

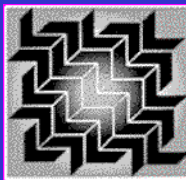
Luminescence of dislocations and oxide precipitates in Si: a search of the origin of the D1 luminescence

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Present status of the matter

Studies on the effect of oxygen on dislocation PL *Wijaranakula et al(1991)*

Studies on the correlation between DLTS and EBIC contrast features (effect of structure and Cu and Au impurities) *Kittler et al(1995)*, *Knobloch et al(2003)*

Studies on the correlation between dislocation PL/CL and DLTS features (effect of structure and oxygen contamination) *Pizzini et al(2002)*

Studies on carrier confinement in the strain fields of dislocations (quantum structures formation?) *Wal Lek Ng et al (2001)*, *H. Weman et al (1990)*

Studies on visible PL from oxygen precipitates *G.P. Karwasz et al(1996)*, *S.Binetti et al (2003)*

Studies on the effect of metallic impurities on the dislocation emission intensity *Kveder et al (2004)*

Studies on the origin of broad bands in oxygen precipitated silicon *S.Pizzini et al (2004)*

Open questions

- Are dislocations the *intrinsic* sources of luminescence?
- Which are the centres responsible for the D1 emission?
- What is the true influence of non-dopant impurities (oxygen, nitrogen)?
- What is the influence of metallic impurities?
- There is an influence of dislocation structure?

Present talk's aims

- **An attempt towards a better understanding of the effect of dislocation structure and oxygen/ metals contamination on the silicon luminescence**
- **An attempt towards the understanding of the origin of the D1 luminescence**

Strategy of the investigation

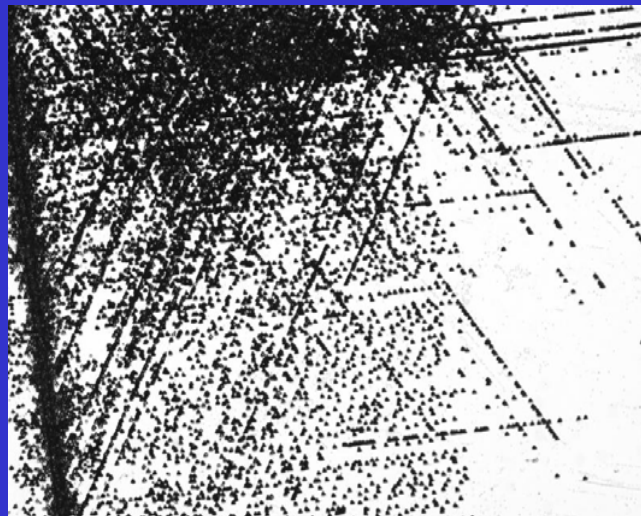
- Preparation of a set of FZ-Si dislocated samples of known structure and purity (intersecting and non intersecting arrays)
- Preparation of a set of Cz-Si dislocated samples of known structure and purity (intersecting and non intersecting arrays)
- Study of dislocated samples in N-doped Si
- Preparation of a set of Cz-Si precipitated samples of known size, with or without punched off dislocations.
- Study of FZ and Cz samples annealed or dislocated under high stress (up to 5GPa)

Samples characterization

- The structural properties of samples were studied with TEM, XR topo, optical microscopy of etched samples
- The optical properties of these samples were studied by photoluminescence spectroscopy. The PL spectra were recorded at 12 K using standard lock-in techniques in conjunction with a grating monochromator and an InGaAs detector (detection range 0.75-1.4 eV)
- Possible contamination effects were studied by DLTS

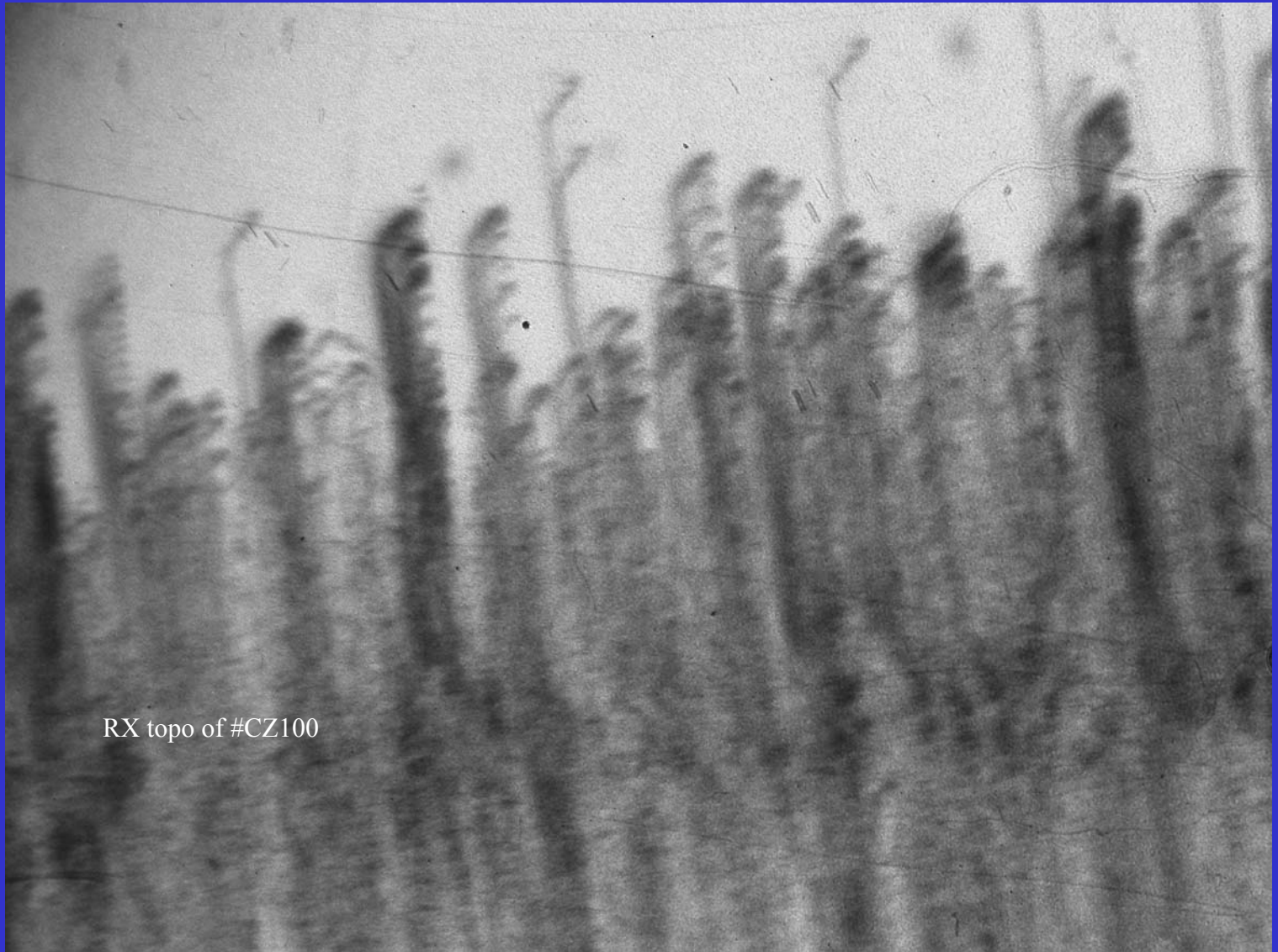
Si (111) samples preparation

This set of dislocated samples was prepared using (111) oriented Cz (p-type, $\rho = 7-17$ Ohm cm) and FZ (n-type, $\rho = 800-1600$ Ohm cm) silicon slabs. Samples have been deformed by scratching the surface along the $[-1-12]$ direction and bending around the $[-110]$ direction at 650°C for 1hr in a very clean environment. The resulting system consists of intersecting half hexagonal loops, with emerging threading arms, which give the regular distribution of etch pits shown below



Si(100) samples preparation: first step

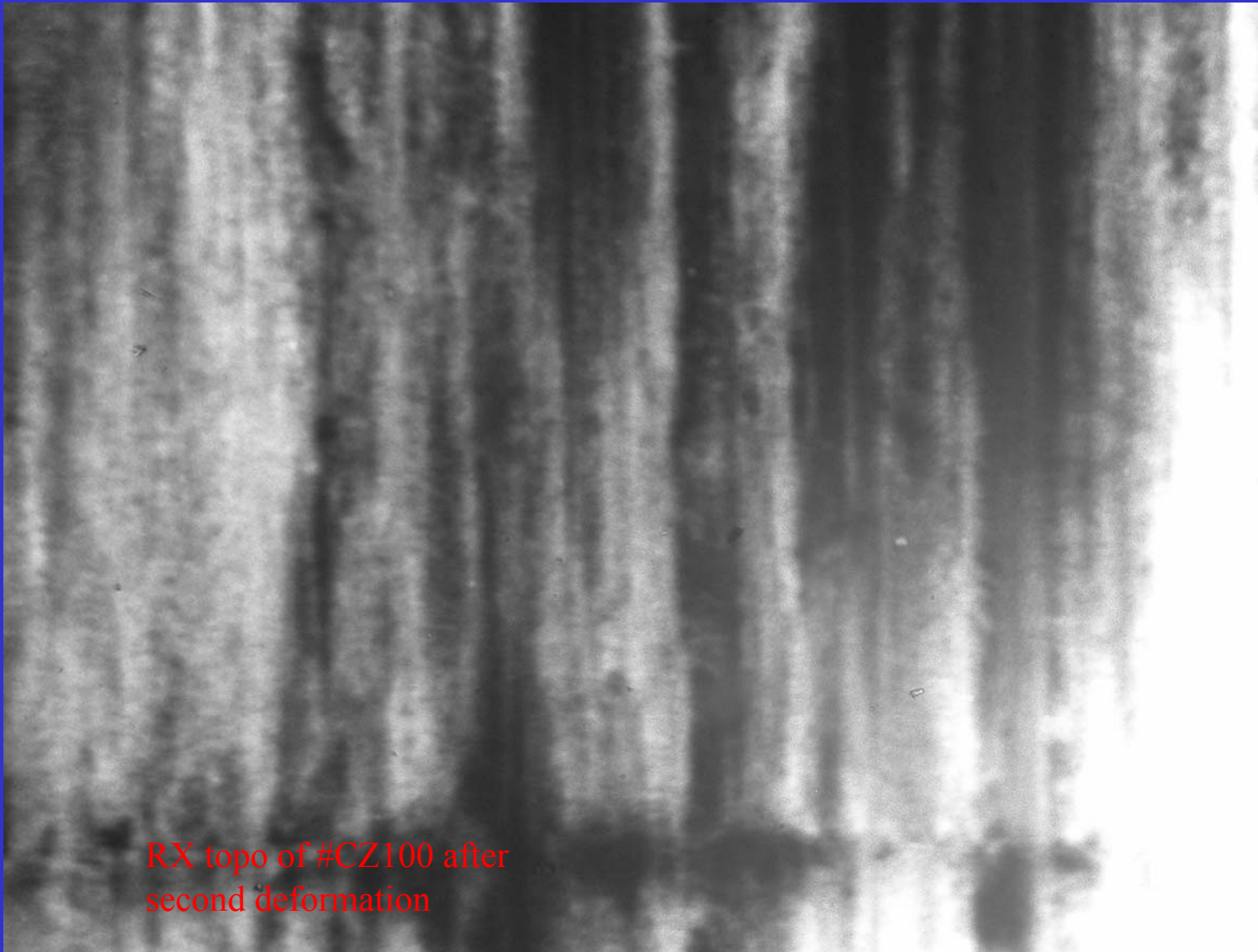
A second set (of dislocated samples) was prepared using (100) oriented (p-type $\rho = 17\text{-}23 \text{ Ohm cm}$) FZ and Cz silicon slabs, by scratching the surface along the $[011]$ direction and bending around the direction $[0\bar{1}1]$ for 1h at $670 \text{ }^\circ\text{C}$ in Argon. The resulting dislocation system consists of four glide systems characterised by a non zero resolved shear stress corresponding to two glide planes containing each one two Burger vectors. Each emerging half hexagonal loops consists of a screw and two 60° segments, with threading arms emerging at the sample surface



