

Hydrogen kinetics in a-Si:H and a-SiC: H thin films investigated by Real-time ERD

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Abstract

Hydrogen effusion from hydrogenated amorphous silicon (a-Si:H) and amorphous silicon carbide (a-Si_{1-x}C_x:H) thin films during a temperature ramp between RT and 600°C was studied by in situ real-time elastic recoil detection analysis. Point to point contour maps show the hydrogen depth profile and its evolution with the ramped temperature. This paper proposes a diffusion limited evolution model to study H kinetic properties from total retained H contents recorded in a single ramp. In a compact a-Si:H layer where H predominantly effuses at high temperatures between 500°C and 600°C, an activation energy value of ~1.50 eV and a diffusion pre-factor of $0.41 \times 10^{-4} \text{ cm}^2/\text{s}$ were obtained. Applied to a non-stoichiometric a-Si_{1-x}C_x:H film in the same range of temperature, the model led to reduced

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values of activation energy and diffusion prefactor of ~ 0.33 eV and 0.59×10^{-11} cm² / s respectively.

Keywords - Kinetic property, activation energy, stoichiometric, depth profile, Arrhenius plot

1. Introduction

Hydrogen plays an important role in Si based opto-electronic devices. In solar cells specifically, H has a beneficial role on the amorphous Si absorber –layer because it passivates a large part of the defects also known as dangling bonds. The hydrogen content has also been linked to the metastability change upon light exposure [1, 2] and its bonding configuration has been reported to influence the structural properties of the material [3] The hydrogen content and its depth profile in Si based thin films depend on the bond chemistry, the chemical reactions, solubility and on the microstructure properties that are themselves strongly influenced by the deposition techniques. It is thus of technological importance that not only the H content is accurately determined in the material but also its depth distribution and kinetic properties be established. For low H concentrations, H diffusion is often determined by secondary ion mass spectroscopy [4]. In a-Si:H and a-Si_{1-x}C_x:H, Fourier transform infrared spectroscopy is widely used to quantify and assign IR active vibrations bonds. Other methods such as thermal desorption spectroscopy have been employed for a long time to study H kinetics in a-Si:H from several ramped anneals [5]. Recently, D. Smeets *et al.* [6] have studied the hydrogen diffusion in a-Si formed by ion implantation using real-time elastic recoil detection analysis (ERDA). While several reports exist on the hydrogen kinetics in a-Si:H thin films, little literature exists on the kinetic parameters in non-stoichiometric a-SiC:H.

This paper reports on hydrogen diffusion kinetics in a-Si:H and a-Si_{1-x}C_x:H thin films in which the hydrogen is incorporated in various forms during the deposition by chemical vapour deposition (CVD) process. In the hydrogen evolution experiments for both films, the temperature is raised monotonically with the time between around 300°C and 600°C while collecting at a constant rate the ERD spectra; the total retained H content throughout this temperature range were obtained from the integration of the simulated content - depth curves. A diffusion-limited evolution model [7, 8] was used to obtain both the activation energy and H diffusion coefficient from a single temperature ramp. It is assumed that no H resides in the used c-Si substrate.

2. Material and methods

Films of a-Si:H, and a-Si_{1-x}C_x:H around 1 µm thick were deposited onto Si(100) substrate by hot-wire chemical vapour deposition (HWCVD) using feed gas mixtures of SiH₄/H₂ and SiH₄/CH₄/H₂ respectively at a low substrate temperature below 400°C; a summary of the deposition conditions is given in Table 1.

Table 1: A summary of the deposition conditions of the films studied.

Sample	Filament T (°C)	Substrate T (°C)	Pressure (µbar)	Feed gas (sccm)	Thickness (nm)
a-Si:H	1600	375	40	SiH ₄ /H ₂ : 12 / 48	900
a-SiC:H	2000	280	150	SiH ₄ /CH ₄ /H ₂ : 2 / 4 / 100	1000

