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Characterisation of SiOX / SiNX Surface Passivation Using Time-of-Flight Elastic Recoil Detection Analysis

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Abstract. An accurate description of the distribution of hydrogen at solar cell interfaces is critical for understanding both passivation and degradation phenomena. Time-of-flight elastic recoil detection analysis (ToF-ERDA) has recently been employed to study this hydrogen distribution by providing a one-dimensional (1D) depth profile. In this work, ToF-ERDA was used to investigate the hydrogen profile in a SiO_X / SiN_X passivating stack. The ability to resolve the interface with the c-Si interface was studied by using polished wafers and thin (20 nm) passivating stacks. This approach, coupled with Monte Carlo ERD (MCERD) modelling, showed that the identification of the interfacial oxide was much more clearly defined compared with previous reports using ToF-ERDA. Annealing the SiO_X / SiN_X at 450 °C for 5 minutes substantially increased the effective lifetime. However, no noticeable change in the H distribution measured with ToF-ERD was observed. We comment on the difficulty of correlating physical hydrogen measurements with the surface recombination properties.

Keywords: Hydrogen, ToF-ERDA, Passivation, Interfaces

1. Introduction

Chemical passivation of c-Si dangling bonds with hydrogen is critical for improving the efficiency of silicon solar cells. It has been a driving force for the increased power output of solar panels over the past 10 years [1], [2], [3]. As well as passivating defects, excessive concentrations of hydrogen can cause undesirable recombination in both the bulk [4], [5] and at the surface [6], [7], [8]. Thus, understanding the distribution of hydrogen at/near the c-Si interface is critical. Direct detection of elemental H in Si structures is usually achieved with secondary ion mass spectrometry (SIMS), a common thin-film analysis tool in which the sample surface is under continuous ion beam sputtering to generate secondary ions [9], [10]. However, reported SIMS results for poly-Si on SiO_X stacks are susceptible to a spread-out and blurring of the H profile at the interfacial oxide, caused by measurement artefacts. Additionally, the presence of residual H_2 gas during the measurement significantly limits the resolution of H with this technique. An alternative approach is to use atom probe tomography (APT), which provides excellent spatial resolution [11], [12]. However, the mass spectra overlap with the background H_2 gas still limits the ability to accurately resolve and quantify H. Low temperature Fourier Transform-Infrared (FT-IR) spectroscopy allows for detection of hydrogen bonded to other species, for example B-H pairs, however, this approach is used for detecting hydrogen in the bulk, not at the surface [13].

In recent work, we investigated the ability of time-of-flight elastic recoil detection analysis (ToF-ERDA) to provide H depth profiles in TOPCon contacts capped with a deuterated SiN_X [14]. ToF-ERDA was shown to be suitable to provide a clear delineation between D and H species, highlighting the strength of this analysis technique [14]. However, in that report, the ability to resolve the interfacial oxide and thus the interface with the c-Si was limited. This was related to (i) the rough surface of the chemically etched silicon surface and (ii) the relatively thick (~130 nm) passivation stack; impacting the technique's depth resolution. In this work, we aim to address these issues by depositing SiO_X/SiN_X stacks on semiconductor grade polished silicon wafers. Additionally, we investigate the use of Monte Carlo ERD (MCERD) modelling [15] to provide a clearer depiction of the interface with c-Si by accounting for multiple scattering events of the incoming ion and recoiled atoms.

2. Methodology

2.1 Sample Preparation

The samples investigated in this work were formed on semiconductor grade polished n-type Cz wafers (~40 Ω·cm, 675 µm). The passivation stack consisted of c-Si / SiO_X (1.5 nm) / SiN_X (20 nm). The thin SiO_X was grown during the RCA2 cleaning process. The 20 nm SiN_X was grown with an Oxford Instruments PlasmaLab PECVD tool at 350 °C. The chamber pressure was kept at 650 mTorr while 400 sccm of 5% SiH_4 and 40 sccm NH_3 were admitted into the chamber. To facilitate hydrogen release, the sample was annealed at 450 °C for 5 mins in a N_2 purged furnace. The effective lifetime was measured using a Sinton Instruments WCT 120.