RX topo of #CZ100

Threading arms suppression

In order to allow dislocation loops expansion with the consequent suppression of threading arms, the samples were submitted to a second deformation procedure identical to the previously described one, after having chemically removed the scratch in order to minimize the dislocation nucleation. The resulting system consists of a regular array of parallel 60° segments

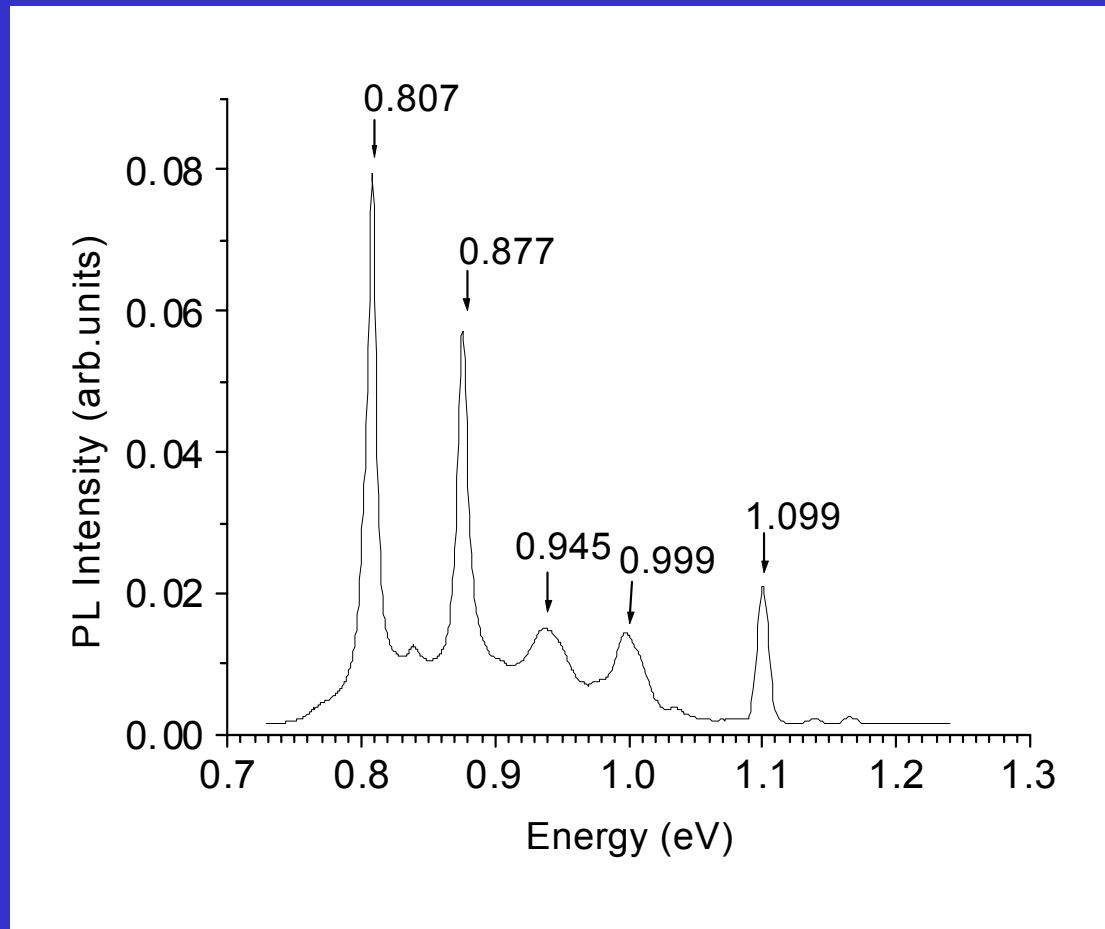


RX topo of #CZ100 after
second deformation

Other samples used in these experiments

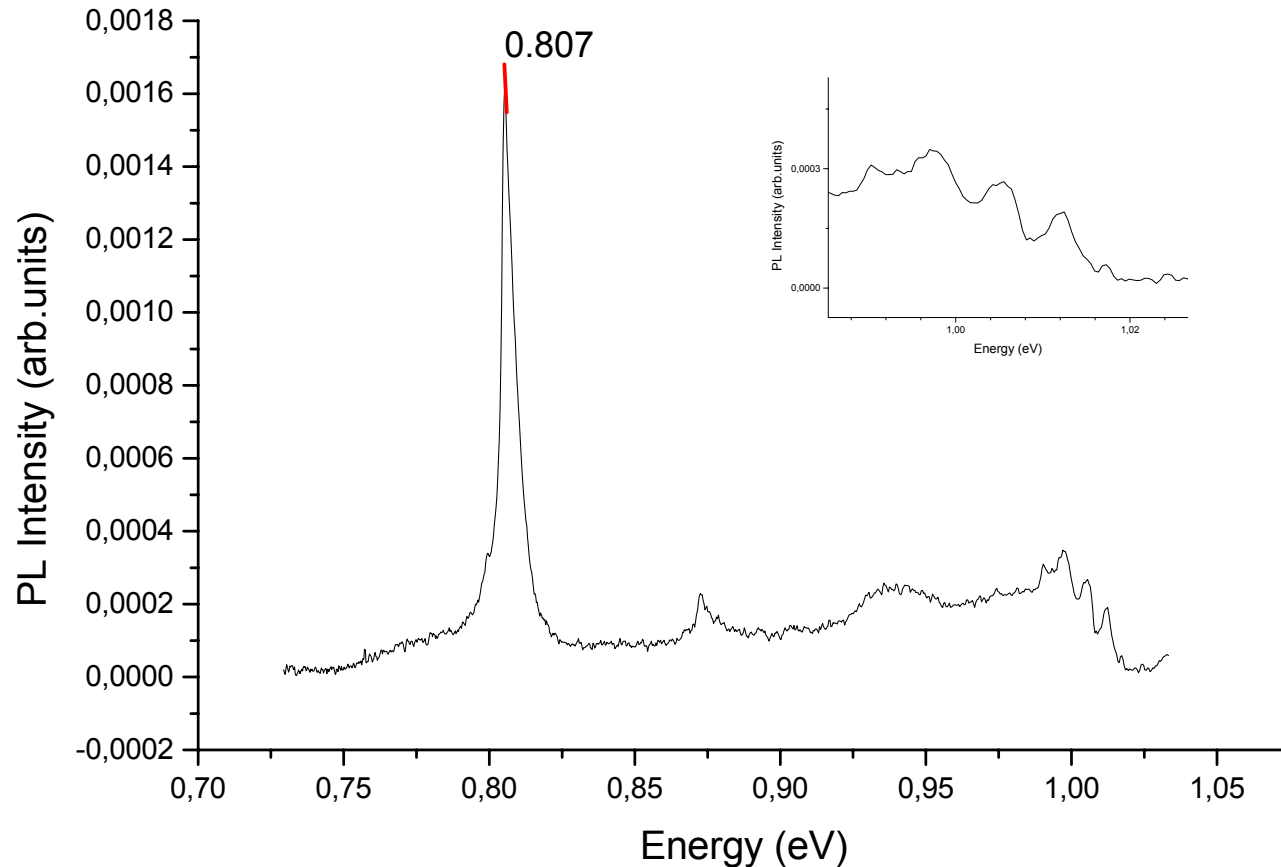
- Another set of samples was prepared by heat treating for 24h at 800°C dislocated and undislocated samples, in order to understand the effect of oxygen segregation.
- Oxygen precipitated samples were prepared using conventional high-low-high treatment in VLSI conditions
- Samples annealed or dislocate under high stress were prepared either in Misiuk's lab or in Rabier's lab

PL spectroscopy of FZ (111) dislocated samples

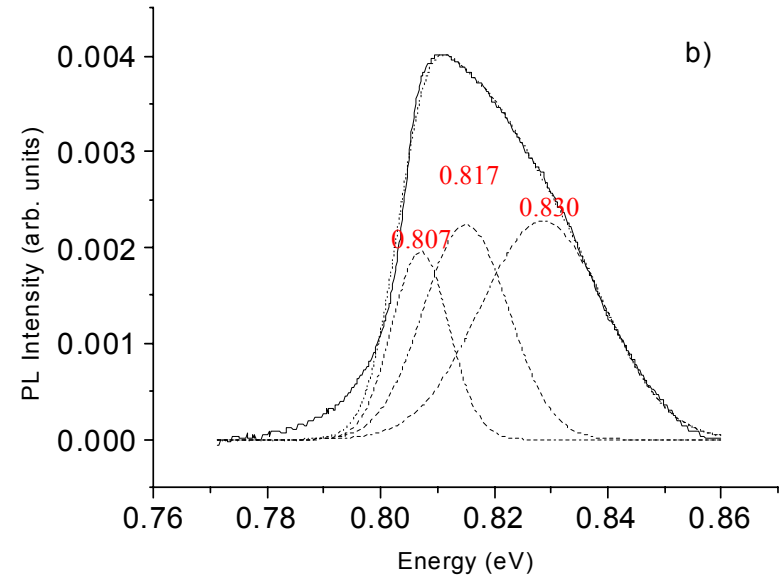
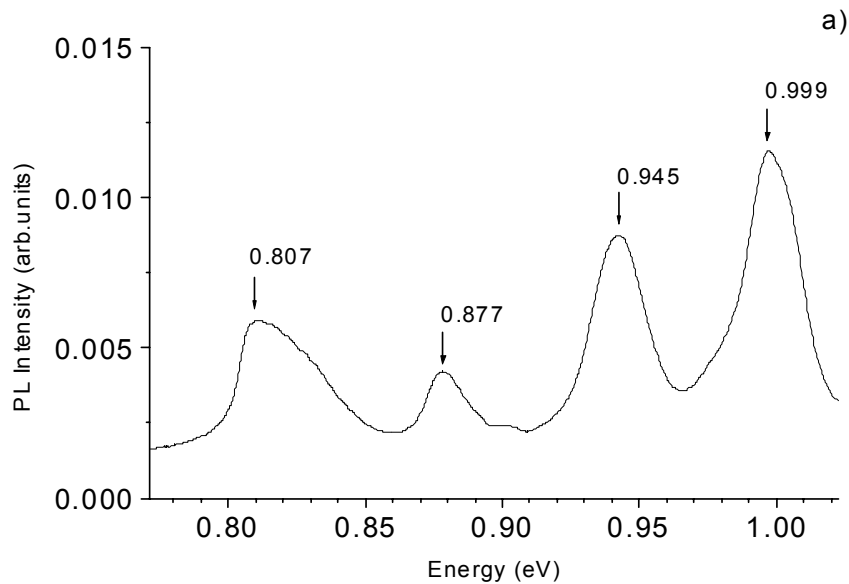


