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Neutron and x-ray reflectometry investigations of amorphous silicon-based surface passivation layers

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Abstract

In this work, films of a-Si:H films exhibiting low surface recombination velocities were deposited onto high lifetime silicon substrates and characterized. The films were made by plasma enhanced chemical vapour deposition with thicknesses ranging from 5 to 40 nm. On one set of samples, the a-Si:H layers was capped by a ~100 nm layer of amorphous, hydrogenated silicon nitride (a-SiN_x:H). The thermal stability of the surface passivation materials was investigated by minority carrier lifetime measurements. The structure and composition of the films were thereafter investigated both before and after annealing using neutron reflectometry (NR) and x-ray reflectometry (XRR) measurements. These measurements give highly accurate information of the physical structure of the films, including their thicknesses and layer densities, and also give an estimate of the H-concentration profiles within the layers. The results show that the degradation of lifetime observed after thermal processing is accompanied by a strong reduction in H concentration throughout the whole bulk of the a-Si:H films.

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1. Introduction

Surface passivation material systems applied to the front and rear sides of the silicon (Si) substrate are key components in all high-efficiency solar cells made from crystalline Si today. Thin films of hydrogenated amorphous silicon (a-Si:H) are well known to yield extremely low densities of interface states on such substrates. This material

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has therefore found widespread use, among others in heterojunction-based solar cell architectures, such as the world record HIT solar cell [1,2]. One challenge with a-Si:H is the lack of thermal stability. When subjected to thermal processing at excessive temperatures, the obtained surface passivation is strongly reduced [3]. This hampers the introduction of a-Si:H into more conventional solar cell processes wherein the application of high temperatures is required as a part of the metallization process. In this work, we present a study of a-Si:H films and a-Si:H/a-SiN_x:H stacks deposited onto high lifetime Si wafers by plasma enhanced chemical vapour deposition (PECVD). The thermal stability of these films and stacks is then investigated by subjecting the samples to subsequent annealing treatments while the minority carrier lifetime is monitored. In order to shed more light on the changes in material properties associated with the observed lifetime variation with temperature, we also investigated the samples using neutron reflectometry (NR) and x-ray reflectometry (XRR) measurements. When combined, these two techniques can give essential information regarding the physical structure of the films, including film thicknesses, film densities and estimated hydrogen (H) concentration profile throughout the films [4,5]. The observed changes in lifetime are correlated with investigations of structure and composition of the films by NR and XRR.

2. Experimental details

All samples presented in this work were made from double side polished wafers of float zone (FZ) Si doped with phosphorous (P) supplied by Topsil. The wafers were of (100) orientation with a thickness of ~280 μm and a measured resistivity of between 3.0 and 3.5 Ω·cm. Prior to deposition, the wafers were cleaned in two consecutive 5% HF solutions, rinsed in de-ionized (DI) water and blow dried with N₂ gas. Thereafter, films of a-Si:H or stacks of a-Si:H and a-SiN_x:H were grown onto the cleaned substrates using a PlasmaLab System 133 PECVD reactor from Oxford Instruments. The thickness of the a-Si:H films ranged between 5 and 40 nm, while a thickness of ~100 nm was used for the a-SiN_x:H capping layer. Process parameters used for the PECVD process of both materials are shown in Table 1 below.

Table 1. PECVD process parameters used for the preparations of samples in this study.

Process parameter	a-Si:H	a-SiN _x :H
Deposition temperature	230 °C	200 °C
Deposition time	38 – 300 s	316 s
Power density	9.4 mW/cm ²	46.8 mW/cm ²
Chamber pressure	300 mTorr	800 mTorr
Flow rate SiH ₄	25 sccm	20 sccm
Flow rate NH ₃	0	20 sccm
Flow rate N ₂	0	980 sccm
Film thickness	5 – 40 nm	100 nm

After deposition, lifetime measurements were performed using quasi-steady state photoconductance (QSSPC) measurements and photoluminescence imaging (PL). QSSPC was performed using a WCT-100 Photoconductance lifetime tester from Sinton Instruments, and PL imaging using a LIS-R1 PL imaging setup from BT imaging. The lifetime of the samples with a-Si:H surface passivating films of variable thickness, both with and without the a-SiN_x:H capping layer, was measured in the as grown state and after annealing at different temperatures to determine their thermal stability. A rapid thermal processing (RTP) system (AccuThermo AW610) was used for this purpose. Single samples were subjected to consecutive annealing treatments at increasing temperatures. The duration of each annealing process was 1 minute.

Two 40 nm thick a-Si:H film samples were thereafter selected for further characterization by NR and XRR, one taken before and the other after annealing at 500 °C. This characterization was performed using a PANalytical XRR instrument at the University of Oslo and the SuperADAM NR instrument at ILL. NR was performed using a neutron wavelength of 4.4 Å.

3. Results and discussion

3.1. Lifetime measurements

In Fig. 1 below, we show the measured effective lifetime after various consecutive annealing steps for the uncapped a-Si:H samples. Although all samples passivated by the single a-Si:H layers initially exhibit high lifetimes, the lifetimes of the as-deposited single a-Si:H layers depend strongly and systematically on the thickness of the deposited layer. The thicker layers result in the highest measured as-deposited lifetime (> 3 ms). When subjected to the annealing process, all samples exhibit a similar trend: The measured lifetimes converge towards values of $\sim 3 - 3.5$ ms for all samples after annealing at a temperature of 350 °C. At this temperature, the passivation quality of all films is relatively equal. Thereafter, the lifetime is degraded quite rapidly, the samples with the thinner surface passivation layers being degraded somewhat faster than the samples with the thicker layers. At a temperature of 500 °C, the surface passivation is completely destroyed.

