

AARHUS UNIVERSITY DEPARTMENT OF PHYSICS AND ASTRONOMY

## Erbium Diffusion in Titanium Dioxide



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#### Colophon

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#### Abstract

Titanium dioxide (TiO<sub>2</sub>) doped with the rare-earth metal erbium (Er) is a very useful material from an optical perspective, since it can be used as an optical up-converter. A material used as an optical up-converter can convert two low-energy photons into one high-energy photon. This process is useful in creating more efficient solar cells since the solar cell will then be able to convert a greater part of the Solar spectrum.

If the Er-doped  $\text{TiO}_2$  is heat treated in the process of producing the solar cell, the Er ions will eventually start to move inside the material. This is known as diffusion. The diffusivity, i.e. how fast this happens, it not known. The aim of this project is to measure this diffusivity.

The experiment involves growth of the materials by magnetron sputtering, heating at various temperatures, and a measurement of the displacement of the Er ions by secondary ion mass spectroscopy.

The diffusion coefficients are found from Fick's second law, where the value of the diffusion coefficients are expected to increase with increasing temperature of annealing. The results obtained from the experiments performed throughout this project are in correspondence with this prediction and will, as expected, follow a slope given by Arrhenius' plot.

#### Resumé

Titaniumdioxid (TiO<sub>2</sub>) dopet med det sjældne metal erbium (Er) er et meget brugbart materiale fra et optisk perspektiv, siden dette kan bruges til optisk opkonvertering. Et materiale, der bruges til opkonvertering, kan konvertere to lavenergifotoner til en højenergifoton. Denne proces er yderst nyttig i produktionen af mere effektive solceller, eftersom solcellen da vil være i stand til at konvertere en større del af Solens spektrum.

Hvis det Er-dopede  $\text{TiO}_2$  udsættes for varmebehandling i produktionsprocessen af solcellen, vil Er-ionerne begynde at bevæge sig inde i materialet. Denne proces kaldes for diffusion. Diffusiviteten, altså hvor hurtigt dette sker, er ikke kendt. Formålet med dette projekt er at måle denne diffusivitet.

Eksperimentet inkluderer opbygning af materialerne ved magnetron sputtering, opvarmning ved forskellige temperaturer samt måling af forskydningen af Er-ionerne ved sekundær ionmassespektroskopi.

Diffusionskoefficienterne er fundet ud fra Ficks anden lov, hvor værdien af diffusionskoefficienterne er forventet at stige i takt med forøgende temperatur. Resultaterne fra de i dette projekt udførte eksperimenter stemmer overens med denne forudsigelse og vil, som forventet, følge en hældning givet ved Arrhenius' plot.

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## Introduction

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The fact that our climate is changing is of great concern. One of the causes for this climate change is the increasing amount of pollution from fossil fueled machinery. For years, scientists have looked for alternatives to fossil fuels in order to prevent further harm to our planet. One suggestion is to replace fossil fuels with energy from resources of renewable energy such as sunlight.

The Sun provides us with an everlasting supply of energy, which can be harvested using solar cells. The Sun emits radiation in a wide range from about 350 nm to 2000 nm. Depending on the solar cell, only a small part of this spectrum can be converted into electrical energy. Photons of too low an energy will not be absorbed by the solar cell, and photons of too high an energy will be absorbed, but will lose energy by thermalization.

Solar cells can be either single-junction or multi-junction. Traditional singe-junction solar cells are only efficient in a small range of the Solar spectrum. Single-junction solar cells have a lower efficiency than multi-junction solar cells, which show efficiencies above 40% (Green et al., 2015). Multi-junction solar cells have several p-n junctions made from the different semiconducting materials which make up the solar cell. Each of these p-n junctions of the materials will be able to produce electric currents from different wavelengths of the incoming light. The multi-junction solar cells are thus more efficient in a wider range of the Sun's spectrum compared to the single-junction.

The efficiency of the solar cell is determined by the band gaps



Figure 1.1: Maximum efficiency of a single-junction solar cell as a function of the band gap,  $E_{\rm g}$ . This figure is made by using equation (5.6) from Shockley and Queisser (1961).

of these semiconducting materials. Solar cells are incapable of absorbing photons with energies lower than the band gaps of the materials and the efficiency of the solar cell is therefore given as a function of the band gap. The maximum efficiency of a singlejunction solar cell is given by the SQ-limit<sup>1</sup>. This limit is shown in Figure 1.1.

As explained, one way of increasing the efficiency beyond the SQ-limit is by producing multi-junction solar cells, where solar cells made from materials with different band gaps are stacked to form one multi-junction solar cell, which is able to convert a greater part of the Solar spectrum.

Another very useful method is upconversion where two lowenergy photons with energies below the band gap are combined to form one high-energy photon, which will have an energy large enough to be absorbed by the solar cell.

<sup>&</sup>lt;sup>1</sup>From its inventors Shockley and Queisser.



Figure 1.2: Schematic view of the diffusion process, where the diffusing ions propagate into the surrounding material. Red points represent the diffusing ions, in this case Er, and gray points represent the doped material, here  $\text{TiO}_2$ . Note that the given Bravais lattice does not represent the lattice structure of the  $\text{TiO}_2$ , which is given by a tetragonal Bravais lattice. The Bravais lattice of  $\text{TiO}_2$  is shown in Figure 1.3.

