Photoluminescence and Raman spectroscopy for defect identification in Silicon, $Cu(In,Ga)Se_2$ and Cu_2ZnSnS_4 materials

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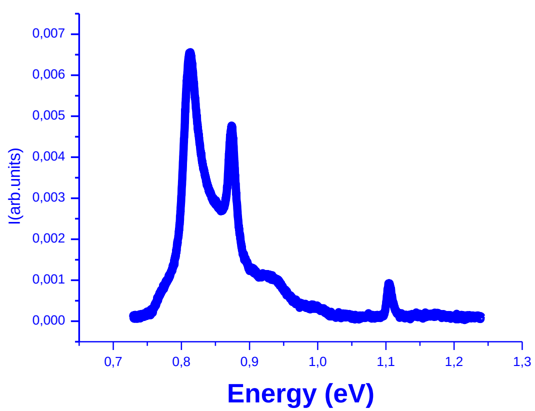
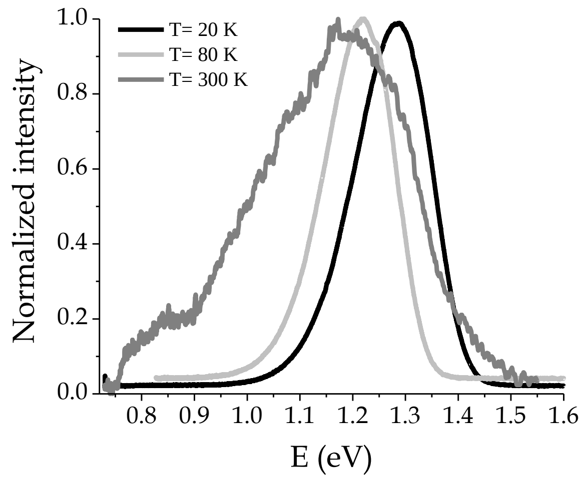
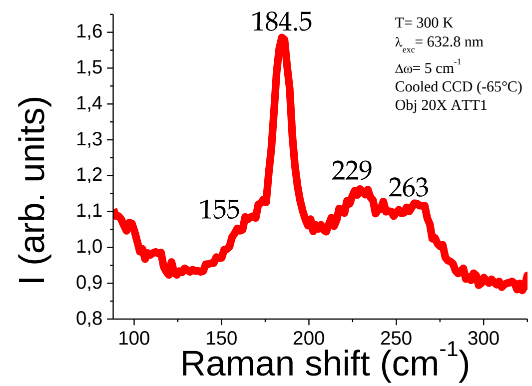






Introduction

- ✓ Purity and low defects density are the most important parameters used to describe the quality of any PV material

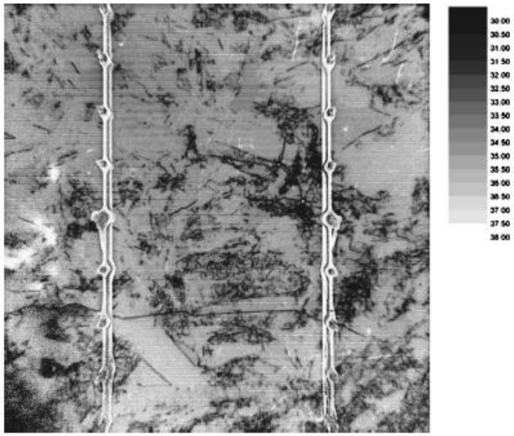
- ✓ Defects and impurities can be detected by spectroscopic tools

  - ✓ The spectroscopic identification of defects and impurities is a fundamental step in the optimization of PV materials : in silicon has been a key factor in the development of silicon based electronic and PV devices. (e.g. oxygen and carbon have been studied for more than 60 years)

The role of defects and defect engineering is a key element in any PV material to get high efficiency

Photoluminescence spectroscopy

✓ Imaging of band edge photoluminescence at room temperature is one of the most useful technique for evaluating the quality of wafers for solar cells *

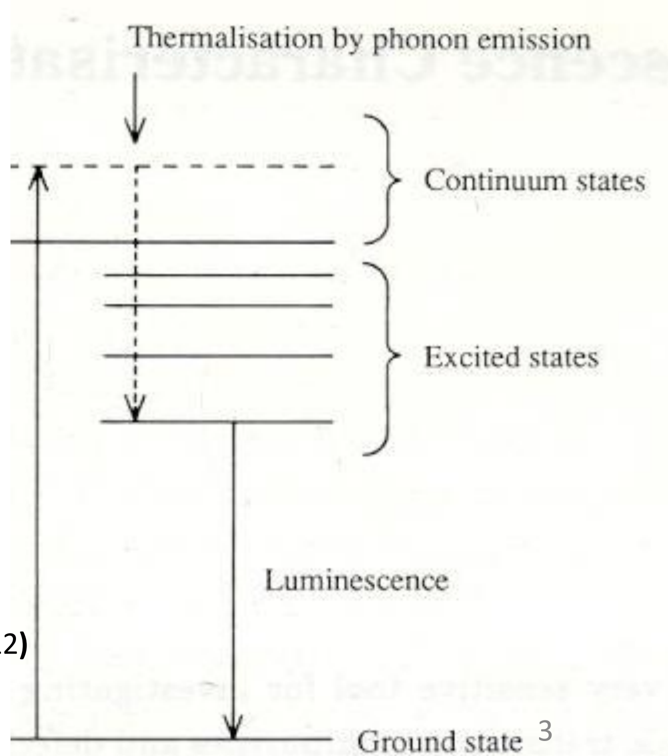


✓ PL is a contactless, nondestructive method of probing electronic properties of materials

PL can be used for :

- Material quality
- Imaging or mapping
- Band gap determination
- **Impurity levels and defect detection**

It is not a quantitative technique



* T. Trupke, R.A. Bardos, M. C. Schubert, W. Warta, Appl. Phys. Lett., 044107, (2006)
M. Bernhard, G., Johannes W. Warta, Wilhelm; IEEE JOURNAL OF PHOTOVOLTAICS, 2, 348 (2012)
Giesecke, J. A.; Niewelt, T.; Ruediger, M.; et al and Warta W. SOLMAT 102, 220-224 (2012)
Giesecke, J. A. M. Kasemann and W. Warta JAP 106. 014907 (2009)

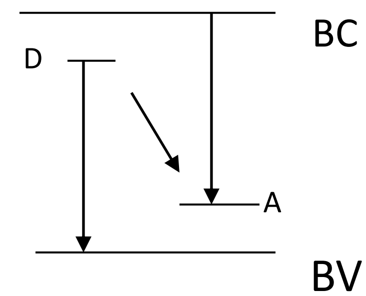
Laser excitation hv> Eg

Electron –hole pairs

Free excitons (FE)

Capture by shallow donors and acceptors

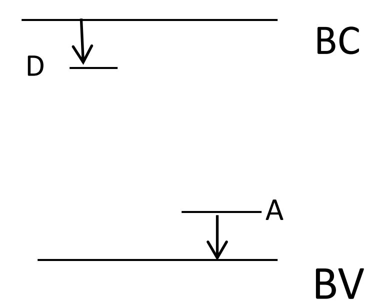
Radiative transition Between a band an impurity states: Deep transitions



T range 4.2 K –300 K

Radiative transition Between a band an impurity states: Shallow transition

T< 12 K



FE luminescence Phonon or no phonon assisted

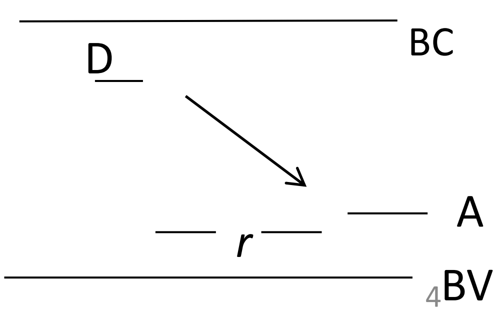
12 K < T< 77 K

Impurity specific BE luminescence No phonon or phonon assisted

4.2 K<T< 12 K

Donor – Acceptor Transitions

T range 4.2 K –300 K



Silicon's case

WEB OF KNOWLEDGE℠ | DISCOVERY STARTS HERE

silicon , impurities, dopants, dislocations and photoluminescence

→ **6'000** articles from 1967

•Most of these works are very old and concerned with fundamental physics

PHYSICAL REVIEW VOLUME 161, NUMBER 3 15 SEPTEMBER 1967

New Radiative Recombination Processes Involving Neutral Donors and Acceptors in Silicon and Germanium

P. J. DEAN,* J. R. HAYNES,† AND W. F. FLOOD

Bell Telephone Laboratories, Murary Hill, New Jersey

(Received 10 April 1967)

(Received 10 April 1967)

- More than 150 luminescence systems are reported, refer to irradiated, heat treated or contaminated silicon or concern silicon for microelectronics

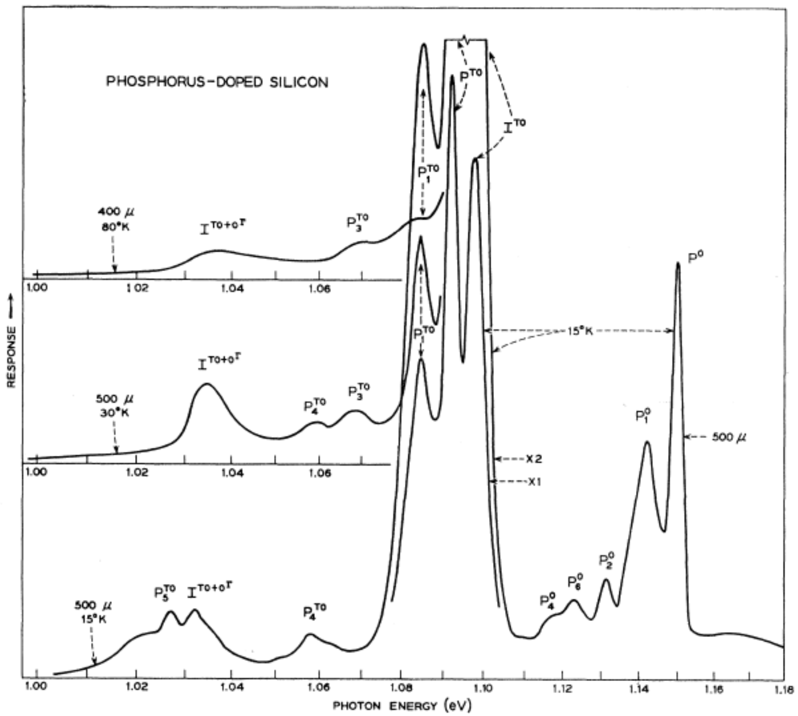
➢Luminescence lines of the most important defects in silicon :
Dopants, oxygen and carbon agglomerates, dislocations.

