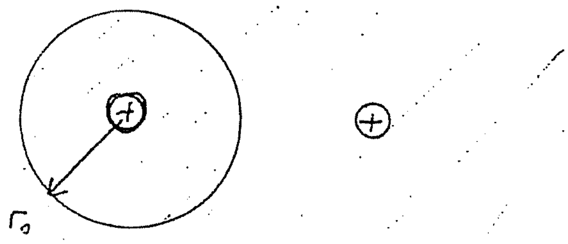
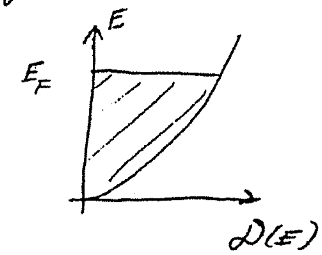
P627 / Chem 541
Surf / Interface Science F 2010
PROBLEM Set 2 - Solutions

1 Consider metal as ⊕ ion imbedded in uniform "free electron gas."



(a) Kinetic energy : Free electrons in 3-dim square well.



Density of States: $\mathcal{D}(E) = \left(\frac{V}{N}\right)\left(\frac{1}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$

filled up to Fermi Level : $E_F = \left(\frac{\hbar^2}{2m}\right)\left(\frac{3\pi^2 N}{V}\right)^{2/3}$

$$\langle E \rangle = \int_0^{E_F} E\,\mathcal{D}(E)\,dE = \int_0^{E_F} \left(\frac{V}{N}\right)\left(\frac{1}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{\frac{3}{2}}\,dE$$

$$= \left(\frac{2}{5}\right)\left(\frac{V}{N}\right)\left(\frac{1}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_F^{\frac{5}{2}} = \left(\frac{2}{5}\right)\left(\frac{1}{2\pi^2}\right)\left(\frac{2m}{\hbar}\right)^{3/2}\left(\frac{V}{N}\right)\left(\frac{3\pi^2 N}{V}\right)^{5/3}\left(\frac{\hbar^2}{2m}\right)^{\frac{5}{2}}$$

$$= \left(\frac{1}{5\pi^2}\right)(3\pi^2)^{\frac{5}{3}}\left(\frac{\hbar^2}{2m}\right)\left(\frac{3}{4\pi r_0^3}\right)^{2/3} = \underbrace{\left(\frac{1}{5\pi^2}\right)(3\pi^2)^{\frac{5}{3}}\left(\frac{3}{4\pi}\right)^{2/3}}_{=\,2.21}\frac{\hbar^2}{2m}\left(\frac{1}{r_0^2}\right)$$

Now $r_s = r_0/a_0$ and $a_0 = \frac{\hbar^2}{e^2 m}$, and 1 Ryd. $= \frac{me^4}{2\hbar^2}$

$$\text{So } \langle E \rangle = 2.21\,\frac{\hbar^2}{2m}\left(\frac{1}{a_0 r_s}\right)^2 = 2.21\,\frac{\hbar^2}{2m}\,\frac{1}{a_0^2}\,\frac{1}{r_s^2} = 2.21\,\frac{\hbar^2}{2m}\left(\frac{e^4 m^2}{\hbar^4}\right)\frac{1}{r_s^2}$$

$$= 2.21\underbrace{\left(\frac{e^4 m}{2\hbar^2}\right)}_{1\ \text{Ryd}}\frac{1}{r_s^2} = \boxed{\frac{2.21}{r_s^2}\ \text{in Ryd.}}$$

