Comparative study of trap-limited hydrogen diffusion in amorphous SiC, Si$_{0.66}$C$_{0.33}$N$_{1.33}$, and SiN$_{1.33}$ films

Comparative study of trap-limited hydrogen diffusion in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ films

H Schmidt[1], G Borchardt[1], U Geckle[2], M Bruns[2] and H Baumann[3]

[1] TU Clausthal, Fakultät für Natur- und Materialwissenschaften, Thermochemie und Mikrokinetik, Robert-Koch-Straße 42, D-38678 Clausthal-Zellerfeld, Germany
[2] Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[3] Institut für Kernphysik, J W Goethe-Universität, August-Euler-Straße 6, D-60486 Frankfurt, Germany

Abstract
Hydrogen tracer diffusion is studied in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ films which were produced by rf magnetron reactive sputtering and which contain about 0.5 at.% of hydrogen. The diffusion experiments were carried out in the temperature range between 700 and 1000 °C with ion-implanted deuterium tracer isotopes and secondary ion mass spectrometry. Effective diffusivities are derived which are nearly identical for all three types of material and which obey Arrhenius behaviours with activation energies of $\Delta E = 3.0$–3.4 eV and pre-exponential factors of the order of $D_0 = 10^{-4}$–10^{-5} m^2 s^{-1}. These results can be explained with a trap-limited diffusion mechanism of hydrogen where the tracer atoms are temporarily trapped by carbon and nitrogen dangling bonds, which have approximately the same binding energy to hydrogen.

1. Introduction

Hydrogen is an essential constituent of the network structure of amorphous semiconductors and is responsible for the reduction of stress and the formation of a metastable equilibrium state. Since this element diffuses at relatively low temperatures compared to other elements, its dynamic behaviour is very important for the thermal stability of these materials. In amorphous hydrogenated silicon (a-Si:H) the diffusion behaviour has been extensively investigated during the last few years [1–8] and it was found that a trap-limited diffusion mechanism is operating. According to this mechanism, the motion of interstitial-like mobile H atoms is connected with the formation of immobile complexes of the form HR at trapping centres R intrinsic to the solid (e.g. dangling bonds) and subsequent dissociation of these complexes. Intrinsic defects like dangling bonds play a decisive role in the application of amorphous semiconductors 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 the 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.

In contrast to silicon, no systematic experiments have been carried out on hydrogenated amorphous compound semiconductors like a-SiN$_{1.33}$ and a-SiC. These materials can be used as components in electronic and optoelectronic devices like solar cells [9–13], light emitting diodes [14–16], photo receptors [17, 18], phototransistors [19], versatile dielectrics, gate dielectrics, and charge storage mediums in non-volatile memories [20–23]. Each of these applications depends on the presence and on the mobility of hydrogen and its interaction with defects.

Recently, we carried out a comprehensive study of hydrogen tracer diffusion in a-SiN$_{1.33}$ as a function of temperature, hydrogen content and pre-annealing conditions [24]. For small hydrogen concentrations of 0.2–0.5 at.% it was shown that the hydrogen transport can also be described by a trap-limited diffusion mechanism, where the tracer atoms are temporarily trapped by nitrogen dangling bonds. Effective diffusivities were 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}. Charging of the films with hydrogen to 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 $D_0 = 3 \times 10^{-6}$ m^2 s^{-1}. In the present study we now investigate the influence of chemical composition on hydrogen diffusion in carrying out comparative studies on amorphous SiC, Si$_{0.66}$C$_{0.33}$N$_{1.33}$, and SiN$_{1.33}$ films.

