

## Diffusion of Hydrogen and Deuterium in Stack Systems of $\text{Si}_x\text{N}_y\text{H}_z$ / $\text{Si}_x\text{N}_y\text{D}_z$ and Crystalline Si

Christoph Boehme and Gerald Lucovsky

Department of Physics, North Carolina State University,  
Raleigh, North Carolina, 27695-8202, U.S.A.

### ABSTRACT

H/D-, N-H/D- and Si-H/D-bond density changes were investigated in stacks consisting of a Cz-Si substrate, a thin layer of  $\text{SiO}_2$ , amorphous deuterated silicon nitride as well as amorphous hydrogenated silicon nitride in order to see if the post deposition anneal of  $\text{a-Si}_x\text{N}_y\text{H}_z$  layers on crystalline silicon wafers can actually lead to a migration of H atoms into the Si-bulk, which is an important question in regard to emitter passivation of Si-solar cells.

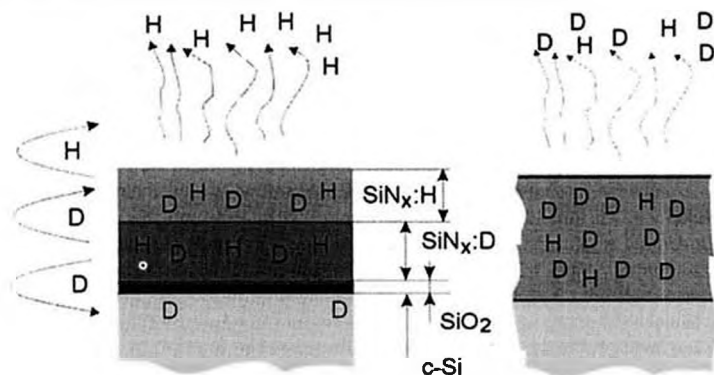
The stacks were grown with remote plasma enhanced chemical vapor deposition (RPECVD). A low temperature ( $\approx 200^\circ\text{C}$ ) process of down stream injected ammonia ( $\text{NH}_3$ ) and silane ( $\text{SiH}_4$ ) activated by an upstream injected He-plasma, produced through RF-radiation (13.65MHz) was used. Thermal treatment was executed by ex situ rapid thermal anneal in Ar ambient. For the measurements of H and D bond densities, FTIR was employed while SIMS determined atomic densities of H, D and O in the c-Si/nitride interface region. The experiments showed that H transport in silicon nitride is determined by several mechanisms including diffusion and dissociation processes and that silicon nitride deposited with high ammonia to silane ratios can produce molecular species like ammonia and  $\text{H}_2$ . The study of the reaction dynamics showed that the production of molecular hydrogen is the most dominant process as long as Si-H-bonds are present in the system. After their exhaustion, an ammonia producing reaction prevails that leads with increasing temperatures to lower densities in the nitride films.

### INTRODUCTION

Even though the release of hydrogen out of amorphous hydrogenated silicon nitride during post deposition anneal has been studied extensively since the end of the 1970s, little attention has been paid to the actual microscopic processes responsible for this effect. In the past ten years improvement through anneal of c-Si solar cells underneath silicon nitride anti reflection layers has repeatedly been observed [1,2]. This effect was assumed to be due to hydrogen passivation by diffusion of hydrogen from the AR-coating into the underlying c-Si bulk. Since hydrogen permeation through the silicon nitride/silicon interface depends mostly on the dynamics of the hydrogen concentration in the silicon nitride, the nature of the microscopic H-transport is of great importance for such a permeation process. A dominance of atomic H diffusion in the  $\text{Si}_x\text{N}_y\text{H}_z$  as described by Bik [3] can lead to a very inhomogeneous H density depth profile and therefore high H densities at the nitride/c-Si interface. However, a dissociative mechanism as proposed by Stein et. al. [7] which consists of the rapid diffusion of molecules with H atoms after a local dissociation out of the network, produces very homogeneous H depth profiles and therefore low H-densities at the interface.