(b) The ion sets up a potential $V = +\frac{e}{r}$

We assemble the sphere of (−) charge with shells: $dp = \rho \cdot 4\pi r^2 dr$

where $\rho = (-e)/(4/3)\pi r_0^3$

$$\text{so} \quad U_c = \int_0^{r_0} \frac{-3e^2}{4\pi r_0^3} \cdot 4\pi r^{\cancel{2}} \cdot \frac{e}{\cancel{r}}\, dr = \frac{-3e^2}{r_0^3}\int_0^{r_0} r\, dr = \frac{-3e^2 r_0^2}{2 r_0^3}$$

$$\text{so} \quad \boxed{U_c = -\frac{3e^2}{2r_0}} = -\frac{3}{2}\frac{e^2}{a_0 r_s^2} = -\frac{3}{2}\frac{e^2 \cdot e^2 m}{\hbar^2}\frac{1}{r_s} = \frac{-3}{r_s}\ (\text{Ryd})$$

(c) The coulomb self-energy is calculated by considering the energy needed to add a spherical shell of charge around an existing sphere of radius r.

$$U_s = \int V\, dp = \int_0^{r_0} \frac{(-e)}{(\frac{4}{3})\pi r_0^3} \cdot \frac{(\frac{4}{3})\pi r^3}{r} \cdot \frac{(-e)}{(\frac{4}{3})\pi r_0^3} 4\pi r^2 dr$$

$$= 3e^2 \frac{1}{r_0^6}\int_0^{r_0} r^4 dr = \boxed{\frac{3}{5}\frac{e^2}{r_0}} = \frac{3}{5}\frac{e^2}{a_0 r_s} = \frac{2\cdot 3}{5}\left(\frac{e^2 \cdot e^2 m}{2\cdot\hbar^2}\right)\frac{1}{r_s}$$

$$= +\frac{6}{5}\frac{1}{r_s}\ (\text{Ryd}).$$

(d) Total energy

$$E(r_s) = \frac{2.21}{r_s^2} - \frac{3}{r_s} + \frac{6}{5 r_s} = \frac{2.21}{r_s^2} - \frac{9}{5 r_s}$$

$$\left.\frac{\partial E}{\partial r_s}\right| = \frac{-2(2.21)}{r_s^3} + \frac{9}{5 r_s^2} = 0 \Rightarrow \frac{+2(2.21)\cdot 5}{9} = r_{s_{eqm}}$$

r_{eqm}

$$= \frac{22.1}{9} = \boxed{2.45 = r_{s_{eqm}}}$$

2] He, $Z_1 = 2$, Ag, $Z_2 = 47$, $E = 2\times10^6$ eV

a)
$$d = \frac{Z_1 Z_2 e^2}{E} = \frac{2\cdot47\cdot14.4\,\text{eV-Å}}{2\times10^6\,\text{eV}} = 6.8\times10^{-12}\text{ cm}$$

b)
$$b = \frac{Z_1 Z_2 e^2}{2E}\cot\frac{\theta}{2} = \frac{d}{2}\cdot\cot\frac{\theta}{2} = 3.4\times10^{-12}\text{ cm}$$
where $\theta = 90°$

c) use σ_T to denote cross-section for scattering through angles $> 90°$

$$\sigma_T = \int_{\pi/2}^{\pi} d\sigma = \int_0^{2\pi}\int_{\pi/2}^{\pi} \sigma(\theta)\cdot\sin\theta\, d\theta\, d\phi$$ where $\sin\theta\cdot d\theta\, d\phi$ is the solid angle

$$= \left(\frac{d}{4}\right)^2 \int_{\pi/2}^{\pi} \frac{\sin\theta\cdot d\theta\cdot 2\pi}{\sin^4\theta/2}$$ where $\int_0^{2\pi} d\phi = 2\pi$

$$= 2\pi\cdot\left(\frac{d}{4}\right)^2 \cdot \int_{\pi/2}^{\pi} \frac{[2\sin\theta/2\,\cos\theta/2]\, d\theta/2\cdot 2}{\sin^4\theta/2}$$

$$= \frac{\pi d^2}{2}\int \frac{\cos\theta/2\cdot d\theta/2}{\sin^3\theta/2} = -\frac{\pi d^2}{4}\sin^{-2}\frac{\theta}{2}\Bigg|_{\pi/2}^{\pi}$$

$$= -\frac{\pi d^2}{4}(1-2) = \pi d^2/4$$

$Nt\sigma_T$ = fraction of beam scattered = probability of scattering

Fraction $= N_A \rho t\cdot\sigma = 6\times10^{23}\times10.5\times10^{-6}\times\pi(6.8\times10^{-12})^2 = 2.1\times10^{-6}$

