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Optical studies of defect centers formed in MCz-Si and FZ-Si by high fluence neutron irradiation

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Topics

Neutron-irradiated samples:

Part 1

- Photoluminescence - native defects, (I_3 and I_4 interstitial complexes) ; thermal dissociation of defects; correlation between I_3 and I_4 ?

Part 2

- Infrared absorption - divacancies; introduction rate

Why photoluminescence?

- **The defects formed during the heat treatment in high purity n-irradiated Si are mainly related to defects formed by the agglomerates of vacancies or silicon interstitials. The excitons are bound to these defects by the local field . Most of them recombine with the emission of the light and new emission lines are observed in the photoluminescence spectrum.**
- **Low temperautre PL is a usefull tool for monitoring these defects**

The main defects in *n*-irradiated high purity Si monitored by LTPL technique

- tri-interstitials silicon – line W (I_3) (1.018eV), EPR signal B5 from I_3^+; donor-like (0/+) Ev+0.1eV; DLTS Ec-0.075 may be related to W center ; Cz-Si and FZ-Si
- tetra-interstitials silicon – line 1.039eV (I_4) , EPR defect B3 (I^+_4), electric level Ev+0.29eV (DLTS) ; Cz-Si and FZ-Si
- hexavacansy V_6 – line 1.108 eV ; Ec-0.04eV acceptor level ; in FZ-Si
- line 1.097 eV - in Cz-Si ; related to oxygen atoms;

Parameters of the samples

- *n- irradiated FZ-Si and MCz-Si (MCz <100>, 1kΩcm, 300 µm and 2-3mm thick ([Oi] = 5×10^{17} cm^{-3}, [Cs] < 5×10^{15} cm^{-3}, FZ 288µm and 3mm thick , 2kΩcm)*
- *Samples were irradiated to fluences of 10^{15} to 10^{16} cm^{-2}, 1 MeV equivalent neutrons at the TRIGA reactor in Ljubljana.*
- *all samples were chemically etched and refreshed before each PL measurement*

Heat treatment parameters

Isochronal annealings:

- ***– 1hour /nitrogen/ 80ºC - 477ºC***
- ***– 0.5h/nitrogen/80ºC(350K) - 380ºC(650K)***

Experimental

Photoluminescence

- Excitation – 514 nm Ar laser line focused to 0.4micrometer. Excitation power 0.5W/mm^2
- Double-grating monochromator – dispersion 1.7nm. Spectral resolution 0.5meV at 1000nm
- Photomultiplier type R5509-72 (Hamamatsu) with InGaAsP cathode.
- Spectral range 1070nm - 1700nm
- Signal collection – lock-in technique
- Closed-cycle cooling system (15K)

Absorption

- Fourier spectrophotometer IFS 113v ; resolution 2cm^{-1} spectral range 4000 cm^{-1} – 400 cm^{-1} (2.5 µm – 25 µm)
- Spectrophotometer Carry 500 resolution 1 nm; spectral range 1µm – 3 µm (monochromatic light)
- Closed-cycle cooling system (8K)

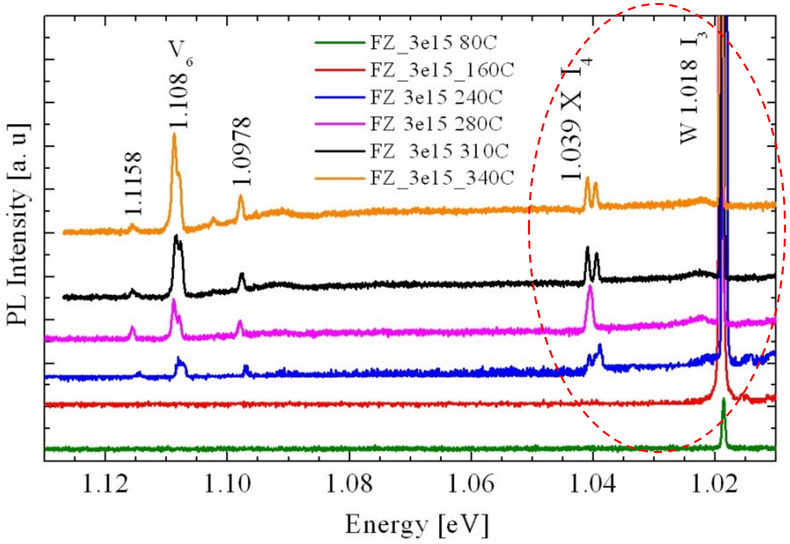
Photoluminescence

Two aspects:

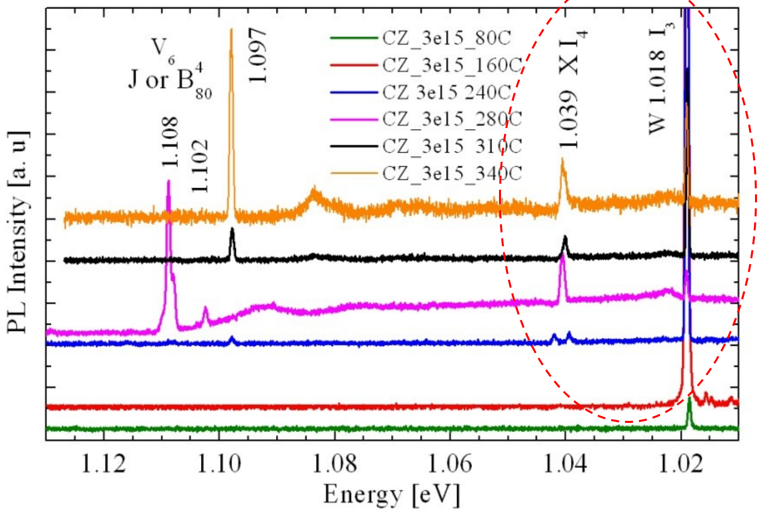
- **study of W (I_3) line behaviors**
- **is I_3 complex a precursor for the formation of I_4 complex ?** (***Decreasing of the intensity of the line W(I_3) (tri-interstitials) is followed by the appearance of new emission at 1.039eV (line I_4) related to the formation of tetra-interstitials***)