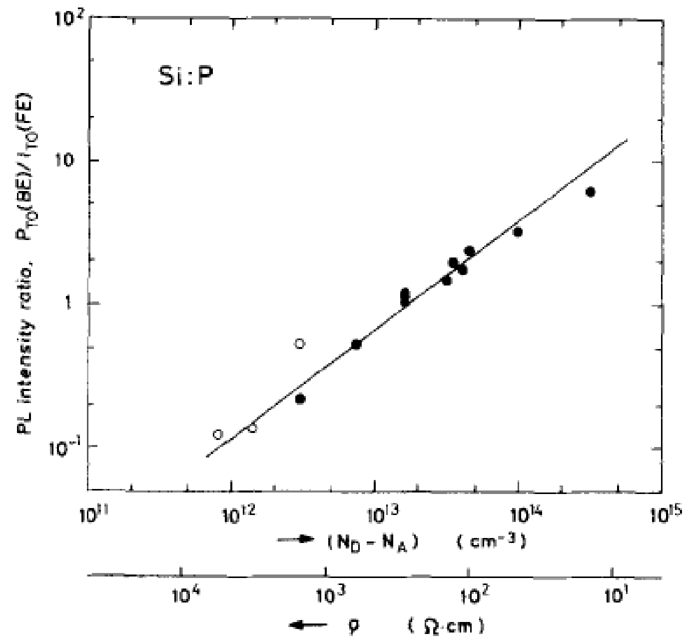
S. Binetti et al . " Solar Energy Materials & Solar Cells 130 696–703 (2014)

Dopant determination by Low T PL

Bound excitons to dopants (As, P, Sb,Bi, Ga,In, Al)

P. J. Dean et Phys. Rev. **161,** 711–729 (1967)





- *M. Tajima Appl. Phys. Lett., 32 719 (1978)*
- *SEMI MF 1389-0704 (2004).*

•A calibration for B, P, Al, As in silicon has been developed based on the ratio between Area of BE peak/ area of FE peak @T=4.2 K

- Advantages:
  - Simultaneous determination of B and P
- Disadvantages :
  - not applicable to concentrations higher than 10^{15}at/cm^3 because the FE lines was almost undetectable.

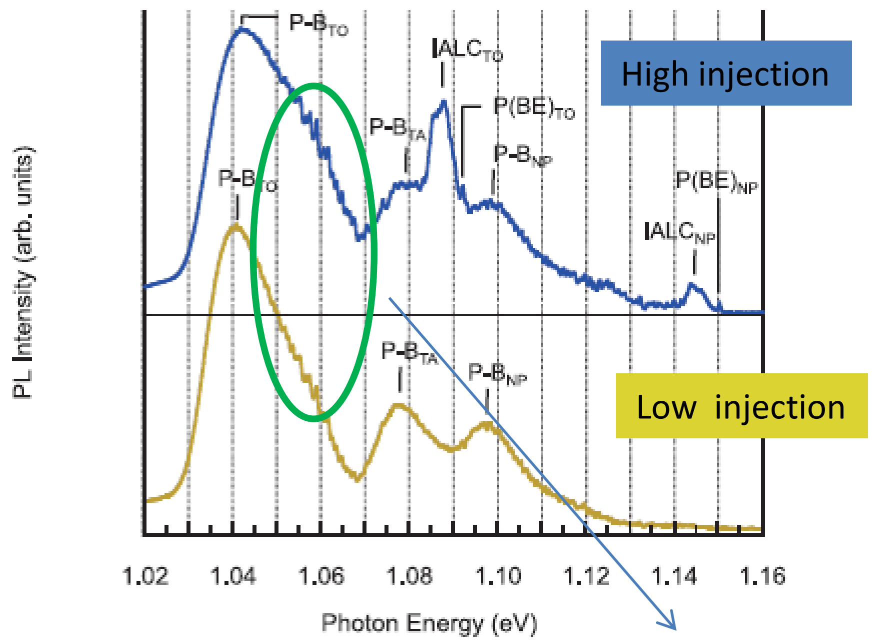
Upper limit of 10^{15} at/cm^3

Donor – Acceptor transition (DAP) in Silicon

- In B-P compensated samples three bands appeared at 1.098, 1.079, and 1.041 eV

M. Tajima, , T. Iwai, H. Toyota, S. Binetti, and D. Macdonald J. Appl. Phys. 110, 043506 (2011) ; M. Tajima, T. Iwai, H. Toyota, S. Binetti, and D. Macdonald, Appl. Phys. Express 3, 071301 (2010)]

R.C. Enck, A. Honig The Physical Review 177 , 1182 (1969)



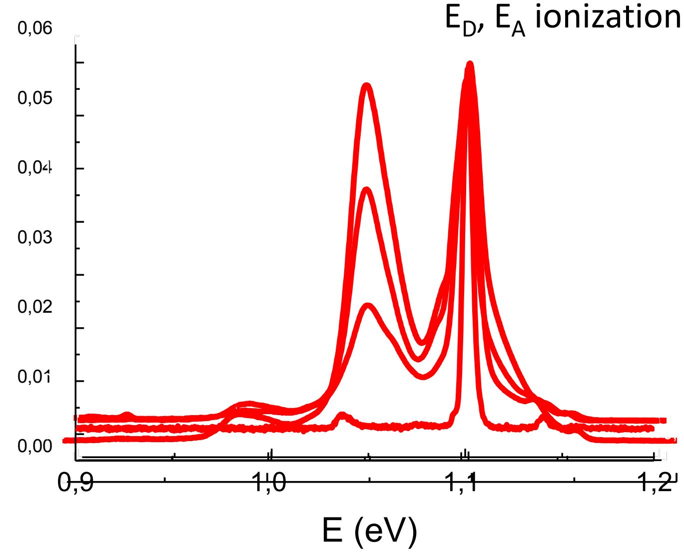
- @T= 12 K, in solar grade silicon a DAP band @ 1.05 eV increases with compensation

Rc=1

R_c= 1,24

Rc=1.68

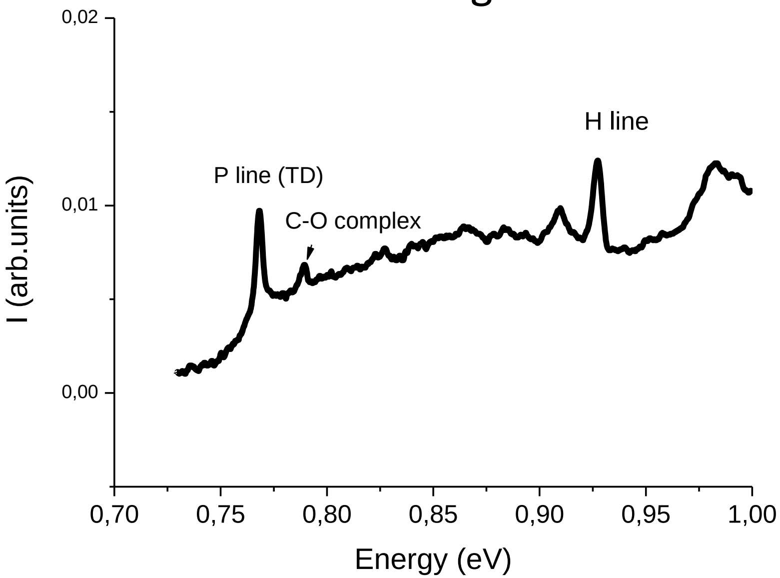
Rc=18,34



Carbon detected by PL

C –related complexes:
G line 0.969 eV $(C_i\text{-}Si_i\text{-}C_s)$
C line* @ 0.789 eV (C_i-O_i) dominant in radiation damaged Si
H line @ 0.926 eV ;

Solar grade silicon



•formation of (C-O)n complex in any codoped C and O silicon samples submitted to heat treatment

•SiC (and SiOx) nanoprecitates: broad band is probably due to strain

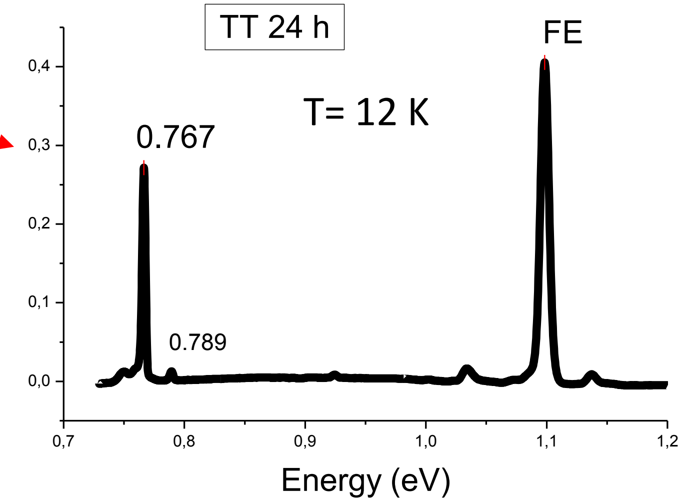
S. Binetti et al. Materials Science and Engineering B **159–160** (2009) 274–277

Oxygen agglomerates detected by PL :

No luminescence lines are associated to Oi
Thermal donors can be detected with BE excitons line

Silicon heated at 450 °C exhibits a strong line at 0,762 eV (P- line)

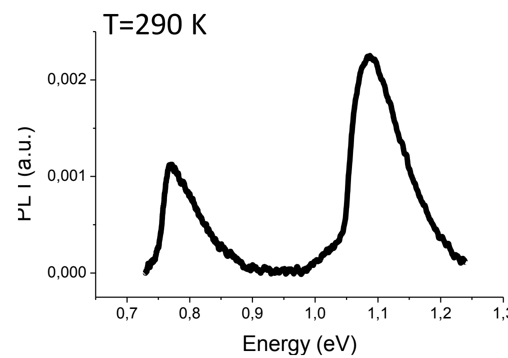
It is not observed in FZ silicon
Carbon isotopic shift (0.079 eV) has been noted in P-line



P line is due to a transition from a TD level (NL8) to a deep center (E_v+0.37 eV) identified by DLTS

M. Acciarri , S. Pizzini, S. Binetti et al. J.Phys. Condensed Matter, 14 13223, (2002)

S. Pizzini, S. Binetti, A. Le Donne et al. MRS Symp. Proc. Vol.692 , 275 (2002)



•visible at room temperature :
can be used a “ diagnostic” line.