3] $E_2/E_0 = 4M_1M_2/(M_1+M_2)^2$

a) Au, $A = M_2 = 197 \Rightarrow \frac{E_2}{E_0} = \frac{4\cdot4\cdot197}{(201)^2} = 0.078$

b) C, $A = M_2 = 12 \Rightarrow E_2/E_0 = 0.75$

c) α, $A = M_2 = 4 \Rightarrow E_2/E_0 = 1$

d) electron, $\frac{E_2}{E_0} = \frac{4M_1 M_e}{(M_1+M_e)^2} \cong \frac{4M_e}{M_1} \cong \frac{(4)(0.51)}{(4000)} \cong 0.0005$

4 From LECT, Pg 16 we have

(1) $$I_A = \sigma_A D \int_{\gamma=0}^{\pi} \int_{\varphi=0}^{2\pi} L_A(\gamma) \iint_{xy} J_0(x,y) T(x,y,\gamma,\varphi,E_A) \int_z N_A(x,y,z)\, e^{\left(\frac{-z}{\lambda_M(E_A)\cos\theta}\right)} dx\,dy\,d\varphi\,d\gamma\,dz$$

Including the assumptions in the notes, and integrating $\int_0^{\infty} dz$ (pure sample) we get

(2) $$I_A = \sigma_A(\hbar\omega) D(E_A) L_A(\gamma_i) J_0 N_A \lambda_M(E_A)\cos\theta \; G(E_A).$$

Further assumptions gives the result on Pg 17:

(3) $$I_A = \frac{B\sigma_A L_A(\gamma_i) N_A^0 \lambda_M(E_A)}{E_A}.$$

(a) For homogeneous solution consider Intensity ratios based on Eqn 3. Then, only surviving factor is $N\lambda$

$$\Rightarrow \frac{I_A}{I_A^0} = \frac{N_A \lambda_{AB}(E_A)}{N_A^0 \lambda_A(E_A)} \qquad \text{given } \lambda_A = 0.41 a_A^{1.5} E_A^{0.5}$$
$$\lambda_{AB} = 0.41 a_{AB}^{1.5} E_A^{0.5}$$

$$\Rightarrow \frac{I_A}{I_A^0} = \left(\frac{N_A}{N_A^0}\right)\left(\frac{0.41\, a_{AB}^{1.5} E_A^{0.5}}{0.41\, a_{A}^{1.5} E_A^{0.5}}\right) = \left(\frac{N_A}{N_A^0}\right)\left(\frac{a_{AB}^{1.5}}{a_A^{1.5}}\right)$$

$$\Rightarrow \left(\frac{N_A}{N_A^0}\right) = \left(\frac{I_A}{I_A^0}\right)\left(\frac{a_A}{a_{AB}}\right)^{1.5}$$

Now, we also have $N_A^0 = a_A^{-3}$; $N_A = a_{AB}^{-3} \chi_A$

So $\frac{N^A}{N_0^A} = \chi_A \left(\frac{a_A}{a_{AB}}\right)^3 \Rightarrow \chi_A = \left(\frac{N^A}{N_0^A}\right)\left(\frac{a_{AB}}{a_A}\right)^3$

or, in terms of intensities:

$$\chi_A = \left(\frac{I_A}{I_A^0}\right)\left(\frac{a_A}{a_{AB}}\right)^{1.5}\left(\frac{a_{AB}}{a_A}\right)^3 = \left(\frac{I_A}{I_A^0}\right)\left(\frac{a_{AB}}{a_A}\right)^{1.5}$$

