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J. Phys.: Condens. Matter **16** (2004) 4233–4244 PII: S0953-8984(04)74689-5

The diffusion of ion implanted hydrogen in amorphous Si_3N_4:H films

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Received 13 January 2004
Published 4 June 2004
Online at stacks.iop.org/JPhysCM/16/4233
doi:10.1088/0953-8984/16/24/005

Abstract

The tracer diffusion of hydrogen is studied in amorphous Si_3N_4:H films which were produced by rf magnetron reactive sputtering. The diffusion experiments were carried out in the temperature range between 700 and 1000 °C with ion implanted deuterium isotopes. Secondary ion mass spectrometry was used for depth profile analysis. While a considerable part of the tracer is immobilized due to the interaction with the implantation damage, the other part migrates freely into the film, wherefrom diffusivities are extracted. These diffusivities coincide with those obtained from a control experiment with a gas exchange technique, demonstrating that the implantation damage has no significant influence on the determination of the correct diffusivities themselves. ^{2}H transport can be described by the concept of trap limited diffusion, where the tracer atoms are temporarily trapped by intrinsic film defects, presumably nitrogen dangling bonds. For the present case of a considerably high dissociation rate of trapped hydrogen, effective diffusivities are derived which obey an Arrhenius behaviour with a large activation energy of $\Delta E = 3.4$ eV and a pre-exponential factor of $D_0 = 5 \times 10^{-4}$ m^2 s^{-1}. The effect on diffusion of pre-annealing the films prior to diffusion in nitrogen and possible structural rearrangements involved, as well as of charging the films with hydrogen up to 2.6 at.%, is analysed.

1. Introduction

During the last few years, there has arisen a considerable experimental and theoretical interest in the migration behaviour of hydrogen in hydrogenated amorphous silicon Si:H [1–10] and related materials [11, 12]. This interest is motivated mainly by two factors. First, hydrogen

is an essential constituent of the amorphous network structure of these materials, responsible for reduction of stress and the formation of a metastable equilibrium state. Since hydrogen diffuses at relatively low temperatures compared to the other elements, its dynamic behaviour is very important for the thermal stability of the material. Second, intrinsic defects of the material like dangling bonds play a decisive role for the application of these materials as electronic and optoelectronic components and limit their performance as devices. Hydrogen is able to passivate these defects and can thus improve the quality of devices. Since the atomic mobility of hydrogen is strongly correlated with the defect densities, investigations of the diffusion properties of hydrogen in these materials may reveal important information on the defect physics, which is of crucial importance for any technological application.

Hydrogenated amorphous silicon nitride (Si_3N_4:H) thin films can be used as a versatile dielectric in IC technology, as a gate dielectric in a-Si:H thin film transistors, and as a charge storage medium in non-volatile memories [13, 14]. Each of these applications depends on the presence and on the mobility of hydrogen and its interaction with defects. To obtain a complete picture on the atomic transport properties of hydrogen we carried out systematic investigations of hydrogen tracer diffusion in a-Si_3N_4:H as a function of temperature, hydrogen content and pre-annealing conditions in the amorphous state. The a-Si_3N_4:H thin films were produced by rf magnetron sputtering. This low-temperature process yields high purity homogeneous samples with low hydrogen content (<0.5 at.%), which enables a specific variation of the hydrogen content by post-annealing the films in hydrogen enriched atmospheres after the deposition process without changing the microstructure of the films due to modified deposition conditions.

Diffusion measurements were performed with ion implanted ^{2}H isotopes as tracers, and secondary ion mass spectrometry (SIMS) was applied for depth profiling. This combination of methods has the advantage that the tracer is deposited directly in the sample. Problems arising from the interaction of the tracer with the sample surface, like an oxide layer which may act as a diffusion barrier and possibly hinders tracer incorporation from the gas phase, are avoided. However, relatively high implantation doses ($>10^{14}$ ions cm^{-2}) are necessary for successful experiments due to the natural abundance of the ^{2}H isotope in the films leading to a background signal during SIMS analysis. Consequently, a non-negligible implantation damage arises which may influence the diffusion behaviour. This problem is also addressed by our experiments.

2. Experimental details

Thin films of silicon nitride were deposited on polycrystalline SiC (BCS, Germany) substrates by rf sputtering using a 3 inch US GUN low profile planar magnetron source (AP&T, Nürtingen, Germany). An operating pressure of 5×10^{-3} mbar of 50 vol.% Ar and 50 vol.% N_2 and a high purity silicon target (B impurities 0.03 ppm, Al impurities <0.01 ppm) were used for reactive sputtering at a sputtering power of 160 W and a substrate temperature of 400 °C yielding deposition rates of about 2 nm min^{-1}. The substrates of dimension $10 \times 10 \times 2$ mm^3 were polished with diamond paste from 6 μm down to 1 μm particle size and cleaned with ethanol in an ultrasonic bath before sputter deposition.