Typical PL spectrum of a dislocated FZ(111) sample

Effect of copper contamination on FZ (111) dislocated samples

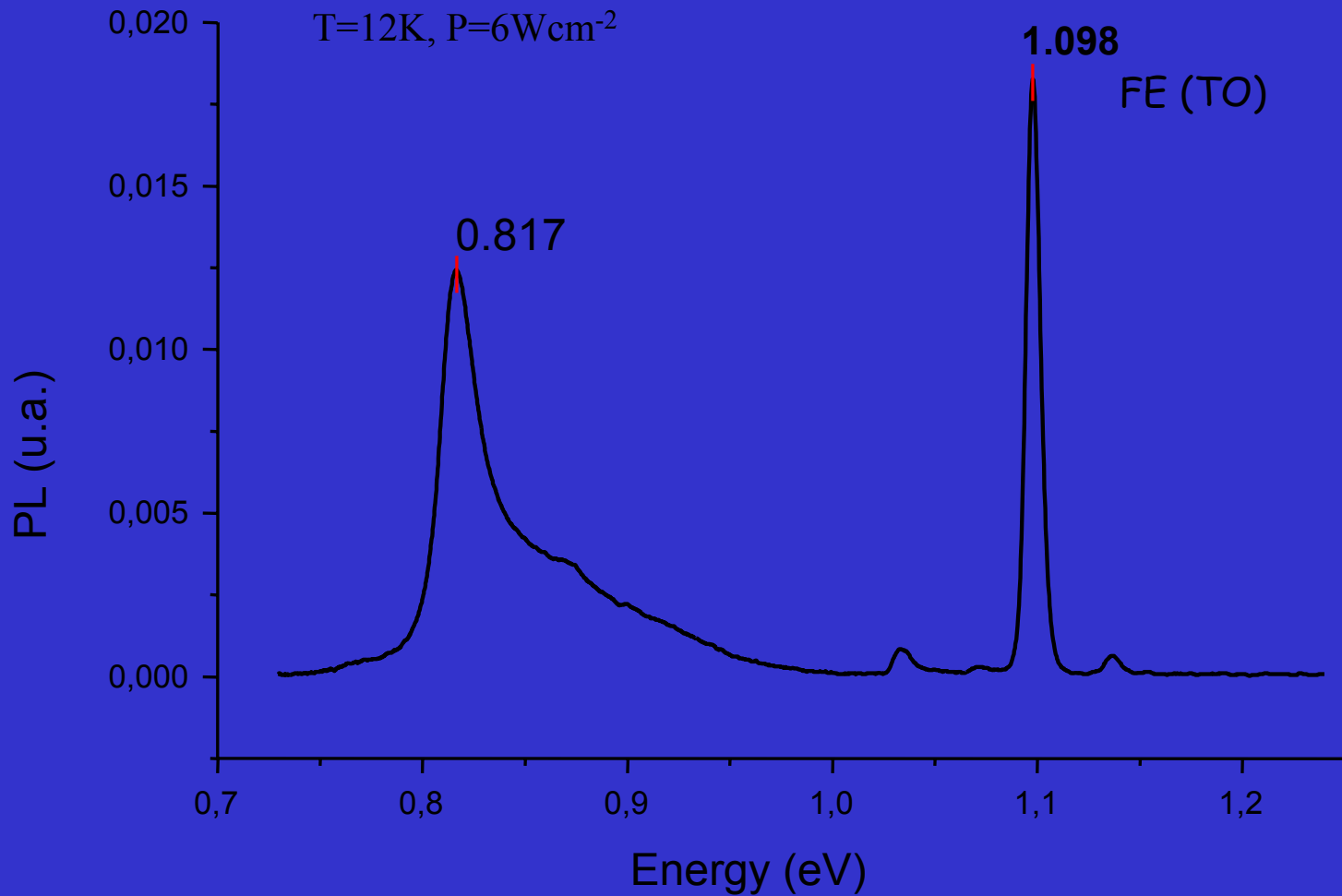


PL spectra of Cz (111) dislocated samples

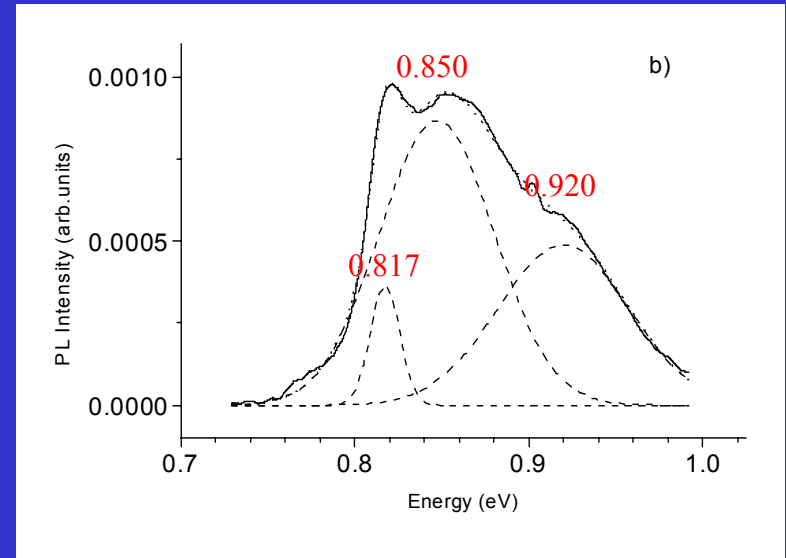
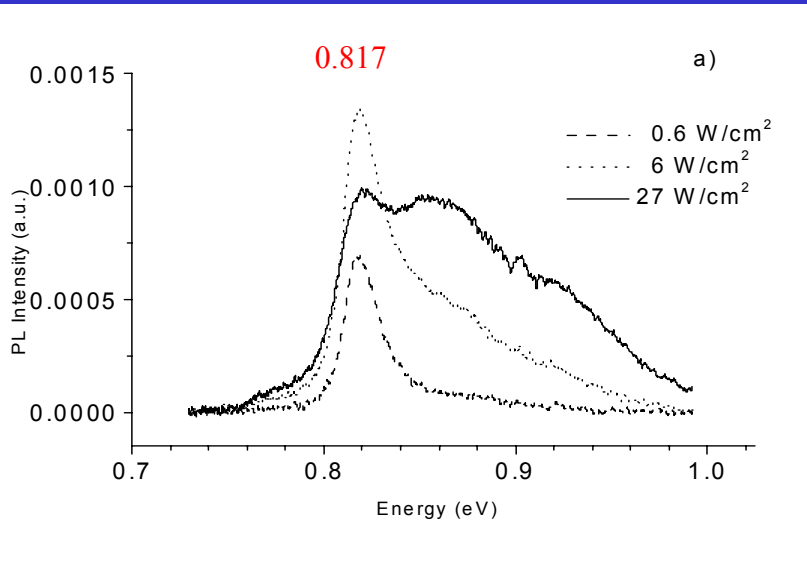


a) PL spectrum of the sample #CZ111 b) deconvolution of the D1 band

PL spectrum of dislocation-free nanometric oxygen precipitates

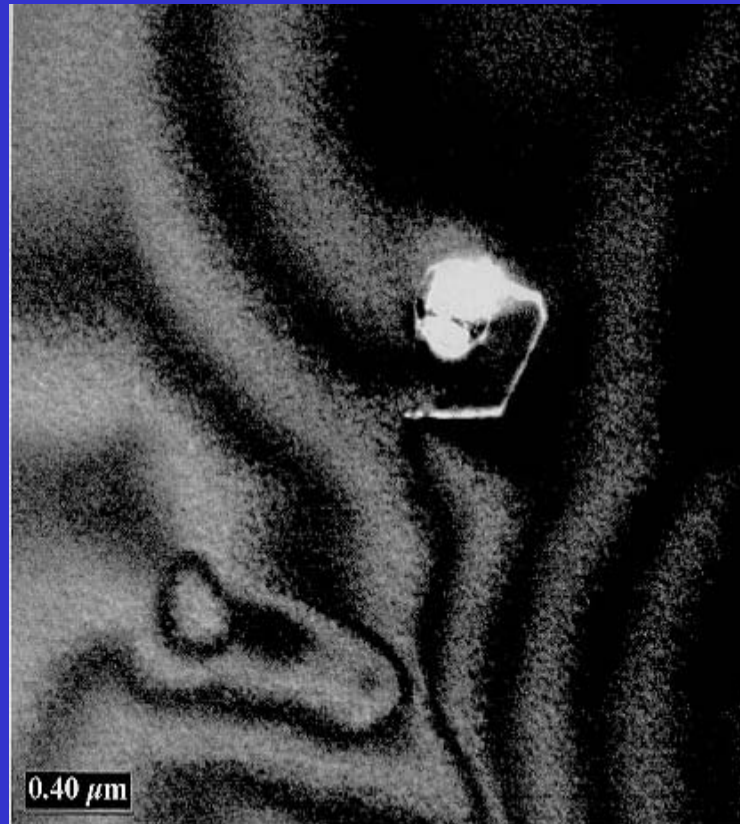


PL spectra of dislocation-free nanometric oxygen precipitates

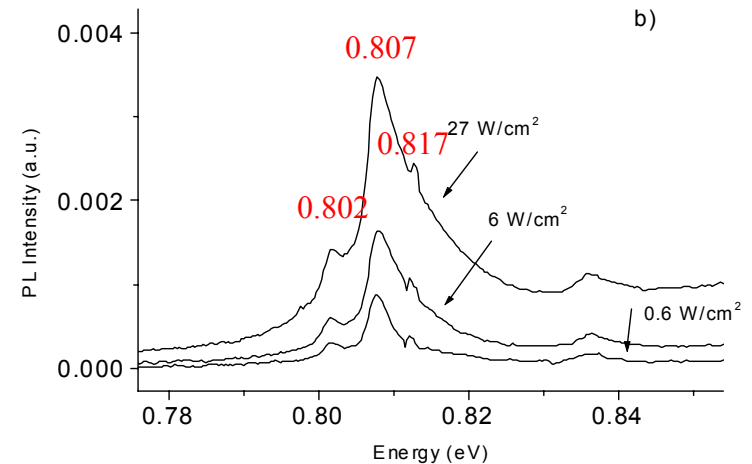
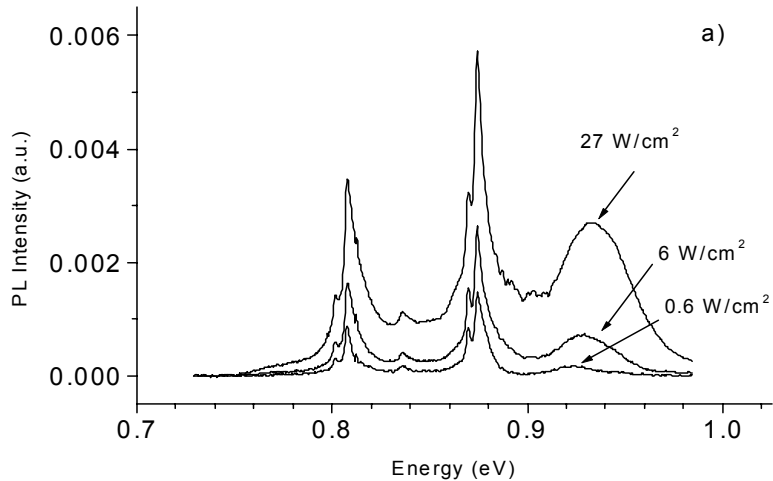


