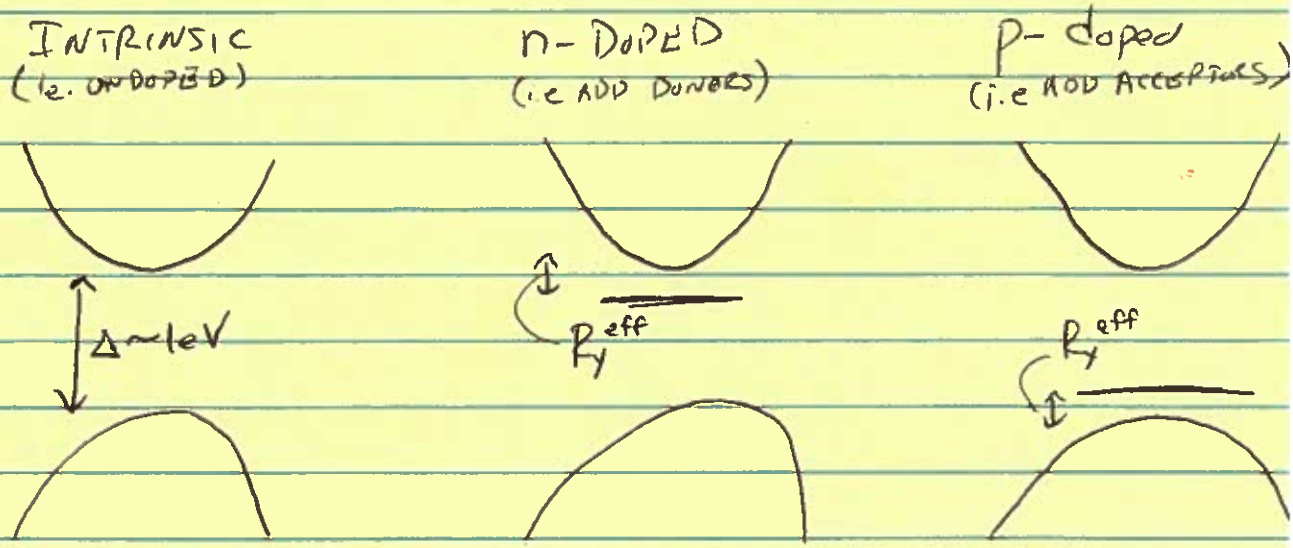
PHYS 460 LECTURE 16

WHEN WE ENDED LAST LECTURE WE HAD WORKED OUT THE APPROXIMATE ENERGY SCHEME FOR A TYPICAL SEMICONDUCTOR DOPED WITH A SMALL NUMBER OF "DONORS" OR "ACCEPTORS". THE RESULT LOOKED LIKE THIS



HERE R_y^{eff} IS THE EFFECTIVE RYBERG CONSTANT, WHICH REPRESENTS THE BINDING ENERGY OF ELECTRONS (HOLES) ON THE SITE OF AN n- (p-) DOPANT. THOUGH THE EXACT ENERGY DEPENDS ON THE LOCAL ENVIRONMENT OF THE EXACT DOPANT SITE, AN ORDER OF MAGNITUDE APPROXIMATION CAN BE FOUND USING

$$R_y^{eff} \approx R_y \times \left(\frac{m^*}{m}\right) \times \left(\frac{1}{\varepsilon_r}\right)^2$$

$$\sim 13.6\,eV \times \left(\frac{1}{10}\right) \times \left(\frac{1}{10}\right)^2$$

$$\sim 0.01\,eV \ll \Delta$$

WE ALSO SHOWED, USING BOLTZMANN STATISTICS BASICALLY, THAT THE NUMBERS OF ELECTRONS AND HOLES IN THESE SYSTEMS AT A TEMPERATURE, T, ARE GIVEN BY

$$n(T) = \frac{1}{4}\left(\frac{2 m_e^* k_B T}{\pi \hbar^2}\right)^{3/2} e^{-\frac{(E_c - \mu)}{k_B T}}$$

$$p(T) = \frac{1}{4}\left(\frac{2 m_h^* k_B T}{\pi \hbar^2}\right)^{3/2} e^{-\frac{(\mu - E_v)}{k_B T}}$$

$$\Rightarrow \boxed{n(T)\,p(T) = \frac{1}{2}\left(\frac{k_B T}{\pi \hbar^2}\right)^3 (m_e^* m_h^*)^{3/2} e^{-\Delta / k_B T}}$$

LAW OF MASS ACTION

IT IS IMPORTANT TO NOTE THAT THE DERIVATION OF THESE EQUATIONS DID NOT DEPEND ON THE MATERIAL BEING "CLEAN". WHAT DO DOPANTS CHANGE? ⟶ THEY ALTER THE CHEMICAL POTENTIAL

TODAY, WE ARE GOING TO SEE HOW TO TRACK CARRIER CONCENTRATIONS IN THE PRESENCE OF DOPANTS.