Four types of samples were investigated during this study (see table 1): films in the as-deposited state (SN0), films annealed for 2 h at 1000 °C (SN1000) or for 2 h at 1200 °C (SN1200) in N_2 (980 mbar), as well as films annealed for 2 h at 1000 °C in a mixture of N_2–6% H_2 (SN1000H). This pre-annealing process was carried out to allow a relaxation of the as-produced amorphous state and to establish a metastable equilibrium.

The elemental composition of the sputtered films was measured with non-Rutherford backscattering spectroscopy (n-RBS), performed with the 7.0 MV van de Graaff accelerator

Table 1. Pre-annealing atmosphere, hydrogen content, activation energies, and pre-exponential factors of hydrogen diffusion for amorphous Si_3N_4:H. Typical errors are about ±0.2 eV for the activation energy ΔE and about ±1.5 for $\ln(D_0/\mathrm{m}^2/\mathrm{s})$.

Sample	Pre-annealing atmosphere	Hydrogen content (at.%)	ΔE (eV)	D_0 ($\mathrm{m}^2\ \mathrm{s}^{-1}$)	Method
SN0	—	0.2 ± 0.05	3.4	5×10^{-4}	Ion implantation
SN1000	N_2	0.4 ± 0.1	3.4	4×10^{-4}	Ion implantation
SN1200	N_2	0.5 ± 0.1	3.5	9×10^{-4}	Ion implantation
SN1000H	N_2–6% H_2	2.6 ± 0.2	2.7	3×10^{-6}	Ion implantation
SN1000HG	N_2–6% H_2	2.6 ± 0.2	2.6	3×10^{-6}	Gas exchange

at the Institut für Kernphysik, Frankfurt, using a 3.5 MeV $^4He^+$ beam. The elastically backscattered particles were detected at an angle of 171°. These parameters were chosen to obtain the enhanced backscattering cross section for ^{14}N compared with the Rutherford cross section [15]. The hydrogen content of the films was determined by nuclear reaction analysis (NRA) using the resonant nuclear reaction $^1H(^{15}N, \alpha, \gamma)^{12}C$ at the resonance energy of about 6.4 MeV.

Tracer deposition was carried out by implanting a mass separated and scanned $^2H_3^+$ molecular ion beam of 20 keV with a fluence between 2×10^{14} and 2×10^{15} ions cm^{-2} at room temperature. After tracer deposition the specimens were diffusion annealed in a powder pack composed of fine powder of Si_3N_4 in the temperature range between 700 and 1000 °C in a N_2 atmosphere (SN0, SN1000, SN1200) and in a N_2–6% H_2 (SN1000H) atmosphere at ambient pressure for times between 0.3 and 68 h. In addition, experiments were carried out with a gas exchange technique where the tracer is incorporated in the sample by annealing in a deuterium enriched N_2–6% $^2H_2$ atmosphere (SN1000HG) and not by ion implantation.

Tracer depth profiles of $^1H^+$ and $^2H^+$ ions were measured by secondary ion mass spectrometry (CAMECA IMS-3F) using an O^--ion primary beam (15 keV, 150 nA). To prevent electrical charging, the samples were coated with a thin layer of gold before SIMS analysis. Depth calibration was obtained by measuring the crater depth with a mechanical profilometer (Alphastep 500, TENCOR), assuming a constant sputter rate. From these data the ^2H concentration versus depth profiles were constructed.

3. Results

3.1. Characterization of film properties

The concentration of the film components Si and N was determined by n-RBS to correspond to stoichiometric Si_3N_4 with an Ar impurity concentration less than 1 at.% and an O impurity concentration less than 0.2 at.%, respectively. The formation of Si–N bonds was proven by photo-electron spectroscopy. The hydrogen content was determined by NRA to be between 0.2 and 0.5 at.% for the as-deposited films and films pre-annealed in N_2 (SN0, SN1000, SN1200), and about 2.6 at.% for the films pre-annealed in N_2–6% H_2 (SN1000H) (table 1). Investigations with SIMS on an as-deposited film (thickness: 1.2 μm) and on the same film annealed at 1200 °C confirm the constant ratio of silicon to nitrogen concentration and indicate a nearly constant depth distribution of hydrogen throughout the film before deuterium is implanted. The presence of an amorphous phase was verified by x-ray diffractometry. A detailed description of the thermal stability of the sputtered Si_3N_4 films, which start to crystallize at 1300 °C, can be found in [16].