Titanium dioxide  $(TiO_2)$  doped with the rare earth metal ion erbium (Er) can be used as an optical upconverter. The upconversion is achieved by the stimulated emission of photons from the dopant ions (Er) in the doped material  $(TiO_2)$ . Light from the Sun in the range 980 nm to 1450 nm excites the Er ions into a state from where they can amplify the light in the 1.5 µm wavelength region by the stimulated emission back to the ground-state (Desurvire et al., 1991).

If the material is subjected to a high temperature, the Er ions will eventually start to move inside the material - a process known as diffusion. A schematic view of such a diffusion process is shown in Figure 1.2.

The diffusivity, i.e. how fast this happens, is not known. The aim of this project is to measure this diffusivity where the main purpose is to measure the diffusion coefficient. The diffusion coefficient, D, is expected to increase with increasing temperature of heating.

This diffusion coefficient is of practical use since the diffusion length, i.e. how far into the material the ions diffuse, is of crucial knowledge in a broad range of experiments.

The experiment involves growth of the material by magnetron sputtering, heat treatment at high temperatures (a process known as annealing), and a measurement of the displacement of the Er ions by secondary ion mass spectrometry (SIMS).



Figure 1.3: Lattice structure of  $\text{TiO}_2$ . Red spheres represent the oxygen, while gray spheres represent the titanium. This lattice is of rutile, which is the most common natural form of  $\text{TiO}_2$  (Penn and Banfield, 1999). This lattice structure is made with inspiration from Bolzan et al. (1997).

## Analysis of Erbium diffusion

The following describes a series of mathematical results connected with the erbium diffusion experiment as derived by Brian Juulsgaard (supervisor).

# 2.1 Definition of experimental parameters

We let  $\rho_{\text{Er}}(x)$  denote the concentration of the Erbium ions at the film depth, x, and we want to determine this concentration experimentally. Ideally, the experimental signal, y(x), would be proportional to  $\rho_{\text{Er}}(x)$ , but in practice, however, the SIMS method gives rise to mixing between the different sub-layers, and we get the experimental signal

$$y(x) = \int M(x - x')\rho_{\rm Er}(x')dx'.$$
 (2.1)

Here M(x - x') denotes the probability function of measuring an Er ion at the time the sputtering reaches the depth x, and x'gives the depth from which the ion actually originated. We expect M to have non-zero values for positive arguments only. M is called the mixing function.

As explained in chapter 1, the main purpose of this project is to measure the diffusion coefficient, D. It would also be very useful to compare the Er density,  $\rho_{\rm Er}(x)$ , of a sample annealed at some temperature,  $T_{\rm ann}$ , for a time,  $t_{\rm ann}$ , to the as-deposited density,  $\rho_{\rm Er}^{\rm (AD)}(x)$ , of another sample, which has not been annealed. The Er density,  $\rho_{\rm Er}$ , is assumed to be connected to the as-deposited density,  $\rho_{\rm Er}^{\rm (AD)}(x)$ , by a folding with a Gaussian as

$$\rho_{\rm Er}(x') = \int \rho_{\rm Er}^{\rm (AD)}(x'')g(x'-x'')dx'', \qquad (2.2)$$

where the Gaussian, g, is given as

$$g(x) = A \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}},$$
 (2.3)

where the front factor A should be of unity.

Note that g has unit area, zero mean, and variance,  $\sigma^2$ . By folding with a Gaussian, diffusion according to Fick's second law is obtained when the variance is given as  $\sigma^2 = 2Dt$ , where t is the time of annealing (Fick, 1855). It can be shown that  $\frac{\partial g}{\partial t} = D \frac{\partial^2 g}{\partial x^2}$ , i.e. the diffusion is indeed described by a Gaussian which spreads out with time. The time, t, is the time at which the sample has been annealed, i.e.  $t = t_{\text{ann}}$ , and the variance is thus

$$\sigma^2 = 2Dt_{\rm ann}.\tag{2.4}$$

### 2.2 Moments of the depth profile

In this section, a discussion will be produced, as to how the mean values and variances of the different physical parameters are connected.

For the mixing function, M, it is assumed that  $\int M(x-x')dx' = 1$ . The mean shift of data is denoted  $\bar{x}_M = \int x M(x)dx$ , and the width of the mixing function is characterized by the variance

$$\operatorname{Var}[x_M] = \int (x - \bar{x}_M)^2 M(x) dx.$$
 (2.5)

The notation Var[...] gives the variance of a depth distribution while Var(...) is used to describe variances which originate from statistical uncertainties.

Let  $\bar{x}_{\rm Er}$  denote the mean physical depth of the Er layer. Then this must be given as

$$\bar{x}_{\rm Er} = \frac{\int x' \rho_{\rm Er}(x') dx'}{\int \rho_{\rm Er}(x') dx'} 
= \frac{\int dx' \int dx'' x' \rho_{\rm Er}^{\rm (AD)}(x'') g(x' - x'')}{\int dx' \int dx'' \rho_{\rm Er}^{\rm (AD)}(x'') g(x' - x'')} 
= \frac{\int dx'' x'' \rho_{\rm Er}^{\rm (AD)}(x'')}{\int dx'' \rho_{\rm Er}^{\rm (AD)}(x'')} 
= \bar{x}_{\rm Er}^{\rm (AD)},$$
(2.6)

from which we can see that the diffusion does not change the mean depth of the Er layer. This is expected to hold true for a well-buried layer, i.e. where the two layers of pure  $\text{TiO}_2$  have a suitable thickness to prevent the diffusion from having any preferred spatial direction.