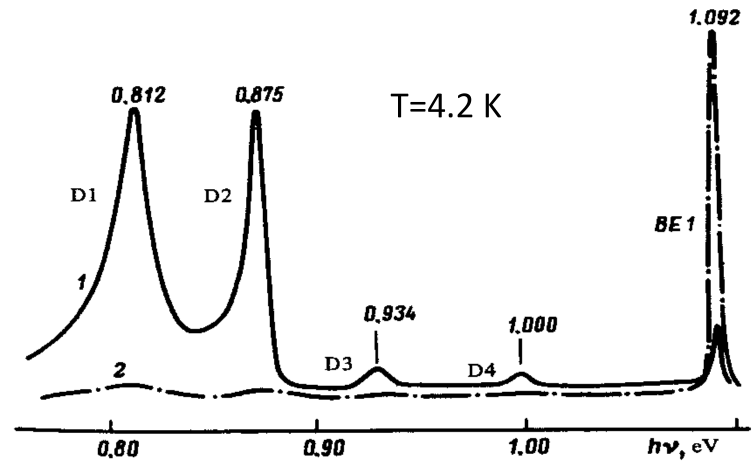
•Fingerprint of ingot thermal history:

Based on the PL intensity of P line at room temperature it was found that the effect of the thermal history of a crystal pulled at 0.8 mm/min was equivalent to an annealing at 500°C for 3 h *

*M. Hamada et al. Jpn. J. Appl. Phys., 35 (1996), 182

Dislocations

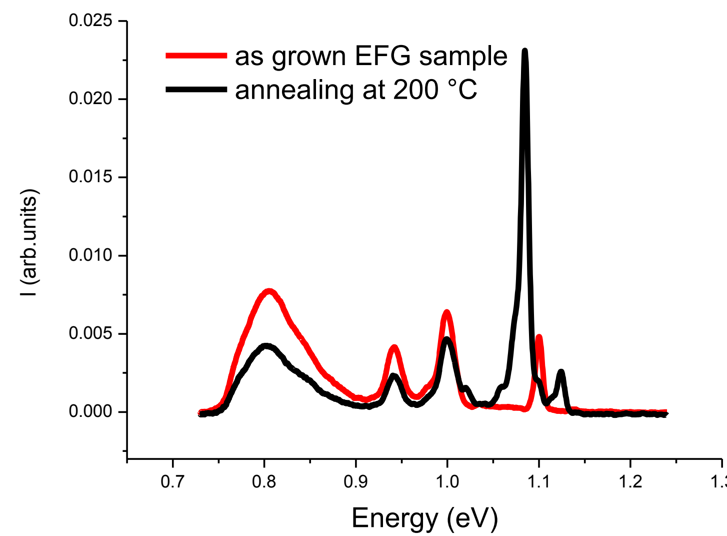
- D1 (E = 0.807 eV)
- D2 (E = 0.870 eV)
- D3 (E = 0.95 eV)
- D4 (E = 0.99 eV)



N.A. Drozdov Sov. Phys. JETP Lett 23, 597 (1976)

The D3/D4 lines are related to the intrinsic nature of dislocations due to the carrier recombination at straight segments of splitted 60° dislocations .

The D1 and D2 emissions do not occur physically together with D3 and D4 supporting the theory that the D1/D2 pair and the D3/D4 pair have different origins



The origin of the D1 and D2 lines is still not understood (impurity , metallic contamination, point like defects etc)

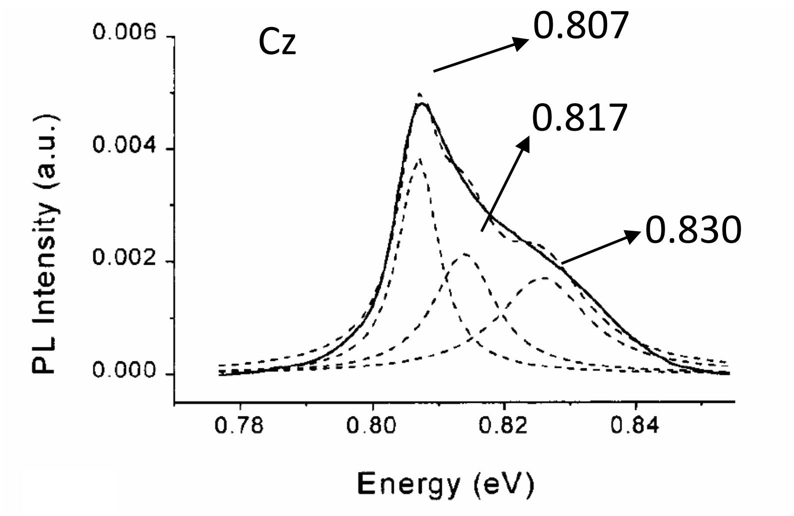
D1 is still present at room temperature

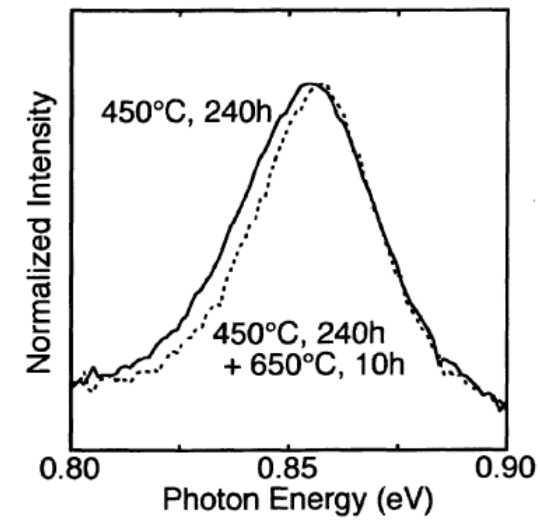
•The relative intensity of D bands can greatly vary from samples to another, can change after heat treatment

M. Suesawa, et al phys. stat. sol. (a) 79, 173 (1983) ; . M. Tajima, M. Ikebe, Y. Ohshita, and A. Ogura, J. Electron. Mater. **39(6), 747 (2010)**.
I. Burud, et al . AIP ADVANCES **2, 042135 (2012)**; M. Kittler and coworkers ; R. Slunjiki B. Pivac, A Le Donne , S Binetti SOLMAT 95 (2011) , 559

Oxygen precipitates by PL

Tajama et al. was the first to assign a luminescence line to oxygen precipitates at around 0.820 eV from 77 K to 150 and at 0.768 eV at 300 K

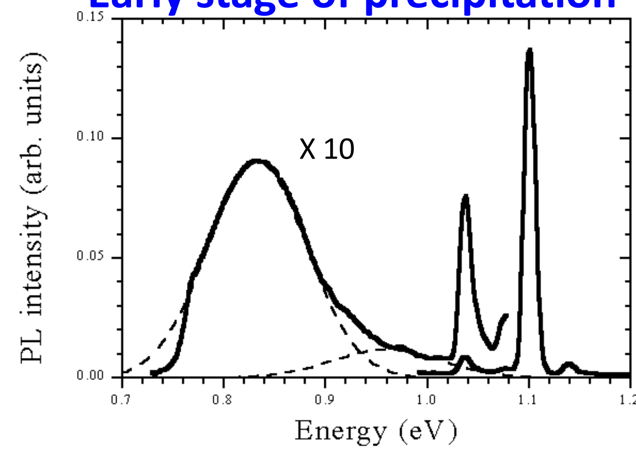




M. Tajima, et al. Mater. Sci. Forum, Vol. 83-87, 1327 (1995)

- 0.807 eV Dislocation
- 0.817 eV SiOx precipitates
- 0.830 eV nuclei
- 0.920 eV nuclei