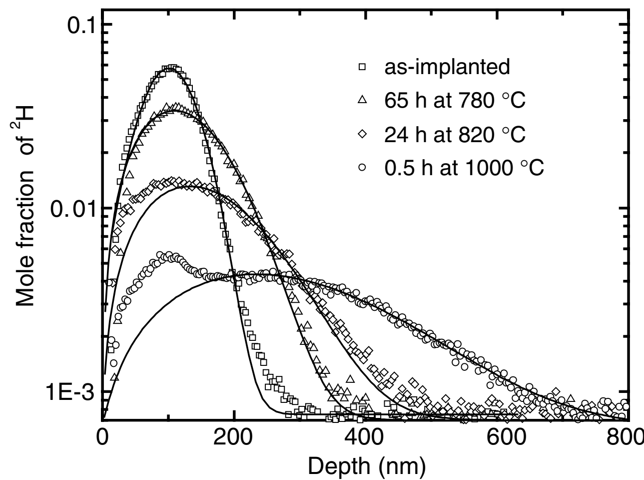

Figure 1. Typical diffusion profiles of ion implanted ^{2}H tracers in amorphous Si_3N_4:H (SN1200) measured with SIMS after annealing at elevated temperatures and annealing times in N_2. The solid curves correspond to a least squares fit of the data to equation (1) in the depth range >170 nm.

3.2. Diffusion measurements with ion implanted ^{2}H tracers

Figure 1 shows typical SIMS depth profiles of implanted ^{2}H in amorphous Si_3N_4:H (SN1200) before and after annealing for different times and at various temperatures. The implantation profile exhibits a nearly Gaussian shape with a projected range of $R_p = 100$ nm and a standard deviation of $\Delta R_p = 38$ nm. For the annealed films a broadening of the profile is observed corresponding to diffusion. For profiles with a large broadening, as obtained for the film annealed at 1000 °C, a cusp is superimposed on the Gaussian profile around 100 nm. This cusp is also observed for other samples and its position does not change during annealing. We attribute this cusp to the fact that defects which are produced by the high-dose implantation process (e.g. agglomerates of vacancies, clusters, etc) act as trapping sites (extrinsic traps) and immobilize a part of the implanted ^{2}H tracer. Only a fraction of the tracer is mobile and diffuses into the sample (Gauss-like diffusion profile). This observation is commonly found in diffusion experiments carried out with a relatively high dose of implanted ions [17, 18], but is less pronounced for light elements like H than for heavier elements like N or Si.

The diffusivities were determined by a least squares fit of the experimental data to the following analytical solution of the diffusion equation

$$c(x,t) = \frac{A}{\sqrt{2\pi(\Delta R_p^2 + 2Dt)}}\left[\exp\left(-\frac{(x-R_p)^2}{2\Delta R_p^2 + 4Dt}\right) - \exp\left(-\frac{(x+R_p)^2}{2\Delta R_p^2 + 4Dt}\right)\right], \tag{1}$$

assuming a sink at the sample surface [19]. Here, $c(x,t)$ is the mole fraction of ^{2}H, A is the fluence of the implanted deuterium, D is the diffusion coefficient, and t the annealing time. The assumption of a sink at the sample surface is justified by the fact that a relatively large amount of the tracer (up to 50%) leaves the sample during the diffusion process. The best possible results are obtained if the fitting procedure is limited to a depth range larger than 170 nm. This means that in order to get an optimised fit, the part of the profile where the influence of the implantation damage is maximum is neglected for fitting purposes. For a justification of this approach see section 3.4. Fitting of a conventional Gaussian distribution to the data does not lead to satisfactory results for the diffusion profile of the film annealed at 1000 °C.

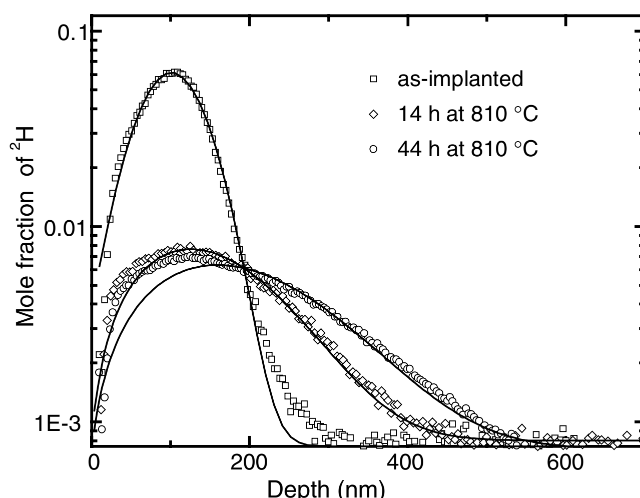

Figure 2. ^{2}H isotope depth profiles for implanted amorphous Si_3N_4:H (SN1000) before and after annealing for 14 and 44 h at 810 °C in N_2, respectively. The solid curves correspond to a least squares fit of the data to equation (1) in the depth range >170 nm.