The variance of the thickness of the physical layer is given as

$$\begin{aligned} \operatorname{Var}[x_{\mathrm{Er}}] &= \frac{\int (x' - \bar{x}_{\mathrm{Er}})^2 \rho_{\mathrm{Er}}(x') dx'}{\int \rho_{\mathrm{Er}}(x') dx'} \\ &= \frac{\int x'^2 \rho_{\mathrm{Er}}(x') dx'}{\int \rho_{\mathrm{Er}}(x') dx'} - (\bar{x}_{\mathrm{Er}})^2 \\ &= \frac{\int dx' \int dx'' x'^2 \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'') g(x' - x'')}{\int dx' \int dx'' \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'') g(x' - x'')} - (\bar{x}_{\mathrm{Er}}^{(\mathrm{AD})})^2 \\ &= \frac{\int d\beta \int dx'' \left(\beta^2 + 2\beta x'' + x''^2\right) \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'') g(\beta)}{\int d\beta \int dx'' \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'') g(\beta)} - (\bar{x}_{\mathrm{Er}}^{(\mathrm{AD})})^2 \\ &= \frac{\int dx'' \left(\sigma^2 + x''^2\right) \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'')}{\int dx'' \rho_{\mathrm{Er}}^{(\mathrm{AD})}(x'')} - (\bar{x}_{\mathrm{Er}}^{(\mathrm{AD})})^2 \\ &= \sigma^2 + \operatorname{Var}[x_{\mathrm{Er}}^{(\mathrm{AD})}], \end{aligned}$$

$$(2.7)$$

with  $\beta = x' - x''$ . This tells us that we may characterize the shape by the variance, no matter the shape of the as-deposited distribution,  $\rho_{\text{Er}}^{(\text{AD})}$ , and that the diffusion will only add on an extra variance,  $\sigma^2$ .

A similar analysis is performed on the experimental signal, y(x). The mean depth and variance of the signal are given as

$$\bar{x}_y = \frac{\int xy(x)dx}{\int y(x)dx} \quad \text{and} \quad \operatorname{Var}[x_y] = \frac{\int x^2y(x)dx}{\int y(x)dx} - \bar{x}_y^2.$$
(2.8)

By inserting the definition of the experimental signal, y(x), as given in equation (2.1), we obtain the mean value

$$\bar{x}_{y} = \frac{\int dx \int dx' x M(x - x') \rho_{\rm Er}(x')}{\int dx \int dx' M(x - x') \rho_{\rm Er}(x')} \\
= \frac{\int d\beta \int dx' (\beta + x') M(\beta) \rho_{\rm Er}(x')}{\int d\beta \int dx' M(\beta) \rho_{\rm Er}(x')} \\
= \bar{x}_{M} + \bar{x}_{\rm Er} \\
= \bar{x}_{M} + \bar{x}_{\rm Er}^{\rm (AD)},$$
(2.9)

and the variance of the experimental depth signal is given as

$$\operatorname{Var}[x_y] = \frac{\int dx \int dx' x^2 M(x - x') \rho_{\mathrm{Er}}(x')}{\int dx \int dx' M(x - x') \rho_{\mathrm{Er}}(x')} - \bar{x}_y^2$$
  

$$= \frac{\int d\beta \int dx' (\beta^2 + 2\beta x' + x'^2) M(\beta) \rho_{\mathrm{Er}}(x')}{\int d\beta \int dx' M(\beta) \rho_{\mathrm{Er}}(x')} - \dots$$

$$(\bar{x}_M^2 + 2\bar{x}_M \bar{x}_{\mathrm{Er}} + \bar{x}_{\mathrm{Er}}^2)$$

$$= \operatorname{Var}[x_M] + \operatorname{Var}[x_{\mathrm{Er}}]$$

$$= \operatorname{Var}[x_M] + \operatorname{Var}[x_{\mathrm{Er}}^{(\mathrm{AD})}] + \sigma^2.$$
(2.10)

Once again, the variance is independent of the actual shape and is just a simple sum of the variances of the mixing function, the as-deposited Er density, and the Gaussian distribution function.

### 2.3 Identifying the Erbium signal

As explained in chapter 1, the displacements of the Er ions are measured by using SIMS. The SIMS method works as follows: (1) A beam of Caesium (Cs) ions is digging into the surface of the sample by sputtering with an energy of 6 keV. The rate of this digging is unknown but assumed to be constant. (2) The analysis is accomplished in positive polarity where another beam of Bismuth (Bi) ions sputters the sample in appropriate time intervals with an energy of 25 keV. The material released is detected by a mass spectrometer. The yield of Si ions,  $y_{Si}$ , works as a normalization parameter for the analyzing sputter rate.

