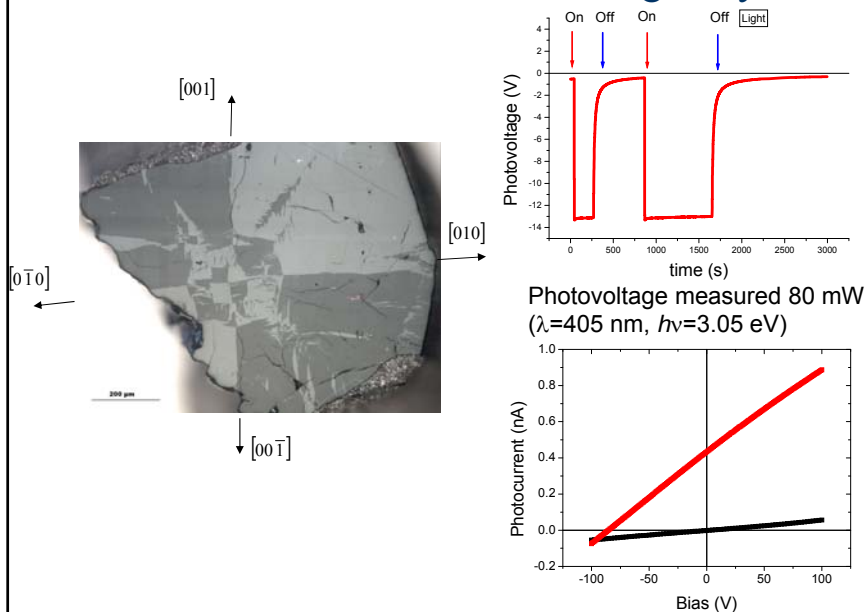


Abnormal photovoltaic effects in ferroelectric (BiFeO_3)

Marin Alexe

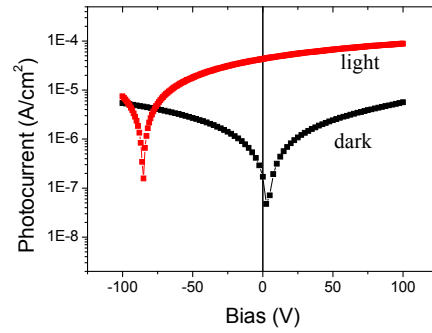
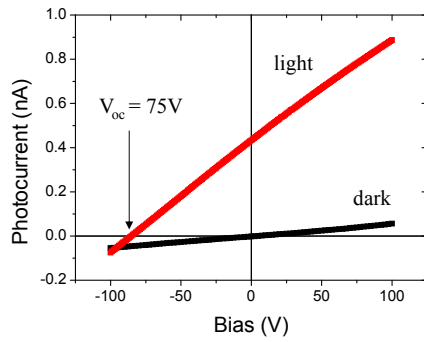
University of Warwick, Physics Department,
CV8 4AL Coventry, UK

Photovoltaic effect in BFO single crystals

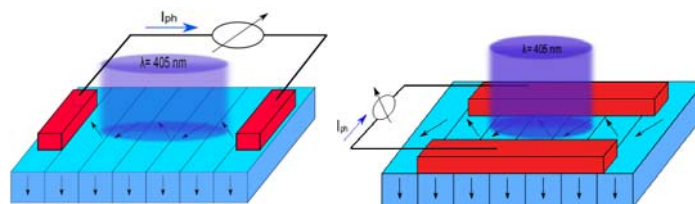
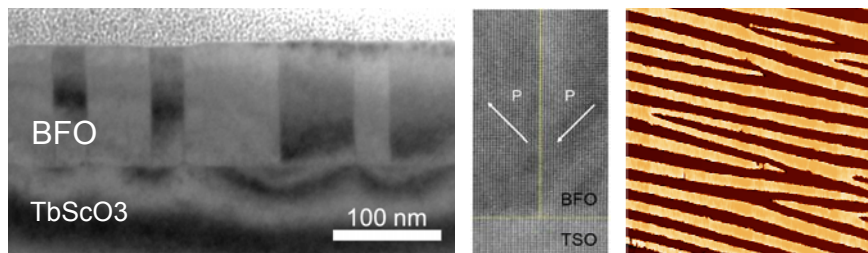