- a) PL spectrum of the sample #62 at increasing excitation
b) Deconvolution (0.817, 0.850, 0.920 eV)

TEM micrograph of a precipitate with POD



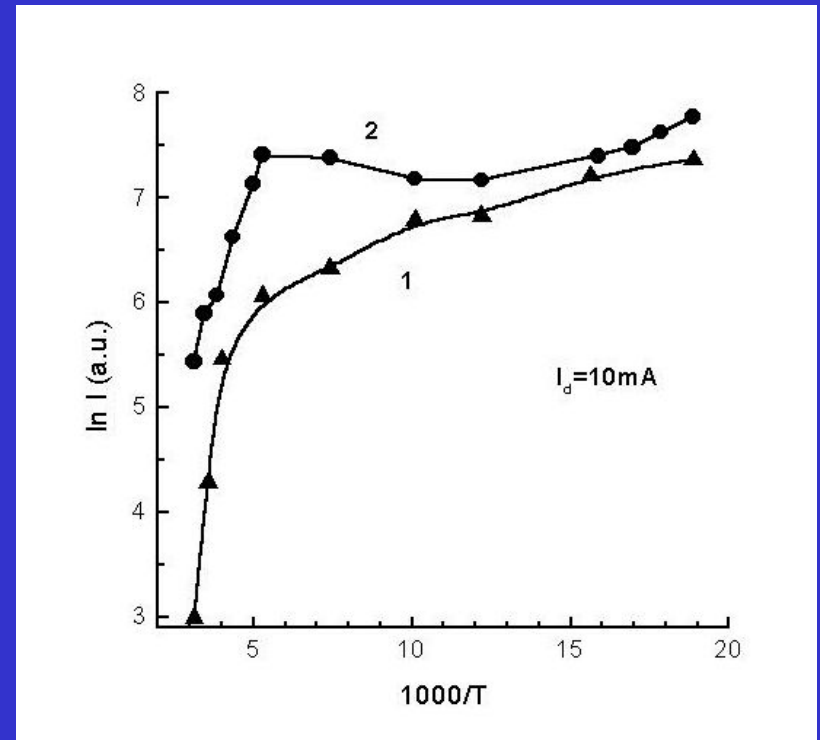
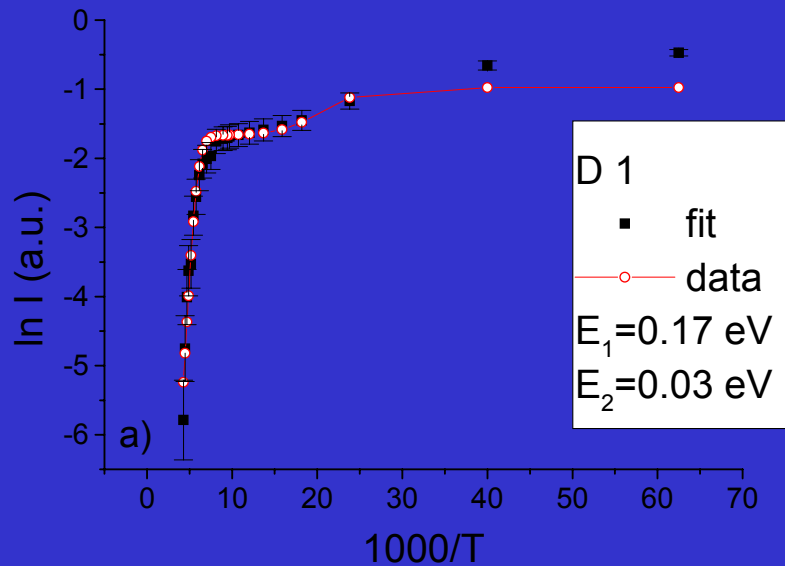
PL spectra of submicrometric oxygen precipitates with PODs



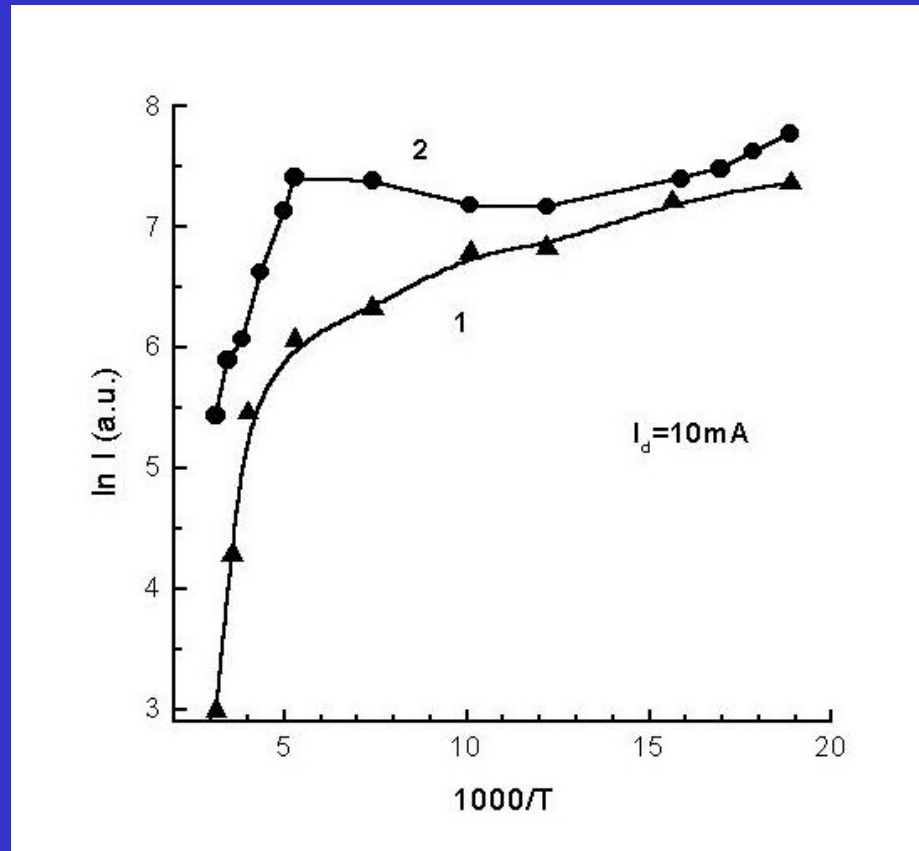
a) High resolution PL spectrum of the sample: b) zoom of the D1 region

Remark the D1/D2 emissions and the broad band at 0.95 eV!

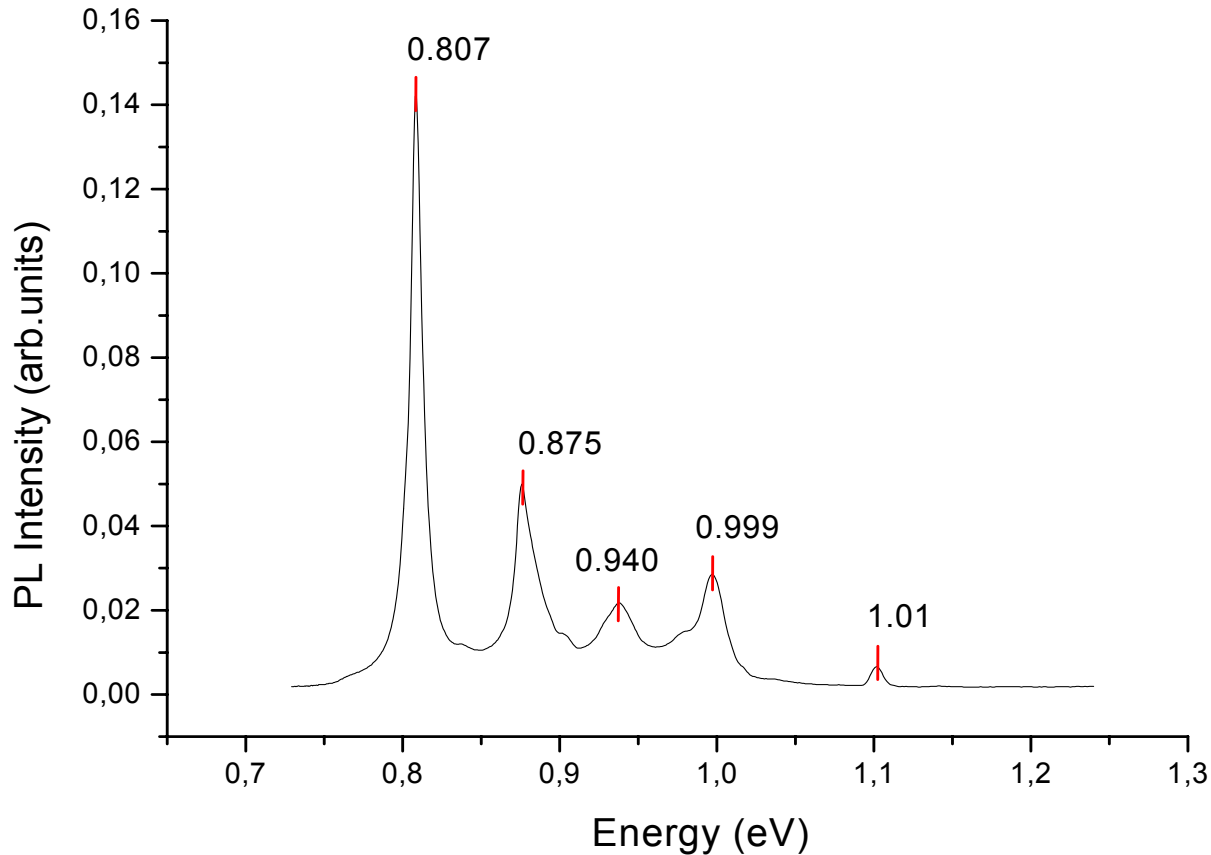
Temperature dependence of D1 band in Cz(111)