Data is distributed according to a Poissonian distribution. The Er signal will be superimposed on a background with a mean value of a few counts. This background signal is given as

$$y_{\text{Er,back}} = \frac{1}{N} \sum_{i} y_{\text{Er,i}} \Rightarrow \operatorname{Var}(y_{\text{Er,back}}) = \frac{y_{\text{Er,back}}}{N}, \quad (2.11)$$

where  $y_{\text{Er},i}$  denotes the *i*'th data point of the raw Er signal, and the sum runs over an appropriate region of the data<sup>1</sup>.

An experimental signal, y(t), proportional to the Er concentration,  $\rho_{\rm Er}$ , at a time, t, in the sputtering process can now be identified. This is defined as

$$y = \frac{y_{\rm Er} - y_{\rm Er, back}}{y_{\rm Si}}.$$
 (2.12)

If N in equation (2.11) is large, these new data points are effectively independent, and y is not expected to follow a Poissonian distribution any longer, since the difference between two Poissonians does not yield a Poissonian. If the count numbers for  $y_{\rm Er}$  are large, the distribution can be considered normal. This, however, is not always the case.

The variance of y is found by neglecting the statistical noise in  $y_{Si}$  entirely. By doing so it is easily obtained that

<sup>&</sup>lt;sup>1</sup>I.e. a region where the tails of the Poissonian distribution have flattened out.

$$\operatorname{Var}(y) = \frac{y_{\mathrm{Er}} + \frac{1}{N} y_{\mathrm{Er, back}}}{y_{\mathrm{Si}}^2}.$$
 (2.13)

It would be more exact to include the noise of  $y_{\rm Si}$ , but since the counts for Si typically lie in the  $10^5$  range, equation (2.13) is sufficient.

There is, however, a practical problem with equation (2.13). The individual data points  $y_{\text{Er},i}$  may be a poor estimator of the mean value,  $\langle y_{\text{Er}} \rangle$  (especially if  $y_{\text{Er},i} = 0$ ). We can make the practical replacement  $y_{\text{Er}} \rightarrow \max(y_{\text{Er}}, y_{\text{Er,back}})$  and then neglect the term  $\frac{1}{N}y_{\text{Er,back}}$  in equation (2.13) and obtain the practical estimate

$$\operatorname{Var}(y) = \frac{\max(y_{\mathrm{Er}}, y_{\mathrm{Er, back}})}{y_{\mathrm{Si}}^2}.$$
 (2.14)

# 2.4 Experimental estimation of moments

The moments from section 2.2 can now be calculated based on the experimental signal. The time parameter, t, is converted into a depth parameter, x, as

$$x = \frac{L \cdot t}{t_{\text{end}}} \equiv v \cdot t, \qquad (2.15)$$

where L is the depth of the sputtered profile (measured e.g. by DekTak), and  $t_{end}$  is the time of the SIMS measurement. The speed of the sputtering process is denoted v.

The mean depth profile,  $\bar{x}_y$ , and the variance of the depth profile,  $\operatorname{Var}[x_y]$ , can be calculated as

$$\bar{x}_y = \frac{\sum_i x_i y_i}{\sum_i y_i} \quad \text{and} \quad \operatorname{Var}[x_y] = \frac{\sum_i (x_i - \bar{x}_y)^2 y_i}{\sum_i y_i}, \qquad (2.16)$$

where data is taken from a suitable range around the Er peak. The *statistical* variances of the above expressions can be calculated from the combination formula<sup>2</sup> to yield

<sup>2</sup>Var(Z) = 
$$\left(\frac{\partial f}{\partial X}\right)^2$$
Var(X) +  $\left(\frac{\partial f}{\partial Y}\right)^2$ Var(Y)

$$\operatorname{Var}(\bar{x}_y) = \sum_{j} \left( \frac{x_j \sum_i y_i - \sum_i x_i y_i}{\left(\sum_i y_i\right)^2} \right)^2 \operatorname{Var}(y_j)$$
(2.17)

and

$$\operatorname{Var}(\operatorname{Var}[x_y]) = \sum_{j} \frac{1}{(\Sigma_i y_i)^6} \left( x_j^2 (\Sigma_i y_i)^2 - \dots \right)$$

$$[2x_j \Sigma_i x_i y_i + \Sigma_i x_i^2 y_i] \Sigma_i y_i + 2(\Sigma_i x_i y_i)^2 \right)^2 \operatorname{Var}(y_j).$$
(2.18)

### 2.5 Diffusion coefficient

With the results obtained so far a specific formula for the diffusion coefficient can be derived. By using equations (2.4) and (2.10) the diffusion coefficient must be given as

$$D = \frac{\operatorname{Var}[x_y] - \operatorname{Var}[x_y^{(\mathrm{AD})}]}{2t_{\mathrm{ann}}},$$
(2.19)

where the variances, Var[...], are given by equation (2.16). The statistical uncertainty on D is given by the standard deviations as

$$\operatorname{Std}(D) = \frac{\sqrt{\operatorname{Var}(\operatorname{Var}[x_y]) + \operatorname{Var}(\operatorname{Var}[x_y^{(\operatorname{AD})}])}}{2t_{\operatorname{ann}}}, \quad (2.20)$$

where the statistical variances, Var(Var[...]), are given by equation (2.18).