To investigate a possible time dependence of the diffusivities, selected films of all series were annealed at two different annealing times. The results are exemplarily illustrated in figure 2 for the case of a film (SN1000) annealed at 810 °C for 14 and 44 h, respectively. The diffusivities determined from the diffusion profiles are the same within an error of about 30%, indicating that no strong time dependence is present.

3.3. The temperature dependence of the diffusivities

In figure 3 the determined diffusivities of ^{2}H are shown as a function of reciprocal temperature for as-deposited films, and for films annealed at 1000 and 1200 °C in nitrogen, prior to tracer deposition and diffusion annealing. During the diffusion experiments the annealing temperatures never exceeded the pre-annealing temperature so that changes in microstructure were avoided. The deuterium tracer diffusivities for all three types of samples obey an Arrhenius law according to

$$D = D_0 \exp\left(-\frac{\Delta E}{k_B T}\right), \tag{2}$$

were D_0 denotes the pre-exponential factor, ΔE the activation energy, and k_B the Boltzmann constant. The experimental error of about 50% attributed to the diffusivities is caused by the error of the depth measurement of the SIMS sputtering crater and by the averaging of different measurements carried out on one sample. The determined activation energies and pre-exponential factors do not vary significantly with the pre-annealing temperature (table 1), resulting in values of $\Delta E \approx 3.4$–3.5 eV and of $D_0 \approx 4$–9×10^{-4} m^2 s^{-1}. Consequently, microstructural rearrangements of the atoms, like relaxation or stress release which occur during the pre-annealing procedure, do not significantly influence the atomic transport properties of hydrogen. It has to be noted that the hydrogen content of the three types of films is well below 1 at.% and shows no substantial variation within estimated errors (table 1).

In figure 4 the temperature dependence of the diffusivities for the films pre-annealed at 1000 °C in N_2 (SN1000) is compared to the films pre-annealed at 1000 °C in N_2–6% H_2

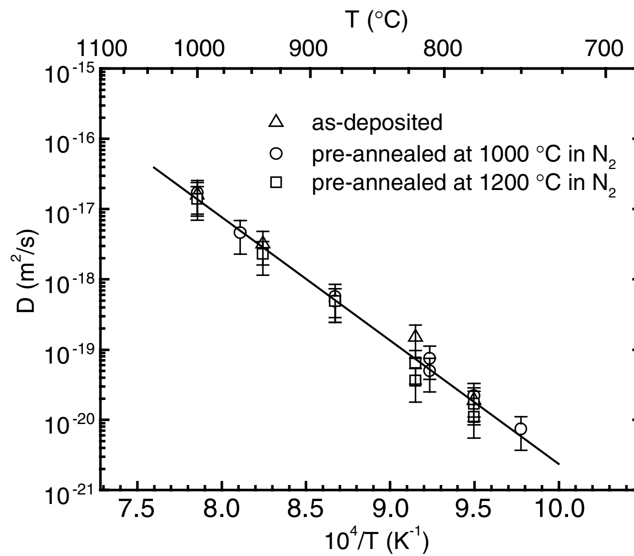

Figure 3. Effective diffusivities of ^{2}H in amorphous Si_3N_4:H as a function of reciprocal temperature for as-deposited films (SN0) and films pre-annealed for 2 h at 1000 °C (SN1000) and 1200 °C (SN1200) in N_2.

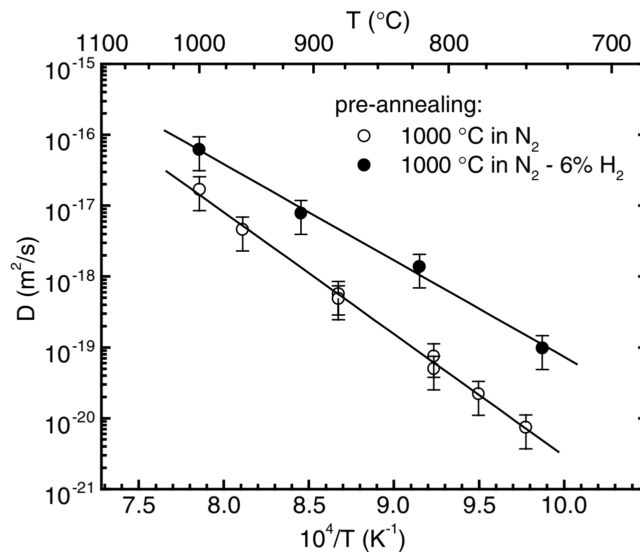

Figure 4. Effective diffusivities of ^{2}H in amorphous Si_3N_4:H as a function of reciprocal temperature for films pre-annealed for 2 h at 1000 °C in N_2 (SN1000) and in N_2–6% H_2 (SN1000H).