2. Experimental details

About 1–2 μm thick films of amorphous SiC, Si$_{0.66}$C$_{0.33}$N$_{1.33}$, and SiN$_{1.33}$ were deposited on single crystalline Si$\langle111\rangle$ wafers (CIS, Germany) by rf magnetron sputtering with a 3″ US GUN low profile planar magnetron source (AP&T, Nürtingen, Germany). An operating pressure of $(1–5) \times 10^{-3}$ mbar and a sputtering power of 80–160 W were used. The silicon nitride films were produced by reactive sputtering of a silicon target (99.999%, Norwegian Talc, Germany) in a gas mixture of 50 vol% Ar and 50 vol% N$_2$ at a substrate temperature of 400 °C. SiC films were made by co-sputtering of silicon and carbon stripes of 5×25 mm^2 (99.99%, Goodfellow, Germany) in argon at a substrate temperature of 200 °C. Films with nominal composition Si$_{0.66}$C$_{0.33}$N$_{1.33}$ were produced by a combination of both methods, as described elsewhere [31]. After deposition, the films were pre-annealed for 2 h at 1000 °C in Ar (SiC) and N$_2$ (Si$_{0.66}$C$_{0.33}$N$_{1.33}$ and SiN$_{1.33}$) for 2 h at 1000 °C, respectively.

The elemental composition of the sputtered films was measured by non-Rutherford backscattering spectroscopy (n-RBS), performed with the 7.0 MV van de Graaff accelerator at the Institut für Kernphysik, Frankfurt, using a 3.5 MeV ^{4}He$^+$ beam. The elastically backscattered particles were detected at an angle of 171°. The hydrogen content of the films was determined by nuclear reaction analysis (NRA) using the resonant nuclear reaction ^{1}H(^{15}N, α, γ)^{12}C at a resonance energy of 6.4 MeV.

Tracer deposition was carried out by implanting a mass separated and scanned ^{2}H$_3^+$ molecular ion beam of 20 keV with a fluence of 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 the film material in the temperature range between 700 and 1000 °C in a N$_2$ or Ar atmosphere at ambient pressure.
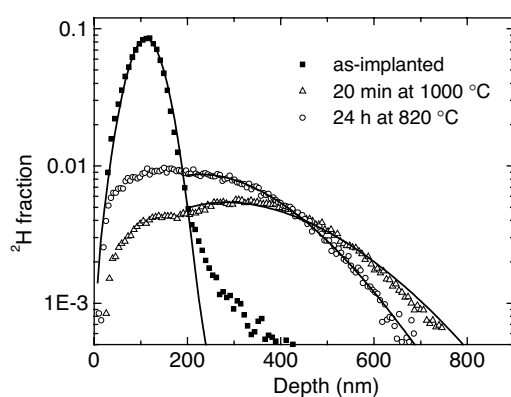
Figure 1. Typical diffusion profiles of ion-implanted ^2H tracers in amorphous SiC measured with SIMS after annealing at elevated temperatures and annealing times in Ar. The solid lines correspond to a least-squares fit of the data to equation (1) in the depth range >200 nm.

Table 1. Hydrogen concentration as well as activation energies and pre-exponential factors of hydrogen diffusion for amorphous Si-based materials.

| Material	Hydrogen conc. (at.%)	ΔE (eV)	$\log (D_0)^a$
SiC	0.4 ± 0.1	3.2 ± 0.2	$-4.1^5 \pm 1.0$
$SiN_{1.33}$	0.4 ± 0.1	3.4 ± 0.2	-3.3 ± 1.1
$Si_{0.66}C_{0.33}N_{1.33}$	0.5 ± 0.1	3.0 ± 0.2	-4.8 ± 1.0

^{a} The units for D_0 are $m^2\ s^{-1}$.

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.

3. Results

The concentration of the film components Si C, and N was determined by (non-)Rutherford backscattering spectrometry to correspond approximately to SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ with an Ar impurity concentration of less than 1 at.% and an O impurity concentration of less than 0.5 at.%, respectively. In the as-deposited state, $Si_{0.66}C_{0.33}N_{1.33}$ is an amorphous material where nominally one silicon atom is replaced by one carbon atom. The presence of an amorphous phase was verified for all types of sample by x-ray diffractometry. A detailed description of the thermal stability of the sputtered films, which start to crystallize at temperatures higher than 1200 °C, can be found in [25, 26]. The hydrogen content was determined by nuclear reaction analysis to be between 0.4 and 0.5 at.% for the films pre-annealed in N_2 or Ar (see table 1). Investigations with SIMS confirm the constant concentration of the Si, C, N, and H film components throughout the film before deuterium is implanted.