## EXPERIMENTAL DETAILS

Two series of experiments were carried out in order to determine the dominant mechanisms and their properties. The first series (Fig. 1, left) consisted of the anneal of a stack system of Cz-Si underneath a thin layer of silicon dioxide, a 400Å thick layer of deuterated silicon nitride and a layer of hydrogenated silicon nitride with the same thickness. The stack system was deposited at 200°C with remote plasma enhanced chemical vapor deposition (RPECVD) and annealed with a Heatpulse 610 rapid thermal annealer at temperatures between 500°C and 1000°C for 20s. Theoretical models of the hydrogen and deuterium loss of the system [4] predicted a much stronger hydrogen loss than deuterium loss for the atomic mechanism and an equally strong loss of both isotopes in case of dominant dissociation mechanisms. The second series (Fig. 1, right) of experiments was a simple rapid thermal anneal of an 800Å thick deuterated silicon nitride layer. Samples deposited at different ammonia to silane flow ratios were annealed at various anneal times between 20s and 800s and anneal temperatures between 500°C and 1000°C. The purpose of this series was the investigation of the dynamics of the different bond concentrations. All nitride layers were deposited at high ammonia to silane deposition flow ratios yielding high densities of NH- or ND-bonds and low densities of SiH- and SiD-bonds which cause film stoichiometries with an index of refraction suitable for AR coatings.



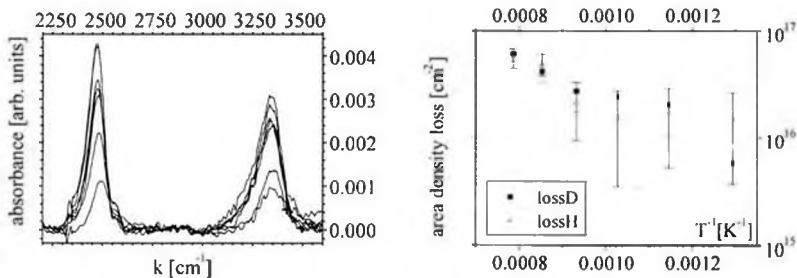
**Figure 1.** The stack for the determination of the dominant transport mechanism (left) and the simple c-Si/  $\text{Si}_x\text{N}_y\text{H}_z$ -stack for the observation of the density dynamics (right).

For all samples measurements of the Si-H, Si-D, N-H and N-D-area-bond-densities were carried out with Fourier transform infrared spectroscopy. The qualitative identification of the bonds was done through the peak center wave number, ( $\approx 1573\text{cm}^{-1}$  for Si-D,  $\approx 2182\text{cm}^{-1}$  for Si-H,  $\approx 2479\text{cm}^{-1}$  for N-D,  $\approx 3336\text{cm}^{-1}$  for N-H) while the quantification took place through integration of the absorbance peaks according to methods of Kim [5] and Lanford [6]. For some samples,

secondary ion mass spectroscopy was used in order to determine the overall atomic H- and D-densities and the depth profiles of the films as well as the confirmation of the FTIR results.

## MEASUREMENTS

The results of the first series of measurements (Fig. 2) show that the loss of N-D- and N-H-bonds is at all temperatures equal within the range of error. The Si-H- and Si-D-bonds were only qualitatively or not at all detectable since the silicon nitride network was deposited with high ammonia to silane ratios.