PL emission at 18K for n-irradiated FZ-Si and MCz-Si (fluence $3x10^{15}$ n/cm^2) vs. annealing temperature for isochronal annealing

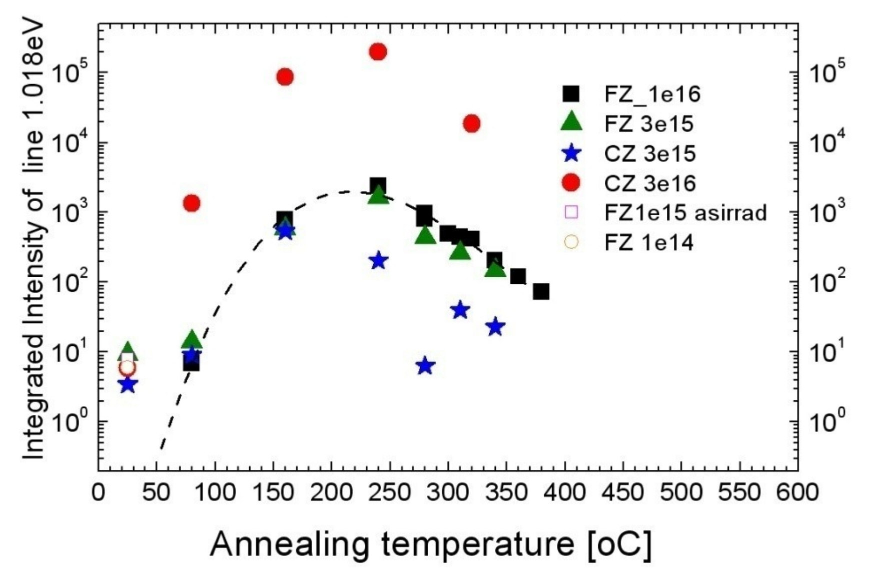
1.039eV tetrainterstitial B3 paramagnetic center

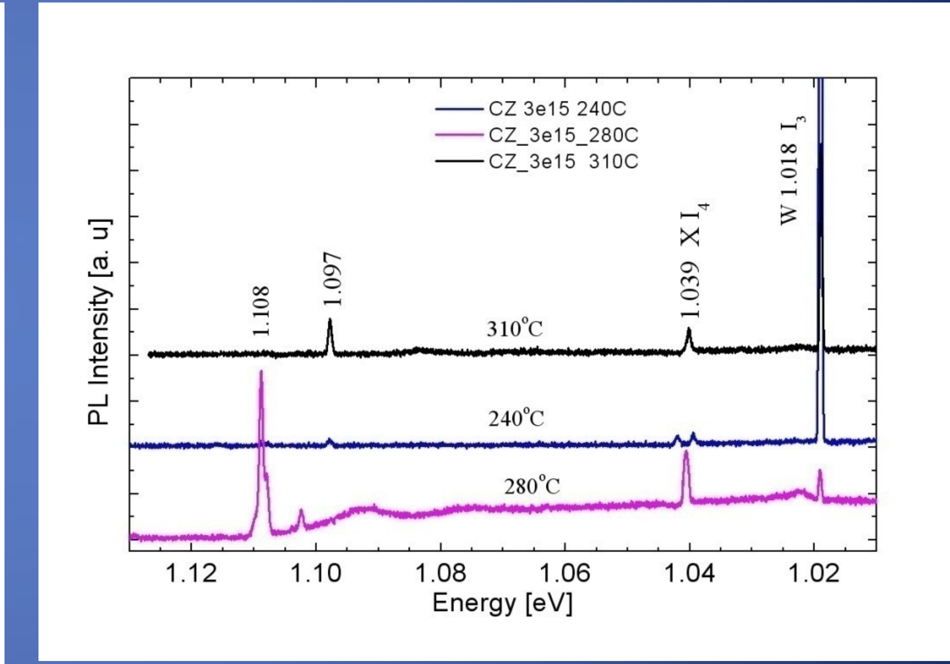


1..097 monoclinic I center - contains O; W source of 1.097line
1.108 trigonal symetry observed in oxygen-lean Si

