Materials Science Forum Vols. 539-543 (2007) pp 3551-3556
Online available since 2007/Mar/15 at www.scientific.net
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doi:10.4028/www.scientific.net/MSF.539-543.3551

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Hydrogen Measurements in SiN_x: H/Si thin films by ERDA

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Key words: Hydrogen; Solar Cells; ERDA; RBS

Abstract. Thin SiN film deposited on Si by plasma enhanced chemical vapour deposition (PECVD) is used for surface passivation of Si. During the PECVD process Hydrogen is incorporated into the SiN film, and the passivation properties of the resulting SiN_x:H layers play an important role in enhancing the energy conversion efficiency of solar cells. It is believed that the Hydrogen present in SiN_x:H is responsible for this enhancement, and therefore its concentration in the passivating layer is an important parameter. The Hydrogen composition and its depth profile in thin SiN_x:H films of 20nm to 200nm was measured by elastic recoil detection analysis (ERDA), using a 1.7MeV He^+ ion beam of $(1x2)mm^2$, generated by a high stability 2MV Tandetron ion beam accelerator. Simultaneously, Rutherford backscattering (RBS) spectra were recorded for each sample. The results show that the Hydrogen concentration in the SiN_x:H layers is dependent of the deposition conditions. Also, Hydrogen was found to be homogenously distributed across the SiN_x:H layer thickness, and the SiN_x:H/Si interfaces were well defined.

Introduction

Thin films of Silicone Nitride with thickness between 20nm and 300nm are used as passivation and antireflection layers in high efficiency solar cells (SC) [1]. When deposited by PECVD, the SiN_x layer can incorporate a certain amount of Hydrogen, which in some conditions can be relatively large. During the subsequent annealing step of the fabrication process, some of the Hydrogen is lost or it may accumulate in pockets buried under the surface, causing blisters and irreparable damage to the SC. A small amount of Hydrogen is diffusing into the substrate and is believed to play a beneficial role by passivating the bulk defects [2], and thus contributing to the enhancement of the SC efficiency conversion.
The complex and important role played by Hydrogen in the passivation process leads to the necessity to monitor its content in the SiH_x:H layer, and one of the few methods capable to measure directly the Hydrogen content in thin films is elastic recoil detection analysis (ERDA).

Experimental

Thin films of amorphous SiN_x were deposited by PECVD on p-type Si (100) wafer. Prior to the deposition, the wafers were cleaned using a standard cleaning procedure (RCA1, RCA2 and HF solutions), and plasma etching [3]. The SiN_x was deposited on both sides of the Si wafer layer using a precursor gas-flow ratio $[NH_3]/[SiH_4]$ of 4.5, at 400°C.

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The Hydrogen content of SiH_x:H was measured by ERDA using a beam of 1.7MeV He^+ ions, impinging on the surface of the samples at an angle of 20°. Using a relatively lower He energy, it may be possible to separate more clearly the Hydrogen originating from the surface from the Hydrogen originating from the bulk of the targets.
In our experiment, the beam shape was rectangular, 1mm width and 2mm hight, and the beam current was 10nA. A schematic of the experimental setup is presented in Fig. 1.
The forward-recoiled H atoms were separated from the He atoms scattered by the surface of the sample by a 6μm thick Mylar ($C_{10}H_8O_4$) foil, with an areal density of 57,680x10^{15}at/cm^2 (Goodfellow). The energy of H atoms was recorded with a Si-barrier detector position at a scattering angle of 40°, and a conventional electronic setup. A rectangular slit (2x10)mm^2, was used in front of the detector, positioned with the larger side vertical.
Simultaneously, the energy of the He ions, Rutherford backscattered (RBS) from the SiN_x:H film and the Si substrate was recorded with a Si-barrier detector positioned at a scattering angle of 170°. In front of the RBS detector rectangular slit (4x10)mm^2 was used as well.

Results

For calibrating the experimental setup, the following procedure was followed. The accelerator energy was calibrated using the $^{27}Al(p,\gamma)^{28}Si$ nuclear reaction, with its narrow resonance at the proton energy E_p of 992keV. A difference of between 2keV and 3keV was typical, resulting in an uncertainty in energy of between 0.2% and 0.3%.