(SN1000H). The hydrogen enriched annealing atmosphere results in a hydrogen charging of the films with an about seven times larger H content for the film series SN1000H. The diffusivities of both sample series can be described by an Arrhenius behaviour, but significant differences arise for the pre-exponential factor and the activation energy. These values are lower for the sample series containing more hydrogen, where ΔE is decreased to 2.7 eV and D_0 by more than two orders of magnitude (table 1).

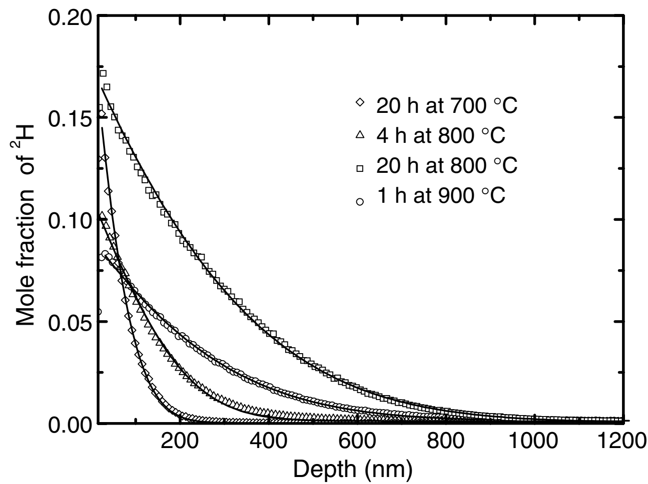

Figure 5. Typical diffusion profiles of ^{2}H in amorphous Si_3N_4:H (SN1000HG) measured with SIMS after annealing at elevated temperatures and annealing times using a gas exchange technique. The curves correspond to a least squares fit of the experimental data to equation (3) with D and k_s as fitting parameters.

3.4. Comparison of tracer deposition by isotope implantation and gas exchange

Often, diffusion measurements which are carried out with ion implanted tracers are criticized by the argument that the damage produced by the implantation process 'disturbs' the real motion of atoms due to the interaction of the tracer with the extended defects. To check a possible influence of the implantation damage on the determination of diffusivities, additional experiments were carried out on films pre-annealed at 1000 °C in N_2–6% H_2 with a gas exchange technique. Here, tracer deposition is achieved by annealing the films in an atmosphere composed of 94% nitrogen and 6% deuterium (N_2–6% $^2H_2$) without producing any damage of the sample. During diffusion annealing an exchange process of ^{1}H in the film and ^{2}H in the gas takes place, resulting in a penetration of the ^{2}H tracer into the film without changing the overall H content of the sample. Some typical depth profiles are displayed in figure 5, wherefrom the diffusivities are extracted by fitting the data to the following solution of Fick's second law

$$c(x,t) = c_g\left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \exp\left(2\frac{x}{2\sqrt{Dt}}\sqrt{\frac{k_s^2 t}{D}} + \frac{k_s^2 t}{D}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{\frac{k_s^2 t}{D}}\right)\right], \qquad (3)$$

assuming an infinite tracer source at the surface [20]. Here, $c(x,t)$ is again the mole fraction of tracer introduced into the sample, $c_g \approx 1$ is the mole fraction of the ^{2}H atoms in the gas phase, and k_s a surface exchange constant.

The data obtained with the gas exchange technique also obey an Arrhenius behaviour with an activation energy of $\Delta E = 2.6$ eV and an pre-exponential factor of $D_0 = 3 \times 10^{-6}$ m^2 s^{-1}. These data are in good agreement with the diffusivities measured with the implantation technique and both data can be fitted with a unique Arrhenius straight line, as shown in figure 6. As a result, we conclude the following on the influence of the implantation damage on diffusion. (a) Trapping of a part of the implanted tracer to extrinsic defects caused by implantation damage results in a deviation of the depth profiles from the ideal behaviour given by equation (1), especially for depths smaller than 200 nm. The occurrence of a stationary cusp in some of the profiles is a special peculiarity of the trapping effect. (b) Implantation damage