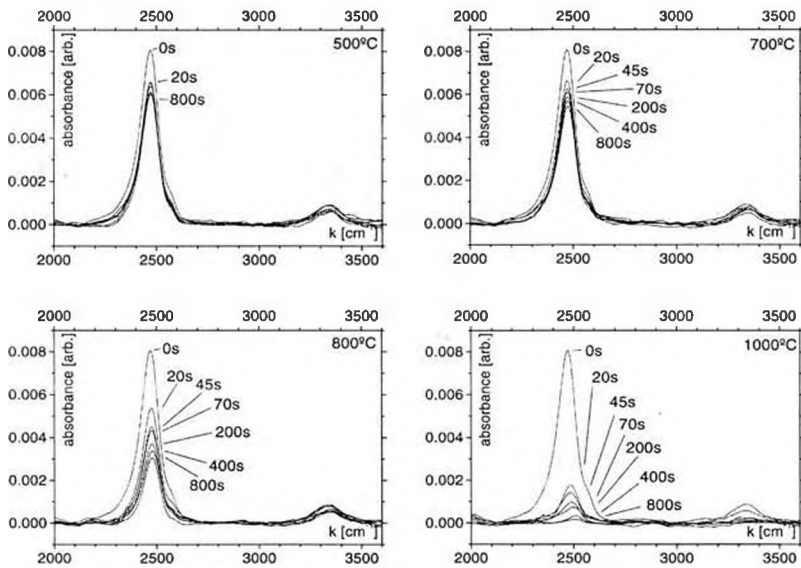
**Figure 2.** The absorbance peaks of the N-D- and N-H-stretch modes at  $2479\text{cm}^{-1}$  and  $3336\text{cm}^{-1}$  (left). Bond area density loss versus the inverse absolute temperature (right).

The second series revealed the development of the area density versus time in a homogeneous stack of silicon nitride deposited with deuterated ammonia ( $\text{ND}_3$ ) flow of  $10\text{sccm}$  and hydrogenated silane ( $\text{SiH}_4$ ) flow of  $1\text{sccm}$ . Figure 3 shows the FTIR spectra for several samples. Figure 4 (left) shows the area density development versus time, normalized to the initial film content. Hydrogen and deuterium loss takes place at all temperatures. At lower temperatures ( $500^\circ\text{C}$  to  $700^\circ\text{C}$ ), the density drop occurs within the first 20s after which the bond content becomes stable at relatively high levels. With higher  $T$ , the stable level decreases while the actual reduction process takes more time.

Figure 4 (right) shows the SIMS profiles for the  $1000^\circ\text{C}$  sample of the first series with heterogeneous stacks. Both the H- and the D-profile have almost proportional shapes and decrease between the silicon/silicon nitride interface and the sample surface. The D-density reduces from  $2.2$  to  $1.8 \times 10^{21}\text{cm}^{-3}$ , the H-density from  $1.8$  to  $1.6 \times 10^{21}\text{cm}^{-3}$ . After 20s of rapid thermal anneal, the original heterogeneous distribution of H- and D-atoms is not recognizable anymore. The concentration reduction within the film is very small in comparison to the overall D- and H-reduction from the non-annealed state. Before heat treatment, the samples had  $2.01 \pm 0.2 \times 10^{21}\text{cm}^{-3}$  H- and D- density which indicates a reduction of about one order of magnitude.

## DISCUSSION

The equivalence of the measured N-H- and N-D-bond loss indicates the dominance of dissociative mechanisms. The slight depth dependence of the H- and D-reduction within the film system as shown by the first series of experiments certainly also indicates that the atomic diffusion mechanism is present in the film system. However, in comparison to the strong overall reduction of the H- and D-contents of the films, this depth dependence is insignificant. Therefore, the dissociative processes are much more dominant than atomic diffusion.