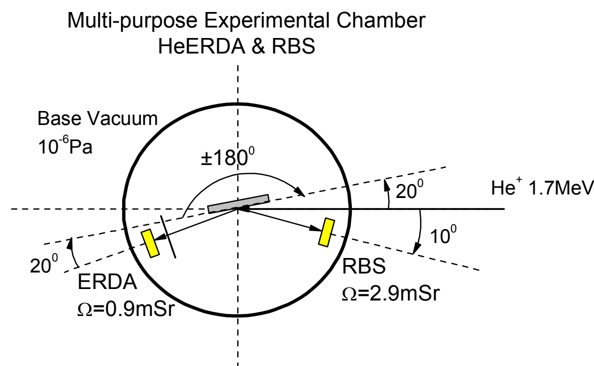

Fig. 1: Schematics of HeERDA/RBS experimental setup

The charge x solid angle (Q x Ω_{RBS}) of the RBS detector was determined using a Si crystal, and the stopping powers for Si published in the literature [4].
In the case of ERDA detector, the (Q x Ω_{ERDA}) product was calculated using a 25μm thick Kapton ($C_{22}H_{10}N_2O_5$) (Goodfellow), which has a small amount of Al possibly in the form of Al_2O_3. The correct stoichiometry of C, N, O in the Kapton target was measured by RBS, shown in Fig. 2, and was found to be C=64at%; N=5.4at%; O=17.1at%; with Al distributed preferentially at the surface of Kapton, at an areal density of 11x10^{15} Al at/cm^2. Using these values and the Hydrogen signal recorded by ERDA from Kapton, the (Q x Ω_{ERDA}) was determined for quantitative Hydrogen measurements.

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An important parameter for solar cell design is the thickness of the passivating SiN_x layer. This was measured by RBS, and compared with the deposition thickness, which was determined based on in-situ deposition measurements (the nominal values) using a crystal quartz balance. Fig. 3 is shows the spectra for amorphous SiN_x:H, with a nominal thickness of around 20nm. The RBS experimental results were fitted with SIMNRA software to determine the thickness of the layers, resulting in a layer thickness of $330x10^{15}at/cm^2$ for the film. Additionally, the stoichiometry of the SiN_x film was determined to be Si=40.2at% and N=55.8at%, with Si/N=0.72, which it is close to the Si/N ratio of the molecular formula Si_3N_4.

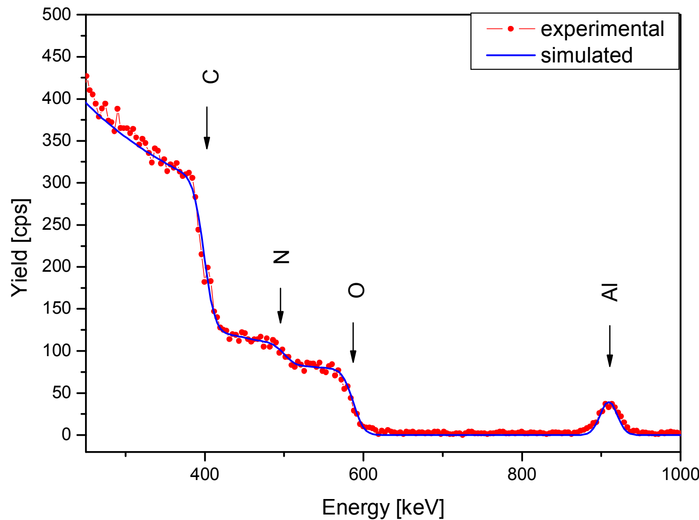

Fig. 2: RBS spectrum of Kapton film with Al surface layer used for calibrating the ERDA solid angle