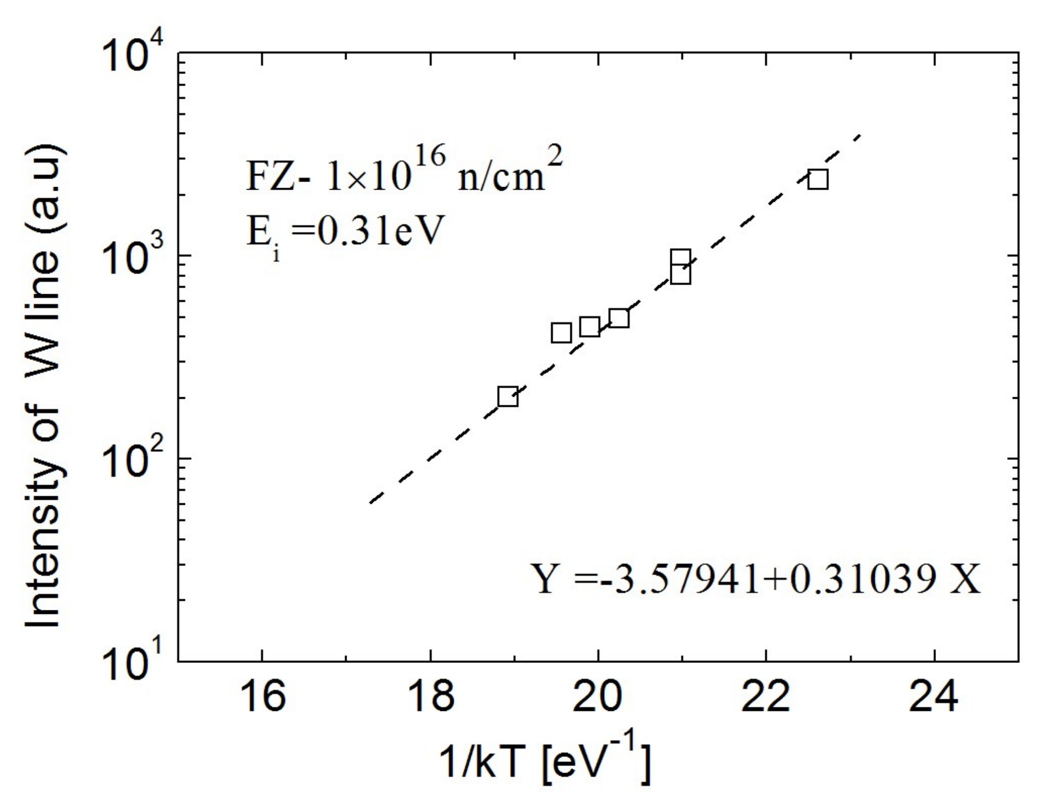


Integrated intensity of W line vs. annealing temperature

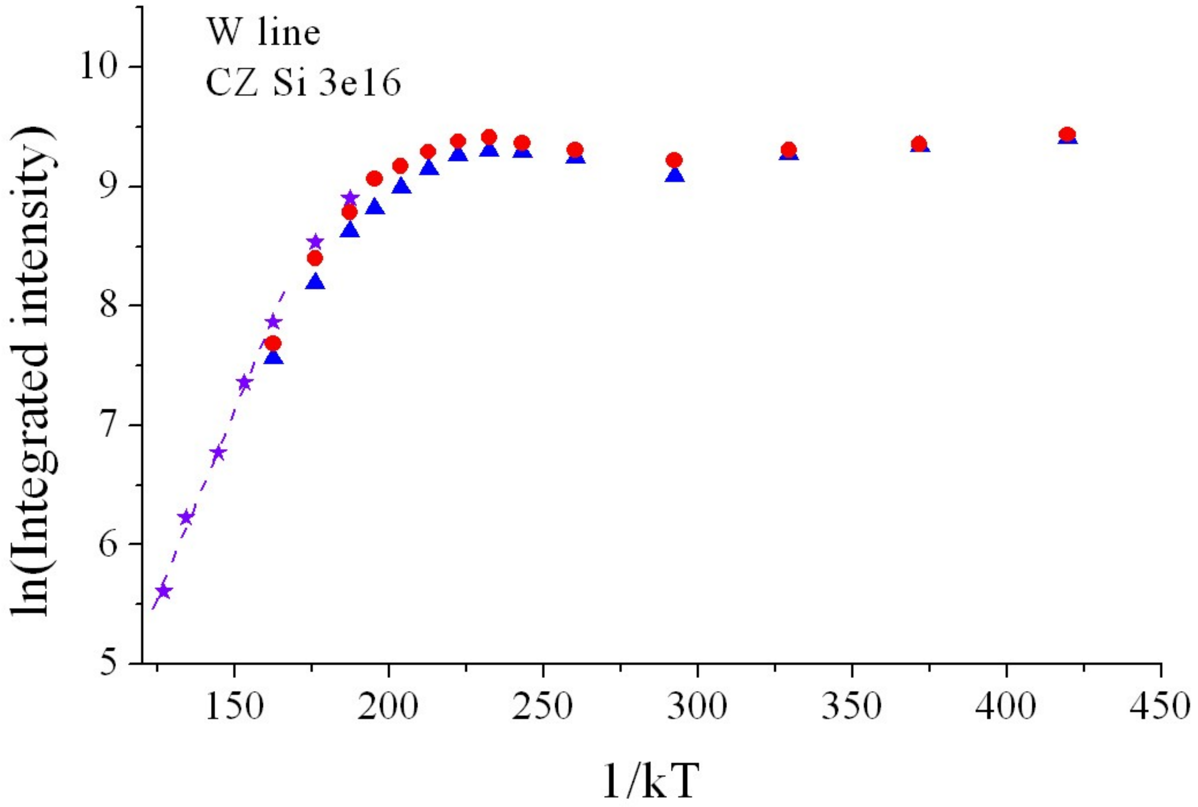




The energy of quenching process for W line from Arrhenius plot was found to be 0.31 eV



Integrated Intensity for W line (1.018eV) vs the temperature of the sample



Fitting procedure

The best fitting was obtained for the following assumptions:

- **Excitons bound with tri-interstitial center (W line) dissociate with thermal energy E**
- **Excitons bound with concurrence centers dissociate thermally with average energy E_t ($E_t < E$)**
- **Excitation of the exciton bound to tri-interstitial center to excited state with energy E_{exc}**