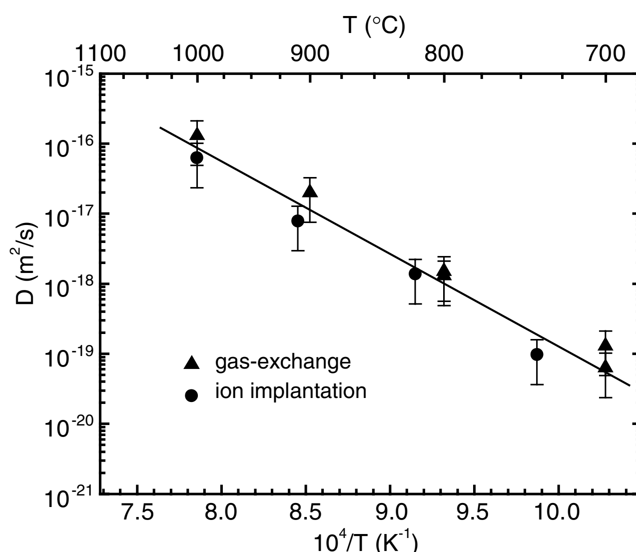

Figure 6. Effective diffusivities of ^2H in amorphous Si_3N_4:H as a function of reciprocal temperature for films pre-annealed for 2 h at 1000 °C in N_2–6% H_2: comparison of ion implanted tracers and gas-exchange.

has a negligible effect on the correct determination of the diffusivities from the measurement data. The hydrogen atoms which are not trapped by the implantation damage diffuse in a manner which is nearly unaffected by the trapping centres, with the same diffusivity as for the implantation damage free case. Therefore, the implantation technique can be considered as an adequate method to determine the correct diffusivities of hydrogen in the present type of materials.

4. Discussion

4.1. Diffusion mechanism

In this study we derived from our experiments very large values for the activation energy of hydrogen diffusion in amorphous Si_3N_4:H films between 2.6 and 3.5 eV. Together with the fact that hydrogen (and also deuterium) present in amorphous silicon nitride is generally bound to the Si and N host atoms [13, 21], we conclude that a trap limited diffusion mechanism is operating in a-Si_3N_4:H. The basic idea of this mechanism is that interstitial-like mobile H atoms (^1H or ^2H) are temporarily trapped by intrinsic defects of the amorphous structure, like dangling bonds. Immobile complexes of the form HR are formed at trapping centres R, which can dissociate again by a thermally activated process. Trapping and subsequent dissociation can be described according to the equation

$$H + R \leftrightarrow HR. \tag{4}$$

For an outline of the theory see, for example, [22–24]. The intrinsic defects discussed here, which are homogeneously distributed over the whole film, should not be confused with the extrinsic defects produced by the implantation damage in a limited depth range close to the surface, which have almost no influence on the diffusion process in the present case. Trap limited diffusion with fairly high activation energies is also observed for amorphous

silicon (∼1.2–2.4 eV) [3], polycrystalline silicon carbide (∼1.7 eV) [25], silicon oxynitride (∼3 eV) [12] and also for impurity doped (e.g. B, Al) mono-crystalline silicon (∼1.7 eV) [22] and silicon carbide (∼1.6–2.5 eV) [23]. In contrast, in undoped mono-crystalline silicon, hydrogen is diffusing via a direct interstitial mechanism with a low activation energy of $\Delta E = 0.48$ eV, and a low pre-exponential factor of $D_0 = 9.4 \times 10^{-7}$ m^2 s^{-1} (see, for example, [26]) due to the absence of trapping centres.

Under the assumption of local equilibrium in reaction (4) and in the case of sufficiently high dissociation rates, which means that the concentration of trapped ^{2}H tracer is smaller than the concentration of traps itself, we obtain a constant effective diffusivity D describing the motion of hydrogen. The effective diffusivity is given by [22]

$$D = D_{\mathrm{H}} \frac{1}{1 + kR_0/\nu}, \tag{5}$$

where R_0 is the concentration of trapping sites, D_{H} is the intrinsic diffusivity of hydrogen, k is the trapping rate, and ν is the dissociation rate of the complexes. The observation of Gauss-like diffusion profiles in our experiments strongly supports the assumption of the limiting case described above, because for low dissociation rates profiles with a non-Gaussian shape are expected [22]. The dissociation rate ν is assumed to follow an Arrhenius temperature dependence of the form

$$\nu = \nu_0 \exp\left(-\frac{\Delta E_{\mathrm{d}}}{k_{\mathrm{B}}T}\right), \tag{6}$$

where ΔE_{d} is the dissociation energy of the HR complex and ν_0 is an attempt frequency. For the trapping rate k we use an expression which is given by the theory of bimolecular reaction rates in solids by several authors [23, 27] as

$$k = 4\pi R_{\mathrm{c}} D_{\mathrm{H}}, \tag{7}$$

where R_{c} is the effective capture radius of a trap. In the case of $\nu/(kR_0) < 1$, but still for sufficiently high dissociation rates (moderately high dissociation limit), we obtain from equations (5)–(7), and (2)

$$D = \frac{\nu_0}{4\pi R_{\mathrm{c}} R_0} \exp\left(-\frac{\Delta E_{\mathrm{d}}}{k_{\mathrm{B}}T}\right) = D_0 \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right). \tag{8}$$

The effective diffusivity is now determined by the dissociation energy of trapped hydrogen, which is approximately a sum of the binding energy of the HR complexes, ΔE_{b}, and the migration energy of the free hydrogen atoms, ΔE_{m}, $\Delta E = \Delta E_{\mathrm{d}} = \Delta E_{\mathrm{b}} + \Delta E_{\mathrm{m}}$ [28].