The studied grown $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ film is not stoichiometric but it instead incorporates an atomic C content x of ~ 7 at. % as it has been determined by EDX studies not given here. Real-time ERDA measurements were performed at iThemba LABS, Faure, South-Africa using the same experimental set-up and scattering details as in [9, 6]. A $15\ \mu\text{m}$ thick mylar ($\text{C}_{10}\text{H}_8\text{O}_4$) was used as a stopper of the scattered He^+ in front of the solid state detector. The analysed spectra were obtained using an incident He^+ beam of 3 MeV while the channel –energies calibration experiment was done using spectra taken from a $125\ \mu\text{m}$ thick Kapton ($\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_5$) foil at beam energies of 3, 2.5 and 2 MeV. For the $a\text{-Si:H}$ sample, a rapid ramp from RT up to 300°C was performed and subsequently a fixed slow ramp rate of 3°C per minute was applied over the range $300 - 600^\circ\text{C}$. In $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ film where a low temperature H effusion was noted, the $3^\circ\text{C}/\text{min}$ slow ramp was initiated at a temperature of 250°C . ERD spectra were saved every 30 seconds. The collected spectra were combined either in four or eight to form a slice of ERD spectra with improved statistics. The formed slices were thus representative of a temperature range of 6°C and 12°C respectively. The simulations of the spectra were done using SIMNRA [10]. The non-Rutherford cross section of Baglin (HHeHHe30.R33) [10] in the energy range between $1 - 3$ MeV and for a recoiled angle of 30° was chosen in the simulations process. The calibrated data of the experimental set-up, obtained from the simulation of a Kapton foil spectrum (i.e. a simulation that reproduced the actual thickness and the hydrogen content in the foil), have been kept fixed during the simulation process of the studied samples' spectra.

3. Results and discussion

Fig.1 compares the profile of few selected ERDA raw spectra of temperature ramped $a\text{-Si:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films ;

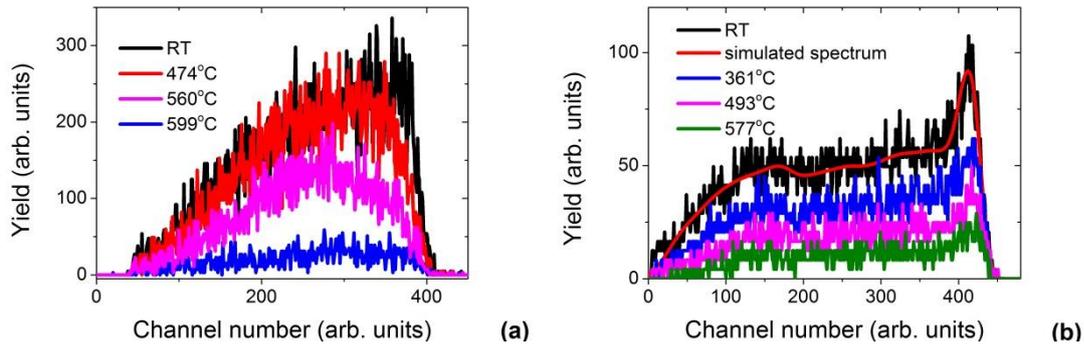


Fig. 1 Selected as-taken spectra (a) the a-Si:H (b) the a-Si_{1-x}C_x:H ramped from RT to 600°C; the red solid curve on the top spectrum of fig. 1(b) is a typical example of the simulation.

the spectrum of the as-deposited a-Si:H sample in (a) shows that H was uniformly distributed throughout the thickness (the reader should note that in ERD spectra, the combined effect of the cross section and of the projectile's energy loss is such that the yield decreases rapidly with depth for the same number N_s of target atoms (i.e. same H content)) in contrast to a-Si_{1-x}C_x:H film in (b) where an inhomogeneous H profile was observed towards the interface. The stacked spectra in fig. 1(b) indicate also that the H effusion starts at lower temperature in the a-Si_{1-x}C_x:H material. Fig. 2 that displays the total simulated hydrogen content as function of the temperature gives more details about the onset of the H effusion.