Theory

$$I(T) = I(O) / \left((1 + F_2) \times \left(1 + F_3 + C_1 \times T^{\frac{3}{2}} \exp(-E/kT) \right) \right)$$

$$F_2 = C_3 / \left(1 + C_1 \times T^{\frac{3}{2}} \exp(-E_t/kT) \right)$$

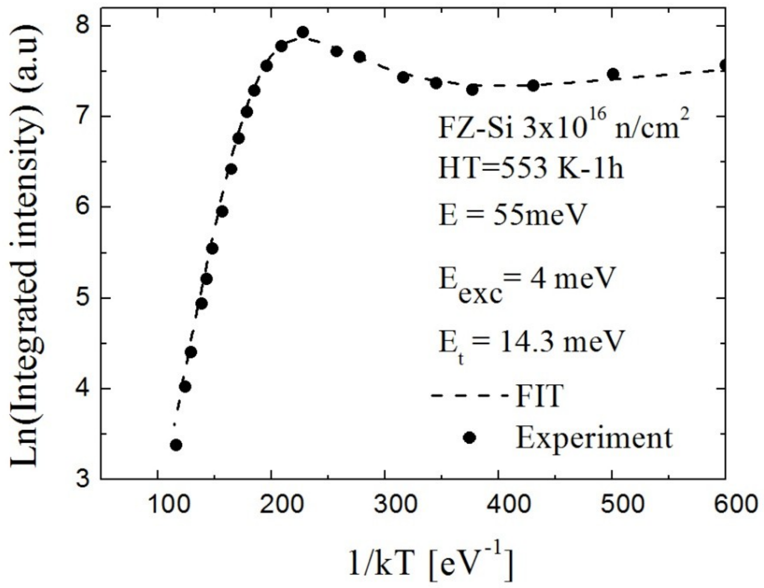
$$F_3 = C_4 \times \exp(-E_{exc}/kT)$$

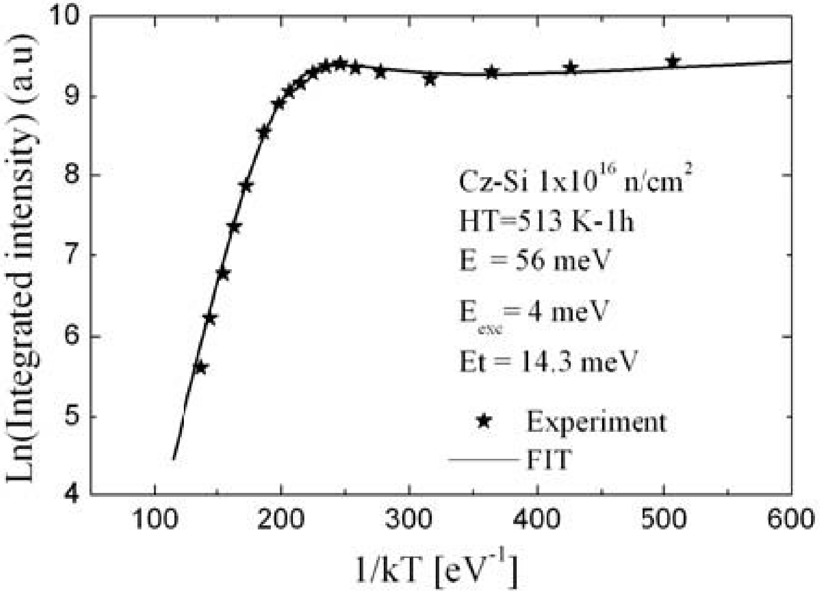
F_2/C_3 – the fraction of concurrence centers that are not ionise so can capture the free excitons

$C_1{*}T^{3/2}$ – the effective density of band continuum states into which the ionisation occurs

C3 - the ratio of trapping cross section for excitons at trap E_t and sum of others traps.

Fitting procedure for W line (1.018eV)





State of art of the knowledge about W line

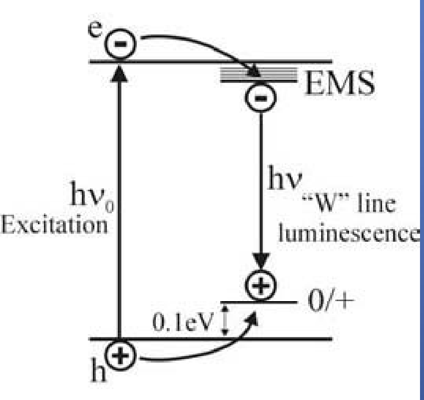
- **W line - defect of trigonal symmetry (C_{3v})**
- **EPR – W line coincides with B5 defect in EPR being a tri-interstitials I_3**
- **Local density functional (LDF) theory calculation showed the defect to have a possible (0/+) donor level close to the VB Ev+0.1eV. (tightly bound hole and loosely bound electron)**