FIRST, RECALL THE CONCENTRATIONS IN THE INTRINSIC CASES WERE GIVEN BY

$$n(T) = p(T) \equiv n_i(T) = \frac{1}{4}\left(\frac{2 k_B T}{\pi \hbar^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-\frac{\Delta}{2 k_B T}}$$

"INTRINSIC"

AND $\mu_i = \frac{E_c + E_v}{2} + \frac{3 k_B T}{4} \ln\left(\frac{m_h^*}{m_e^*}\right)$

OK, HOW DO THINGS CHANGE IN THE EXTRINSIC CASE? WELL, AS NOTED, THE BIG CHANGE IS TO THE CHEMICAL POTENTIAL. HOW, FROM THE FORM OF $n(T)$, $p(T)$ WE KNOW

$$n(T) = N(T)\, e^{-\frac{(E_c-\mu)}{k_B T}}, \quad \text{WHERE } N(T) = \frac{1}{4}\left(\frac{2m_e^* k_B T}{\pi \hbar^2}\right)^{3/2}$$

$$= N(T)\, e^{\frac{\mu-\mu_i}{k_B T}} e^{-\frac{(E_c-\mu_i)}{k_B T}}$$

$$= e^{\frac{\mu-\mu_i}{k_B T}}\, n_i(T)$$

AND $$p(T) = e^{-\frac{(\mu-\mu_i)}{k_B T}}\, n_i(T)$$

THUS

$$\Delta n \equiv n(T) - p(T) = n_i(T)\left(e^{\frac{\mu-\mu_i}{k_B T}} - e^{-\frac{(\mu-\mu_i)}{k_B T}}\right)$$

$$\boxed{\frac{\Delta n}{n_i} = 2\sinh\left(\frac{\mu-\mu_i}{k_B T}\right)}$$

THIS TELLS US TWO THINGS

(1) $\Delta n \neq 0$, AND IT DEPENDS ON THE LOCATION OF μ

(2) UNLESS $\Delta n \gg n_i$ BY ORDERS OF MAGNITUDE, μ IS WITHIN $k_B T$ OF μ_i $\longrightarrow$ STILL IN THE GAP! (AND STILL HARD TO PEG)

OK THEN, WHAT CAN WE SAY WITHOUT μ?

FIRST, RECALL THAT THE LAW OF MASS ACTION HAD NO μ DEPENDENCE AND REMAINS VALID!

$$n(T)\,p(T) = n_i^2$$

USING THIS TOGETHER WITH THE DEFINITION $\Delta n = n(T) - p(T)$, WE CAN CALCULATE

$$(\Delta n)^2 + 4n_i^2 = n^2 + p^2 - 2np + 4np$$

$$= (n+p)^2$$

$$\Rightarrow \quad n(T) = \left((\Delta n)^2 + 4n_i^2\right)^{\frac{1}{2}} - p$$

$$= \left((\Delta n)^2 + 4n_i^2\right)^{\frac{1}{2}} + \Delta n - n(T)$$

$$\rightarrow \quad \boxed{n(T) = \frac{1}{2}\left(\sqrt{(\Delta n)^2 + 4n_i^2} + \Delta n\right)}$$

SIMILARLY

$$\boxed{p(T) = \frac{1}{2}\left(\sqrt{(\Delta n)^2 + 4n_i^2} - \Delta n\right)}$$