## Experimental setup

#### 3.1 Initial wafer

The initial wafer prepared in the magnetron sputtering system consisted of a base of pure p-type Si, a layer of pure  $\text{TiO}_2$  (200 nm), a layer of Er doped  $\text{TiO}_2$  (20 nm), and a top layer of pure  $\text{TiO}_2$  (25 nm). The concentration of Er in the  $\text{TiO}_2$  is 1 at%. The composition of this wafer can be seen in Figure 3.1.

The top layer of pure  $\text{TiO}_2$  was supposed to have a thickness of 200 nm just like the bottom layer, but due to a shutdown of the magnetron sputter over night the sputtering process stopped after the 25 nm.



Figure 3.1: Side view sketch of the composition of the initial sample. Not to scale. Made with inspiration from Lu et al. (2010).

Despite the incomplete top layer, we chose to continue with this sample to get an indication of in which temperature range the annealing should take place.

The sample was cut into smaller pieces and annealed at 1000 °C for one hour. In order to observe diffusion, the temperature should be high enough to overcome the energy barriers to atomic motion, since molecules diffuse through random molecular motion (Heitjans and Kärger, 2005). We chose a temperature of 1000 °C since this was the highest possible stable temperature the oven in question could reach.

After the wafer had cooled, we performed SIMS (Secondary Ion Mass Spectrometry) both on the original sample and on the annealed samples. The SIMS method is explained in details in section 2.3.

From the SIMS method we were able to retrieve distribution information of the samples, i.e. the intensity of certain ions as a function of the depth. The distributions of interest were the ones for the  $\text{ErO}^-$  ions and  $\text{Si}^-$  ions. Recall, that we for the annealed sample should detect a flattening of the  $\text{ErO}^-$  distribution profile. This, however, was not detected as explained in section 4.1.

We then tried annealing the sample in the RTA oven. RTA stands for Rapid Thermal Annealing and will, as the name indicates, rapidly reach the desired temperature. This oven will reach a temperature of 1200 °C, but only for a restricted time period before shutting down due to overheating.

When heating a sample, the oven injects nitrogen into the oven chamber in order to prevent the sample from oxidizing. This process of oxidation is only possible if, simultaneously, a reduction of one or more elements occurs. This is not a desired outcome, hence the nitrogen injection.

As explained in section 4.1 the results from this wafer were inadequate partly due to the structure of the wafer.

### 3.2 Second wafer

A new wafer was produced by the same process as for the initial wafer. The Er doped  $\text{TiO}_2$  used here also had a concentration of Er of 1 at%.

Temperature [°C]	Annealing time [s]	Oven
800	3600	Small furnace
850	3600	Small furnace
900	3600	Small furnace
900	900	RTA, small furnace
945	900	Small furnace
960	900	RTA
980	900	RTA, small furnace
1000	900	RTA
1020	300	RTA

Table 3.1: Annealing times and temperatures for the second, improved sample. Two different ovens were used; a small furnace and an RTA oven.

On the new wafer, the thickness of the bottom layer of TiO<sub>2</sub> was increased to 300 nm in order to prevent the Si from diffusing up through the sample and thus interfering with the diffusivity of Er, as it did on the initial wafer, as explained in section 4.1. The thickness of the middle layer with the Er doped TiO<sub>2</sub> (shown in blue in Figure 3.1) was decreased to 10 nm. Along with these alterations, the thickness of the top layer of TiO<sub>2</sub> was increased to 100 nm in order to ensure that the thickness of the TiO<sub>2</sub> was larger than the diffusion length and thus to completely bury the Er in the TiO<sub>2</sub>.

This wafer was annealed at several temperatures in two different ovens. These temperatures along with the annealing times can be seen in Table 3.1.

These were all analyzed by performing SIMS. From the SIMS measurements, an intensity distribution was obtained. The intensity, i.e. the number of counts, is given as a function of the sputtering time. In the sputtering where the Cs and Bi ions remove material from the sample a crater is formed. By measuring the depth of this crater with a profilometer, the rate of digging as a function of time can be found, as shown in equation (2.14), and the intensity as a function of the depth of the crater can thus be obtained. This conversion from time to depth was obtained under the assumption that the rate of sputtering was constant during the entire SIMS

measurement.

The profilometer used is a Veeco Dektak 150 surface profilometer. The profilometer works by placing the sample on a movable X-Y stage. The surface profilometer then takes surface measurements using techniques from contact profilometry. The profilometer has a 4 Å step-height repeatability which it uses to perform very precise step-height measurements of thin samples down to 10 Å and thick samples of up to several hundreds microns in thickness (Veeco, 2009).

## Experimental results

#### 4.1 Data selection

The initial sample was cut into smaller pieces and annealed at  $1000 \,^{\circ}\text{C}$  for  $15 \,\text{min}$  and  $1 \,\text{h}$ , at  $1100 \,^{\circ}\text{C}$  for  $1 \,\text{min}$ , and at  $1160 \,^{\circ}\text{C}$  for  $17 \,\text{s}$  in the RTA oven. The annealings at  $1100 \,^{\circ}\text{C}$  and  $1160 \,^{\circ}\text{C}$  should have lasted  $15 \,\text{min}$ , but due to overheating, the oven shut down before reaching the  $15 \,\text{min}$  mark.