similarly:

$$\chi_B = \left(\frac{I_B}{I_{B}^0}\right)\left(\frac{a_{AB}}{a_B}\right)^{1.5}$$

$$\Rightarrow \frac{\chi_A}{\chi_B} = \left[\frac{I_A/I_A^0}{I_B/I_B^0}\right]\left[\frac{a_{AB}/a_A}{a_{AB}/a_B}\right]^{1.5}$$

$$\boxed{\frac{\chi_A}{\chi_B} = \left[\frac{a_B}{a_A}\right]^{1.5}\left[\frac{I_A/I_A^0}{I_B/I_B^0}\right]}$$

where $I_{A,B}$ is intensity of element $\binom{A}{B}$ in mixed sample

and $I^0_{\substack{A\\B}}$ — " ——— — " — standard.

→ (b) CASE II

Consider steps between eqn ① + ② above. If we make all the same assumptions but do not perform z-integration, Then

$$I = I_0 \int_{z_0}^{\infty} e^{-\frac{z}{\lambda_m(E_A)\cos\theta}} \, dz$$

Now, from exposed portion of surface

$$I = C' \int_0^{\infty} e^{-\frac{z}{\lambda\cos\theta}} \, dz = -C' \lambda_B(E_B)\cos\theta \int_0^{\infty} e^{-u} du$$

now $\int_0^{\infty} e^{-u} du = e^{-u}\Big|_0^{\infty} = (-1) \Rightarrow I = C' \lambda_B(E_B)\cos\theta \equiv I_B^0$

Since a fraction of the surface Θ_A is covered,

$$I_{B\,\text{exposed}} = (1-\Theta_A) I_B^0$$

For fraction of B below A, we have: $I_B = C \int_{a_A}^{\infty} e^{-\frac{z}{\lambda\cos\theta}} \, dz$

So $I_{B\,\text{covered}} = C(-\lambda_A(E_B)\cos\theta) \int_{a_A/\lambda\cos\theta}^{\infty} e^{-u} du = C(-\lambda\cos\theta)\, e^{-\frac{a}{\lambda\cos\theta}}(-1)$

$$= I_B^0 \, e^{-\frac{a_A}{\lambda\cos\theta}}$$ from fraction Θ of surface

$$\Rightarrow I_B = (1-\Theta) I_B^0 + \Theta_1 I_B^0 \, e^{-\frac{a_A}{\lambda\cos\theta}})$$

$$\boxed{I_B = I_B^0 \left(1 - \Theta\left(1 - e^{-\frac{a_A}{\lambda\cos\theta}}\right)\right)}$$

Signal from I_A:

$$I = C \int_0^{a_A} e^{-\frac{z}{\lambda\cos\theta}} dz = C(-\lambda\cos\theta)\left[e^{-\frac{a_A}{\lambda\cos\theta}} - 1\right]$$

$$= I_A^\circ \left[1 - e^{-a_A/\lambda\cos\theta}\right] \quad \text{for fraction } \Theta_A$$

$$\Rightarrow \frac{I_A}{I_B} = \left(\frac{I_A^\circ}{I_B^\circ}\right) \frac{\Theta_A\left\{1 - e^{-a_A/\lambda\cos\theta}\right\}}{\left\{1 - \Theta_A\left[1 - e^{-a_A/\lambda\cos\theta}\right]\right\}}$$

(c) CASE III Similar to case II:

$$I_B = C \int_{d_A}^{\infty} e^{-z/\lambda\cos\theta} dz = C(-\lambda\cos\theta)\left[0 - e^{-\frac{d_A}{\lambda\cos\theta}}\right](-1)$$

$$= I_B^\circ \, e^{-d_A/\lambda\cos\theta}$$

$$I_A = C \int_0^{d_A} e^{-z/\lambda\cos\theta} dz = C(-\lambda\cos\theta)\left[e^{-d_A/\lambda\cos\theta} - 1\right](-1)$$

$$\Rightarrow \frac{I_A}{I_B} = \left[\frac{I_A^\circ}{I_B^\circ}\right]\left\{\frac{1 - e^{-d_A/\lambda\cos\theta}}{e^{-d_A/\lambda\cos\theta}}\right\}$$