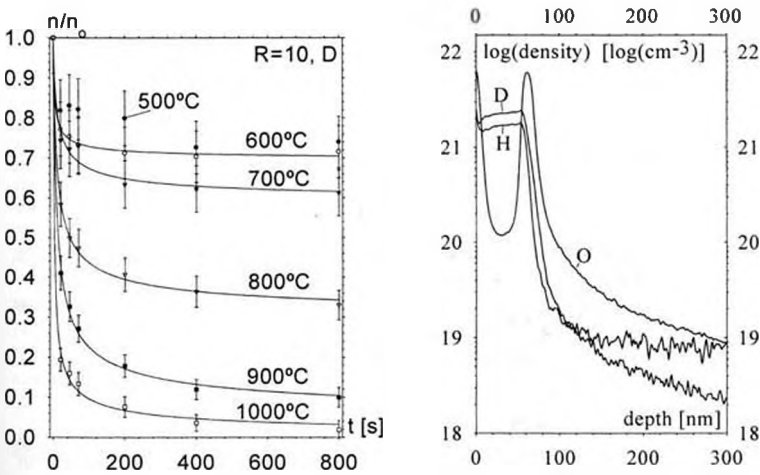


**Figure 3.** The dynamics of the absorbance peaks of the N-D- and N-H-stretch modes at  $2479\text{cm}^{-1}$  and  $3336\text{cm}^{-1}$  for ammonia rich deposited deuterated 800Å layers at  $500^\circ\text{C}$ ,  $700^\circ\text{C}$ ,  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  (left).

For the determination of the dissociation reactions as well as their products, the theoretical bond dynamics of several model reactions were calculated and compared to the measurements of the second series. Common for all these models was the assumption, that the diffusion constants for the reaction products is very high, since the dissociating molecules have hardly stable sites within the amorphous network and their diffusion therefore has a very low activation energy. This assumption is supported by the homogenous SIMS profiles of films annealed at various temperatures and anneal times. Any possible density gradient within the network is instantly compensated by fast diffusion and the overall density reduction is merely due to the reaction rates of the dissociation processes. This assumption also implies that the reverse reactions of the

dissociation do not take place and that the system never gets into a chemical equilibrium since such an equilibrium is shifted instantly as soon as it appears because of the constant loss of the reaction products out of the film.

Another input of the reaction models was the experimentally observed existence of a static minimum density of H-bonds that can't participate to the reaction. This static part of the initial concentration is apparently due to the locality of the dissociation reactions, which cease when the average distance of the H-bond-centers becomes too large.



**Figure 4:** The normalized area density of the second series of film systems during anneal at several temperatures versus the anneal time as well as the theoretically predicted development for a dominant ammonia dissociation (left). The SIMS profiles for D, H and O (right). The oxygen was used as interface marker between the nitride and c-Si.

Even though an amorphous hydrogenated silicon nitride network only contains three different types of atoms, a large variety of isometrically possible reactions had to be found by solving a set of systems of linear equations [4]. The most likely reactions were then selected by its enthalpies obtained from Sanderson [8]. Finally, few reactions turned out to be likely, which produced molecules like molecular hydrogen, silane, hydrazine, disilane and ammonia. By comparison of the correlation between the theoretical reaction dynamics predicted by these models with the data obtained by FTIR, the different dissociation reactions at different anneal temperatures and times were identified.

Figure 4 (left) shows the theoretically predicted dynamics when ammonia dissociation out of three N-H-bonds (enthalpy:  $\Delta E = -0.43 \text{ eV}$ ) is dominant. The correlation factors of all the fits above 600°C was above 0.9 while the other models hardly exceeded 0.3. At 500°C an even more endothermic reaction of one Si-H- and one N-H-bond into molecular hydrogen seems to be

dominant ( $\Delta E = -1.86\text{eV}$ ) which ceases after the exhaustion of the Si-H-bonds that carry only about 20% of the bonded hydrogen. This reaction has also been confirmed before by Lu et. al. [9]. At higher temperatures, this reaction is also dominant; however, the spectroscopic data indicates that beyond 600°C the Si-H has already dissipated at the time of the first measurement after 20s, so that the less exothermic ammonia reaction can prevail.

## SUMMARY

Hydrogenated amorphous silicon nitride, deposited with high ammonia to silane ratios, shows strong H-loss during post deposition anneal due to the rapid diffusion of small H-containing molecules that dissociate out of the network in advance. Atomic H-diffusion does not play an important role. The dissociation mechanisms consist of an initial development of molecular hydrogen followed by larger amounts of ammonia. Since most of the unwanted H-loss at the c-Si/nitride interface is due to the ammonia reaction, the future investigation of anneal processes in ammonia ambients is proposed.

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