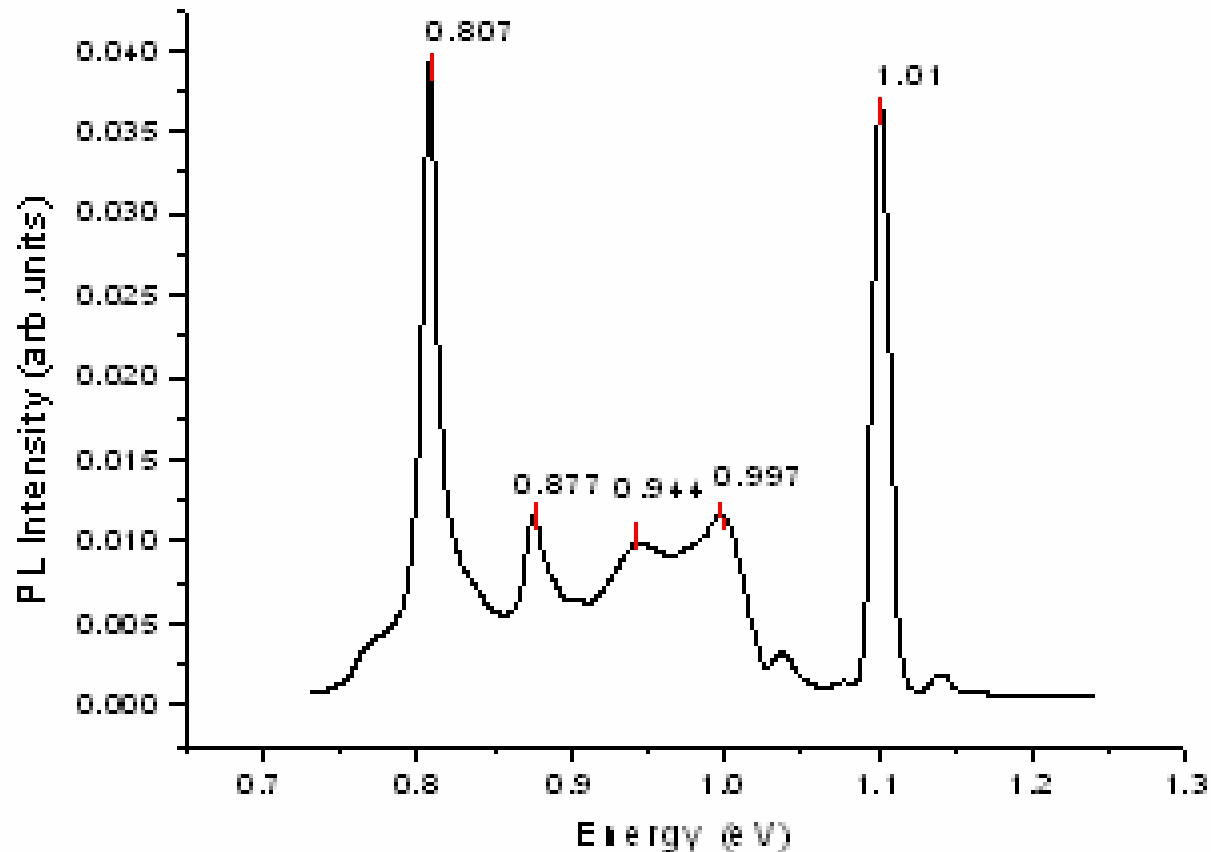
Effect of external gettering and passivation on the intensity of D luminescence



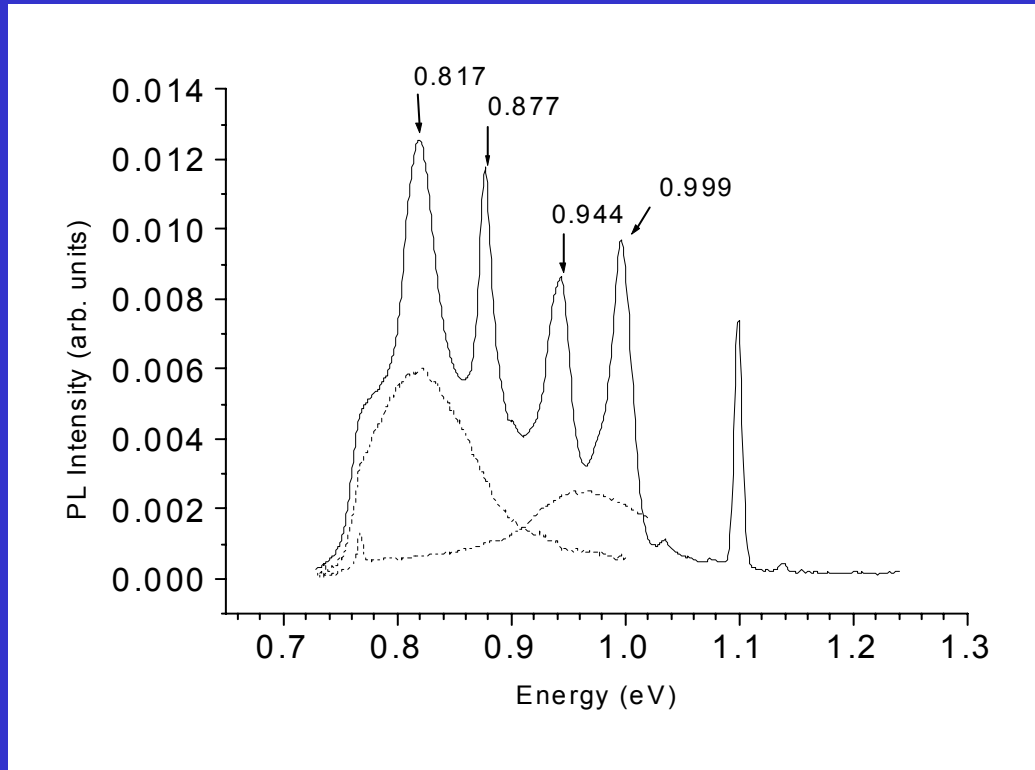
PL spectrum of a FZ (100) sample after 1h deformation and 1 h heating at 650°C (60° dislocations and threading arms)



PL spectrum of a FZ (100) dislocated sample (only 60° segments)

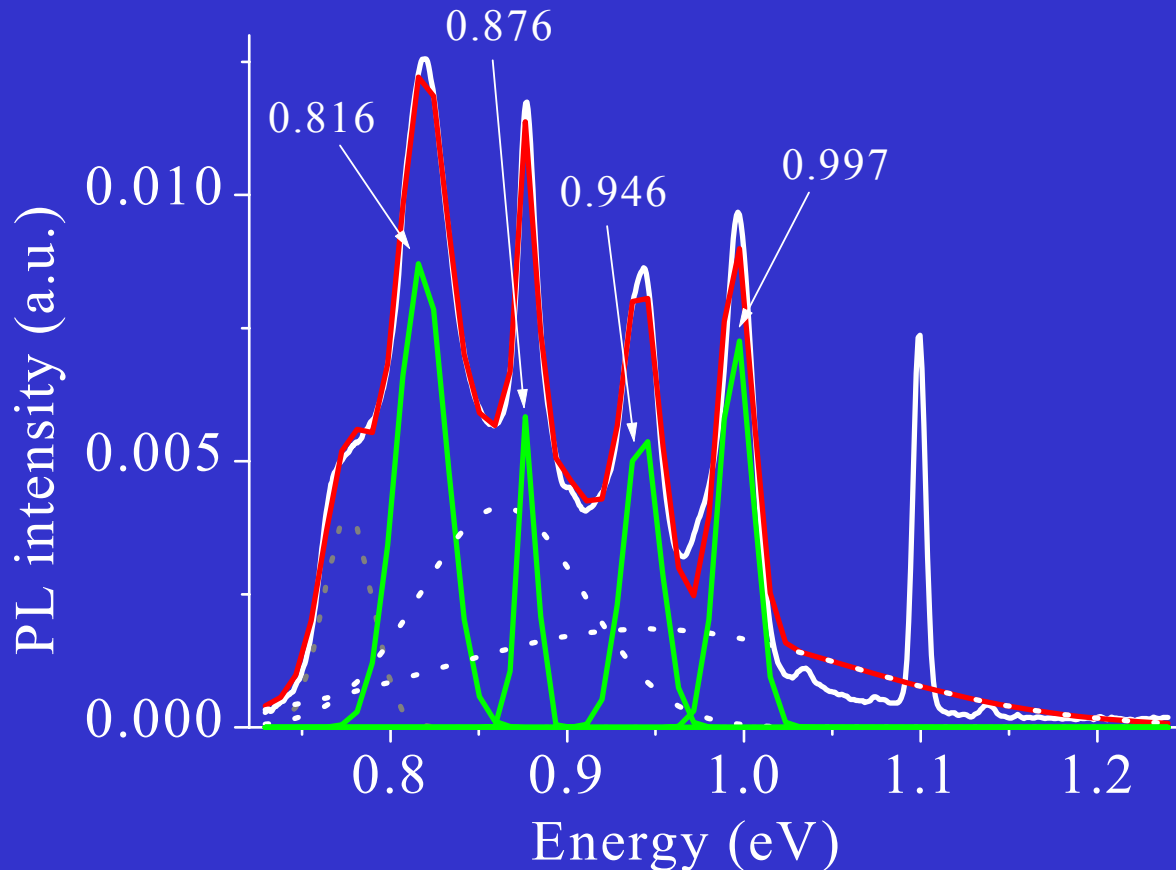


PL measurements on CZ (100)

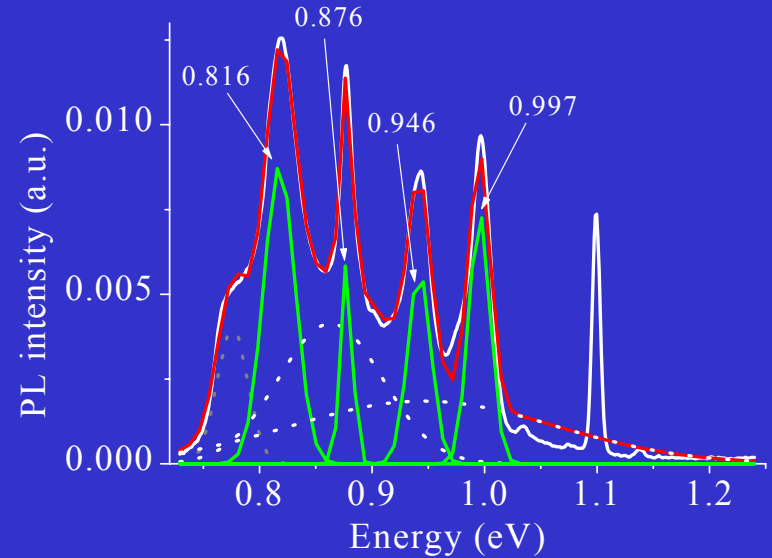
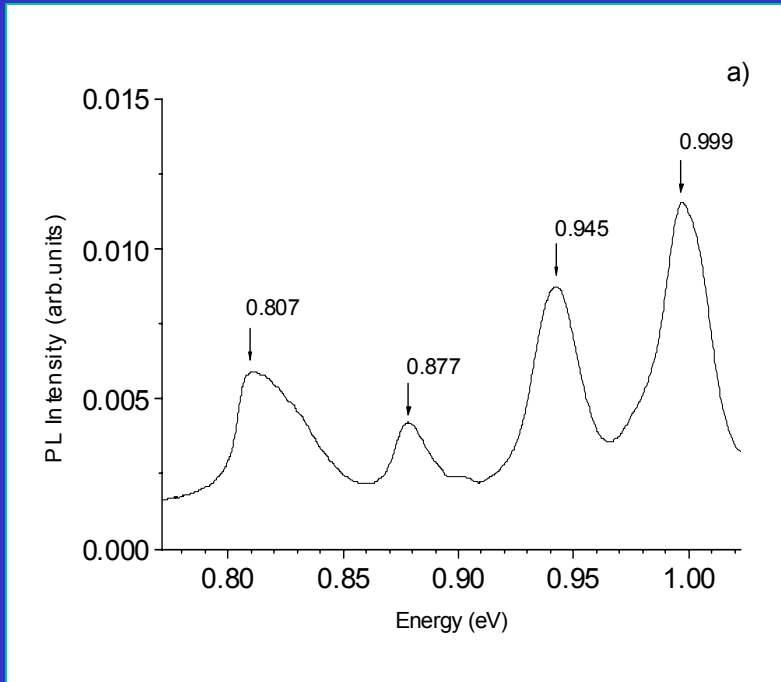


PL spectrum of a #CZ100 sample (continuous line) : PL spectra of oxide precipitates from oxygen rich and oxygen poor CZ silicon (dotted lines)