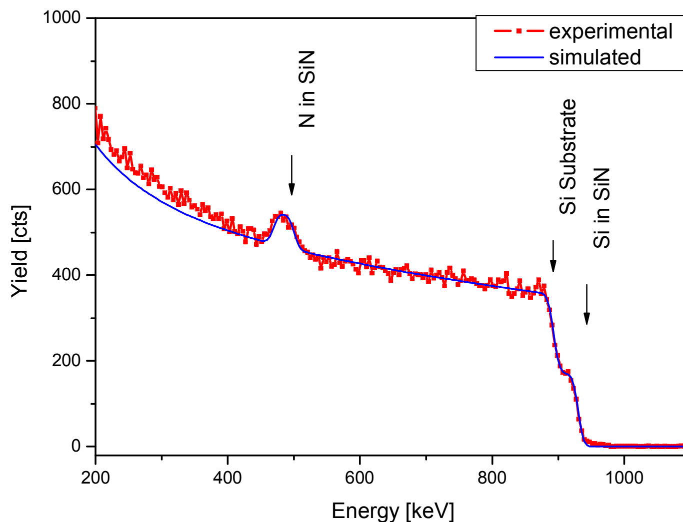

Fig. 3: RBS spectra of a thin a-SiN_x:H/Si sample

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Similarly, the thickness of the thicker SiN_x film, with a nominal thickness of around 70nm, was measured by RBS, and the result is presented in Fig. 4. In this case, the RBS-thickness was measured to be $605x10^{15}at/cm^2$, and the stoichiometry of the film was Si=39.5at% and N=55at%, with Si/N=0.718.
The physical thickness of the thin and the thick SiN_x:H films grown on Si was also assessed using ellipsometry, and the result was 46nm and 85nm respectively. With these values and the areal densities from RBS and ERDA measurements, the atomic density of the amorphous SiN_x:H was calculated to be $7.17x10^{22}at/cm^3$ for the thin film and $7.11x10^{22}at/cm^3$ for the thick film.
The raw HeERDA spectra of the thin and thick amorphous SiN_x:H films are shown in Fig. 5, together with the data obtained from a bare Si wafer used as the substrate for the deposition of the films.

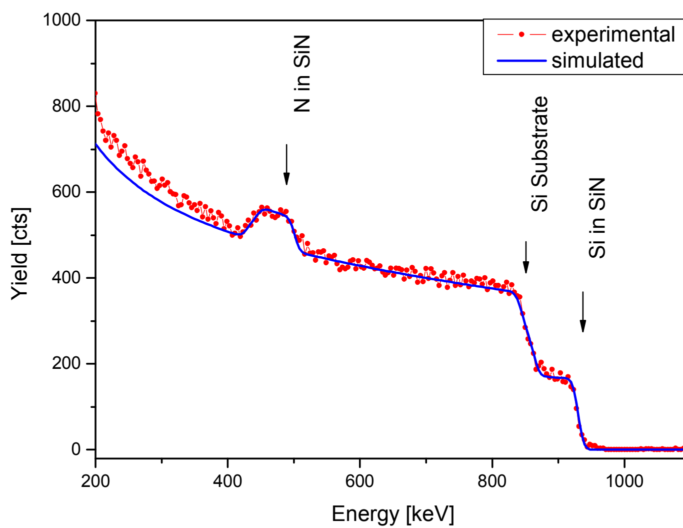

Fig. 4: RBS spectra of a thick SiN_x:H/Si sample

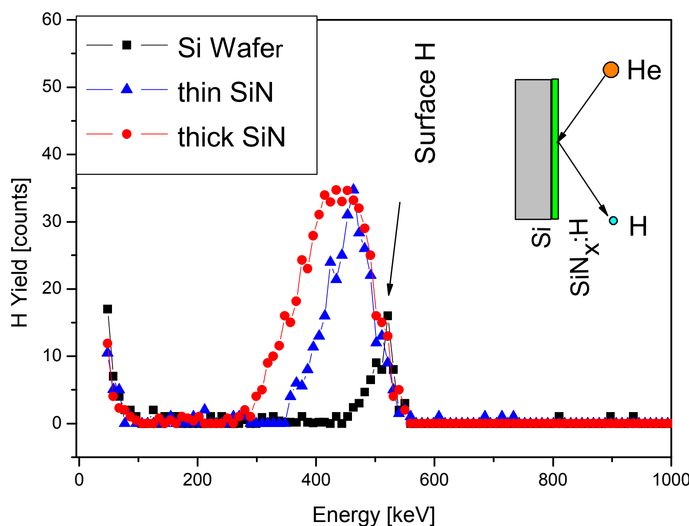

Fig 5: HeERDA Spectra from Si (■), thin SiN_xH (▲) and thick SiN_xH (●) thin films

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Using the kinematics of the He-H interaction and the SRIM2000 stopping powers, the energy of the Hydrogen recoiled from the surface of the samples was calculated to be 786keV, and after passing through the 6μm Mylar foil (the filter), the energy of the recoils decreases to 550keV. As seen in Fig. 5, a distinct peak is present at around 550keV, indicating that the the Hydrogen is indeed present at the surface of the sample. This Hydrogen present at the surface was not removed by the standard cleaning procedure, described before suggesting that it is tightly bonded to the surface of Si.
For the thin and thick amorphous SiN_x:H films, two peaks are present in the Energy versus H yield spectra. These peaks overlap, but are still distinct. The first peak is at around 550keV, originating from the surface of the films and a second, more intense, originating from the bulk, and extending over a wider energy region. The increase of the Hydrogen yield at the low energy end of the spectrum is due to the He atoms scattered from the surface of the samples which are not completely stopped by the Mylar foil.
For a thin film containing Hydrogen, the total yield from the surface to the maximum depth is given by [5]:

$$H = \frac{Q\Omega N\sigma}{\cos\theta}\int_0^t \sigma(E)dx \tag{1}$$

where Q is the charge, Ω is the detector solid angle, N is the number of Hydrogen atoms recoiled from the sample, σ is the differential cross section, θ is the incidence angle of the He ions, measured from the normal to the sample and t is the thickness of the film. As σ is a function of energy of the recoiled H ions, and it decreases continuously from the point of He-H impact at the maximum depth to the surface of the sample, the Equation 1, and the dE/dx for He and for H ions in Si were used to relate the Hydrogen yield at a particular energy to the depth x in the sample where the Hydrogen has originated from. The results of these calculations are presented in Fig. 6.

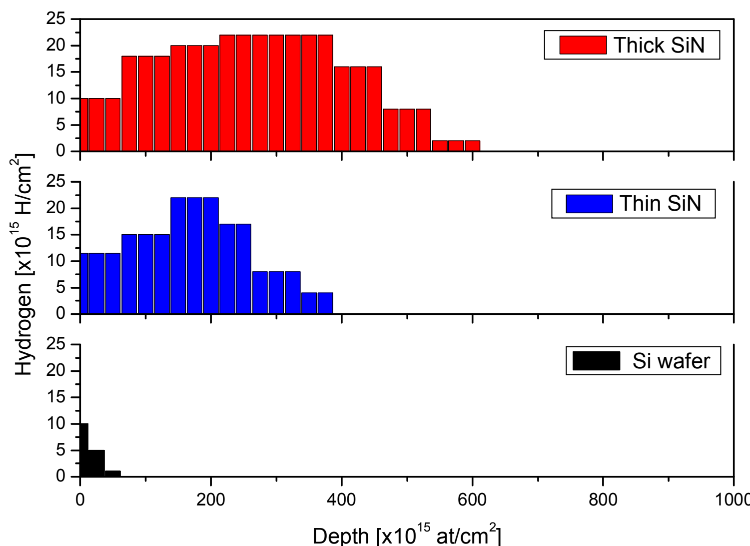

Fig. 6: The Hydrogen depth profiles in Si, thin SiN_x:H and thick SiN_x:H films

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The amount of Hydrogen present at the surface of the Si wafer, was determined to be 16×10^{15} H atoms/cm^2. This value is somewhat larger than the amount of Hydrogen usually found on the surface of cleaned Si, which is about 2-3x10^{15}at/cm^2.
In the case of the thin and thick a-SiN_x:H sample, the amount of Hydrogen measured was 213×10^{15} H atoms/cm^2, and 390×10^{15} H atoms/cm^2 respectively.
A key question regarding the measured samples was where the Hydrogen is absorbed: in the SiN_x:H film only, or partly in the film and partly in the substrate. A closer inspection of Fig. 6 shows that in both the thin and the thick SiN_x:H film cases, the Hydrogen presence is extended to a depth which corresponds approximately to the thickness of the films, determined above by RBS to be 330×10^{15}at/cm^2 and 605×10^{15}at/cm^2.

Summary

The effective passivation of atomically smooth Si surfaces is achieved with amorphous SiN_x films, which contain a variable amount of Hydrogen. We measured the Hydrogen content of a-SiN_x:H thin films grown on Si by PECVD using ERDA, with 1.7MeV He^+ ions. At this energy, the surface Hydrogen peak was resolved from the bulk signal.
Most of the Hydrogen was contained in the films, and thus available to afford an effective passivation to an atomically smooth Si surface.
An amorphous SiN_x film of 330×10^{15}at/cm^2 thick contains, following the deposition process, a total amount of Hydrogen of 213×10^{15}at/cm^2, and a SiN_x film of 605×10^{15}at/cm^2 thick contains, a total amount of Hydrogen of 390×10^{15}at/cm^2.
The thickness of the a-SiN_x:H films was measured by RBS, compared to the physical thickness of the films measured by ellipsometry, and the density for these amorphous films was calculated. For the thin a-SiN_x:H film the density was 7.17×10^{22}at/cm^3 and for the thick a-SiN_x:H film the density was 7.11×10^{22}at/cm^3.

Acknowledgement

This work was partly supported by ARC through grant no LP0455328, and partly by AINSE through the grant no 05140.

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THERMEC 2006
doi:10.4028/www.scientific.net/MSF.539-543

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doi:10.4028/www.scientific.net/MSF.539-543.3551

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