D. Pierreux and A. Stesman Phys. Rev. B 71, (2005), 115204.

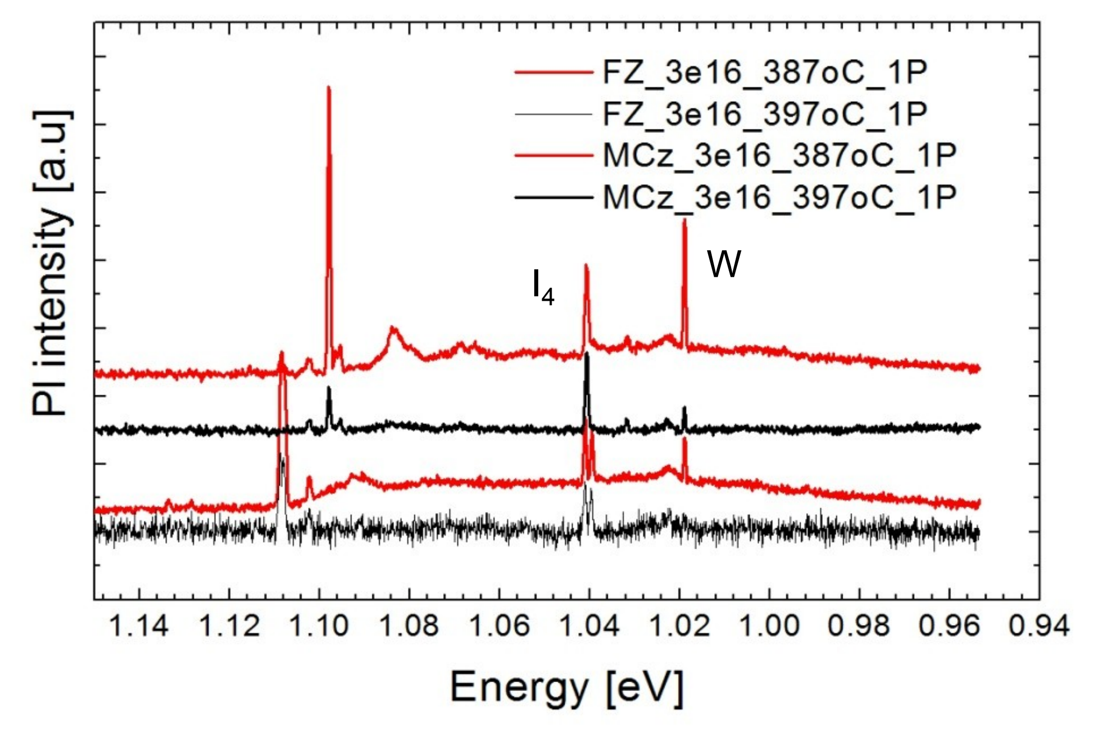
*B. J, **Coomer** J. P. Goss, R. Jones, S. Osberg, and P. R. Briddon J. Phys.: Condens. Matter V13, (2001), L1-L7,*

Our results

- **Taking band gap energy at 15K E_g=1.1695eV**
- **Energy distance of W line from E_g : E_g -hν_w=0.1513eV**
- **E_t=57meV for lightly bound species**
- **153.1meV-57meV =96.1meV for tightly bound species**
- ***Close to calculated 0.1 eV.***



Are tri-interstisials (W) the precoursors for the formation of tetra-interstitials (I_4)?



Theory

- **The rate of the exciton capture by center *i* is equal:**
    - $P_i = \sigma_i N_i n_{ex} v_{ex}$
- **where :**

σ_i – *the capture radii of i-th centre*

v_{ex} – ***thermal velocity of excitons***

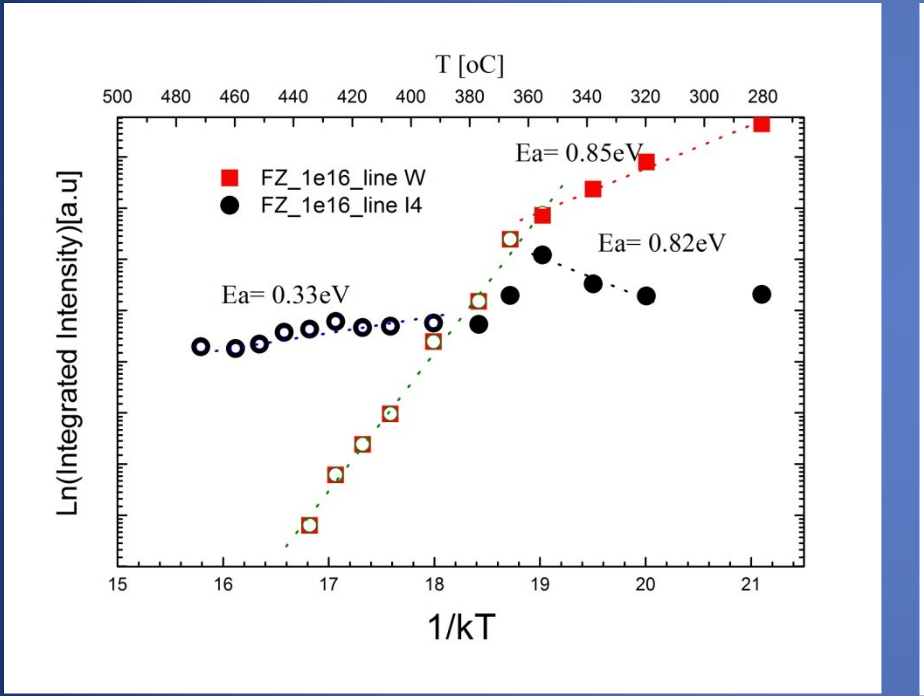
N_i – ***concentration of i-th centre***

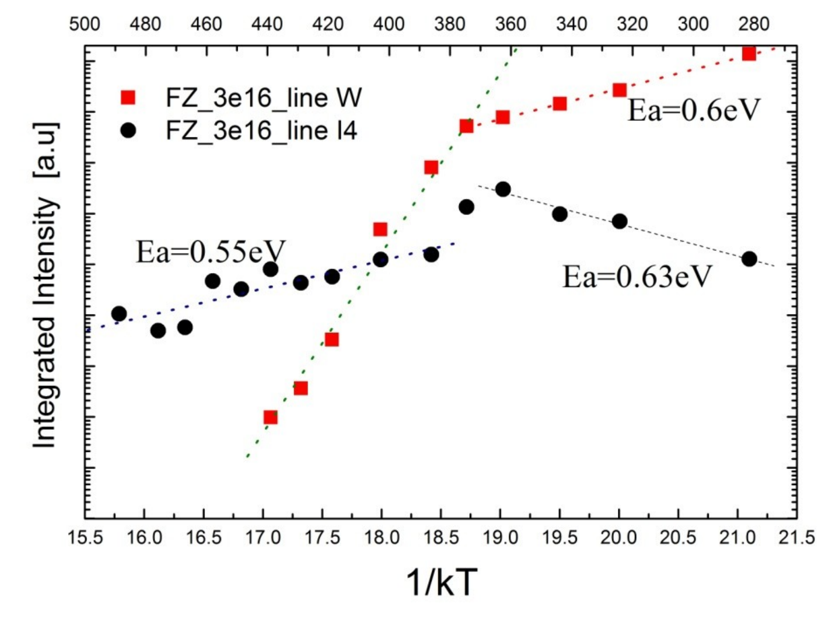
n_{ex} – ***concentration of excitons***