Early stage of precipitation

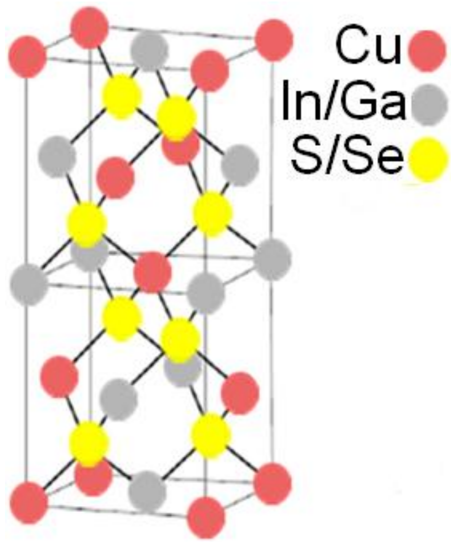


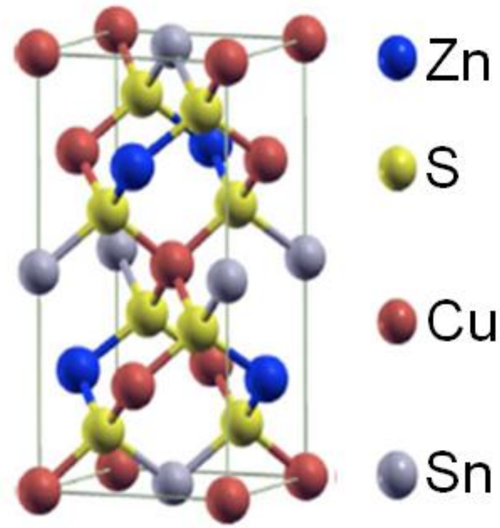
Gap states:

T2 trap (Ev+ 0.42 eV) related to the emission at 0.817 eV : F –C line (Ec- 0.37 eV) related to 0,807 eV

M. Tajima, et al Mater. Sci. Forum, Vol. 83-87, 1372 (1992) S. Binetti et al. J. Appl. Phys. 92, 2437 (2002)
E. Leoni, S. Binetti, et al, Eur. Phys. J.: Appl. Phys. 27, 123 (2004) ; D. Cavalcoli, S.Pizzini, S.Binetti App. Phys. Lett. 86, 162109, (2005)

PL spectroscopy on CIGS ($CuInGaSe_2$) and CZTS (Cu_2ZnSnS_4)





- ✓ no stoichiometric thin film
- ✓ intrinsic p-type doping due to point defects related levels in the bandgap (V_{Cu} for $Cu(In,Ga)Se_2$ and Cu_{Zn} for Cu_2ZnSnS_4)
- ✓ large number of both acceptor and donor levels associated to point defects
- ✓ Direct bandgap

➢The correlation among defects type and defect density and the growth processes is far to be completely understood and it is a key point in defining a pathway to future performance improvements

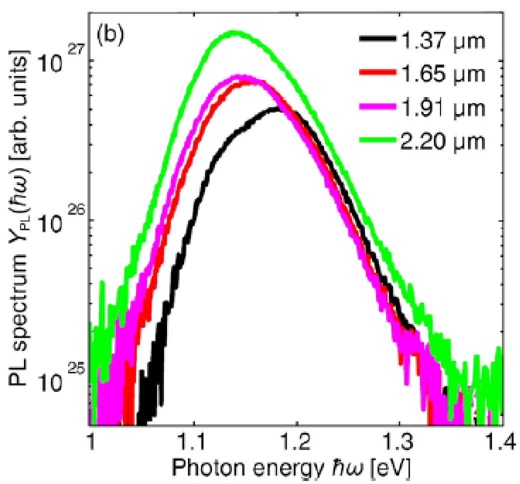
PL spectroscopy on $Cu(In,Ga)Se_2$ (CIGS)

➢PL spectra have been extensively studied, depend on stoichiometry of CIGS material

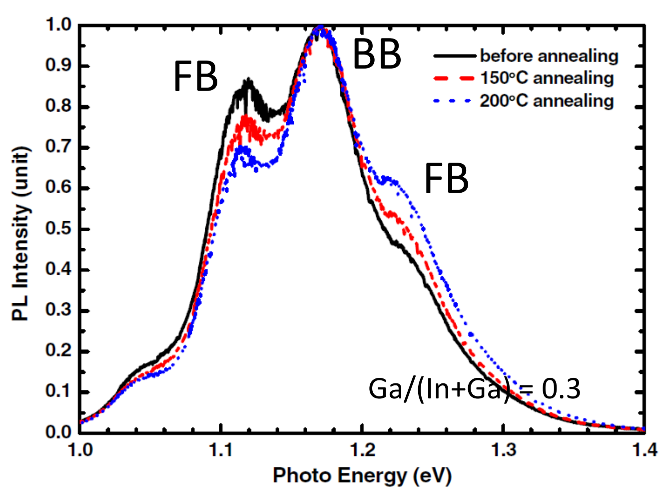
➢The PL spectra of solar cells, exhibit broad peaks, often merging into one featureless maximum

➢Donor–acceptor , free–to–bound and excitonic transitions can be inferred by P and T dependencies

➢Donor defect V_{Cu} (Ec+0.03 eV), acceptor defect V_{Se} (Ev-0.06 eV), deep level antisite defect In_{Cu} (Ec-0.16 eV) and many other defects all have been detected by PL ((V_{Cu}) as the acceptor and In_{Cu} as the donor involved in the DA recombination)

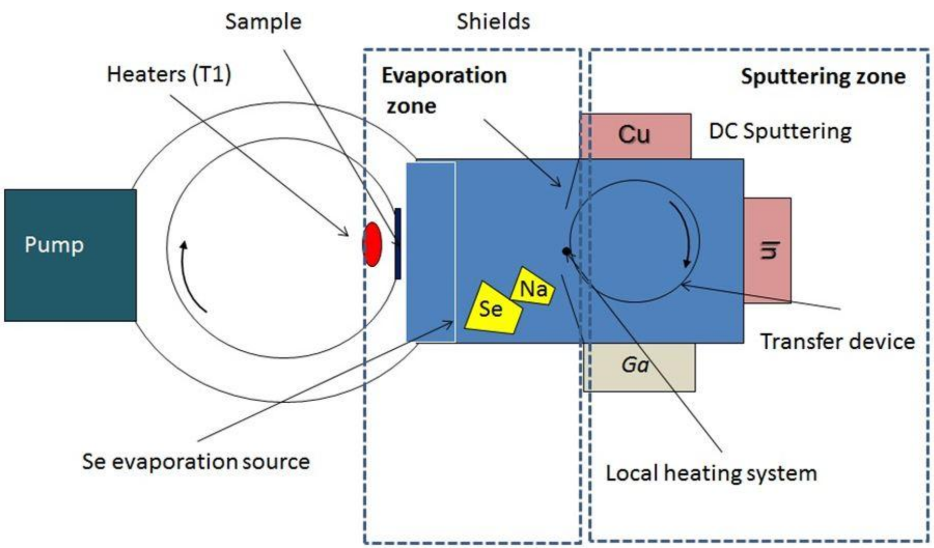


W. Witte et la . PIP 23, 717 (2015)



S.H. Chen et al., ECS Journal of Solid State Science and Technology, 4, 347(2015)

Optimization of hybrid sputtering /evaporation growth process * by PL

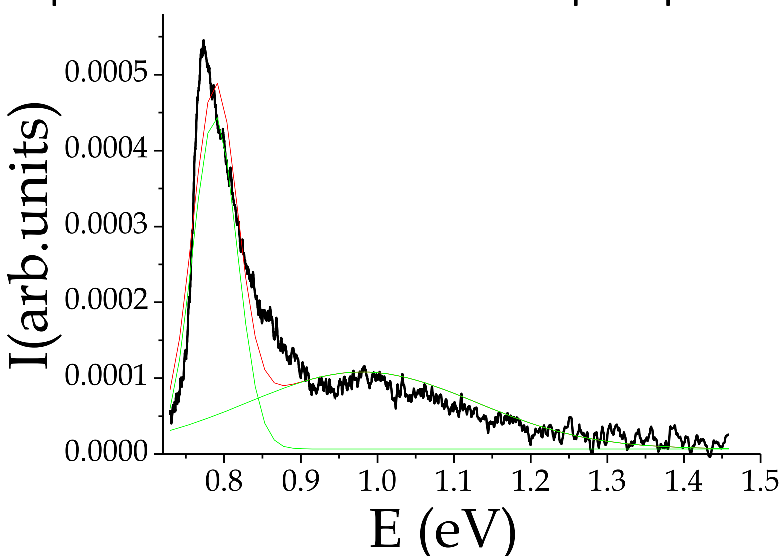


Substrate	Eff (%)	Voc (mV)	Jsc (mA/cm2)	FF (%)
130um Glass	13.2	496	38.9	68.6
Stainless steel	13.8	534.2	37.5	69.02
Upilex	11.7	512	35.6	64.34

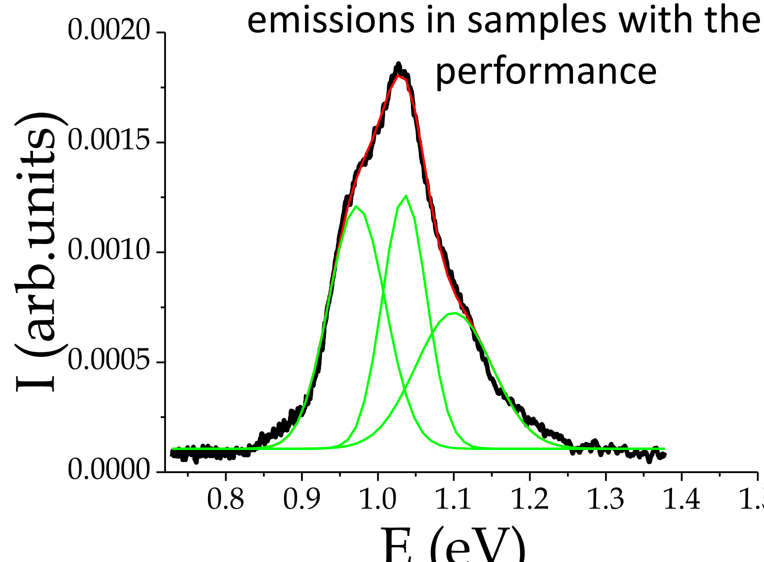
T_{dep}= 450 °C
Na by PDT

*S. Binetti et al. , Semicond. Sci. Technol. 30 (2015) 105006
-European Patent 2013 n° EP 13425019.0

