of N centres with a dangling bond, which have also been identified as possible trap

states in a-SiN<sub>x</sub> [20, 21]. Again the density of these defects close to the interface is reduced when the interface gradient is increased.

### Effects of the gradient interface on recombination

We now present a simplified model, based on our calculated trap densities, and estimations of the carrier concentrations, of the degree to which we would expect recombination to occur in the various gradient interfaces.

As Si in an indirect bandgap semiconductor, the dominant source of recombination will be due to bulk traps. Recombination can be considered as a process of electron and hole capture, which can be described by Shockley-Read-Hall (SRH) statistics[15]. According to the SRH model the rate of capture is given by

$$U = \left[ 1 - \exp \frac{F_t - F_n}{kT} \right] f_{pt} \rho_T \times \int_{e_c}^{\infty} f(E) N(E) c_n(E) dE \quad (1)$$

Here  $F_t$  is the Fermi energy of the trap and  $F_n$  is the quasi Fermi level, which is related to the intrinsic Fermi level, and is located almost at mid-gap for non-doped systems.  $f_{pt}$  is the probability that a trap is empty (thus available to the carrier) and  $\rho_T$  is the trap density. The integral runs from the bottom of the conduction band ( $e_c$ ) to all higher levels and the terms in the integrand are the fraction of states occupied by electrons  $f(E)$ , the number of quantum states  $N(E)$  and the probability per unit time that an electron will be trapped. In our analysis we replace the integral of  $f(E)N(E)dE$  by a carrier density  $\rho_n$ . The density of carriers, in a non-degenerate n-type semiconductor, is given by

$$\rho_n = N_V \exp \left( \frac{-E_F - E_V}{kT} \right), \quad (2)$$

where  $E_V$  is the valance band minimum energy,  $E_F$  is the Fermi energy. Since the Fermi energy for an intrinsic semiconductor lies very close to the middle of the band-gap, and as we do not expect the SiN<sub>x</sub> layer to have a significant dopant population we estimate the value  $E_F - E_V$  to be half the value of the band-gap.  $N_V$  is the effective density of states in the conduction band and is given by

$$N_V \equiv 2 \left( \frac{2\pi m_{de} kT}{h^2} \right) \quad (3)$$

where  $m_{de}$  is the effective mass of an electron in the conduction band. The value for  $m_{de}$  in c-Si is  $0.33m_e$ [22] and that in SiN<sub>x</sub> is  $\sim 0.5m_e$ [23–25]. The variation of the band gap of SiN<sub>x</sub> with stoichiometry has been calculated by Robertson[26]. In figure 6 we present the variation of the band gap with stoichiometry and the resultant variation in carrier concentration in the SiN<sub>x</sub> layer as calculated using equation 2.

The trap density is then calculated from the trajectories of the MD simulations, with the active trap density defined as

$$\rho_T(z) = \rho_K(z) + \rho_N(z)\delta, \delta = \begin{cases} 1 & \text{if } x \geq 1, \\ 0 & \text{if } x < 1 \end{cases} \quad (4)$$

where  $\rho_K(z)$  is the density of K centres not passivated by hydrogen,  $\rho_N(z)$  is the density of N centres not passivated by hydrogen and the  $\delta$  is 1 when  $x$  in  $\text{SiN}_x$  is greater than 1 and 0 when  $x$  is less than 1, to reflect the fact that below  $x = 1$  the N centre is no longer active in the band-gap of  $\text{SiN}_x$  as illustrated in figure 1. This results in very little contribution to trapping from N centres in the gradient interface, since by the time the band-gap is wide enough for the N-centre to be active, the carrier population is vanishingly small. Thus we ignore the contribution from

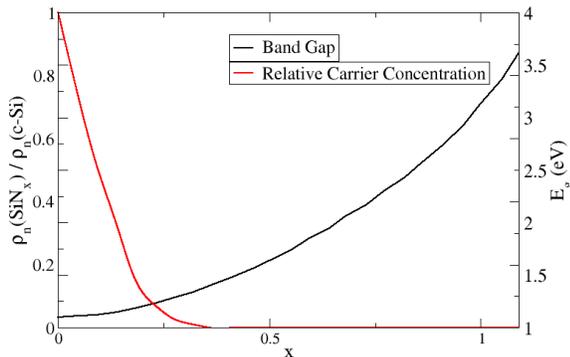


FIG. 5. (Colour online). Band gap dependence on the stoichiometry of  $\text{SiN}_x$ , as calculated by Robertson[26], and the resultant electron carrier population normalized by the hole population in pure c-Si, calculated from equation 2.

N centres to trapping in gradient interface systems. The rate of capture at the K centre will depend on the difference between  $F_t$  and  $F_n$  in equation 1. Since  $F_t$  is located at almost mid-gap as is  $F_n$  for the K centre[27], and given that the band gap opens almost symmetrically about mid-gap[26] across the  $\text{SiN}_x$  composition range, this dependence will not change across the composition range either. Thus we can say that the probability of a carrier being trapped by it will be proportional to the trap density and the carrier density in the system.

$$P_T = \int_0^Z \rho_T(z)\rho_n(z)dz \quad (5)$$

where the the integral is calculated from the c-Si/ $\text{SiN}_x$  interface at zero, to the edge of the  $\text{SiN}_x$  layer at  $Z$ . The active trap density is given by

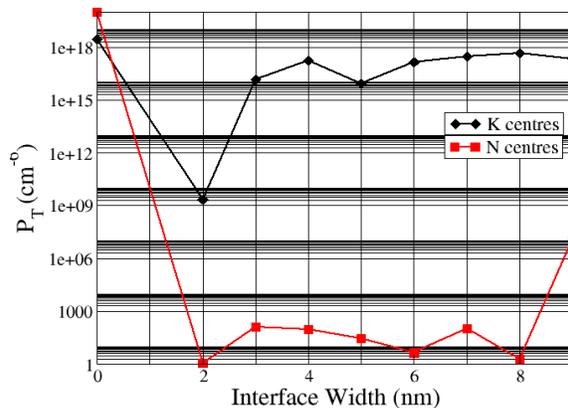


FIG. 6. (Colour online). Probabilities of carrier trapping at defect centres depending on interface gradient thickness, calculated from equation 5.

## Conclusions

In conclusion, we have performed molecular dynamics simulations to investigate the effect of a N density depletion layer at the interface between c-Si and a-SiNx:H. In particular we have concentrated on how the width of the depletion layer affects the density and distribution of a number of bond types and defect states which have previously been shown to be important for the performance of solar cells when a-SiNx is used as an ARC.

By considering the density of Si-Si and Si-H bonds, the density of K-centre defects and the locations of K- and N- centre defects we believe that these results suggest that a gradual interface with a gradient in  $\rho_N$  can be designed to improve device efficiency. Furthermore we believe that the results suggest that there should be an optimal width of the  $\rho_N$  gradient, which would result in the best balance between layer stability, fixed charge and concentration of recombination centres at the interface. Although we realise that due to the complexity of the factors which affect operational solar cells means that we can only consider a small number of important aspects, we believe that our simulations suggest that an a-SiNx gradient layer of around 7 nm would provide the best compromise between layer stability and electrical performance.

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