The sample annealed at 1000 °C for 1 h was annealed in a red oven, which was only used this one time. The reason for this oven only being used for this annealing was that a flattening of the ErO<sup>-</sup> distribution profile was not detected as shown in Figure 4.1.

The sample annealed at 1160 °C had changed its surface appearance after the annealing. This temperature burns the surface and further analysis will thus not be performed on this sample. The same goes for the sample annealed at 1100 °C. On this sample, however, only the edges had changed their visual appearances, where the Si had diffused up through the sample. This diffusion of Si can be seen in Figure 4.2. These photos were taken by using a light microscope and then applying a green filter. The areas of lighter green shading indicates the presence of Si at the surface of the sample.

At these high temperatures, we can possibly see the Si and the  $TiO_2$  creating vacancy diffusion, where the diffusing Si particles migrate from vacancy to vacancy in the  $TiO_2$ .

The sample annealed at  $1000 \,^{\circ}$ C did show the expected diffusion

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Figure 4.1: Distribution of  $\text{ErO}^-$  before (blue crosses) and after (red crosses) annealing at 1000 °C for 1 h in a small, red oven. Here we do not detect the expected flattening of the distribution profile. This oven was thus only used for this one annealing.



Figure 4.2: Surface of sample annealed at  $1160 \,^{\circ}\text{C}$  for  $17 \,\text{s}$ . The areas of lighter green show the Si at the surface of the sample. Left: Area 1 mm across. Right: Area  $0.5 \,\text{mm}$  across.

of the Er ions. The Er ions had however not diffused into the pure  $\text{TiO}_2$  as desired, but instead into the now Si contaminated  $\text{TiO}_2$ , since the Si also at this temperature had diffused into the  $\text{TiO}_2$  layers.

The analysis of the diffusion coefficients will thus be focused on the distribution profiles of the improved wafer from section 3.2.

### 4.2 Erbium distribution profiles

In order to find the diffusion coefficient as a function of temperature, D(T), the intensity distribution of Er at the given temperatures were compared to that of the as-deposited sample. Recall from section 2.3 that data is distributed according to a Poissonian, which spreads out with time. The Er SIMS profiles were fitted to this Gaussian by  $\chi^2$ -minimization. This  $\chi^2$  is used as a measure of goodness of fit and it gives the weighted sum of the squared errors.  $\chi^2$  is inversely proportional to the variance,  $\sigma^2$ .

We would therefore expect the intensity profiles of the Er distribution to spread out when annealed since the process of annealing speeds up the diffusivity. The distributions of Er of the as-deposited sample and a sample annealed at 960 °C for 15 min can be seen in Figure 4.3. The remaining distribution profiles can be found in appendix A, where  $\chi^2_R$  varies between 0.218 and 0.733.

Here, it is readily apparent to see that the annealed distribution profile is flattened compared to the as-deposited. Furthermore, the distribution seems to have shifted deeper into the wafer, i.e. towards the Si at the bottom.

When analyzing the intensity distributions extracted from the SIMS measurements of the different temperatures, the mean depth of the Er distribution can be found. An average of these mean depths was used throughout the analysis. By doing so the assumption of equal mean depths for every SIMS measurement was introduced. This was not a bad assumption, since all the samples were from the same wafer, and the real depth must thus be the same. The mean depth for 12 measurements are given in Figure 4.4. Here, the average mean depth is shown by the dashed line.

Each of the mean depths have all been assigned an uncertainty of  $\pm 2\%$ . These are shown as the vertical errorbars in Figure 4.4.



Figure 4.3: Comparison between SIMS measurement of the Er distribution of the as-deposited sample and the sample annealed at 980 °C. Blue crosses represent the as-deposited data, and red crosses represent the data of the annealed sample. The black line gives the folding of the as-deposited and the Gaussian as explained in section 2.1. The parameter  $A_{\rm fit}$  gives the front factor in equation (2.3) which should be of unity. The Gaussian fits the data to a value of  $\chi^2_R$  of 0.634. The black, horizontal line gives the diffusion length as explained in section 4.4.

When measuring the depth of the sputtered crater the sputtering rate was assumed to be constant. We do not, however, know if this is true. Therefore, when converting the distribution function from being a function of the sputtering time to one of the sputtering depth an uncertainty must be applied. 4.2. Erbium distribution profiles



Figure 4.4: Mean depths of every sample along with the mean depth averaged over all samples plotted as the dashed line. The dotted lines represent the uncertainty on the average mean depth. The red crosses represent the Si-filtered data. The mean depths have as expected approximately the same value.

The average mean depth is found to be  $(127.9 \pm 4.9)$  nm. We see that the mean depth of all of the measurements are aligned around the averaged mean depth. This is in agreement with the assertion that the diffusion should not change the mean depth of the Er as explained in equation (2.6).

As shown in Figure 4.4 four of the data points (plotted as red crosses) have been Si-filtered. This filtration was performed since the Si was not, as initially expected, homogeneously distributed over the area of which the SIMS measurements took place. This is easily seen in a 3D-measurement of the sample. These are shown in Figure 4.5. Therefore, a filtration of the Si in the sample was made in order to observe whether or not the heterogeneous distribution of the Si affects the diffusion of Er in the sample.