In figure 1, typical SIMS depth profiles of ion-implanted ^2H are shown in a-SiC before and after diffusion annealing at various temperatures. The implantation profile exhibits a Gaussian shape with a projected range of about $R_p = 110$ nm and a standard deviation of about $\Delta R_p = 40$ nm. For the annealed films, a broadening of the profile is observed corresponding
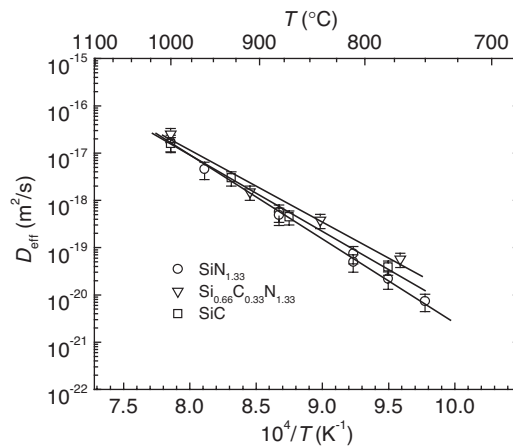
Figure 2. Effective hydrogen diffusivities in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ as a function of reciprocal temperature.

to diffusion. For certain profiles, especially with a large broadening (e.g. at $1000\,°C$), a cusp is superimposed on the Gaussian profile at 110 nm, whose position does not change during annealing. As extensively discussed in [24], this cusp is associated to the immobilization of implanted hydrogen atoms by implantation damage. Only a small fraction of the tracer is mobile and diffuses into the film in form of a Gaussian-like diffusion profile. As demonstrated for the case of a-$SiN_{1.33}$ [27], the experimentally obtained diffusion profiles can be numerically simulated by computer calculations based on the concept of trap-limited diffusion where the tracer atoms form immobile complexes with: (a) intrinsic film defects like dangling bonds, and (b) extrinsic defects caused by the implantation damage. As shown in [27], a least-squares fit of the experimental data to the following solution of the diffusion equation [28]

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

in the depth range >200 nm leads to the same diffusivity as obtained by numerical calculations. This demonstrates that for the present case the implantation damage has no influence on the determination of the effective diffusivities and equation (1) can be used for analysis. In equation (1), $c(x, t)$ is the mole fraction of deuterium, A is the fluence of the implanted deuterium, D is the diffusivity, and t is 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 diffusion profiles for $Si_{0.66}C_{0.33}N_{1.33}$ and $SiN_{1.33}$ are qualitatively identical to those obtained for SiC and are consequently not discussed in further detail.

In figure 2 the determined hydrogen diffusivities are shown as a function of reciprocal temperature. During the diffusion experiments the annealing temperatures never exceeded the pre-annealing temperature so that changes in microstructure were avoided. The diffusivities for all three types of sample 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. Activation energies of $\Delta E \approx 3.2$ eV (SiC), $\Delta E \approx 3.0$ eV ($Si_{0.66}C_{0.33}N_{1.33}$) and

$\Delta E \approx 3.4$ eV ($SiN_{1.33}$) as well as pre-exponential factors of $D_0 \approx 7.1 \times 10^{-5}$ m^2 s^{-1} (SiC), $D_0 \approx 1.5 \times 10^{-5}$ m^2 s^{-1} ($Si_{0.66}C_{0.33}N_{1.33}$), and $D_0 \approx 5.0 \times 10^{-4}$ m^2 s^{-1} ($SiN_{1.33}$) are derived. As can be seen in figure 2, the diffusivities of all three types of material are nearly identical. Taking into account the error limits attributed to the activation energies and pre-exponential factors (see table 1), these quantities are also identical.