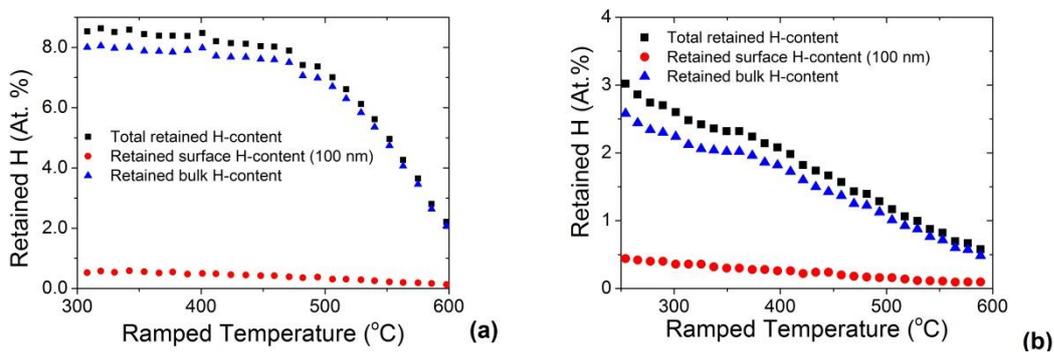


Fig. 2 Measured retained H content obtained by simulation, as function of the ramped temperature

(a) a-Si:H ; (b) a-Si_{1-x}C_x:H

It is clear that only a high temperature H effusion process, starting at $\sim 500^\circ\text{C}$ is observed in a-Si:H sample (fig. 2(a)) while on the other hand a continuous loss of H can be seen to occur throughout the plotted temperature range on the a-Si_{1-x}C_x:H profile in fig. 2(b).

We have plotted in fig. 3 point by point contour maps of the depth profile of the retained hydrogen content at different temperatures, using the simulated results. It follows from fig. 3(a) that the bulk hydrogen is fairly stable up to a temperature of $\sim 500^\circ\text{C}$. The H effusion in the a-Si:H film at a high temperature of $500 - 600^\circ\text{C}$ suggests a compact dense material [11]. This is consistent with earlier published results [12] that stipulate that hydrogen incorporation in high quality a-Si:H materials is predominantly in the form of isolated Si-H.

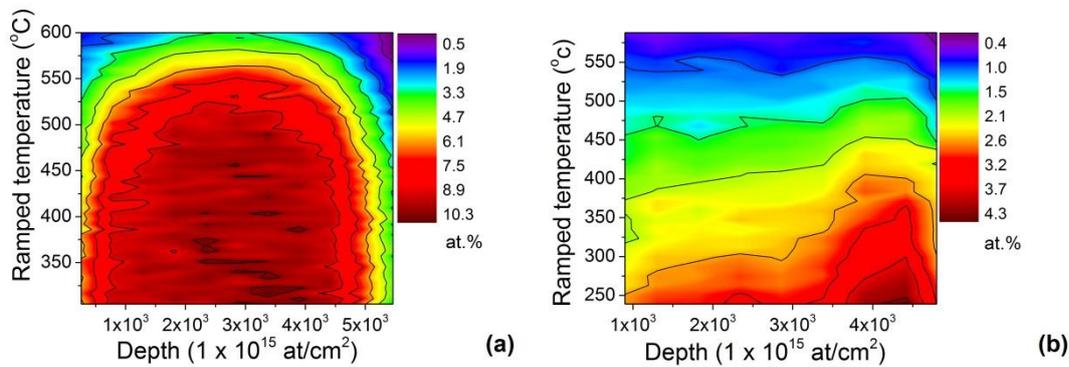


Fig. 3 Contour plot maps indicating the depth profile of hydrogen at different ramp temperatures:

(a) a-Si:H, (b) a-Si_{1-x}C_x:H. The appended contour lines are there as a guide to the eye.

Fig. 3(b) displays the contour plot of the a-Si_{1-x}C_x:H film annealed at a slow constant rate from around 250°C to 600°C . A continuous loss of H is observed throughout the range of temperature studied. Low content of C in a-Si films (mainly in a-Si_{1-x}C_x:H_n form) has thus the effect of straining the a-Si network. This is in agreement with the work of Williamson [13] that concluded that a-SiC alloy's growth often results in a void-rich structure.

In order to extract the kinetics properties i.e. the activation energy E_a and the pre-factor diffusion coefficient D_0 , the solution of the diffusion equation was used. For a diffusion-

limited evolution, the hydrogen concentration profile $c(x,t)$ across the film must be compatible with the diffusion equation [7, 8]

$$\frac{\partial c}{\partial t} = D(t) \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where D is a time-dependent diffusion coefficient $D(T(t))$. The general solution is written [8]:

$$c = \sum_{m=1}^{\infty} (A_m \sin \lambda_m x + B_m \cos \lambda_m x) \exp(-\lambda_m^2 D t), \quad (2)$$