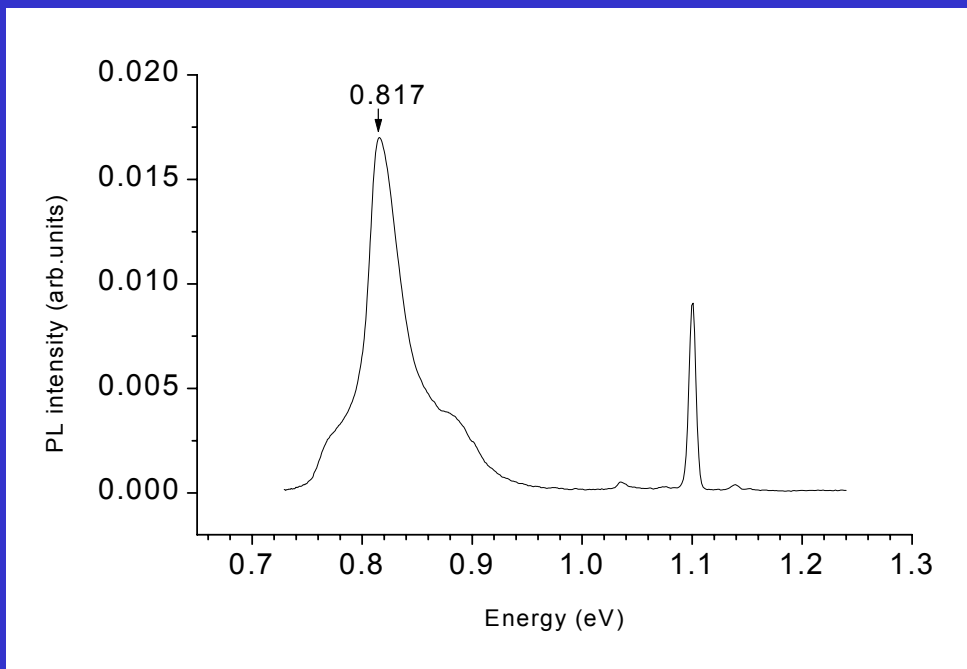
PL spectrum of the CZ (100) dislocated sample



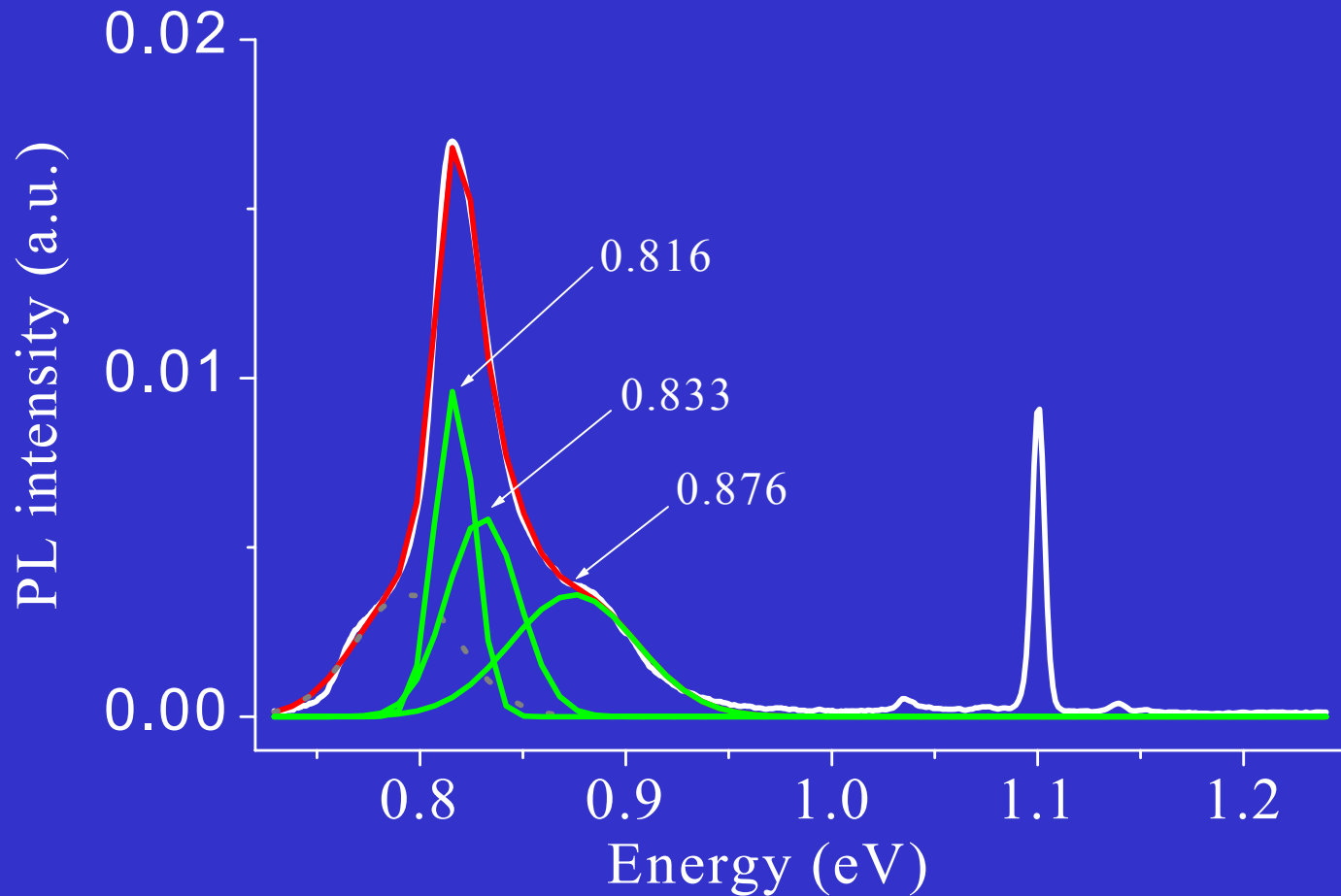
Comparison of PL spectra of Cz (111) and Cz (100) dislocated samples



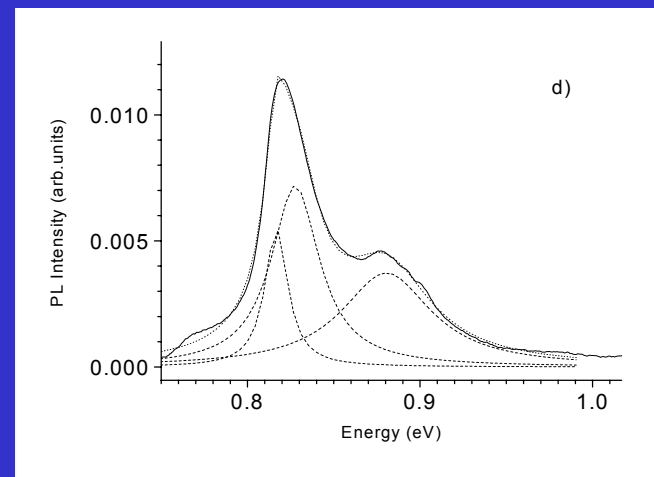
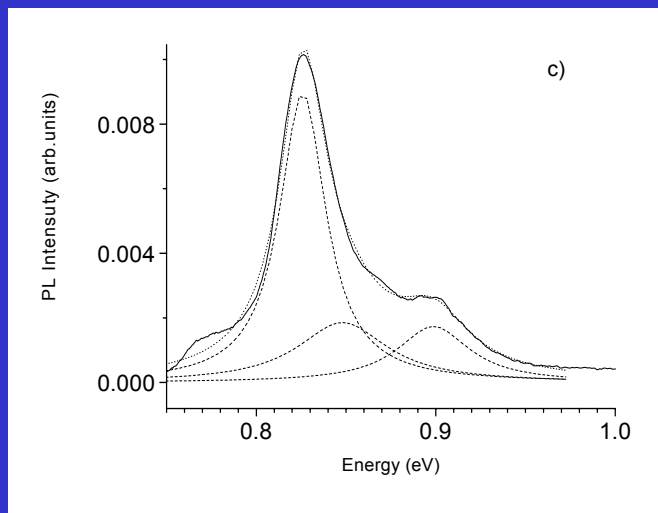
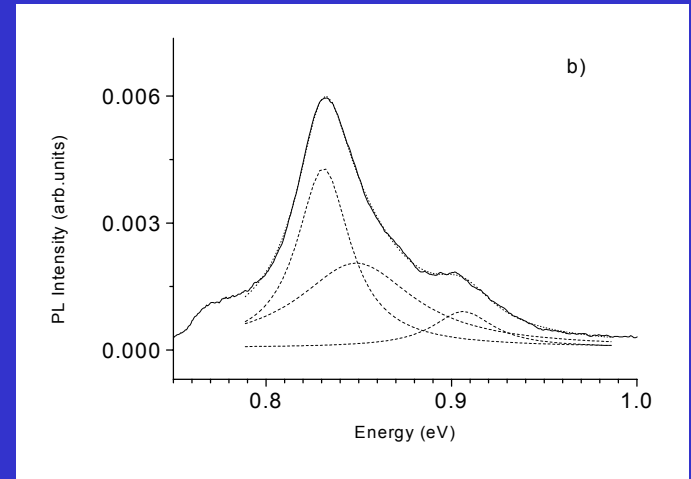
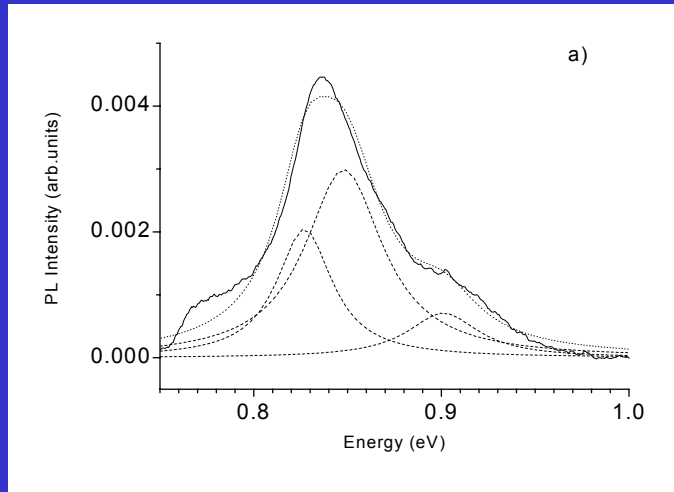
PL measurements on CZ (111) TT dislocated samples



Deconvolution of the PL spectrum of the CZ (111) TT sample



PL measurements of #CZ 100 TT at increasing dislocation density



Summary of PL/DLTS measurements

Sample	Treatments	D1 band components (eV)	Other bands	Notes
#FZ(111) n type	1hD650	0.807	D2,D3,D4	Dislocation half loops, +F lines (DLTS)
#CZ(111)	1hD650	0.807+0.817+0.830	D2,D3,D4	Dislocation half loops, F +P2 + Fe lines (DLTS)
#CZ(111) TT	1hD650+24hTT800	0.817 +0.830	broad shoulder @ 0.9 eV	
#FZ(100) n type	1hD650+e+1hD650	0.807	D2-D4	60° dislocation segments, C line
#FZ(100)*n type	1hD650+1hTT650	0.807	D2-D4	60 ° dislocation segments and threading arms
#CZ(100) p type	1hD650+e+1hD650	0.817	D2-D4 & broad bands @ 0.82 and 0.93 eV	60 ° dislocation segments Fe(O)+P2
#CZ(100)* p type	1hD650+1hTT650	0.817	D2-D4	60 ° segments and threading arms
#CZ(100) TT p type	1hD650+e+1hD650 +24h800	0.817+0.830+0.850	D2	Fe(O)+ F line
#62 (p-type)	4h650+4h800+4h1000	0.817+0.855+0.920		Dislocations absent P1 and P2 lines (DLTS)
#87 (p-type)	64h650+4h800+16h1000	0.802+0.807+0.817	D2 & broad band @ 0.93 eV	POD, P1+P2