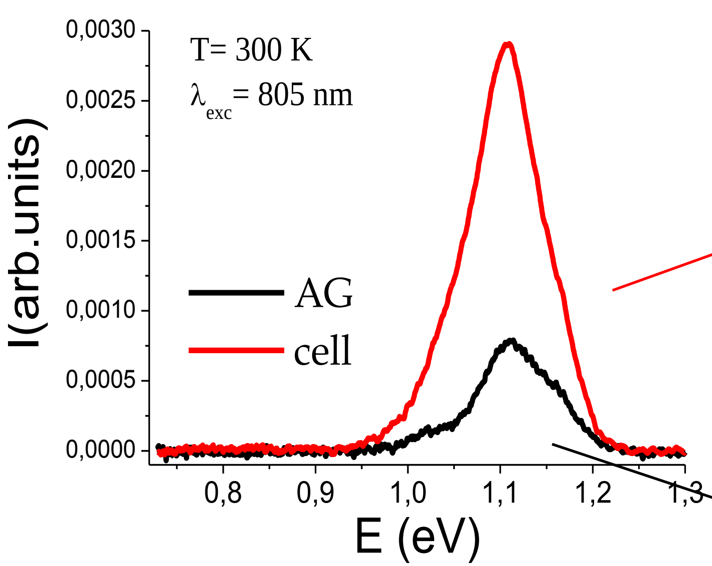
Higher intensity of emission from deep levels in samples with low Voc and overall poor performance

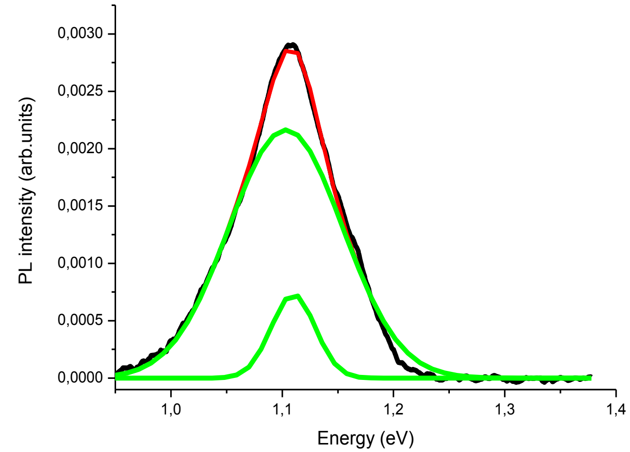


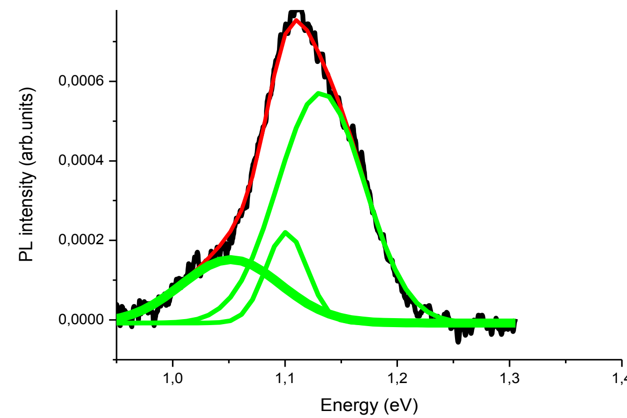
Higher intensity of DAP and BB emissions in samples with the best performance



PL investigation of surface passivation effects by Cd diffusion

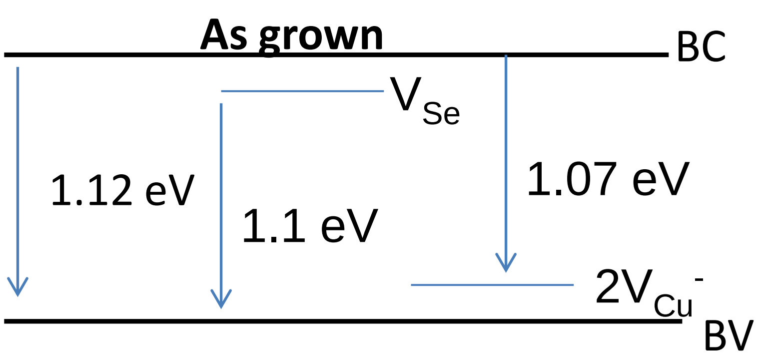


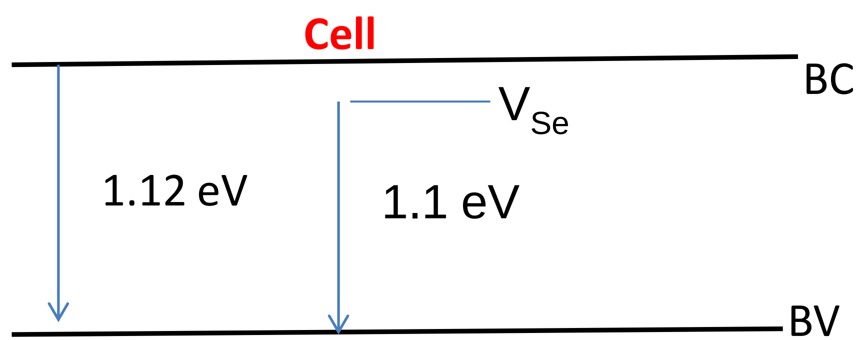




Cd (CdS) + V_{Cu} (CIGS) $\longrightarrow$ Cd_{Cu} (CIGS)

Hypothesis :



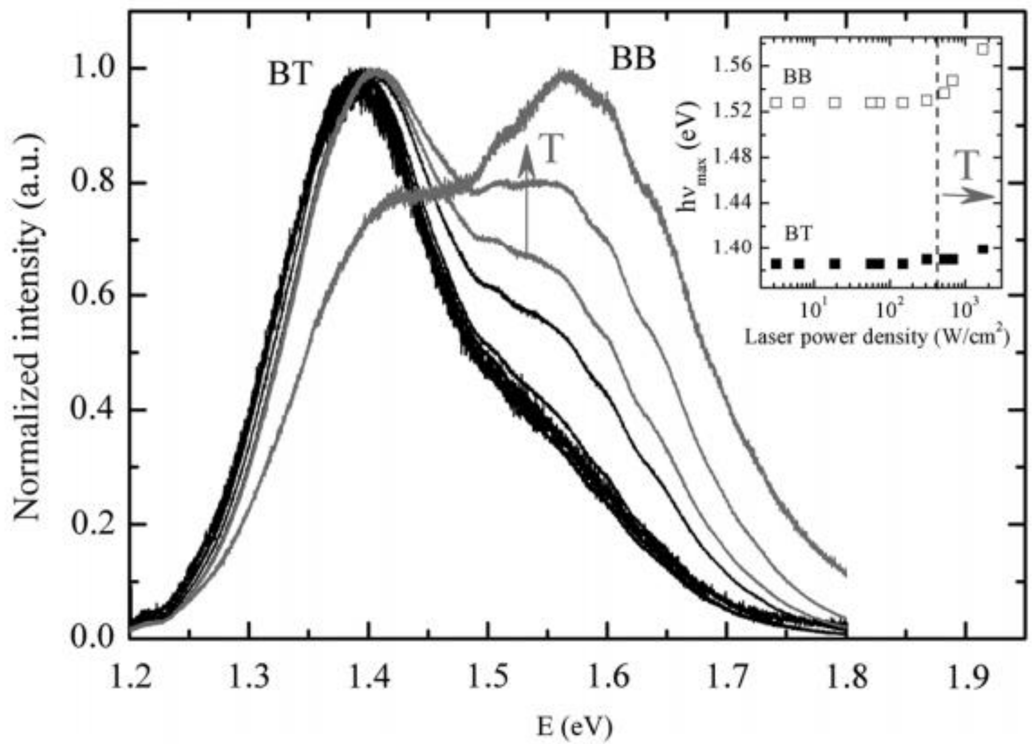


PL spectroscopy on $Cu_2ZnSnSe_4$ (CZTS)

A broad and asymmetric PL band has been detected in many studies.
It has been attributed both to donor–acceptor pair recombination and to free-to-bound recombination.