#### 4.2. Erbium distribution profiles



Figure 4.5: 3D-measurements of the sample showing the heterogeneous distribution of Si. Top: X-Z view of one selected scan. Bottom: X-Y view of all scans added.

#### 4.3 Diffusion coefficient

The experimental diffusion coefficient can be described by the equation

$$D(T) = D_{T_0} \exp\left(\frac{-\Delta E}{k_{\rm B}} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right),\tag{4.1}$$

where  $k_{\rm B}$  is the Boltzmann constant, T is the temperature, and  $T_0$  is the reference temperature (both measured in units of Kelvin). The front factor,  $D_{T_0}$ , denotes the value of the diffusion coefficient at the reference temperature, and  $\Delta E$  is the activation energy of the diffusion process. This activation energy is given as a function of the enthalpy.

The experimental diffusion coefficients found from the setups given in Table 3.1 are shown in Figure 4.6. Here  $\Delta H$  denotes the enthalpy of the system, i.e. the total energy including the work needed to make room for this energy (assuming constant pressure).

In diffusional mixing of (ideal) gases the diffusion is driven by an increase in entropy. In solids and liquids additional enthalpy effects prevents the formation of diffusion (Mittemeijer, 2011).

Equation (4.1) is called Arrhenius equation. A plot of  $\ln D$  as a function of 1/T should result in a straight line with a slope given by  $-\Delta E/k_{\rm B}$ . This plot is called Arrhenius plot and can be seen in Figure 4.6 as the black line. This slope is obtained by using only 10 out of the 11 calculated diffusion coefficients and thus excluding the diffusion coefficient found at a temperature of 1020 °C. This temperature was found to burn the surface of the wafer. From Figure 4.7 we see that the distribution profile of the Er has changed drastically from that of the as-deposited.

The change of enthalpy is found to be  $\Delta H = (1.9 \pm 0.2) \text{ eV}.$ 

From Figure 4.6 it is clear to see that the diffusion coefficients as a function of the annealing temperature follow Arrhenius' plot.

These diffusion coefficients have all been obtained by comparing the annealed Er distributions to the original as-deposited sample. These distributions can also be compared to the as-deposited sample, where 16% of the area of the Si has been removed as explained in section 4.2. These diffusion coefficients can be seen in Table 4.1. We see from this that changing the reference as-deposited sample



Figure 4.6: Diffusion coefficients as a function of temperature. Blue squares represent the samples annealed in the RTA, red crosses represent the Si-filtered samples, and green circles represent the samples annealed in the small furnace. The black, straight line denotes the fit to data with a slope given by Arrhenius' plot.

to the Si-filtered as-deposited sample does not have any significant effect on the diffusion coefficients.

## 4.4 Diffusion length

From the experimental diffusion coefficients (found by using equation (4.1)), the diffusion length can be calculated. This is found as



Figure 4.7: Distribution profile of Er obtained at a temperature of 1020 °C at 5 min (red crosses) compared to the distribution profile of the as-deposited sample (blue crosses). At this temperature the profile has flattened too much in order to produce a valid diffusion coefficient. This profile is therefore not included when finding the slope in the Arrhenius plot.

$$L = 2\sqrt{Dt_{\rm ann}}.\tag{4.2}$$

The diffusion length provides a measure of how far the diffusing element has propagated into the material. Semiconductor materials which are heavily doped result in shorter diffusion lengths. The higher the diffusion length, the longer lifetime of the semiconducting material (Fick, 1855).

Temperature	Time	$D_{ m ref}$	$D_{\rm Si \ rem.}$
[°C]	$[\mathbf{s}]$	$[10^{-15} \text{cm}^2  \text{s}^{-1}]$	$[10^{-15} \text{cm}^2 \text{ s}^{-1}]$
900	900	$0.21\pm0.02$	$0.21\pm0.02$
960	900	$0.36\pm0.04$	$0.36\pm0.04$
980	900	$0.44\pm0.04$	$0.45\pm0.04$
1000	900	$0.65\pm0.03$	$0.65\pm0.03$
1020	300	$2.63\pm0.84$	$2.64\pm0.84$
900	900	$0.14\pm0.02$	$0.14\pm0.02$
945	900	$0.32\pm0.03$	$0.32\pm0.03$
980	900	$0.45\pm0.05$	$0.46\pm0.05$
800	3600	$0.032\pm0.003$	$0.033 \pm 0.003$
850	3600	$0.041 \pm 0.003$	$0.042\pm0.003$
900	3600	$0.099 \pm 0.007$	$0.100\pm0.007$

Table 4.1: Comparison between diffusion coefficients found from using the original as-deposited sample and the Si-filtered as-deposited sample.

The values of the diffusion coefficients and the diffusion lengths at a given temperature and annealing time are given in Table 4.2.