For the present case of Si_3N_4, the trapping centres can be associated tentatively with silicon (Si-) or nitrogen (N-) dangling bonds. Consequently, the migration of the ^{2}H tracer has to be connected with the dissociation of an Si–H or N–H bond with a binding energy of several electronvolts, and the formation of a mobile H species and a dangling Si- or N-bond due to equation (4). In order to have a hydrogen atom escape from a trap in the amorphous solid it is necessary to supply the dissociation energy of the HR complex, ΔE_{d} (see figure 7(a)). After de-trapping, the mobile ^{2}H tracer can migrate freely in a fast transport mode corresponding to an interstitial-like diffusion process with a low migration energy ΔE_{m} until it is re-trapped again. In [13] the energy levels of Si–H and N–H bonds in Si_3N_4 are calculated to about −3 and −4 eV with respect to the value in free space. Since the experimentally determined activation energy of $\Delta E = 3.4$ eV obtained for the samples with low hydrogen content exceeds the binding energy of Si–H it becomes clear that breaking of N–H bonds should be the rate limiting step in this case. This assumption finds strong support by Fourier transform infrared (FTIR) spectroscopy on CVD derived SiN_x:H films, where N–H was identified to be the dominating bond configuration of hydrogen and deuterium [21].

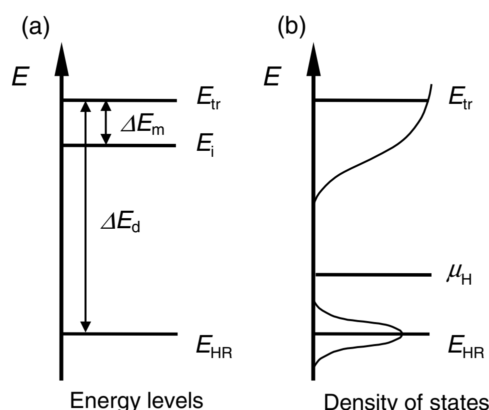

Figure 7. (a) A schematic sketch of the energy level schema assuming a trap limited diffusion process. E_{RH} is the energy level of hydrogen bonded to a trap (dangling bond), E_i is the energy level of an interstitial-like hydrogen position, E_{tr} is the energy level of freely migrating hydrogen, ΔE_d is the dissociation energy of a RH bond, and ΔE_m is the migration energy of untrapped hydrogen. (b) If a site energy distribution arises due to disorder, the process is governed by a hydrogen chemical potential μ_H.

A consequence of equation (5) is that the intrinsic hydrogen diffusivity D_H cannot be extracted from the experimental data because of the fact that different combinations of the quantities ν, k, R_0, and D_H, which are in principle unknown, result in the same effective diffusivity D. This quantity might be orders of magnitudes smaller compared to D_H, depending on the values of ν, k, and R_0. However, from the experimentally determined pre-factor D_0 it is possible to estimate the concentration of traps R_0 by equation (8) to be $R_0 = \nu_0/(4\pi R_c D_0)$. The value of the attempt frequency ν_0 which corresponds approximately to the Debye frequency ν_D (see [23] for the case of crystalline SiC) is essentially unknown for amorphous Si_3N_4:H. We used an estimated value of $\nu_0 \approx 1 \times 10^{13}\ s^{-1}$ for our considerations. The capture radius is usually set to a value of the same order of magnitude as the interatomic distance in the lattice $R_c \approx 0.1$ nm. From these data a trap concentration of $R_0 = 10^{19}$ atoms cm^{-3} is derived, which is a quite reasonable value for the dangling bond concentration in nitrogen-rich SiN_x ($x \approx 1.33$) films [13].

For the sample series SN1000H containing nearly 3 at.% of hydrogen, the activation energy and the pre-exponential factor are strongly decreased compared to the nearly hydrogen free case. These findings can in principle be explained with equation (8) if two different kinds of traps are assumed to be present in Si_3N_4. For the case of low H content, diffusion is controlled by a relatively small amount of deep traps (nitrogen dangling bonds) as indicated by comparatively large values of ΔE_d and D_0. If the hydrogen content is increased, the system rearranges itself and the deep traps are saturated by the additional hydrogen present in the amorphous matrix and become ineffective. For a sufficiently high H concentration the rate limiting step is now the breaking of an Si–H bond, which is reflected in a reduction of the activation energy. The smaller pre-factor indicates a decrease of the ratio $\nu_0/(4\pi R_c R_0)$. Since the frequency $\nu_0 \approx \nu_D$ and the capture radius R_c are relatively static material parameters for a given system, the smaller pre-factor should reflect an increase of the number of trapping centres R_0 (more shallow Si traps than deep N traps). Unfortunately, we obtain a high concentration ($R_0 \approx 10^{21}$ atoms cm^{-3}) of Si dangling bonds as trapping centres, which is not very realistic for a hydrogen content of almost 3%, as long as multiple trapping processes are not considered.