5)

$$I(z_0) = c\int_0^{z_0} e^{-z/\lambda\cos\theta}\,dz = I^\circ\left[1-e^{-z_0/\lambda\cos\theta}\right]$$

For $\theta=0$; $\cos\theta=1 \Rightarrow I = I^\circ\left[1-e^{-z_0/\lambda}\right]$

$I(z_0 \to \infty) = I_0$

So $\frac{I(z_0=\lambda)}{I^\circ} = \left[1-e^{-1}\right] = \left[1-0.368\right] = 0.632$

$\frac{I(z_0=2\lambda)}{I_0} = \left[1-e^{-2}\right] = 0.865$; $\frac{I(z_0=3\lambda)}{I_0} = 0.95$

Now, let $\theta = 80^\circ \Rightarrow \cos\theta = 0.17$

$\Rightarrow I(z_0) = I_0\left[1-e^{-\frac{z_0}{0.17\lambda}}\right] = I_0\left[1-e^{-\frac{5.76 z_0}{\lambda}}\right]$

$\Rightarrow \frac{I(\lambda)}{I_0} = \left[1-e^{-5.76}\right] = 0.997$; $\frac{I(2\lambda)}{I_0} = .999 \to 1.0$

At synchrotron can choose $h\nu$ to place KE of desired core level at minimum of mfp. For example, choose $h\nu \sim 130\,eV$ to place Si 2p peak @ $\sim 30\,eV$.

5) If we take the simplest model of isolated charges + assume charge transferred goes into a thin sphere of radius $r = 1Å$ around Si core, then for charge xfer of $4e^-$:

$$\Delta V = \frac{1}{4\pi\epsilon_0}\frac{q}{r} = \frac{(9\times10^9)4(1.6\times10^{-19}C)}{(10^{-10}m)} =$$

$$= (9)(4)(1.6) = 57.6 \text{ Volts} \Rightarrow \Delta E = 57.6\,eV.$$

<u>But</u> this is in Si, which has a dielectric const. of ~ 12

$$\Rightarrow \quad \Delta V = \frac{\Delta V_0}{12} = 4.8\,eV,$$

quite close to 4.0 eV measured.

In reality, charge xfer is not exactly $4e^-$ (not purely ionic). Also, charge is distributed over Si atom, not just in thin shell.

The first of these effects brings ΔV lower, closer to 4 eV.
The second effect $\Rightarrow$ ΔV larger near core as compared to far from core. As a result, the 1s level, which is closer to core, would have a larger ΔE compared to 2p level, which is more delocalized.