CZTS polycristal *
BB@ 1.53 eV
Band to tail (BT) @1.3 eV

Spatial potential fluctuations

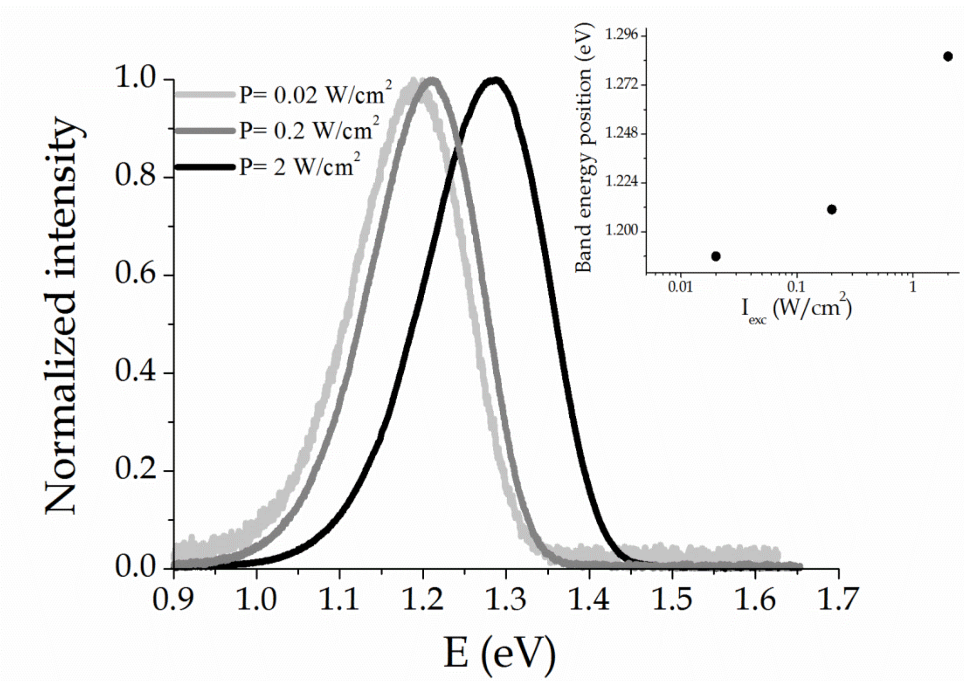


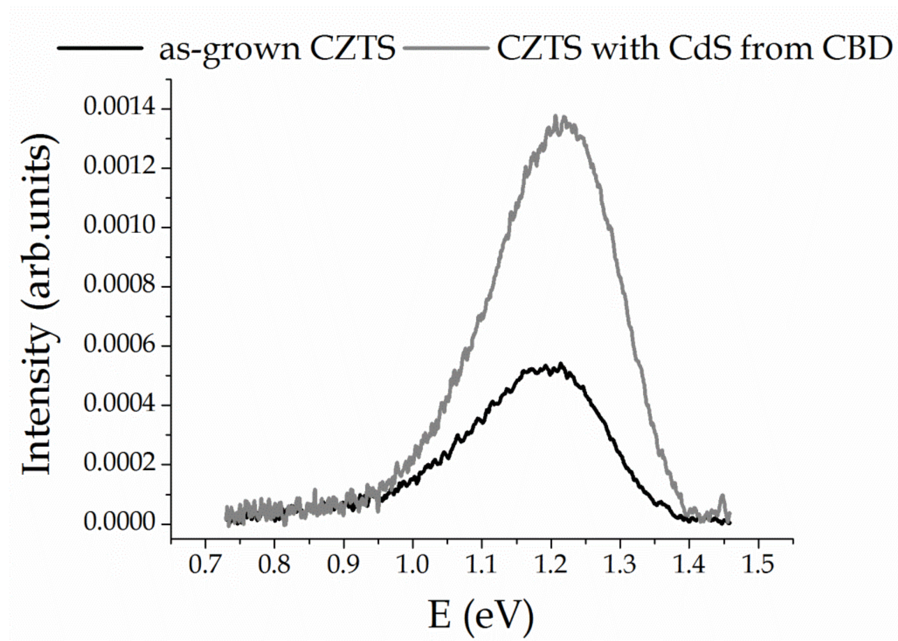
*M. Grossberg et al . Journal of Photonics for Energy 3 (2013) 030599

M.V Yakushev Thin solid films 582 (2015) 154

CZTS grown by sulphurization of stacked metal precursors deposited by RF sputtering: defects analysis by PL and effect of CdS buffer layer*

in Cu-poor/Zn-rich conditions : our best performance : η = 4 %





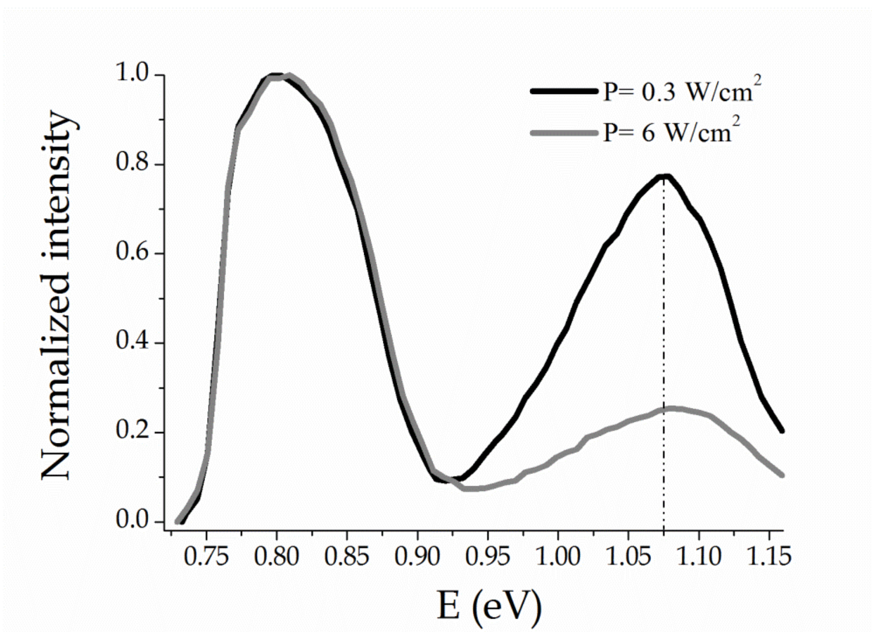
•Broad band centred around 1.21 eV: large blue shift for increasing excitation power ⇒ quasi-donor-acceptor pair (QDAP) transition, which involve potential fluctuations:

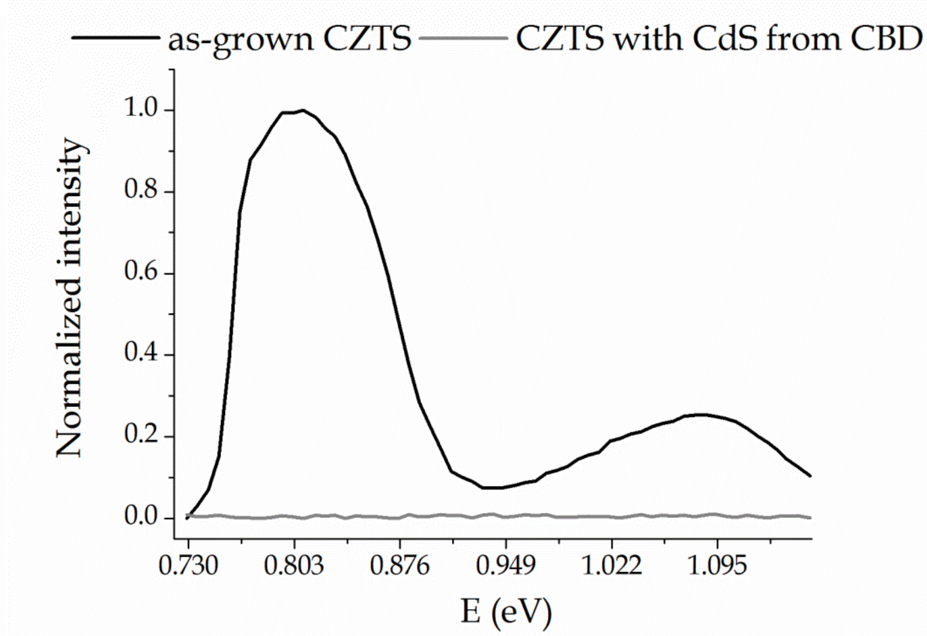
- the Cu_{Zn} acceptor level at 0.12 eV above the VB could be involved in the transition.

No passivation of the point defects involved in this emission by Cd atoms occurs at the CdS/CZTS interface as a consequence of the CBD process.

* S. Marchionna, et al & S. Binetti Thin Solid Films 542 (2013) 114–118;
A . Le Donne et al. & S. Binetti International Journal of Photoenergy Article ID 583058 - S. Chen et al., Physical Review B 81 (2010) 245204

Below bandgap excited PL (λ_{exc}=1064 nm-E_{exc}=1.165 eV) and effect of CdS buffer layer*





Luminescence peaks at 1.075 and 0.85 eV : an occupied acceptor level should be present at about 0.335 eV from the VB.

According to theoretical calculations**, Cu_{Sn} or Zn_{Sn} are probably involved in the absorption process of the 1064 nm radiation and in the emission at 1.075 eV, while $V_S$can be responsible for the emission at 0.85 eV.

The emissions at 1.075 and 0.85 eV both disappear in CZTS solar cells, : point defects involved in these emissions are passivated by Cd atoms at the CdS/CZTS interface

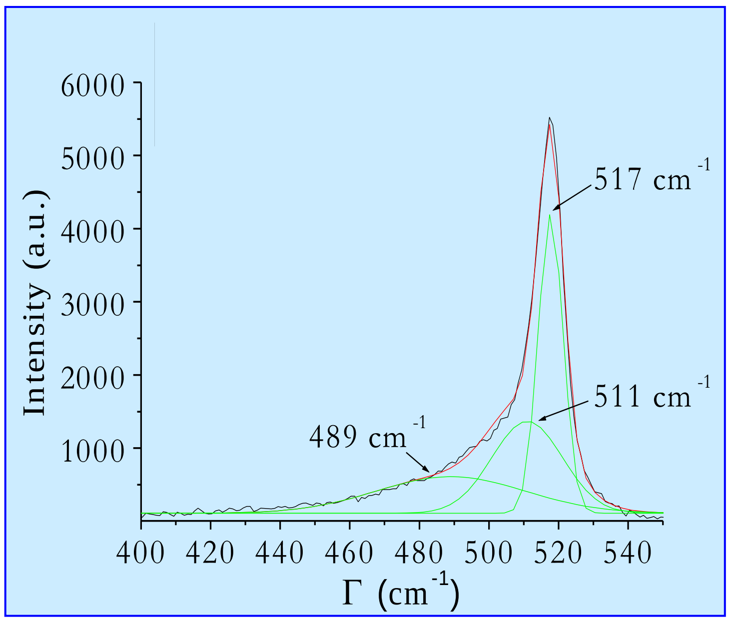
* A . Le Donne et al. & S. Binetti International Journal of Photoenergy Article ID 583058
**S. Chen et al., Physical Review B 81 (2010) 245204

Raman spectroscopy

- Raman spectroscopy is an optical techniques for the study of impurities and defects
- The line shape and position of the Raman bands are strongly sensitive to the presence of defects, strain, chemical composition and presence of secondary phases