4. Discussion

The three materials investigated in this study differ mainly in their elemental composition and/or in their local short-range crystallographic order. For amorphous $SiN_{1.33}$ and SiC, tetrahedrally coordinated silicon atoms are present, whereas the nitrogen or carbon atoms are connected to a three-dimensional amorphous network structure [29, 30]. For $Si_{0.66}C_{0.33}N_{1.33}$, it was shown by FTIR measurements [31] that the corner-linked SiN_4 tetrahedra are connected via N=C=N bridges in order to form a three-dimensional network, the so-called carbodiimide structure, which was recently also verified in polymer-derived Si–C–N materials [32]. The results show that these different structures with different atoms, atomic distances, bonds, and bond angles show nearly the same diffusion behaviour of hydrogen as long as the hydrogen concentration is low and approximately the same (see table 1). The observed behaviour can be understood in the framework of a trap-limited diffusion mechanism. The basic idea of this mechanism is that interstitial-like mobile H atoms (^{1}H or ^{2}H) 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

$$H + R \leftrightarrow HR. \tag{3}$$

For an outline of the theory see for example [33, 34]. Assuming high dissociation rates of the traps, which means that the concentration of trapped deuterium tracer is smaller than the concentration of traps itself, a constant effective diffusivity D is given by [33]

$$D = \frac{\nu_0}{4\pi R_c R_0} \exp\left(-\frac{\Delta E_d}{k_B T}\right), \tag{4}$$

where R_0 is the concentration of open trapping sites, R_c is the effective capture radius of a trap, and ν_0 is an attempt frequency. The activation energy of diffusion ΔE can be identified with ΔE_d, the dissociation energy of an HR complex, which is a sum of the binding energy of an HR complex, ΔE_b, and the migration energy of free hydrogen, ΔE_m.

In case of a-SiC, the trapping centres can in principle be associated with silicon or carbon dangling bonds and hydrogen migration has to be connected with the dissociation of a Si–H or a C–H bond according to equation (3). In order to achieve such a dissociation it is necessary to thermally supply the dissociation energy ΔE_d. After de-trapping mobile hydrogen can migrate freely in a fast interstitial-like transport mode until it is trapped again. In [22] the energy levels of Si–H and C–H bonds in SiC are calculated to be about -3.1 and -4.2 eV with respect to the value in free space. Since the experimentally determined dissociation energy of $\Delta E_d = 3.2$ eV is the same as (or exceeds) the value of a Si–H bond it becomes clear that breaking of C–H bonds has to be the rate-limiting step in the present case. After de-trapping, the hydrogen atoms are in the interstitial state and are not transferred to free space, which means that $\Delta E < \Delta E_d$ has to be valid.

From the experimentally determined pre-exponential factor D_0 it is possible to estimate the concentration of traps R_0 by equation (4) to be $R_0 = \nu_0/(4\pi R_c D_0)$. For the attempt frequency, which corresponds approximately to the Debye frequency, ν_D, we used an estimated value of
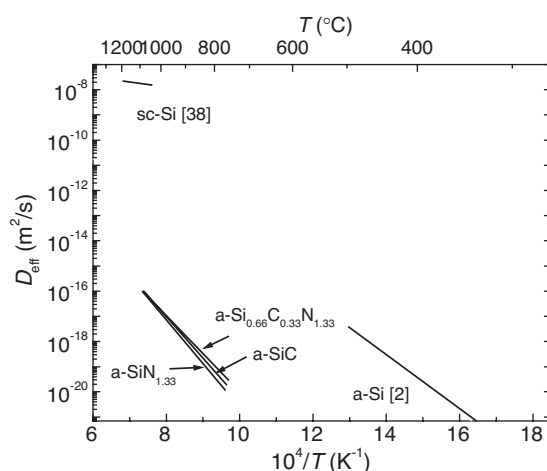
Figure 3. Effective hydrogen diffusivities in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ in comparison to literature data on single crystalline (sc-) and amorphous (a-) Si.