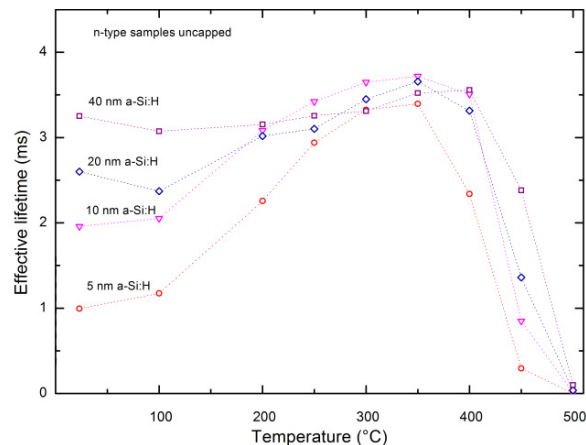


Fig. 1. Plot of the measured lifetime before and after annealing of single a-Si:H films with thicknesses from 5 to 40 nm.

In Fig 2 below, the measured lifetime after consecutive annealing steps is shown for the capped samples. Here, the observed changes in lifetime with temperature are different. Initially, all samples exhibit quite similar lifetimes in the as-deposited state, regardless of the a-Si:H layer thickness. The increase in lifetime at temperatures up to 350 °C, which is observed for the single a-Si:H layers, is not as clear a trend for the capped samples. However, as in the case for the uncapped samples, the lifetime of the capped samples is also strongly reduced by annealing at a temperature of 500 °C. The degradation of the thinnest films with temperature seems to occur somewhat later for the thinnest films, but more samples combined with additional annealing processes at intermediate temperatures needs to be performed before this behaviour is sufficiently verified. It should be noted that the passivation quality of the low temperature a-Si_x:H layers when applied to wafers without an intermediate a-Si:H layer is poor.

The measured lifetimes are strongly dependent not only on deposition temperature, but really on the total thermal budget of the PECVD process, as well as on any subsequent thermal processing. For further optimization of the single a-Si:H layers, it seems clear that an optimum process temperature must be found for each a-Si:H layer thickness if a subsequent annealing process is to be avoided, at least for films with thicknesses well below 40 nm. The application of a capping layer makes a subsequent annealing step to maximize lifetime unnecessary.

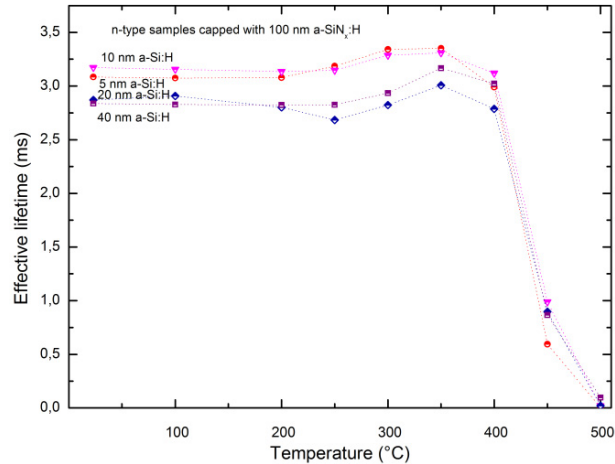


Fig. 2. Plot of the measured lifetime before and after annealing of single a-Si:H films with thicknesses from 5 to 40 nm capped by a-Si:H films with a thickness of ~100 nm.

3.2. Neutron and x-ray reflectometry measurements

One of the major motivations of the experiments presented in this work was to determine the practical usefulness of NR and XRR measurements for the characterization of surface passivating, silicon-based thin film materials deposited by PECVD. The combination of the two techniques can give information regarding film thicknesses and film densities, as well as allow for the determination of H concentration profiles throughout the films. The latter is particularly interesting for the materials investigated in this work, since H is well known to be important in determining the surface passivation quality in a-Si:H.

In order to shed some light on the actual changes in the material properties of the deposited a-Si:H films that caused the observed lifetime changes, several samples were selected for XRR and NR measurements. In general, XRR gave good information both with respect to layer thicknesses and densities for both capped and uncapped samples. The information regarding the physical structure of the films was used as input to the NR measurements to allow for the calculation of scattering length density (SLD) plots and, subsequently, the H concentration profiles.

Here, we will discuss the results of measurements on two samples, both with single layer a-Si:H films of 40 nm thickness, one before and one after annealing at 500 °C. The NR measurements of the as-deposited a-Si:H films, which exhibited high lifetimes, show that the films contain a high concentration of H, with a H/Si ratio of ~0.35. The H concentration remains relatively constant throughout the entire film thickness, apart from in the region closest to the a-Si:H/air interface. No significant accumulation or depletion of H is observed at the Si/a-Si:H interface. For a similar sample where the surface passivation is destroyed after annealing at 500 °C, a strong, uniform reduction of the H concentration in the bulk of the 40 nm layer is observed in the NR measurements. This confirms that H is important in determining surface passivation quality, as expected. Also here, no accumulation or depletion of H is observed at the Si/a-Si:H interface.

4. Conclusion

In this work, we have processed and characterized a-Si:H layers of varying thickness both with and without a capping layer of a-Si_x:H. The lifetimes of the samples is strongly affected by subsequent annealing, in addition to the deposition process itself. We also used XRR and NR to investigate the changes in material properties responsible for the observed changes in lifetime. Combined, these techniques are powerful tools for quantitative investigations of the structure and H distribution of silicon-based thin film materials.

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