An alternative, more plausible explanation for the decrease of the values ΔE and D_0 with increasing H content can be given if the present system is not considered as a system with mono-energetic traps only. Following the theoretical concepts of Street [29], Beyer [2, 3], and Kirchheim [30], the trapping process can be described as a quasi-equilibrium process which is governed by a hydrogen chemical potential μ_H. Here, a site energy distribution exists for the traps, resulting from the disorder of the Si–N–H network, which tends to broaden the energy levels (for a schematic sketch see figure 7(b)). A modified effective diffusivity is given by

$$D = D_{00} \exp\left(-\frac{E_{tr} - \mu_H}{k_B T}\right), \tag{9}$$

where E_{tr} is the energy of the hydrogen transport path. If low energy sites are saturated, additional hydrogen atoms have to occupy sites with higher energy, which gives rise to an increase of μ_H and consequently to a decrease in the overall activation energy of diffusion. A changing linear temperature dependence of the chemical potential relative to the hydrogen transport path according to $\mu_H = \mu_H^0 - \beta T$ may then cause a decrease of the pre-factor by $D_{00}^* = D_{00} \exp(-\beta/k_B)$, where $\Delta E = E_{tr} - \mu_H^0$ is the activation energy of diffusion. This should lead to a continuous variation of pre-factor and activation energy with H concentration and not to a discrete one as expected for the model with mono-energetic traps. This is a point which has to be clarified by further experiments.

5. Comparison to literature data

Literature data on the investigation of hydrogen diffusion in Si–N:H films resulting in quantitative diffusivities and activation enthalpies are relatively limited. Yu *et al* [31] measured a diffusivity of 1×10^{-23} m^2 s^{-1} at room temperature with the potential-pH response method in a silicon nitride film whose state (composition, hydrogen content) was not more closely specified. This measurement temperature is completely out of our measurement range, and consequently the determined diffusivity is of less significance for a comparison to our results. Arnoldbik *et al* [21] carried out measurements on chemical vapour deposited near-stoichiometric Si_3N_4 consisting of a double layer of hydrogenated and deuterated films (3.5 at.%) with elastic recoil detection analysis (ERDA) in the temperature range between 700 and 1000 °C. Unfortunately, the thermodynamic state of the films (amorphous or crystalline) was not given. The obtained diffusivities are very close to our data of the SN1000 series within error bars, but a lower activation enthalpy of 2.94 eV is derived. The larger hydrogen content of about 3.5 at.% compared to ours of 0.4 at.% indicates a possible influence of the preparation method on diffusion. Nevertheless, the rate limiting step of diffusion, the breaking of N–H bonds, seems to be the same.

6. Summary

In this study we have presented an experimental investigation of the diffusion of ion implanted ^{2}H tracers in amorphous hydrogenated Si_3N_4 films as a function of temperature, pre-annealing state and hydrogen content. The diffusion profiles were measured with secondary ion mass spectrometry. Our main results are summarized as follows.

(1) The diffusion of ^{2}H in amorphous hydrogenated Si_3N_4 films follows the kinetics expected for a trap limited diffusion mechanism with the formation and dissociation of immobile complexes between hydrogen and intrinsic defects, presumably nitrogen dangling bonds.

(2) It is shown by a comparison of experiments carried out with ion implanted tracers and a gas exchange technique that implantation damage has negligible influence on the determination of diffusivities.
(3) The atomic motion of hydrogen for the present case of moderately high dissociation rates of the trapped hydrogen can be described by an effective diffusivity with a high activation energy of about $\Delta H = 3.4$ eV and a pre-exponential factor of about $D_0 = 5\times10^{-4}$ m^2 s^{-1}.
(4) Pre-annealing of the as-deposited Si_3N_4 films in N_2 and possible structural rearrangements involved have no influence on the effective diffusivity.
(5) Charging of the films with hydrogen up to about 2.6 at.% leads to a significant increase of the diffusivities of more than one order of magnitude due to a decrease in both the activation energy to $\Delta E = 2.7$ eV and the pre-exponential factor to $D_0 = 3\times10^{-6}$ m^2 s^{-1}. These findings can be explained with a site energy distribution of traps and a temperature dependent hydrogen chemical potential increasing with hydrogen content.

Acknowledgments

The authors would like to thank E Ebeling and U Geckle for their assistance in film preparation. Funding by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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