10/12

Use peak heights

$h_{In\,3d_{5/2}} = 4.8\,mm$ $\sigma_{In\,3d} \cong 0.6$ $\#e^- = 6$

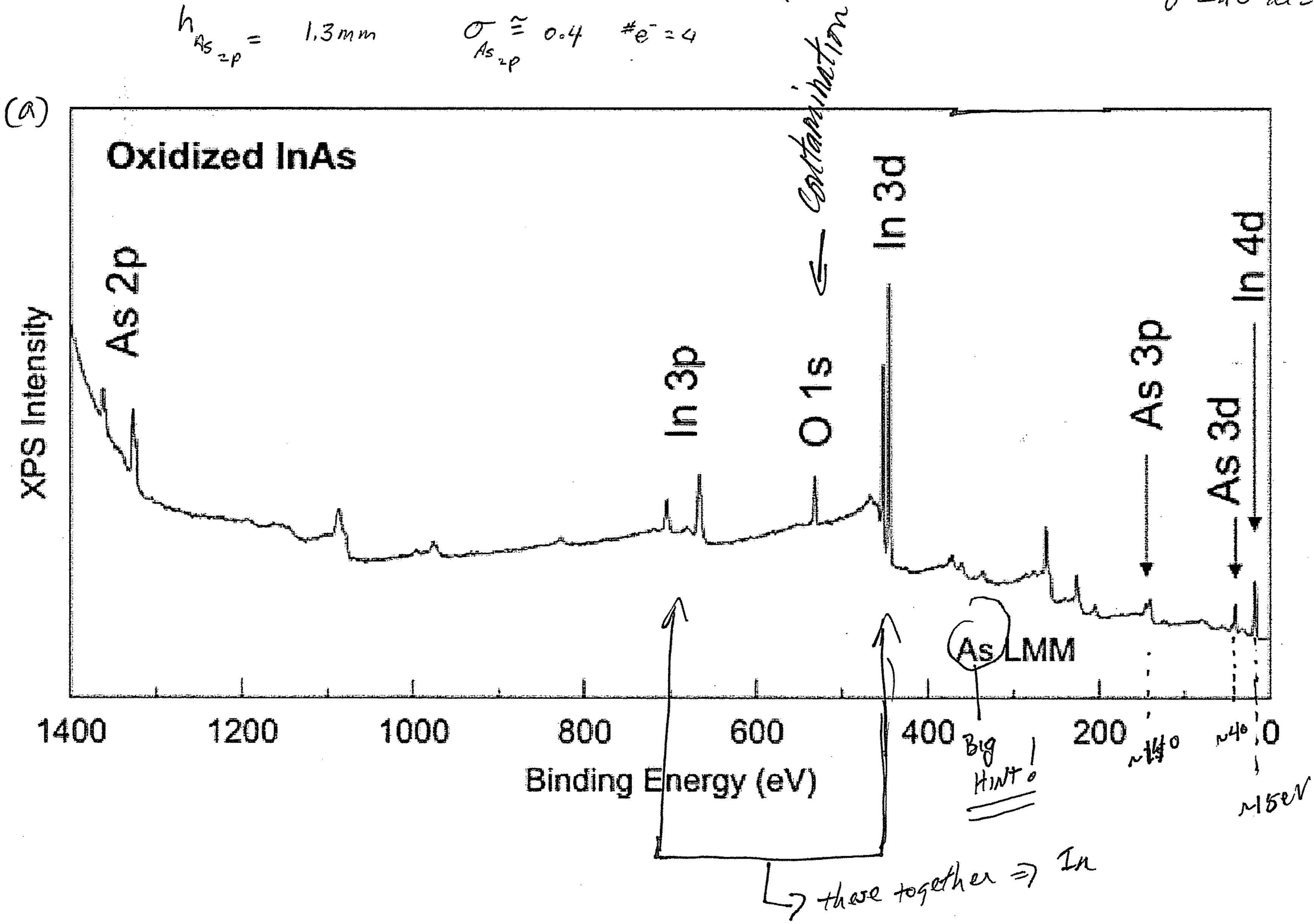
$h_{As\,2p} = 1.3\,mm$ $\sigma_{As\,2p} \cong 0.4$ $\#e^- = 4$