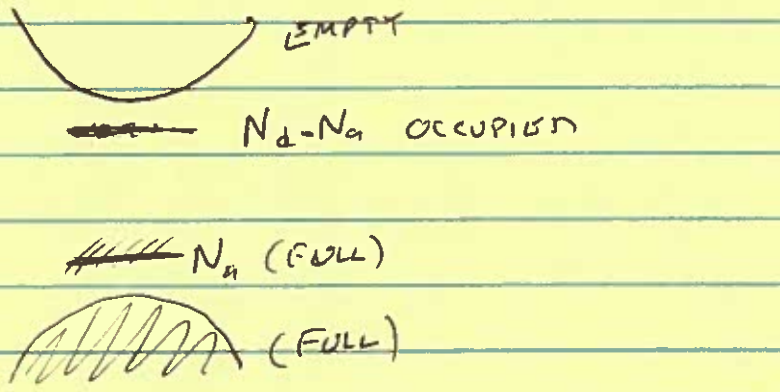
SO, THIS AT LEAST TELLS YOU THAT IN THE LIMIT $\Delta n \gg n_i$, THEN [redacted] (IF $\Delta n > 0$, FOR EXAMPLE)

$$n(T) \approx \Delta n$$

$$p(T) \approx \frac{\Delta n}{2}\left(1 + \frac{n_i^2}{\Delta n}\right) - \frac{\Delta n}{2} \approx \left(\frac{n_i}{\Delta n}\right)^2$$

So IN THE CASE THAT ONE CARRIER DOMINATES, THE MINORITY CARRIER IS ALMOST GONE. PERHAPS OBVIOUS. NOTE THOUGH, THIS EQUATION ALSO SAYS THAT IF INTRINSIC CARRIER CONCENTRATION IS LOW (i.e AT LOW TEMPS), THEN YOUR SYSTEM WILL ~~#~~ ONLY HAVE CARRIERS OF A SINGLE TYPE!

THIS MAKES SENSE TOO. CONSIDER THE CASE WHERE ONE HAS N_d DONOR ATOMS AND N_a ACCEPTOR ATOMS PER UNIT VOLUME, AND LET $N_d > N_a$. THEN AT $T=0$, N_a OF THE DONOR ELECTRONS WILL FALL INTO THE EMPTY STATES ON THE ACCEPTOR ATOMS, LEAVING $N_d - N_a$ DONOR ELECTRONS.



THEN, AS $k_B T > R_y^{eff}$, YOU END UP WITH NO HOLES AND $N_d - N_a$ ELECTRONS IN THE CONDUCTION BAND. AT HIGHER TEMPS

$$n(T) + n_d(T) = N_d - N_a + p(T) + p_a(T)$$

($n_d(T)$: # FILLED STATES ON DONOR SITES; $p_a(T)$: # EMPTY STATES ON ACCEPTOR SITES)

LET'S GET MORE SPECIFIC. USING BOLTZMAN STATISTICS, WE CAN FIND THE MEAN NUMBER OF ~~ELE~~ ELECTRONS ON A DONOR SITE. THERE ARE FOUR POSSIBILITIES

1. NO ELECTRONS ON SITE
2. 1 SPIN UP ELECTRON
3. 1 SPIN DOWN ELECTRON
4. 2 ELECTRONS

THE LAST CASE HAS A COULOMB COST, SO IT IS HIGHER ENERGY. FOR SIMPLICITY, LET'S IGNORE IT FOR NOW.

ACCORDING TO BOLTZMAN

GENERAL DEFINITION →

$$\langle n \rangle = \frac{\sum_j N_j e^{-\frac{(E_j - \mu N_j)}{k_B T}}}{\sum_j e^{-\frac{(E_j - \mu N_j)}{k_B T}}}$$

ε_d = ENERGY OF DONOR LEVEL

$$= \frac{0 + 2e^{-\frac{(\varepsilon_d - \mu)}{k_B T}}}{1 + 2e^{-\frac{(\varepsilon_d - \mu)}{k_B T}}}$$

$$\Rightarrow \boxed{n_d(T) = \frac{N_d}{\frac{1}{2} e^{\frac{(\varepsilon_d - \mu)}{k_B T}} + 1}}$$