Theory

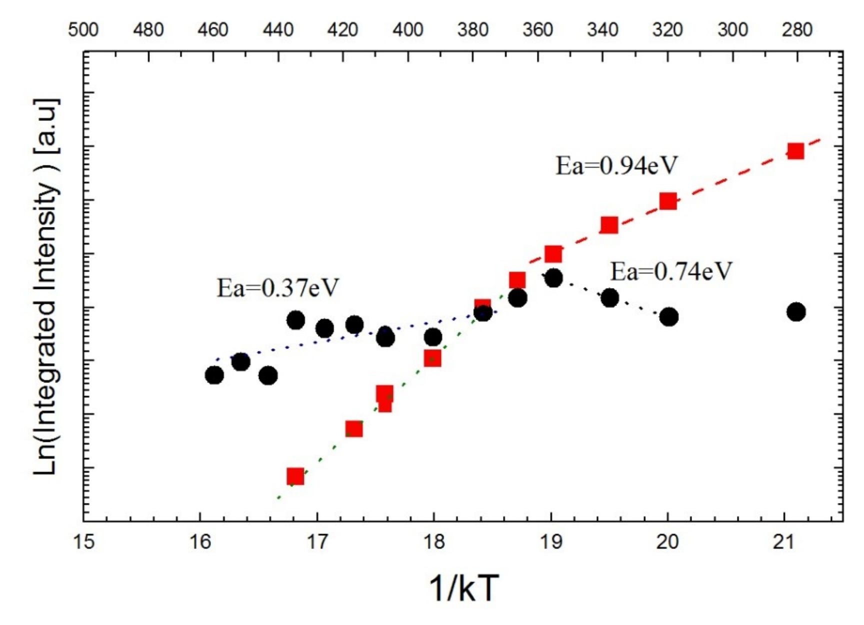
$$P_i / P_{total} = \sigma_i N_i n_{ex} v_{ex} / \sum_k \sigma_k N_k n_{ex} v_{ex}$$

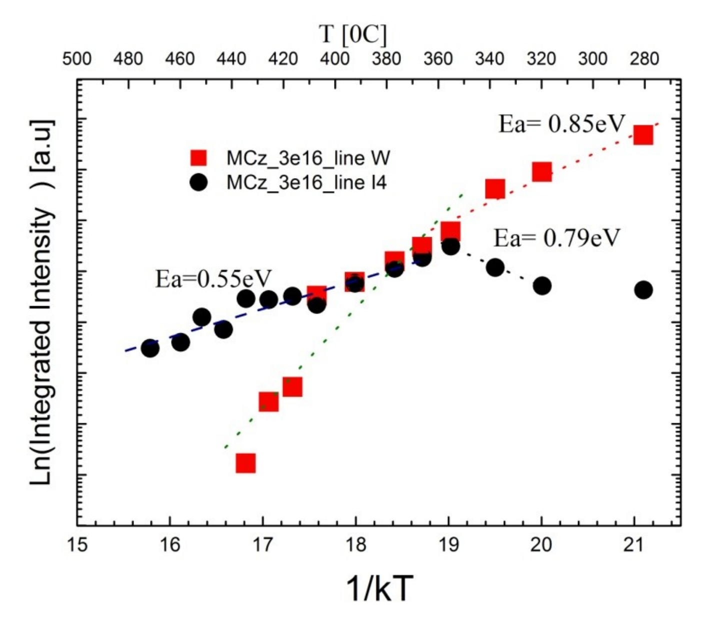
Arrhenius plot for FZ-Si samples





Arrhenius plot for MCz-Si samples





Activation energy for diffusion for interstitials

- **D_I=0.335*exp(- 1.86 eV/kT)**

  D. Maroudas and R. A./ Brown Appl Phys. Lett V62, (1993), 172s
- **D_I=0.19*exp(- 1.58 eV/kT)**

  J. Tershof, Phys. Rev. Lett. V56, (1986), 632-635
- **D_I=0.72*exp(- 1.35 eV/kT)**

  F. H. Stillinger and T. A. Weber, Phys. Rev. B, 31, (1985), 5262-5271
- **D_I=0.242exp(-0.937/kT)**

  T. Sinno, R. A. Brown, W. Von Ammon, E. Dornberg , Appl.Phys.Lett. V70(17) (1997).2250-2252

Activation energy for diffusion for vacancies

- **D_V=0.001exp(-0.457/kT)**

  T. Sinno, R. A. Brown, W. Von Ammon, E. Dornberg , Appl.Phys.Lett. V70(17) (1997).2250-2252
- **Dv=1000exp(-2.838/kT)**

  J. Vanhellemont Appl. Phys. Lett. 69. (1996), 4008-4010

Part II

Absorption measurements

Divacancies

- Neutron irradiation creates cluster damage and „point defect’ damage and to a first approximation they behave independently of each other.

- Assume that we can separate the damage into cluster damage and ‘point defect’ damage.

- The point defects evolve and form the agglomerates of native defects or interact with impurities.