So $C_{In} \cong \dfrac{4.8}{(0.6)(6)} = 1.3$

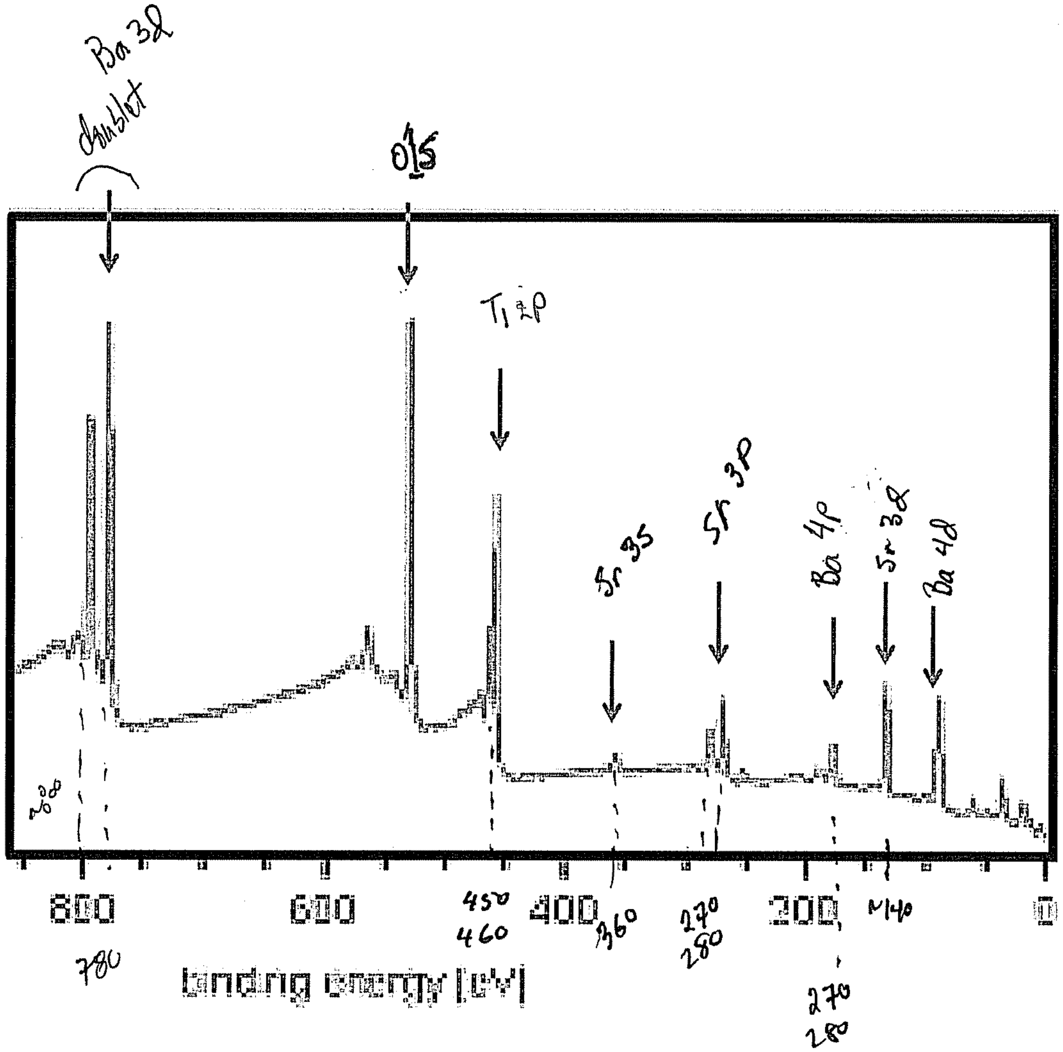
$C_{As} \cong \dfrac{1.3}{1.6} = 0.9$

Should be equal for InAs. However, oxidized surface has excess of InO at surface.

(a)