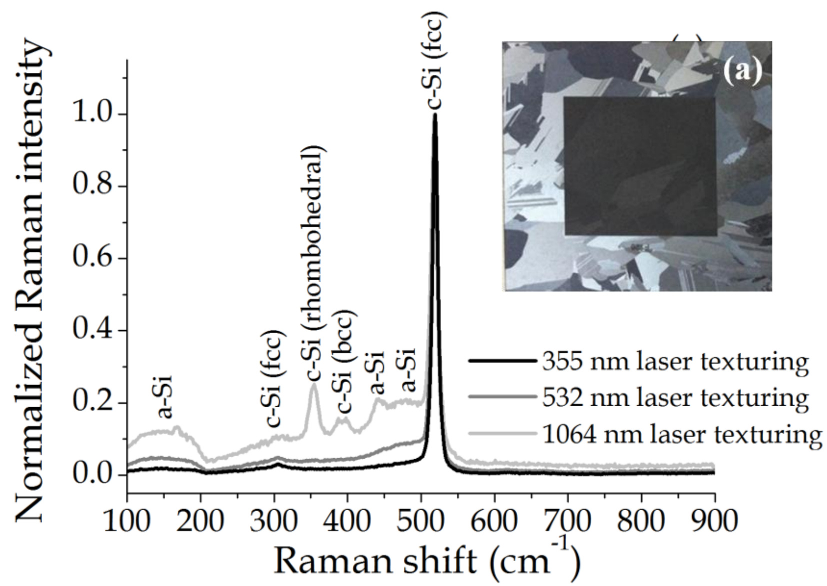
Silicon

nc- Si solar cell: cristallinity %



ALe Donne et al & Binetti Applied Surface Science 254, (2008)
S. Binetti et al. , Thin Solid Film **487**, 19, (2005)
P. L. Novikov et al .Appl. Phys. Letts **94**, 051904 (2009)

Picosecond laser texturization of mc-Silicon

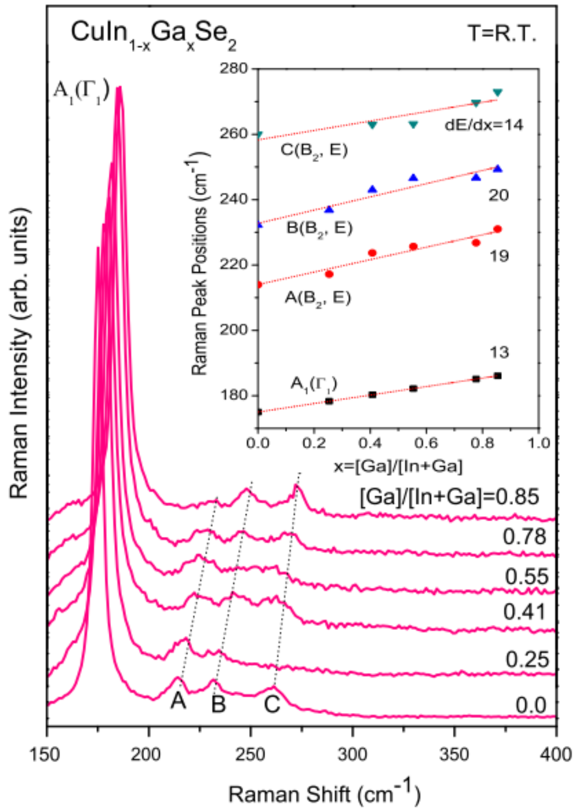


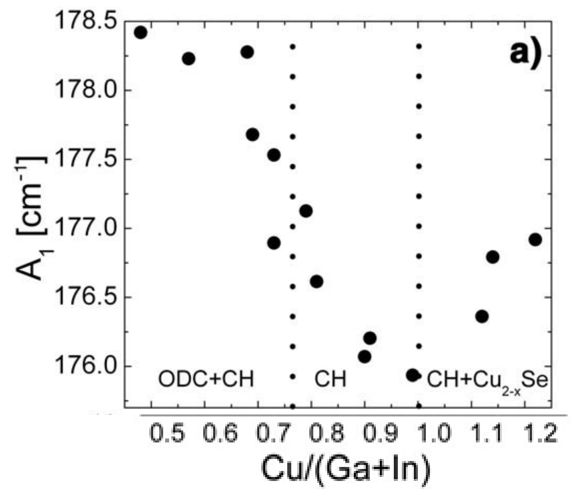
S. Binetti in Proceed. of CLEO: Applications and Technology, 2015 p.1021

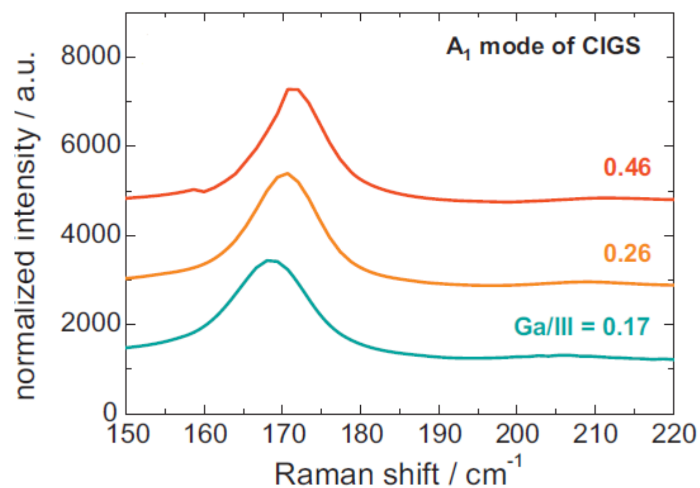
S. Binetti et al. submitted to Applied Surface Science (2016)

Raman spectroscopy in CIGS

- The main Raman mode A1 (vibration of the Se anions in the x-y plane with the cations at rest) increases linearly with increasing Ga content (from 174 cm^{-1} for CIS to 184 cm^{-1} for CGS): its position can be used to make a quantitative estimation of the mean [Ga]/[Ga]+[In] and its depth gradient – and depends on the relative Cu content
- a shoulder at 150–170 cm^{-1}, is attributed to the OVC (ordered vacancy compound) phase



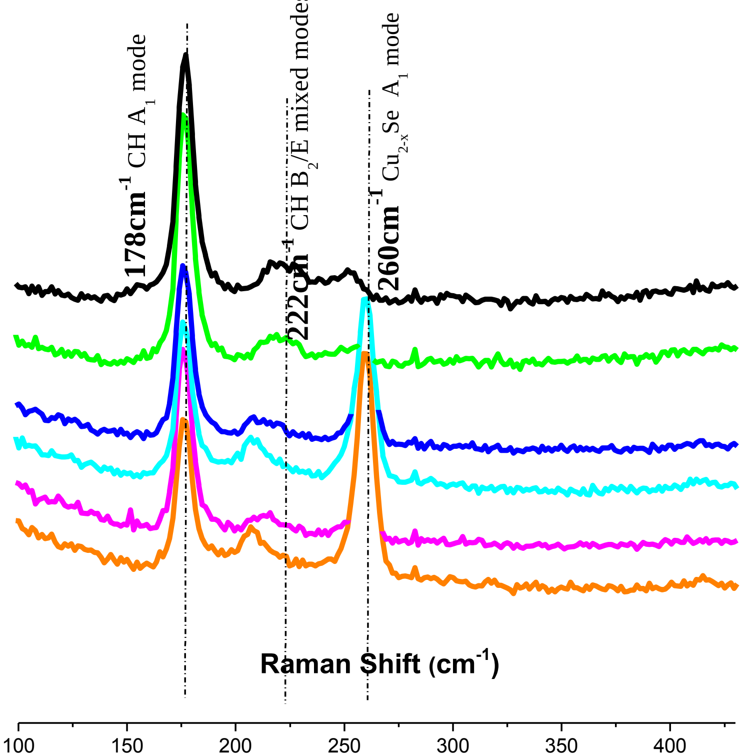


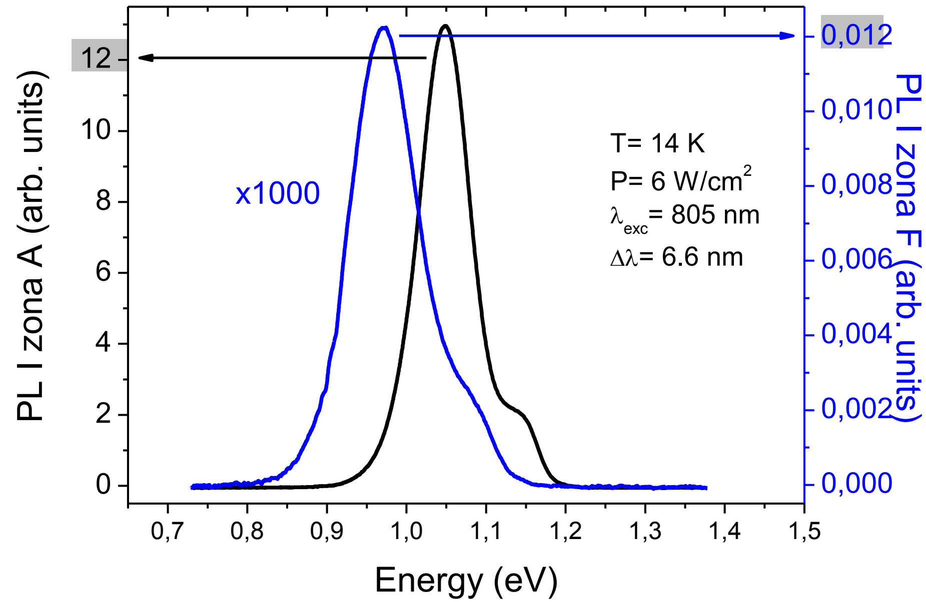


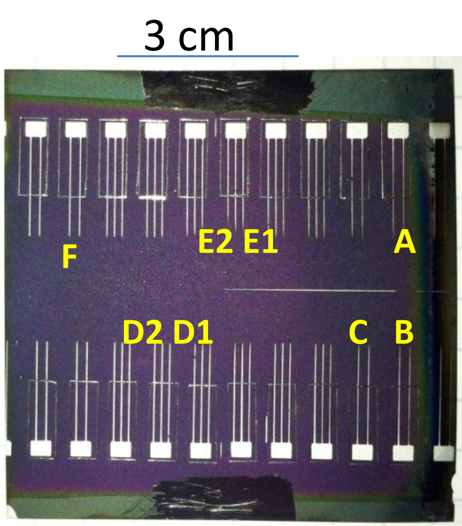
W. Witte et al . Thin Solid Films 517 (2008) 867–869;