where A_m , B_m and λ_m are determined by initial and boundary conditions for any particular problem. In order to determine the hydrogen diffusion coefficient from ERD retained H contents, we consider a typical diffusion out of a plane sheet of thickness L and we assume, for temperatures in the diffusion regime, a hydrogen concentration profile $c(x)$ with $c \sim 0$ at both the film surface and the film substrate interface. The same assumption was made by W. Beyer *et al.* [7] in their H effusion experiments, for a temperature close to the peak evolution rate. The support for this assumption is justified by the hydrogen profiling experiments which show a decreasing retained H content at the film surface and film-substrate interface compared to the content in the bulk. While the depletion of hydrogen near the film surface can be understood in terms of hydrogen effusion following the high temperature ramping, the reason for its decrease near the interface compared to bulk is less evident as no diffusion is expected through the c-Si substrate. A lateral diffusion along the film-substrate interface is most likely and it has been proposed previously by Beyer *et al.* in amorphous Si material [7]. The lateral diffusion along the interface depends strongly on the microstructure (e.g. compactness and oxidation state) of the interfacial layer as well as on the film adhesion on the substrate. With the above assumptions, the initial and boundary conditions are written as in [8]:

$$C = C_0, 0 < x < L, t = 0 \quad (3)$$

$$C = 0, x = 0, x = L, t > 0. \quad (4)$$

Applying the above initial and boundary conditions, equation (2) becomes [8]:

$$C = \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \exp \left\{ -Dt \left(\pi \frac{2n+1}{L} \right)^2 \right\} \sin \left(\frac{2n+1}{L} \pi x \right) \quad (5)$$

In our experiments, the boundary condition given by equation (4) is valid at high temperature of anneal where the Arrhenius theory is applicable; the generated particular equation (5) is thus only used at a temperature above $\sim 500^\circ\text{C}$ in the diffusion regime.

The resultant numerical solution to equation (5) shows that it is dominated by the first few leading terms because they decrease significantly as the order of n increases; here follow the 1st three terms that were used in the numerical estimation of the diffusion coefficient D :

$$C(x, t) = \frac{4C_0}{\pi} \left\{ \exp \left(-\frac{D\pi^2 t}{L^2} \right) \sin \left(\frac{\pi x}{L} \right) + \frac{3}{2} \exp \left(-\frac{9D\pi^2 t}{L^2} \right) \sin \left(\frac{3\pi x}{L} \right) + 2 \exp \left(-\frac{25D\pi^2 t}{L^2} \right) \sin \left(\frac{5\pi x}{L} \right) \right\} \quad [6]$$

The average concentration of the retained hydrogen at time t can be estimated by integrating $C(x, t)$ over the entire thickness L and dividing the integral by L

$$C_{average}(t) = \frac{1}{L} \int_0^L C(x, t) dx \quad (7)$$

This expression, after integration of the equation (7), reduces to

$$C_{average}(t) = \frac{4C_0}{5\pi^2} \exp \left(-25Dt \frac{\pi^2}{L^2} \right) \left\{ 4 + 5 \exp \left(\frac{16D\pi^2 t}{L^2} \right) + 10 \exp \left(\frac{24D\pi^2 t}{L^2} \right) \right\} \quad (8)$$

Using the set ramp constant $\beta = (T - T_0)/t$ and the value of the initial temperature T_0 when the temperature ramp was initiated, the time t can be found from the continuously monitored ramped temperature T .

As all other parameters featuring in equation (8) are either constant or can be determined experimentally, the diffusion coefficient can be determined numerically; in our analysis, the quantity C_0 and $C_{average}$ are estimated through integration of the H content before anneal and the integrated retained H at different ramped temperatures respectively. The kinetic

parameters D_0 & E_a are found using the Arrhenius equation from the temperature dependent diffusion's expression (over a small temperature range in the diffusion regime)