ELECTRONS ON DONOR SITES

FOR ACCEPTOR LEVELS, WE SAY THEY ARE SINGLY OCCUPIED (HAVE ONE HOLE) OR DOUBLY OCCUPIED (HAVE ~~TWO~~ 0 HOLES) BUT NOT EMPTY (HAVE TWO HOLES)

$$\text{ACCEPTOR } \langle n \rangle = \frac{2e^{-\frac{(\varepsilon_a - \mu)}{k_B T}} + 2e^{-\frac{(2\varepsilon_a - 2\mu)}{k_B T}}}{2e^{-\frac{(\varepsilon_a - \mu)}{k_B T}} + e^{-\frac{(2\varepsilon_a - 2\mu)}{k_B T}}}$$

$$= \frac{e^{\frac{(\mu - \varepsilon_a)}{k_B T}} + 1}{\frac{1}{2} e^{\frac{\mu - \varepsilon_a}{k_B T}} + 1}$$

$$\boxed{p_a(T) = N_a \cdot (2 - \langle n \rangle) = \frac{N_a}{\frac{1}{2} e^{\frac{(\mu - \varepsilon_a)}{k_B T}} + 1}}$$

NOW IF $\varepsilon_d - \mu \gg k_B T$ AND $\mu - \varepsilon_a \gg k_B T$ > LEVELS NEAR EDGE OF GAP

THESE FORMULAS SAY

$$n_a(T) \approx 2N_d e^{-\frac{(\varepsilon_d - \mu)}{k_B T}} \ll N_d$$

AND $$p_a(T) \approx 2N_a e^{-\frac{(\mu - \varepsilon_a)}{k_B T}} \ll N_a$$

$\Rightarrow$ LEVELS ARE ALMOST COMPLETELY EMPTY

IN THIS LIMIT

$$\Delta n = n(T) - p(T) = N_d - N_a + p_a(T) - n_e(T)$$

$$\simeq N_d - N_a$$

DETERMINED COMPLETELY BY DOPANT ATOM LEVELS. WE CONTROL THOSE!

ALSO

$$n(T) = \frac{1}{2}\left(\sqrt{(N_d - N_a)^2 + 4n_i^2} + N_d - N_a\right)$$

$$p(T) = \frac{1}{2}\left(\sqrt{(N_d - N_a)^2 + 4n_i^2} - N_d + N_a\right)$$

CHECK LIMITS

$$N_d, N_a \ll n_i \rightarrow \begin{Bmatrix} n(T) \\ p(T) \end{Bmatrix} = n_i(T) \pm \frac{(N_d - N_a)}{2}$$

$$N_d, N_a \gg n_i \rightarrow \begin{Bmatrix} n(T) \\ p(T) \end{Bmatrix} = \begin{cases} N_d - N_a \\ \frac{n_i^2}{N_d - N_a} \end{cases} \quad \text{FOR } N_d > N_a$$

$$\begin{Bmatrix} n(T) \\ p(T) \end{Bmatrix} = \begin{cases} \frac{n_i^2}{N_a - N_d} \\ N_a - N_d \end{cases} \quad \text{FOR } N_a > N_d$$

SINCE $n_i(T)$ GROWS WITH TEMPERATURE, THIS NATURALLY LEADS TO THE CONCLUSION THAT SEMICONDUCTORS HAVE INTRINSIC (HIGH T) AND EXTRINSIC (LOW T) TEMPERATURE REGIMES

ONE LAST ITEM: WE HAVE SHOWN HOW TO DETERMINE CARRIER TYPE AND ADD EXTRINSIC CARRIERS. IS THERE ANY WAY TO CONTROL THE NUMBER OF INTRINSIC CARRIERS, ASIDE FROM TEMPERATURE? ACCOMPLISHING THIS FEAT DEMANDS CONTROL OVER THE SIZE OF THE BAND GAP WHICH IS A MATERIAL PROPERTY. FREQUENTLY, ONE SIMPLY JUST SEEKS A MATERIAL WITH THE GAP SIZE DESIRED. EMPIRICALLY, HOWEVER, IT IS FOUND THAT ALLOYING IS A USEFUL TOOL.

EXAMPLE (GIVEN IN SIMON, CH 18)

$\Delta_{GaAs} \approx 1.4eV$

$\Delta_{AlAs} \approx 2.7eV$

Al & Ga HAVE SAME VALENCE, SO ONE CAN SUBSTITUTE x% OF Ga ATOMS WITH Al WITHOUT INTRODUCING CARRIERS. HOWEVER THE GAP SIZE GOES LIKE

$$\Delta(x) = (1-x)\,1.4eV + x\,2.7eV$$

ON AVERAGE

SO WITH BOTH DOPING AND ALLOYING, MATERIALS SCIENTISTS HAVE EXCELLENT CONTROL OVER MOST IMPORTANT MATERIALS PROPERTIES