Park et al., J. of Alloy and Comp. 513 (2012)068

Optical properties and cells parameters of samples grown by hybrid sputtering /evaporation process : Raman/PL investigations





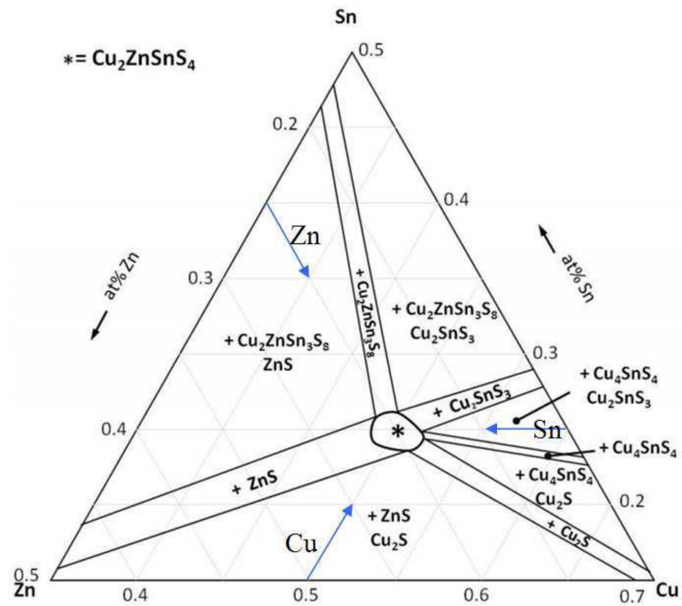


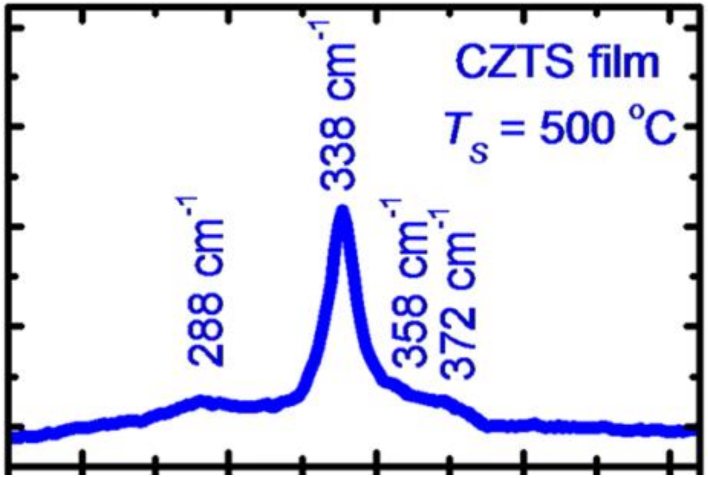
- inhomogeneity ; presence of $Cu_{2-x}Se$;
- Different radiative recombination paths

Substrate: steel foil							
Zona	*cella*	*η[%]*	*Voc[mV]*	*FF[%]*	*Isc[mA]*	*Jsc[mA/cm^2]*	*Cu/In+Ga*
A	2f_4p_a	7.63	490.33	48.22	4.84	32.27	0.76
F	2f_2p_a	0.03	11.57	22.29	1.59	10.63	1

Raman spectroscopy in CZTS

Different CZTS films synthesis approaches are under investigation .
Some of them are simple to implement but the process that lead to CZTS formation may be complex. Moreover, secondary phases are a particularly serious problem for CZTS because they are likely to occur as a consequence of the rather small existence region of single phase CZTS.

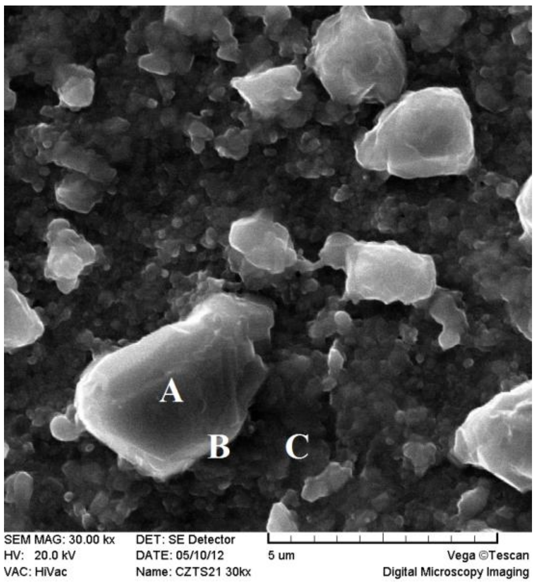


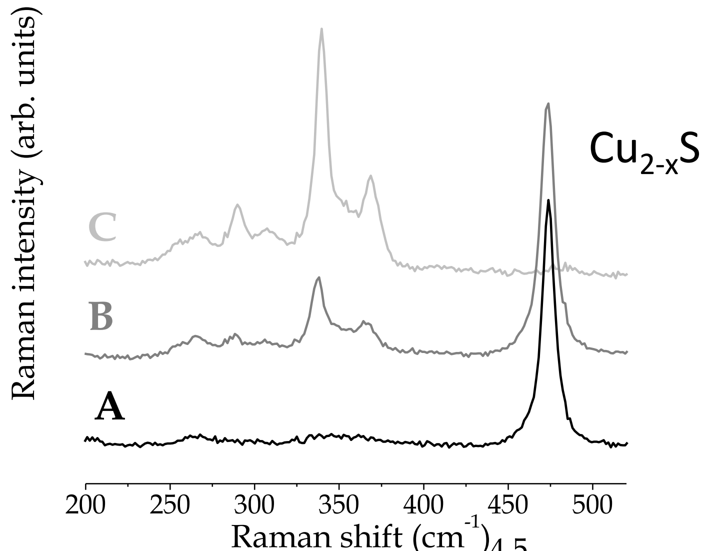


Most detrimental secondary phases:
- $Cu_{2-x}S$ heavily doped semi-conductor (metallic behaviour) (264, 475 cm^{-1})
- Cu_2SnS_3 intrinsic p-semiconductor with low E_g (298 , 336 , 351 , 355 cm^{-1})
-SnS_2 n-type semiconductor (315 cm^{-1})
- ZnS insulator (350 , 274 cm^{-1})

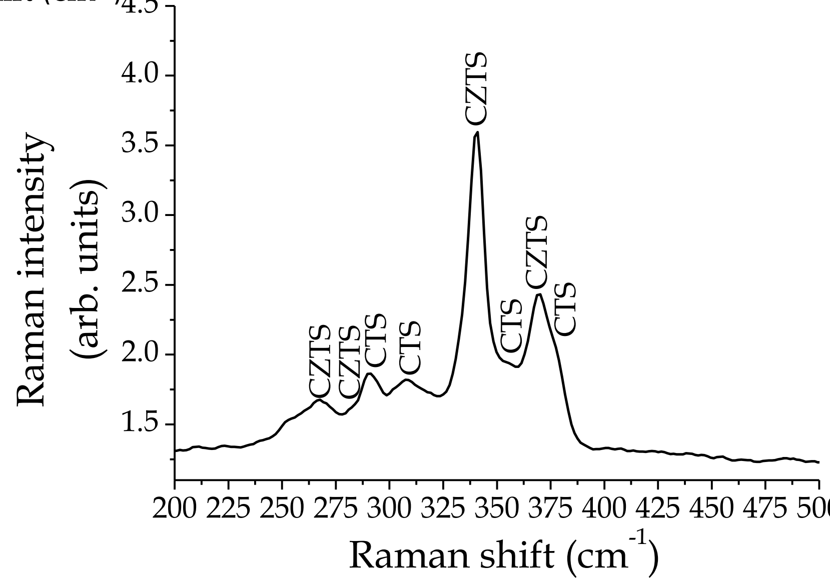
A-J Cheng J. Vac. Sci. Technol. A, 29,(5) 051203, (2011)

CZTS grown by sulphurization of stacked metal precursors deposited by RF sputtering *: Raman analysis





Cu rich conditions



Cu poor/Zn rich conditions: best performance

* S. Marchionna, et al & S. Binetti Thin Solid Films 542 (2013) 114–118; A . Le Donne et al. & S. Binetti International Journal of Photoenergy Article ID 583058

Conclusions

✓A lot of impurities, defects and complexes can be detected by PL and Raman spectroscopy

✓Advantages of PL and Raman spectroscopy:

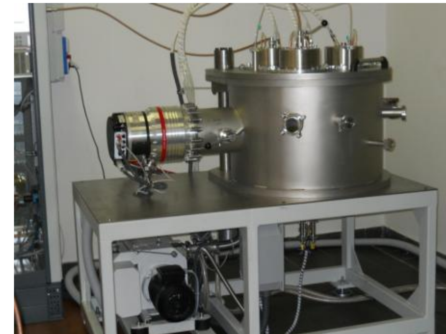
- are non-destructive techniques
- no particular sample preparation and handling are necessary
- impurities and defects can be detected even at low concentration
- are sensitive to the chemical species
- easy to used

✓Critical points

- No quantitative information
- small samples only and in some cases low temperature
- time consuming to map big samples

✓A lot of data and information are already in literature, but the application on own materials is not always straightforward

Thank you for your attention !



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