$$D(T) = D_0 e^{-E_a/k_B T} \quad (9)$$

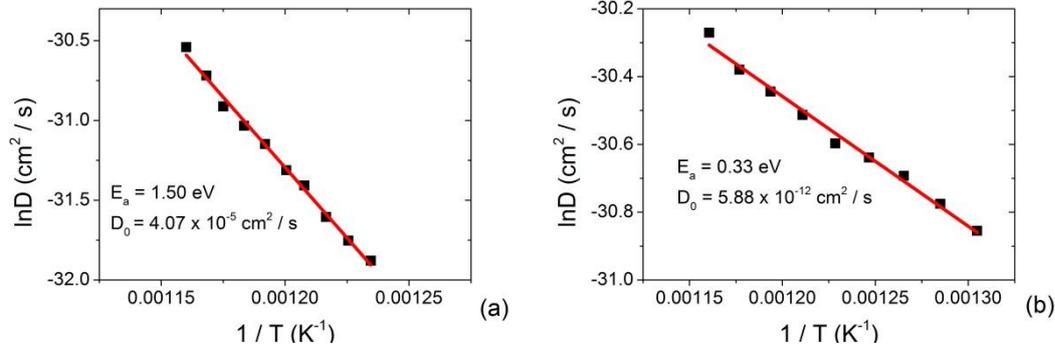


Fig. 4 Arrhenius plots of the diffusion coefficient against inverse temperature and the best fits obtained (red solid lines) (a) the a-Si:H sample and (b) the a-Si_{1-x}C_x:H film. The obtained values of the kinetic parameters are inserted.

Figure 4(a) displays the Arrhenius plot obtained from the analysis of the a-Si:H film. Values of (1.50 ± 0.04) eV and 0.41×10^{-4} cm²/s for the activation energy E_a and the diffusion pre-factor respectively were calculated; they are close to those previously reported for compact a-Si:H with a hydrogen content of ~10 at.% [7, 11, 12, 14]. Applied to the a-Si_{1-x}C_x:H sample in the high temperature regime (above 493°C) where the H effusion is known to be diffusion limited for a-Si:H films, this model has yielded activation energy E_a and D_0 values $(0.33 \text{ eV} \pm 0.01)$ eV and 0.59×10^{-11} cm²/s respectively as seen in fig.4(b). The obtained values of E_a and D_0 for the a-Si_{1-x}C_x:H film are particularly low; this points to a void rich microstructure that leads to the instability of hydrogen at the void surfaces and thus its easy desorption. The influence of the change in microstructure with anneal is also visible in a slight scattering of the experimental data constituting the Arrhenius plot around the best linear fit. The dispersion in the diffusion process due to the change in the microstructure has been previously reported

by other authors [15, 16]. The obtained values of the kinetic parameters are however in very good agreement with the expected values from the previously reported linear dependence curve between the prefactor D_0 and the hydrogen diffusion energy E_D for amorphous, microcrystalline and single-crystal silicon materials [12]. Williamson [13] attributes the presence of voids in a-SiC:H to the difference in binding energy to H between the alloy C and the host Si atoms. We conclude thus that the random incorporation of C in a-Si:H has an adverse effect of straining the Si network. The rate of the rupture of Si-H and H desorption from internal surfaces of voids seems to be the main limiting factor in low C-content a-Si_{1-x}C_x:H alloys. This is also consistent with the observed continuous loss of H starting at low temperature as observed in fig. 2(b) and 3(b). Beyer [5] had established that H diffusion and H surface desorption in Si were considerably affected by *p*-doping with boron where the low temperature effusion peak shifted towards lower values; it appears that alloying the Si network with smaller atoms like C in small amounts results also in the same effect. It had also been found earlier that the properties of the impurity (e.g. its size) not only influence the rate limiting step of the diffusion process [17] but also the effective entropy of diffusion [18].

4. Conclusion

We have studied H effusion from a-Si:H and a-SiC:H films by realtime ERD using a single thermal annealing ramp. In the a-Si:H, the hydrogen exited the sample significantly above 500 °C while for a-Si_{1-x}C_x:H, the out-diffusion was observed to start below 300 °C. A diffusion limited evolution model, based on the solution of the diffusion equation, was applied to extract the kinetic parameters from the integrated retained H content. The results obtained on the a-Si:H sample are in the range of the reported values for intrinsic a-Si:H with similar hydrogen content indicating that the method of analysis is appropriate. Applying the

same analytical method to a HWCVD grown a-SiC:H with a low C content of ~7 at. %, a lower activation energy value and consequently low H diffusion coefficient were observed; this result points to a defective microstructure resulting from the non-stoichiometric alloying of C in a-Si:H. This method of analysis has proved to be sensitive to small variations in the microstructure, future studies will explore the hydrogen kinetics in a-SiC:H with different degrees of C alloying.

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