2.2 Time-of-Flight Elastic Recoil Detection Analysis

We aim to introduce ToF-ERDA as a technique that can be used to analyse buried interfaces and passivating contact structures. ToF-ERDA works by bombarding the surface of a sample with heavy ions at high energies. In this work, the incident species was 10 MeV $^{35}Cl^{5+}$. Unlike SIMS, where the sputtered ions are measured using a mass spectrometer, in ToF-ERDA, the velocity and energy of the recoiled atoms are measured. Due to the relationship between kinetic energy, velocity and mass, the traces from different elements can be clearly separated based on the different masses. The correlation of energy and velocity relates to the depth in the sample for each element, allowing a depth profile for all the elements present in each sample to be created. In this work, the coincidence spectra were converted into 1D depth profiles using the software, potku [16]. The raw event data for the timing foils and GIC detector are used by the software to remove false coincidences (for example different atoms triggering a start and stop pulse in the timing foils) to create the coincidence spectra with only true coincidences. Then each region is selected and allocated to an element. Potku can then generate a depth profile in an iterative process, which corresponds to the histogram. Figure 1 shows a schematic of the ToF-ERDA setup at the Surrey Ion Beam Centre. When the atoms recoil from the sample, the system measures i) the time of flight between two timing foils (shown as T1 and T2) and ii) the energy using a gas ionization chamber (GIC).

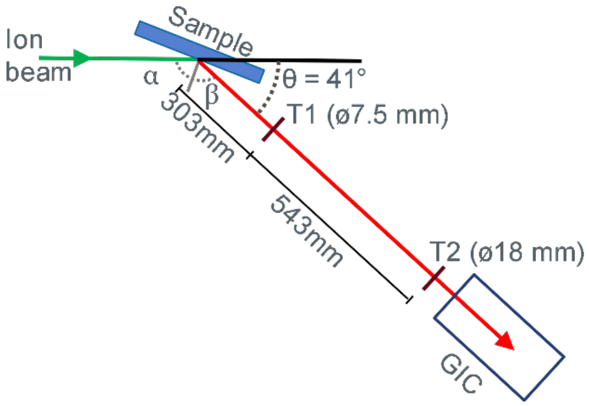

Figure 1. *Schematic illustration of the ToF-ERDA experimental setup at Surrey Ion Beam Centre.*

3. Results and Discussion

Figure 2 displays the ToF-ERDA coincidence spectra for the as-deposited c-Si / SiO_X (1.5 nm) / SiN_X (20 nm) sample. The regions for each element show the relationship between the measured energy and time-of-flight. As atoms are recoiled from deeper in the sample, they lose more energy and have a higher time-of-flight. The relationship between kinetic energy, velocity and mass dictates the parabolic shape of the curves. A logarithmic colour scale is used to show the density of detection counts, which can be related to the population of the element. To better understand the distribution of hydrogen, such coincidence spectra can be converted to depth profiles using the potku analysis software [16].

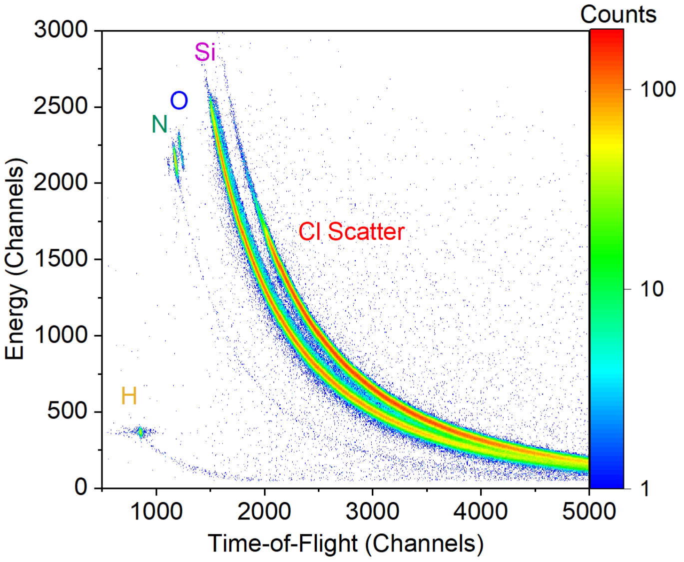

Figure 2. *ToF-ERD coincidence spectra for as-deposited c-Si/SiO_X/SiN_X structure.*