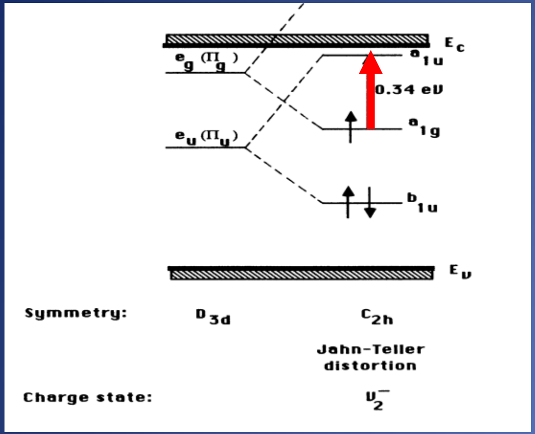
- Among the as-irradiated defects V_2 is one of the most important. V_2 can be formed inside and outside the clusters.

Divacancies

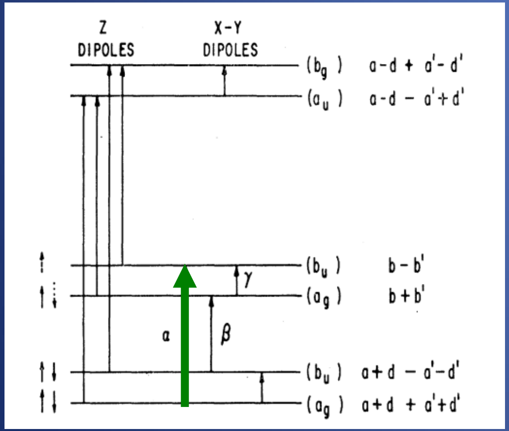
$V_2^+ + e^-$ ✡ V_2^0 $E_v+0.31$ eV

$V_2^0 + e^-$ ✡ V_2^- $E_c-0.41$ eV

$V_2^- + e^-$ ✡ V_2^{2-} $E_c-0.23$ eV



J. H Svensson et all PRB V36, 4192p, (1988-II)



I.J. Cheng et all PR V152, 761p, (1966)

Infrared optical absorption:

-peak at 0.31 eV (3.9μm) - transition from VB to V_2^+ state

-peak at 0.34eV (3.6μm)- intracenter transition in V_2^- charge state

- peak at 0.69 eV (1.8μm) – intracenter transition in V_2^0 charge state

Measurement conditions

- In high purity n type silicon at room temperature V_2 are in neutral state V_2^0. One can observe intra-center transition at 1.8μm
- At low temperature under strong illumination V_2^0 are easily transformed to negatively charge state V_2^- (*the case of Fourier IFS 113v spectrophotometer conditions*) and we observe intra-center transition in V_2^- charge state
- Cooling in darkness and illumination with monochromatic light does not change the charge state of V_2 and one can observed the intra-center transition at 1.8μm for V_2^0 (*the case of Carry 500 spectrofotometer conditions)*

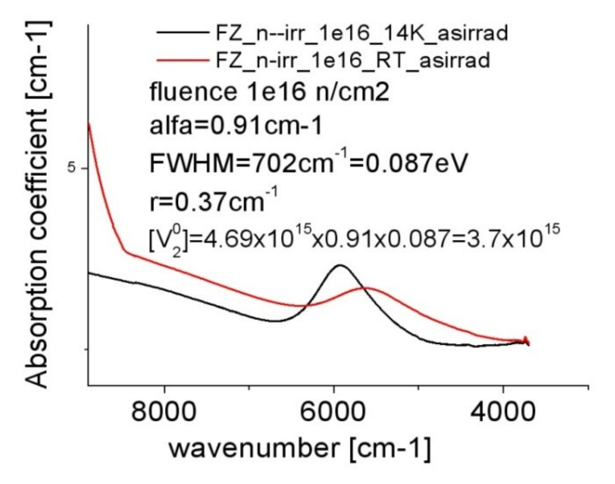
The main Questions !

Do V_2^0 change the charge state under illumination into V_2^- state inside and outside the clusters?

Do the deformation field inside the clusters influences the position of the Fermi level under illumination ?