Conclusions : *about the 0.807 eV emission*

0.807 eV emission :

- the only component of the D1 line in dislocated FZ (111) and FZ (100) samples (sharp peak)
- It occurs with other emissions in dislocated Cz(111) silicon.
- It is also the predominant emission in oxide precipitates with punched off dislocations. It occurs in environments which are “locally” oxygen-free.
- It is the signature of 60° dislocations
- When present, we observe the C line in DLTS spectra of the n-type FZ samples and the F line in p-type samples
- metals, when present, influence its intensity, not its energy position

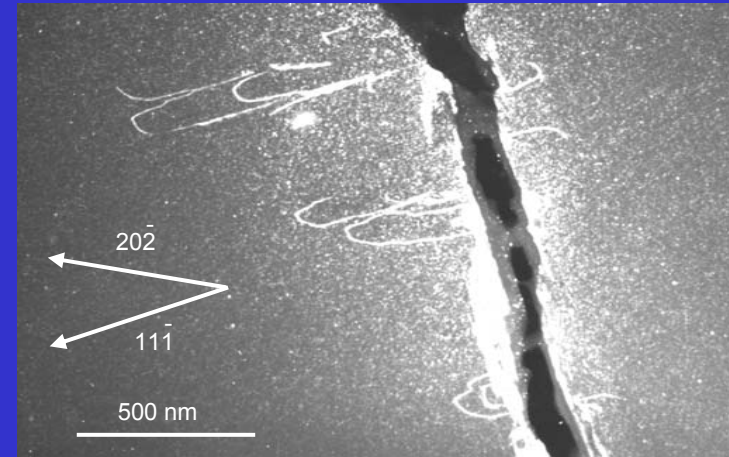
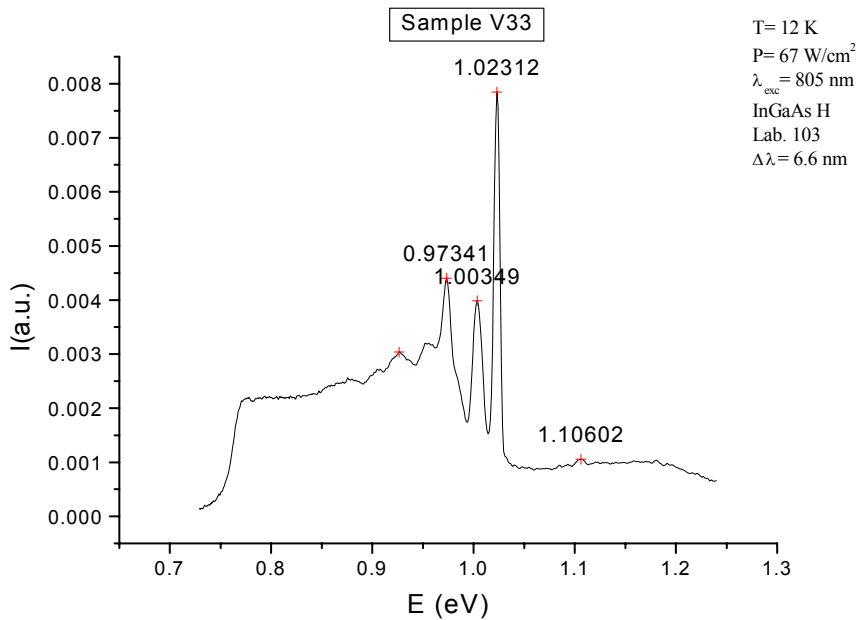
Conclusions: *about the emission of oxide precipitates*

1. The emissions at 0.817, 0.830 and 0.920 eV are the signatures of oxygen precipitates
2. the emission features of oxide precipitates depend on the absence or presence of punched-off dislocations:
 - *Without dislocations* the predominant “D1” emission is the 0.817 eV component at low injection: at high injection broad bands at 0.830+0.920 eV do also occur
 - *With dislocations* the D1 is the convolution of three sharp lines (0.802, 0.807 and 0.817 eV)

Conclusions: *About the role of dislocation structure on the segregation of oxygen*

Oxygen segregation occurs in both the CZ (111) and CZ (100) samples but is favoured in CZ (100), where only 60° dislocations do occur. The hydrostatic stress field around a 60° dislocation (4.8 GPa close to the core) is sufficient to overcome the activation barrier also for the segregation of high pressure phases

The strain field associated to 60° dislocations favours the oxygen segregation



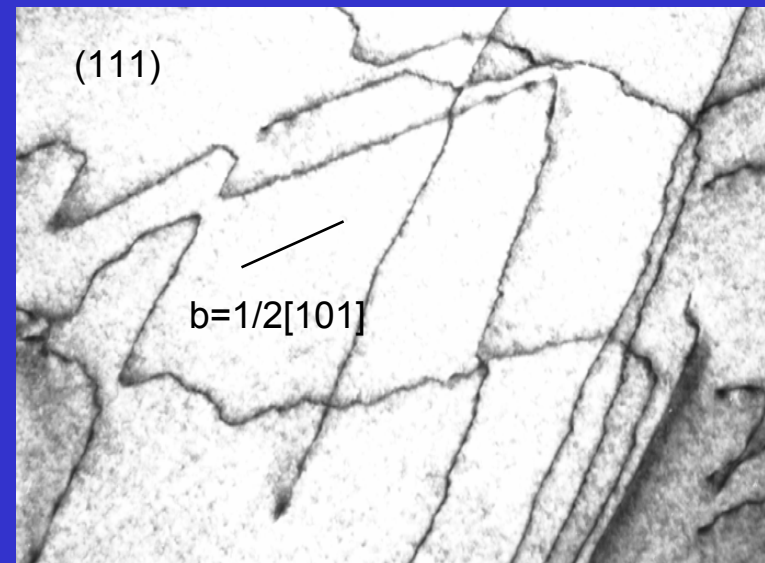
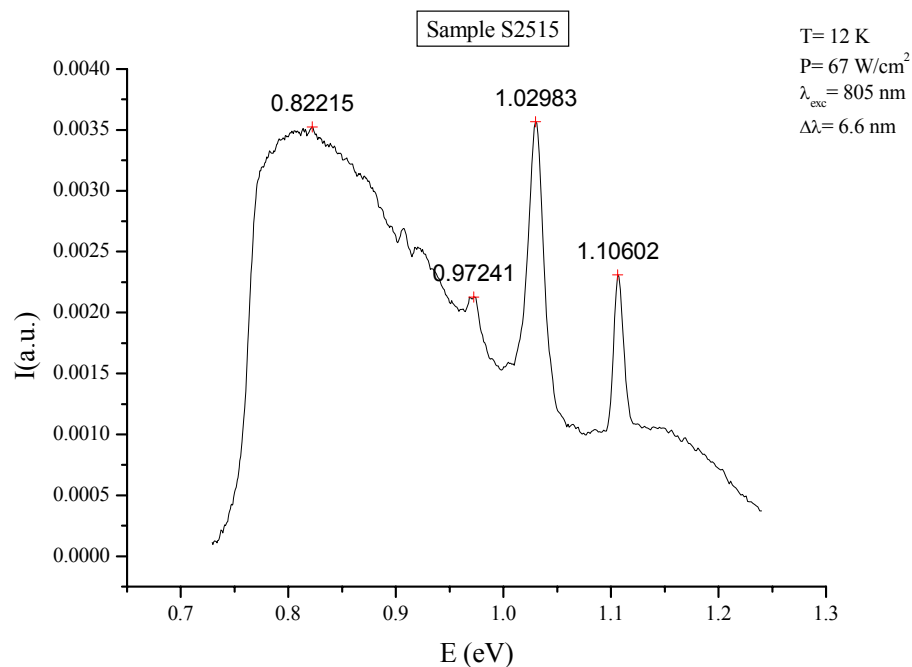
Comments:

The free silicon exciton emission is quenched

The dislocation related emissions D1, D2, are absent,
 D3 and D4 (presence of glide system dislocations ?)

The emission at 1.020 could be related to point defects as it has been observed also in irradiated samples

A broad band around at 0.8 eV , is present, cutted by the detector cut off at about 0.75 eV.



Comments:

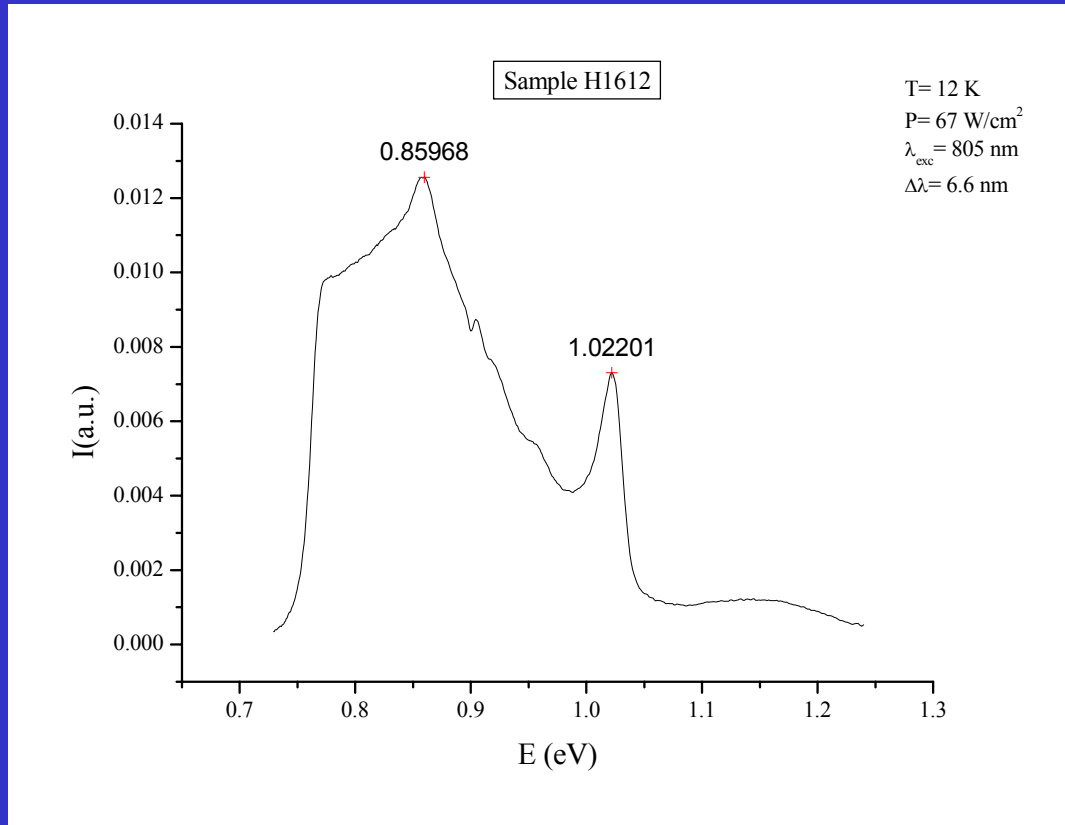
Free exciton (1.1 eV) emission is present