Figure 3 (a) displays the corresponding 1D depth profile of the spectra shown in Fig. 2. This shows the relative elemental concentration as a function of depth, shown in thin film units (TFU), with units 1×10^{15} atoms/cm^2. The green represents N, which indicates the SiN_X surface region. The O trace displays a peak at the edge of the SiN_X region (~180 TFU), which corresponds to the interfacial SiO_X. This peak is significantly sharper compared with previous results on TOPCon samples [14]. In this region, we can see the distribution of H, which has an average concentration of 15.3 at.%. Figure 3 (b) displays the 1D depth profile for the sample after annealing at 450 °C for 5 mins in a N_2 purged furnace. It was expected that this H profile would change following annealing, as annealing of hydrogen-containing dielectrics allows hydrogen to diffuse to the interface to passivate defects. Somewhat surprisingly, the H profile in Fig. 3(b) shows no significant change following annealing.

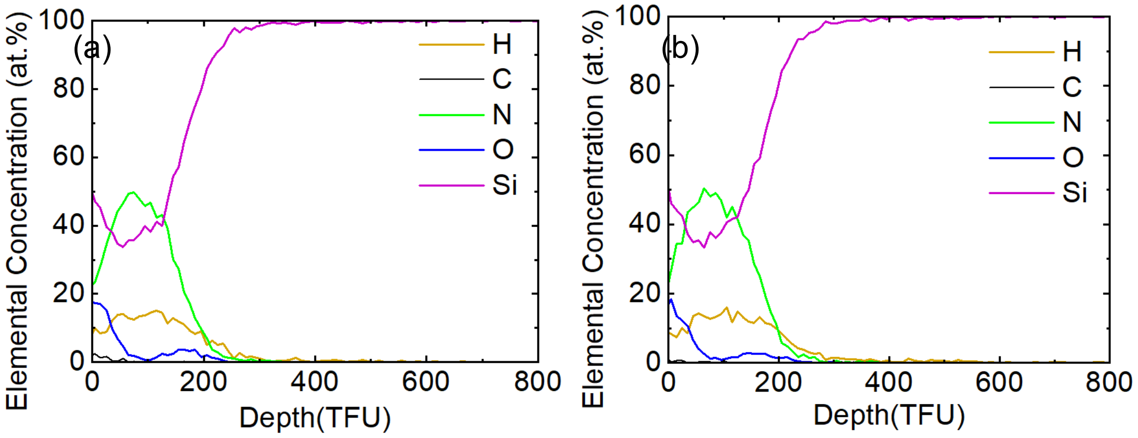

Figure 3. *Depth profiles from ToF-ERDA depicting Si, N, O, H distributions (a) as-deposited and (b) after annealing at 450 °C.*

The impact of annealing on the effective lifetime and surface recombination saturation current (J_0) are shown in Table 1. The effective lifetime displayed was extracted at an injection level of 1×10^{15} cm^{-3}. The annealing increases the lifetime from 1.25 ms to 2.08 ms, which corresponds to a 52% reduction in J_0. This indicates that the anneal is allowing for the diffusion of hydrogen to the c-Si interface to passivate defects and reduce surface recombination. However, no noticeable change in the H distribution is shown in Fig. 3 (b). Assuming a spatial resolution of 3 nm and a relative concentration certainty limit of 0.5 at.%, we calculate that the rough absolute minimum resolution of measuring H in silicon using ToF-ERDA is ~7×10^{15} cm^{-2}.

When considering the chemical passivation at the c-Si interface, a critical parameter is the areal density of recombination active defects (D_{it}), which can originate from Si dangling bonds and lattice strain. For a poorly passivated interface, a D_{it} on the order of 1×10^{12} cm^{-2} would be expected. However, the excellent surface passivation required to reach record voltages has D_{it} on the order of 1×10^{10} cm^{-2}. Comparing such defect density to the detection floor of analytical techniques illustrates the many orders of magnitude discrepancy. The resolution limits of physical H measurements is much worse than that required to identify the densities of recombination sites that hydrogen is passivating. It is likely that hydrogen is moving to the interface and passivating defects, which causes the vast reduction in J_0. However, this quantity of hydrogen is so small that it is ‘hidden’ within our measurements. SIMS measurements are also susceptible to this problem. H concentrations are typically shown as the intensity of counts, which provides no quantitative information, or as a volumetric density on the order of > 1×10^{19} cm^{-3}. This idea calls into question the validity of previous reports that draw a direct correlation between H concentration near an interface and the measured recombination properties.