We see that the diffusion lengths are in the range 7 nm to 16 nm (when excluding the diffusion length found at a temperature of 1020 °C). Compared to those found by Lu et al. (2010) where the diffusion of Er in SiO<sub>2</sub> at a temperature of 1100 °C resulted in a diffusion length of 31 nm, the diffusion lengths obtained in this experiment are a bit shorter. The diffusion length as a function of temperature at a fixed annealing time of 900 s can be seen in Figure 4.8. The fitted line found has the function  $L(T) = (-52.11 \pm 7.08) \text{ nm} + (0.067 \pm 0.007) \text{ nm K}^{-1} \cdot \text{T}_{\text{ann}}$ . Extrapolating this to a temperature of 1100 °C we get  $L = (21.04 \pm 7.08) \text{ nm}$ .

Throughout the experiment performed by Lu et al. (2010), the concentration of Er in the SiO<sub>2</sub> was at 0.2 at% compared to 1 at% of Er in TiO<sub>2</sub> in this experiment. Recall that a lower concentration leads to a longer diffusion length and that a heavily doped semiconductor material leads to shorter diffusion lengths.

The extrapolated diffusion length at 1100 °C only amounts to about 2/3 of the 31 nm found by Lu et al. (2010), but it has rather large uncertainties. This diffusion length of  $(21.04 \pm 7.08)$  nm is

Table 4.2: Diffusion coefficients and diffusion lengths at a given temperature and time of annealing. The 11 diffusion coefficients are found by using two different ovens.

$D_{\rm ref} \left[ 10^{-15} {\rm cm}^2 { {\rm s}}^{-1} \right]$	$T_{ann} \ [^{\circ}C]$	$t_{ann} \ [s]$	$L \; [nm]$	Oven
$0.21 \pm 0.02$	900	900	$8.70\pm0.45$	RTA
$0.36\pm0.04$	960	900	$11.33\pm0.56$	RTA
$0.44\pm0.04$	980	900	$12.59\pm0.61$	RTA
$0.65\pm0.03$	1000	900	$15.30\pm0.33$	RTA
$2.63\pm0.84$	1020	300	$17.76 \pm 2.85$	RTA
$0.14\pm0.02$	900	900	$7.14\pm0.40$	Si-filtered
$0.32\pm0.03$	945	900	$10.66\pm0.45$	Si-filtered
$0.45\pm0.05$	980	900	$12.73\pm0.64$	Si-filtered
$0.032\pm0.003$	800	3600	$6.84 \pm 0.29$	$\mathbf{SF}$
$0.041 \pm 0.003$	850	3600	$7.71\pm0.32$	$\mathbf{SF}$
$0.099 \pm 0.007$	900	3600	$11.96\pm0.43$	$\mathbf{SF}$



Figure 4.8: Diffusion length as a function of temperature. These data points are for the measurements annealed at 900 s, i.e. the first seven measurements given in Table 4.2 (excluding the measurement at  $1020 \,^{\circ}$ C).

however still shorter than that found by Lu et al. (2010).

From Table 4.2 we see that the diffusion length increases with temperature as expected, since  $L \propto D^{1/2}$ , which increases with temperature as shown in Figure 4.6.

## Conclusion and outlook

In this project I have successfully found a linear relation between diffusion coefficients and temperature with a slope given by Arrhenius' equation and thereby by the activation energy.

Throughout this project I have investigated the temperature dependency of the diffusion coefficient of Er diffusion in  $TiO_2$ . The diffusion coefficients were obtained by annealing a sample of Er doped  $TiO_2$  buried in pure  $TiO_2$  at a range of temperatures. The samples were then analyzed by SIMS measurements and from this, the diffusion coefficients could be found from Fick's second law.

These diffusion coefficients are found to closely follow a straight line with a slope given by the activation energy.

Due to the diffusion of Si into the  $TiO_2$ -layer as explained in section 4.1 the Er ions diffused into slightly contaminated  $TiO_2$  and not pure  $TiO_2$  as desired.

From the results we see that the Er ions at temperatures ranging from 800 °C to 1000 °C and with time of annealing of either 900 s and 3600 s diffuse between 7 nm and 16 nm into the surrounding layers of TiO<sub>2</sub>. In order to prevent surface effects the Er should therefore be buried in layers of TiO<sub>2</sub> with a minimum height corresponding to a few diffusion lengths at that given temperature the material is heat treated at, and at that given time in which the heat treatment takes place.

For further experiments, the  $TiO_2$ -layers could be built onto quartz instead of Si. Quartz is a mineral found in the Earth's continental crust. The crystal structure of quartz is based on the structure of  $SiO_2$  (silicon-oxygen tetrahedra). Each oxygen atom is shared between two tetrahedra, making the overall chemical structure of quartz as that of  $SiO_2$ . This structure is shown in Figure 5.1.

The idea is that the Si ions are more tightly bound in  $SiO_2$ than in pure Si, and the Si should thus not diffuse into the  $TiO_2$ . This hypothesis can be validated by experiments similar to those explained throughout this project, where the  $TiO_2$ -layers are build on top of a wafer of quartz instead of pure Si.



Figure 5.1: Schematic lattice structure of  $SiO_2$  and therefore of quartz. Blue spheres represent Si and red spheres represent O. The real structure is three-dimensional. The unit cells in 2D and 3D are shown in the bottom right corner. Each Si is bound to three O, hopefully making the Si more tightly bound and thus preventing diffusion of the Si into the TiO<sub>2</sub>-layer.

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## Appendix

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