D3

Broad band around 0.8 eV

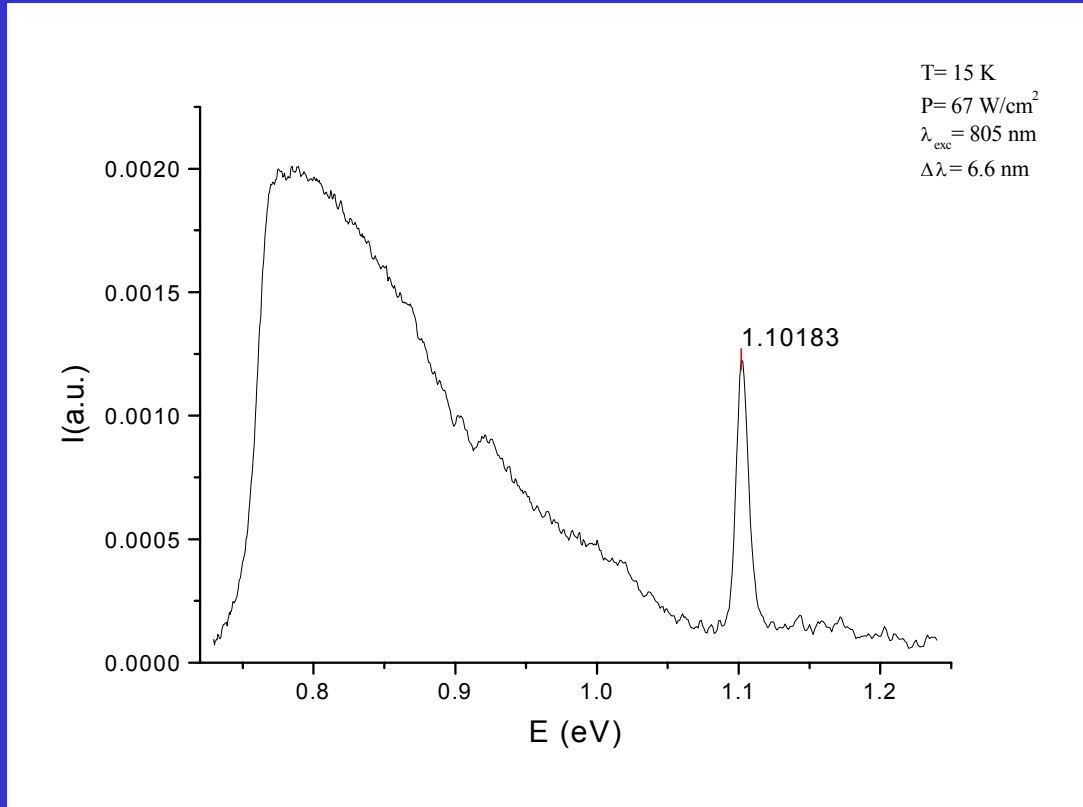
Peak at 1.02 eV related to point defects, slightly asymmetric with FWHM greater than in V33 spectrum

SAMPLE H1612-deformed at 275° C and 5 GPa along <123>



SAMPLE H1846-deformed at RT and 9 GPa along <123> : no PL signal

Effect of oxygen :CZ Si deformed at 150°C under 5GPa along <123>



Structural details ?

CZ Si deformed at RT under 5GPa along <123> : no signal

Acknowledgments

This work has been carried out in the frame of the
INTAS Project 01-0194.

Thanks to:

- Elisa Leoni
- Alessia Le Donne

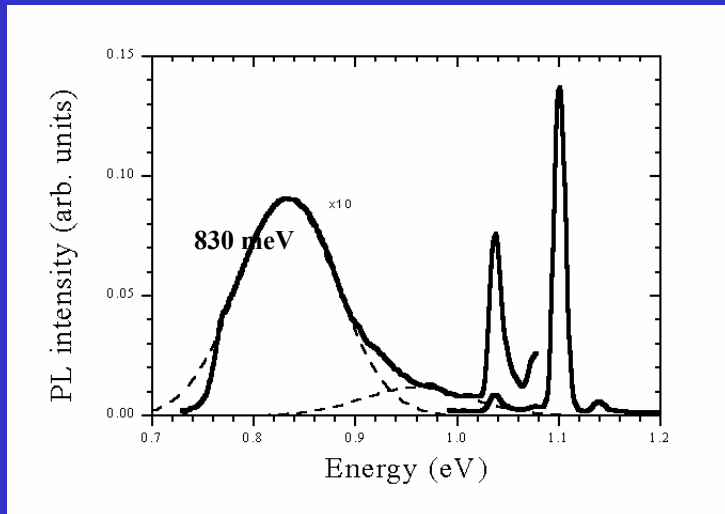
About the origin of broad bands

- According to Weman et al. *Phys Rev B*(1990) and A.N. Safonov et al *Physica B* (2001) the strain field of precipitates and the intrinsic strain field of interstitial oxygen might induce band-gap shrinkage and line shift and broadening.
- Line shifts of the order of 0.3 eV are expected for local strains $\Delta a/a$ of the order of 3% : the bands at 0.92 and 0.85 eV might be strain induced
- Broadening of oxide bands should depend on a wide distribution of particle sizes and shapes

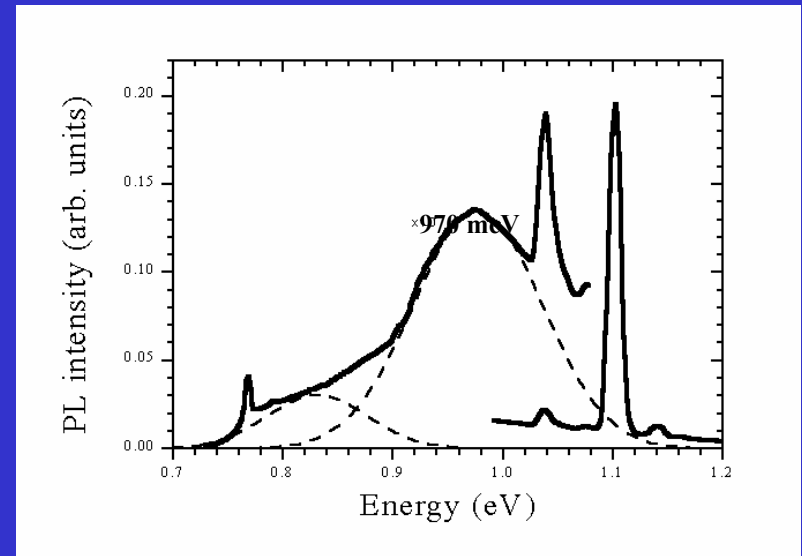
PL spectra of oxygen nuclei

15' at 1000 °C + 120h at 650 °C

N1 (medium oxygen, 16 ppma)



N2 (high oxygen, 18.5 ppma)



*At $T = 650^{\circ}\text{C}$ the difference in the total driving force $\Delta G_t = \Delta G_f + \Delta G_o$ for the nucleation of vitreous, cristobalite or and coesite-type of oxide precipitates is of the order of 1 Kcal/mole. The difference in the ΔG_o coming from $\Delta O_i = 2.5$ ppma is = 1.266 Kcal/mole

coesite rodlike- shaped

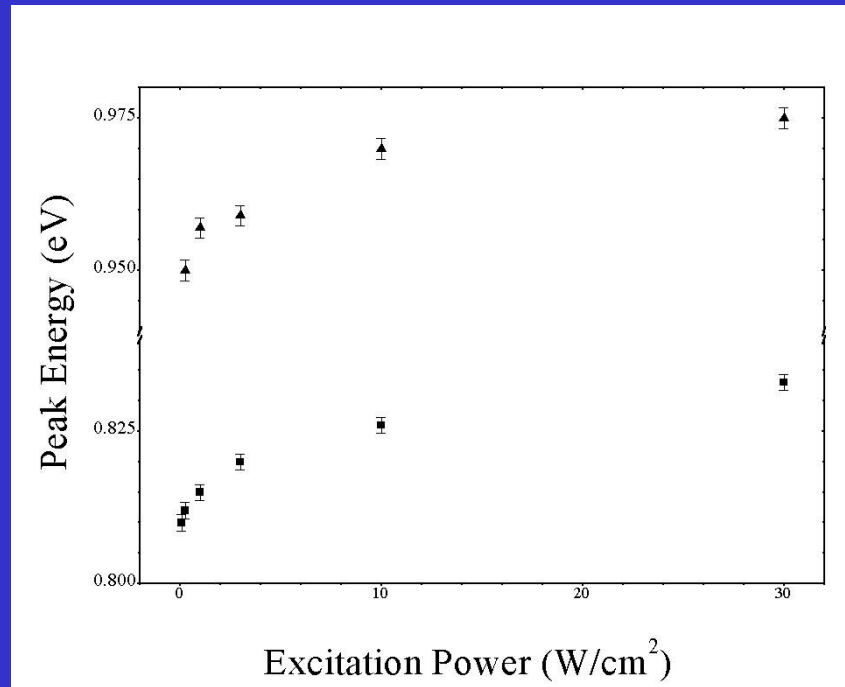


amorphous platelike-shaped



High sensitivity of PL

Peaks position vs Excitation power



➤ due to local shrinkage of the band gap introduced by the oxygen precipitates, due to a presence of a compressive strain field

Weman et al. Phys. Rev. B, 42 (5), 3109 (1990)

➤ due to Donor-Acceptor (D-A) transition from a deep donor level at the Si/SiO_x interface to an acceptor level

S.T. Pantelides, et al. MRS Symp. Proceedings, 490, 59 (1998)

Introduction

Dislocations are potential sources of light. Their emission occurs in a wavelength region (1.15 μm) interesting in the field of optical communications and have a radiative lifetime short enough to enable high quantum efficiency values. Moreover, the strain field of dislocations might be used to get carrier confinement effect and drainage of impurities, and might behave as possible sources of 1D quantum structures.

Impurities are known to influence both the optical and electrical properties of dislocations

Introduction

- The achievement of (internal) high quantum yield

$$\eta = \tau_p / \tau \sim \beta n \tau_p \text{ (high injection limit)}$$

(τ_p =lifetime of minorities, τ is radiative lifetime, n = carrier concentration)

in c-silicon EL at rt was considered, until 2001, an almost impossible, although fascinating, basic research objective (no direct applicative interest of the 1.1 eV emission).

Today, η values around 0.1% or more are obtainable under high injection *Th. Dittrich et al (2001), A.M. Emelyanov et al (2003)* or by device optimization *M.A Green et al (2001)*

- Most of the work for vis and IR emission has been carried out on a-Si, nc-Si, Er-doped Si, and dislocated silicon, all of which still present unknowns and challenges.

Remarks on CZ(100) TT

- 0.817 eV emission only at high N_D
- 0.830 eV emission increases with N_D
- 0.850 eV emission decreases with N_D
- D2 intensity constant

DLTS and PL comparison (p-type samples)

	E_T (eV)	#62	#87	Cz111 as grown	Cz111 dislo	FZ 111 as grown	FZ 111 dislo
T1 (P1,F)	~ 0.27 $\sigma=10^{-15}$	●	●		●		
T2 (P2)	~ 0.45 $\sigma=10^{-15}$	●	●				
T3 (Fe)	~ 0.40 $\sigma=10^{-16}$		●	●	●		
T4	~ 0.38 $\sigma=10^{-16}$				●		
D1a 0.807 eV			●		●		●
D1b 0.816 eV		●	●		●		