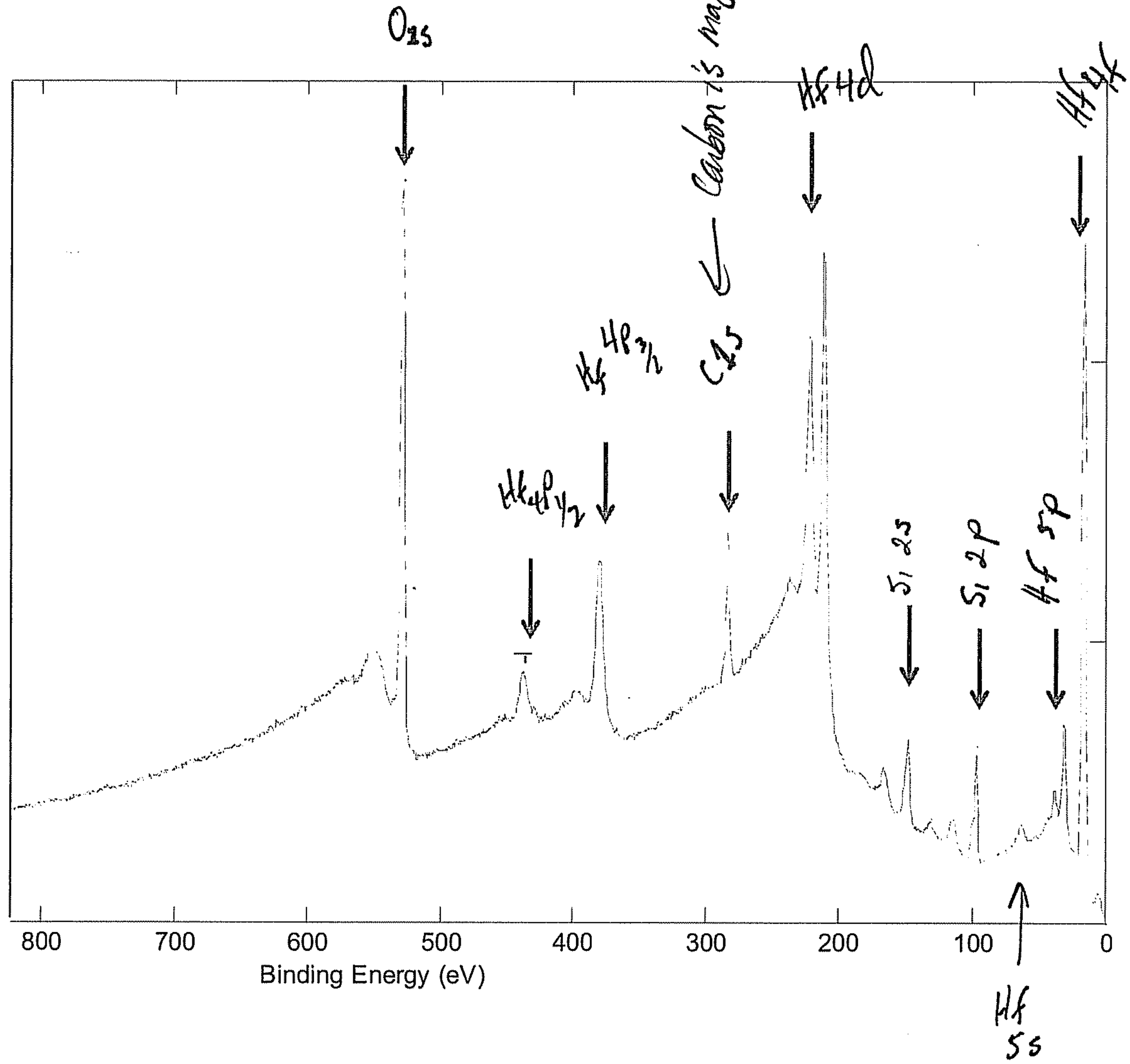


(b)


Ba 3d
doublet
O1s
Ti 2p
Sr 3S
Sr 3P
Ba 4P
Sr 3d
Ba 4d
800
600
400
200
0
780
450
460
360
270
280
140
binding energy [eV]

Ba Sr Ti O_x

(c)


O 1s
Carbon is major contaminant.
Hf 4d
Hf 4f
Hf 4p 1/2
Hf 4p 3/2
C 1s
Si 2s
Si 2p
Hf 5p
Hf 5s
800
700
600
500
400
300
200
100
0
Binding Energy (eV)