Absorption measurements

V_2^0



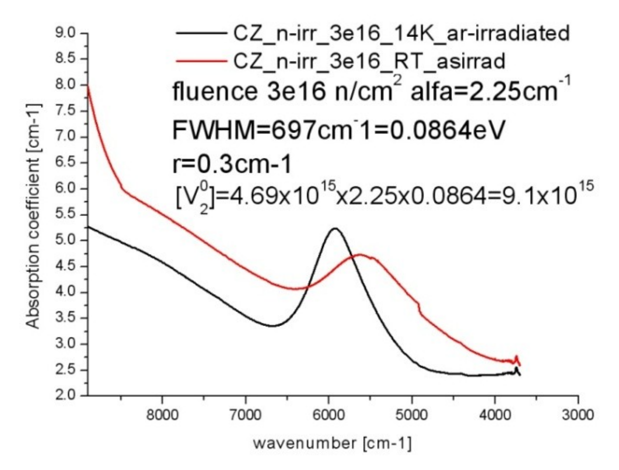
fluence 1e16 n/cm2

alfa=0.91cm-1

FWHM=702cm^{-1}=0.087eV

r=0.37cm^{-1}

$[V_2^0]=4.69\times10^{15}\times0.91\times0.087=3.7\times10^{15}$



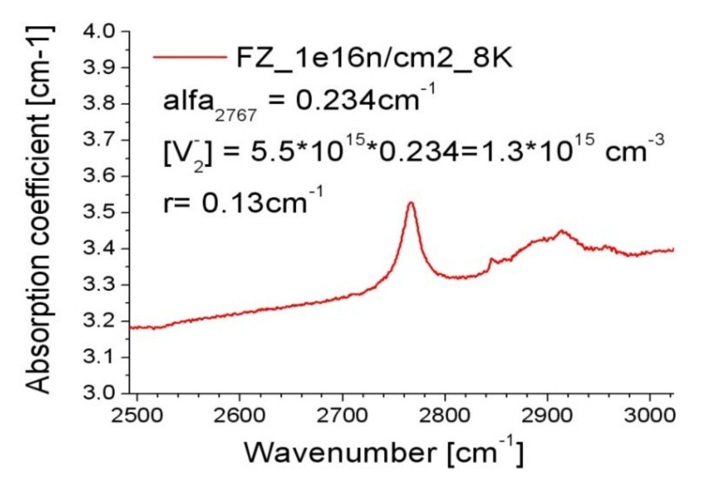
fluence 3e16 n/cm^2 alfa=2.25cm^{-1}

FWHM=697cm^{-1}=0.0864eV

r=0.3cm-1

$[V_2^0]=4.69\times10^{15}\times2.25\times0.0864=9.1\times10^{15}$

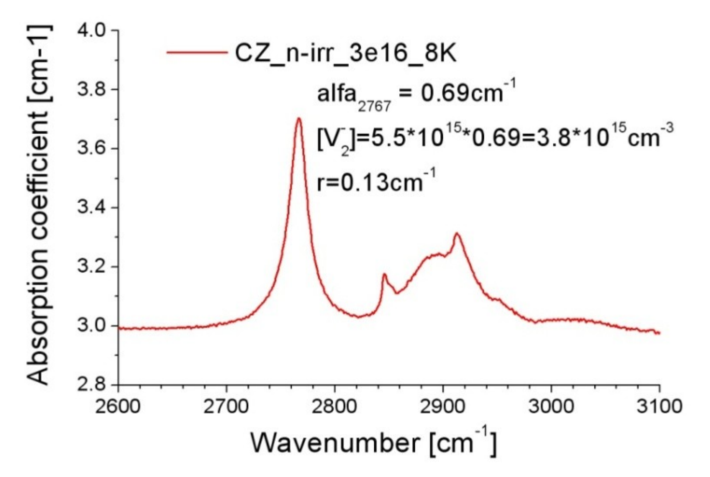
V_2^-



alfa$_{2767}$ = 0.234cm^{-1}

$[V_2^-] = 5.5*10^{15}*0.234=1.3*10^{15}$ cm^{-3}

r= 0.13cm^{-1}



alfa$_{2767}$ = 0.69cm^{-1}

$[V_2^-]=5.5*10^{15}*0.69=3.8*10^{15}$cm^{-3}

r=0.13cm^{-1}

Calculations

The concentration of V_2^0 (1.8µm)

$$[N_{V2}] = 4.69 * 10^{15} * \alpha\,\Gamma_{FWHM}\ [\mathrm{cm}^{-3}]$$

According to the rule

$$N \times f = 8{,}21 \times 10^{16} \frac{n}{\left(n^2 + 2\right)^2} \int \alpha\left(E_{h\nu}\right) dE_{h\nu}$$

Where :

N – concentration of defects [cm^{-3})

f - oscillatore strength

n –refraction index

α– absorption coefficient (cm^{-1})

$E_{h\nu}$ – photon energy (eV)

Concentration of V_2^-

The concentration of V_2^- (3.6µm)

$$[N_{V2}] = 5.5 * 10^{15} * \alpha \ [cm^{-3}]$$

G. Davies et all., PRB, V73, 165202,(2006)

Experimental results

Sample	Fluence cm^{-2}	$[V_2^0]$ [cm^{-3}]	Introduction rate [cm^{-1}]	$[V_2^-]$ [cm^{-3}]	Introduction rate [cm^{-1}]
FZ	$1*10^{16}$	$3.7*10^{15}$	0.37	$1.3*10^{15}$	0.13
MCz	$1*10^{16}$	$3.39*10^{15}$	0.34	-	-
FZ	$3*10^{16}$	$9.7*10^{15}$	0.32	-	-
MCz	$3*10^{16}$	$9.1*10^{15}$	0.3	$3.8*10^{15}$	0.13

Conclusions

- **Low temperature photoluminescence measurements have been applied to studying self-interstitial aggregates in MCz and FZ silicon irradiated with neutron fluences from 3x10^{15} to 3x10^{16} cm^{-2} and subjected to isochronal annealing up 480°C**

- **It has bees stated that exciton is thermally bound to W center with energy of 57meV and from this the energy for tightly bound spices has been found to be around 96 meV. This value well coincides with theoretical prediction of (0/+) donor -like level at E_v+0.1eV.**

Conclusions

- The changes in the normalised photoluminescence intensity for tri- and tetra-interstitials with the annealing temperature were determined and the Arrhenius plots for the defects thermal stability were plotted
- The increase of the 1.039 eV emission intensity was observed in the temperature range from 280 to 350°C
- The activation energy for increasing the 1.039 eV (I_4) line intensity was found to be nearly the same as that for decreasing the 1.018 eV (W line) intensity and was equal 0.75 +/- 0.15 eV.
- The annihilation of the tetra-interstitials was observed at a temperature higher than 350°C

Conclusions

- **Infrared absorption measurements have been used for determination of divacancies concentrations in neutral (V_2^0) and singly negative (V_2^-) charge states in silicon irradiated with neutron fluences of $1*10^{16}$ and $3*10^{16}$ cm^{-2}**
- **The introduction rates of V_2^0 and V_2^- are found to be around 0.3 cm^{-1} and 0.13 cm^{-1}, respectively**
- **Both for MCz and FZ Si, the concentration of V_2^0 was found to be approximately tree times higher than that of V_2^-**
- **There are two reasons that can explain the observed difference in the concentration of V_2^0 and V_2^- :**
  - **the error in the values of the calibration factors,**
  - **the V_2^0 located in clusters are fully transformed into V_2^-.**
- **The possible influence of the clusters can be cleared up by additional experiments using the electron irradiated material.**

Text

Text