

## PROBLEM 200-8

- a) Calculate the vacancy concentration for intrinsic Si at 1100 °C.  
b) Then calculate the equilibrium vacancy concentration at room temperature.

Discuss whether equilibrium is likely at room temperature.

(Intrinsic silicon means in this context there are an equal concentration of electrons and holes, equal to the so-called intrinsic carrier concentration at the temperature. In practical terms it would mean that it is undoped or low doped)

[‘Hint’ : Calculate this problem, before Problem 9, then possibly reflect on it again]

**> restart;**

We need to look up some formulae, expressions and values of relevant parameters.

We look first in the text book

We have there given equation 2.1

**> eq2\_1:=Nv0=N\_0\*exp(-Ea/k/T);**

$$eq2\_1 := Nv0 = N\_0 e^{-\frac{Ea}{kT}}$$

Here it is stated that N\_v\_0 is the 'vacancy concentration'. N\_0 is the density of Si atoms = 5.02e22\*cm^-3 and Ea is the activation energy being around 2.6 eV. The book gives the answer: 1 in 10^44 atoms being a vacancy at RT so N\_v\_0 = 1e-22 We will check that.

**> numbers:={k=8.617e-5\*eV/K,Ea=2.6\*eV,N\_0=5.02e22\*cm^(-3)};**

$$numbers := \left\{ Ea = 2.6 \text{ eV}, N\_0 = \frac{5.02 \cdot 10^{22}}{cm^3}, k = \frac{0.00008617 \text{ eV}}{K} \right\}$$

**> answer\_a:=simplify(subs(numbers union {T=(1100+273)\*K},eq2\_1));**

$$answ\_a := Nv0 = \frac{1.434467013 \cdot 10^{13}}{cm^3}$$

We should compare this concentration to the atomic density of Si - 5e22cm^-3. So the equilibrium relative density appears very small. Also, say compared to a typical doping concentration 1e15(low) 1e17 (medium) 1e19 (hi) this vacancy concentration is low.

**> answer\_b:=simplify(subs(numbers union {T=(20+273)\*K},eq2\_1));**

$$answ\_b := Nv0 = \frac{9.492769639 \cdot 10^{-23}}{cm^3}$$

So we see the books number for RT , 1 in 10^44 is OK.

The calculated number for vacancy concentration at RT is very low, - at equilibrium

If we had a piece 1 cm^3 we would not have any vacancies in it.

We would on the average need a volume of 1e22 cm^3 in order to have one vacancy!!,

1e7x1e7x1e7 cm=1e5x1e5x1e5=10kmx10kmx10km= 1 x 1 x 1 mil

But you should know that some of your fellow students study vacancies at room temperature of below, so you should from that think that, maybe either

1. The theory is wrong,

2. The calculation numbers are wrong
3. We don't have equilibrium

Option 3 is considered correct. In order to have equilibrium, the vacancy concentration would have to adjust.

That requires atomic mobility. Diffusion. At room temperature, many vacancies will be frozen in.

But, hey! we have learned that the vacancy can exist in many charge states.

Thus we have a certain concentration for each charge state, - given the Fermi level.

By reading a little further in the text book, looking at equations (2.4)-(2.6) you may take the parameter  $N_{v0}$  of eq (2.1) to mean the concentration of neutral vacancies at equilibrium - the  $v$  without a sign signals the charge state and the 0 signals equilibrium.

In the textbook the concentration of negative charged vacancies is given by equation (2-4) ( $N_{vm} = N_v$  minus)

```
> eq2_4:=Nvm=Nv0*(n/ni)*exp((Ei-Evm)/k/T);
```

$$eq2\_4 := N_{vm} = \frac{N_{v0} n e^{\frac{E_i - E_{vm}}{k T}}}{n_i}$$

(Where  $N_{v0}$  the concentration of neutral vacancies ( $v$  without sign being neutral, the 0 signaling equilibrium. If so then what we have calculated above is the neutral concentration)

Similarly 2.5 and 2.6

```
> eq2_5:=Nvp=Nv0*(p/ni)*exp((Evp-Ei)/k/T);# for positively charged vacancy
```

$$eq2\_5 := N_{vp} = \frac{N_{v0} p e^{\frac{E_{vp} - E_i}{k T}}}{n_i}$$

```
> eq2_6:=Nvmm=Nv0*(n/ni)^2*exp((Ei-Evmm)/k/T);# for double negative charged vacancy
```

$$eq2\_6 := N_{vmm} = \frac{N_{v0} n^2 e^{\frac{E_i - E_{vmm}}{k T}}}{n_i^2}$$

We need to look up the temperature dependence of the energy levels to use these.

NB the Handout on defects indicate this and give values for 1400 K, see example 5 in "Defects in Semiconductors", But really 1400 K is not far from 1373 K = 1100 C, so we could have used that.

We can also recheck the more original publication Van Vechten in the Handbook Fig 26 a page 80 for  $T=1375$  we read off  $E_v^- = 0.07$  eV,  $E_v^+ = T$  independent  $= 0.35$ ,  $E_{vmm} = 0.55$  eV,  $E_c = 0.61$  eV, So  $E_i = 0.305$ .

```
> numbers2:={Evm=0.07*eV,Evmm=0.55*eV,Ec=0.61*eV,Ei=0.305*eV,Evp=0.35*eV,k=8.37e-5*eV/K,T=1373*K};
```

```
numbers2 := {Ec = 0.61 eV, Ei = 0.305 eV, Evm = 0.07 eV, Evmm = 0.55 eV, Evp = 0.35 eV, T
```

$$= 1373 \text{ K}, k = \frac{0.0000837 \text{ eV}}{\text{K}} \}$$

```

> eq11:=evalf(subs(numbers2 union {n=ni},eq2_4));
      eq11 := Nvm = 7.728378095 Nv0
> eq12:=evalf(subs(numbers2 union {p=ni},eq2_5));
      eq12 := Nvp = 1.479310955 Nv0
> eq13:=evalf(subs(numbers2 union {n=ni},eq2_6));
      eq13 := Nvmm = 0.1186098195 Nv0
> eq14:=NT=Nvm+Nvmm+Nv0+Nvp;
      eq14 := NT = Nvm + Nvmm + Nv0 + Nvp
> eq15:=subs({eq11,eq12,eq13},eq14);
      eq15 := NT = 10.32629887 Nv0
> answa_2:=subs(answ_a,eq15);
      answa_2 := NT =  $\frac{1.481273510 \cdot 10^{14}}{\text{cm}^3}$ 

```

OK, so we get a factor of 10 between the total and just the neutral at this temperature and doping concentration, If we had calculated for strongly n-type we would have gotten considerably more