$\nu_0 \approx 1 \times 10^{13}$ s^{-1}. The capture radius is usually set to a value of the same order of magnitude as the interatomic distance in the lattice $R_c \approx 0.2$ nm. From these data a trap concentration of $R_0 \approx 10^{19}$–10^{20} atoms cm^{-3} is derived, which is of the same order of magnitude as the dangling bond density found by electron spin resonance measurements [35].

According to equation (4), the effective diffusivities of different materials are identical if the dissociation energy and the trap concentration are equal. The calculations of Robertson [22] show that the energy levels of C–H and N–H bonds in a-$SiN_{1.33}$ and a-SiC are located at almost the same energy of about -4 eV with respect to the value in free space, leading to the same dissociation energy. This means that if the rate-limiting step of effective diffusion is identified with the dissociation of the C–H and/or the N–H bonds, the diffusivities of the investigated a-SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ films are identical if the trap concentration is approximately the same. This assumption seems to be fulfilled here, probably due to the fact that the same hydrogen concentration is present.

In the literature, diffusion data of hydrogen in amorphous SiC or $SiN_{1.33}$ are very scarce. Arnoldbik *et al* [23] carried out measurements on chemical vapour deposited near-stoichiometric hydrogenated $SiN_{1.33}$ films with elastic recoil detection analysis. The obtained diffusivities are nearly identical with our data on $SiN_{1.33}$ within error bars, but with a slightly lower activation enthalpy of 2.94 eV. For amorphous SiC there are no systematic data on hydrogen diffusion, only for polycrystalline and doped single crystalline material [36, 37]. In contrast, hydrogen diffusion in amorphous silicon has been extensively studied (see e.g. [2]). Hydrogen diffuses there with a trap-limited diffusion process, while the activation energy strongly depends on the hydrogen concentration. In figure 3, diffusivities in a-Si, measured on films with approximately the same low hydrogen concentration of 0.5 at.% as for the films investigated in this study, are given for comparison (from figure 13 in [2]). An extrapolation to higher values shows that the diffusivities in a-Si are higher by several orders of magnitude than those in a-SiC, a-$Si_{0.66}C_{0.33}N_{1.33}$, and a-$SiN_{1.33}$. Approximately the same pre-exponential factor of the order of 10^{-4} m^2 s^{-1}, but a lower activation energy of $\Delta E = 2.1$ eV, are found. For higher hydrogen concentrations (up to 15%) lower activation energies (down to 1 eV [2]) and lower pre-exponential factors occur. Consequently the value of 2.1 eV is an approximate upper limit for the activation energy of diffusion which may result from trapping at Si dangling

bonds (if this mechanism is assumed to be valid in a-Si). Following these argumentations, we conclude that the slower hydrogen diffusion in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ compared to Si is a result of trapping at N and C dangling bonds instead of trapping at silicon dangling bonds. Also shown in figure 3 are the diffusivities of hydrogen in single crystalline silicon [38]. These diffusivities are much higher, with an activation energy of only 0.48 eV, reflecting the diffusion via a direct interstitial mechanism, due to the absence of trapping centres.

5. Conclusion

In this study we have presented an experimental investigation on the diffusion of hydrogen in amorphous SiC, $Si_{0.66}C_{0.33}N_{1.33}$, and $SiN_{1.33}$ films with low hydrogen concentration of about 0.5 at.%. We demonstrated that the diffusivities are nearly identical within error limits in all compounds investigated and can be described with an activation energy of the order of 3.0– 3.4 eV. The results can be explained with a trap-limited diffusion mechanism, where nitrogen and carbon dangling bonds act as trapping centres. The activation energies are significantly higher than the values of 2.1 eV found in amorphous silicon, where trapping takes place at silicon dangling bonds.

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