Table 1. *Impact of the 450 °C anneal on effective lifetime and J_0 of 20 nm SiN_x:H passivated samples.*

	Lifetime (ms)	**J_0 (fA/cm^2)**
As Deposited	1.25	351
Annealed	2.08	171

Although the surface is semiconductor grade polished and the stack is only ~ 20 nm, the O peaks displayed in Fig. 3 are fairly broad, making it difficult to identify the interface with the c-Si. There are various experimental effects that can broaden the depth profile as displayed in the potku analysis shown in Fig. 3. This includes both geometrical and multiple scattering, which are respectively due to the glancing angles along with ions and recoil atoms undergoing multiple collisions before detection. To sharpen the interface resolution by taking these experimental effects into account, MCERD modelling was employed [15]. MCERD or Monte Carlo ERD is a software that simulates the experiment and can be used to account for experimental effects such as multiple scattering and finite beam spot. The simulated energy spectra are fitted to the experimental energy spectra for each element individually, using set composition layers (hence the stepwise shown in Fig. 4). MCERD also allows the user to set individual densities to each layer for more accurate depth profiles in terms of nanometres rather than TFU. Figure 4 displays the stepwise MCERD modelled profile, overlayed with the data from potku shown in Fig. 3 (a). This allows for a much clearer identification of the interface. The O peak from the potku data is broad, however, the MCERD peak is sharp (3 nm). This correlates with the sharp reduction in the N signal, providing further evidence for the presence of the interfacial oxide. Additionally, the depth scale converted from TFU to nm using an assumed density for each layer. This is unlike potku, which uses a global density across the whole stack.

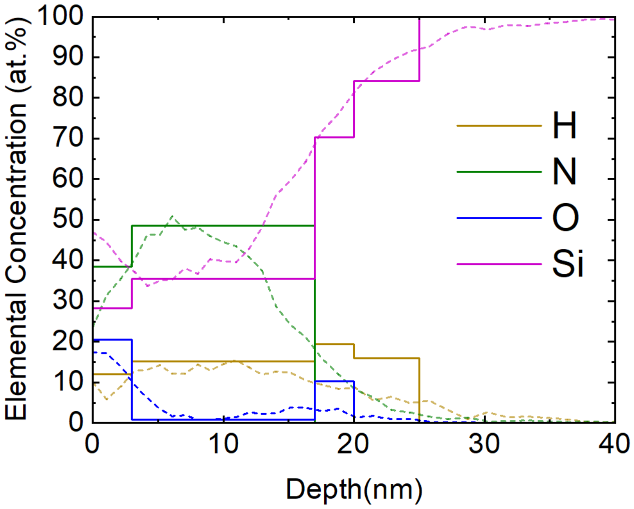

Figure 4. *Depth profile displaying dotted lines for potku data and solid lines for MCERD modelling analysis for Si, N, O, H.*

4. Conclusion

In this work, we investigated SiO_X / SiN_X surface passivation properties with ToF-ERDA. The experimental design of samples included a semiconductor grade polished surface and thin passivating stack, which allowed for clearer depiction of the interface compared with TOPCon stacks in prior work. Monte Carlo ERD (MCERD) modelling was employed to account for scattering events, which allowed for better interface resolution. The goal of using ToF-ERDA was to provide insights into the role of hydrogen diffusion during thermal processes on the chemical passivation at the c-Si interface. Interestingly, we were not able to correlate the H distribution from ToF-ERDA with the recombination properties. We discuss broadly the inability to accurately correlate such physical measurements with recombination, which has implications for prior interpretation of such results using other techniques.

Data availability statement

All data created during this research and published in this article is openly available from the Oxford University Research Archive and can be downloaded free of charge from http://ora.ox.ac.uk.

Author contributions

M. Wright: conceptualization, investigation, data curation, formal analysis, writing – original draft, writing – review & editing. **M. Sharpe:** formal analysis, data curation, software, supervision, resources, investigation, writing – review & editing. **C. McAleese:** formal analysis, data curation, software, investigation, writing – review & editing. **Y. Wang:** investigation, writing – review & editing. **Y. Shi:** formal analysis, writing – review & editing. **R.S. Bonilla:** project administration, funding acquisition, supervision, writing – review & editing.

Competing interests

The authors declare that they have no competing interests.

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