Thin film vs single crystal

Open circuit voltage – single crystal bulk



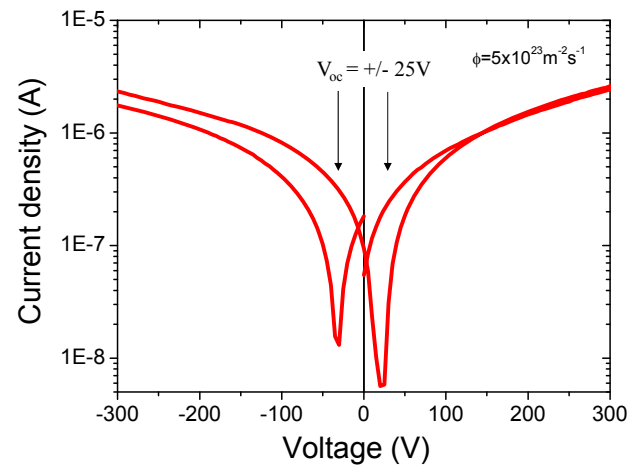
Thin film vs single crystal



Thin film vs single crystal

Open circuit voltage – Thin film

Parallel



- Origins of the abnormal PV effect

Photoelectric effect

Photoconductive effect

The left side shows two diagrams of a photoconductor. The top diagram shows a photon ($h\nu$) incident on a material with Fermi level E_F , generating an electron-hole pair. The bottom diagram shows the same material under an electric field E , with the generated carriers contributing to a current I . Below these is a graph of current I versus voltage V . A red line labeled 'illum' shows a linear increase in current with voltage, while a black dotted line labeled 'dark' shows a much lower, nearly constant current.

The right side shows energy band diagrams. Diagram (a) illustrates the Auger process where energy is transferred to a free electron or hole, and the radiative emission of a photon. Diagram (b) shows four stages of carrier capture and emission: (1) Electron capture, (2) Electron emission, (3) Hole capture, and (4) Hole emission. The bands shown are conduction band (E_C), valence band (E_V), and trap levels (E_t).

S.M. Sze, Physics of Semiconductor Devices, Wiley 1981

Photovoltaic effect

p-n junctions

The left side shows a p-n junction under illumination ($h\nu$). Below are four diagrams: (a) shows the depletion region with net donor density ($N_D - N_A$) and net acceptor density. (b) shows the area-diffusion potential ϕ_m . (c) shows the built-in potential V_{bi} . (d) shows the energy band diagram with conduction band (E_C), valence band (E_V), and Fermi level (E_F) across the junction.

The right side shows a graph of current versus voltage for a p-n junction. The curves shift upwards as the light level increases, showing an increase in short-circuit current (I_{sc}) and a decrease in open-circuit voltage (V_{oc}). Below the graph is a circuit diagram of a solar cell connected to a load R_L , showing the current I_L , diode current I_D , shunt current I' , and reverse saturation current I_S .

$$I_0 = I_L - I_D - I' = I_L - I_S \left(\exp \frac{eV_D}{kT} - 1 \right) - I' \dots$$

$$V_{oc} = \frac{kT}{e} \ln \left(\frac{I_L - I'}{I_S} + 1 \right)$$

I_L – photogenerated current
 I_D – diode current
 I' – shunt current
 I_S – reverse saturation current

SM Sze, Physics of Semiconductor Devices, Wiley 1981

Microscopic origins of APV

THE ORIGIN OF THE PHOTO-EMF IN FERROELECTRIC AND NON-FERROELECTRIC MATERIALS

W. RUPPEL, R. VON BALTZ and P. WÜRFEL

Department of Physics, University of Karlsruhe, D-7500 Karlsruhe, West Germany

(Received June 3, 1981)

$$f_{\text{ph}}(\mathbf{r}, \mathbf{k}) = f_{\text{eq}}[\epsilon_k - \eta(\mathbf{r})] + \delta f(\mathbf{r}, \mathbf{k})$$

Carrier distribution function under photo-excitation

$$f_{\text{eq}}(\epsilon_k - \eta) = \{1 + \exp[(\epsilon_k - \eta)/k_B T]\}^{-1}$$

Carrier distribution function at equilibrium,
Symmetric in k-space, can not generate current

$$\delta f(\mathbf{r}, \mathbf{k}) =$$

$$\tau \cdot G_{\text{opt}}(\mathbf{r}, \mathbf{k}) + \frac{\partial f_{\text{eq}}(\epsilon_k - \eta)}{\partial(\epsilon_k - \eta)} \cdot v_k \cdot \nabla_r \eta(\mathbf{r})$$

lifetime (pointing to τ)
Generation rate (pointing to G_{opt})
internal field (pointing to $\nabla_r \eta(\mathbf{r})$)

ϵ_k - energy; η = quasi-Fermi level

9

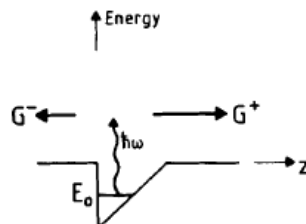
Microscopic origins of APV

1. $\nabla \eta(\mathbf{r}) \neq 0$ Classical case: gradient in Fermi level (chemical potential)
2. $G(+k) \neq G(-k)$ APV case: Generation rate asymmetric in k-space

$$\delta f^{as}(k) = \frac{1}{2} [G(+k) - G(-k)] \tau = G^{as} \tau$$

$$\mathbf{j}_{PG} = \sum_k -e \tau v_k G^{as} = -e l (G^+ - G^-), \quad \text{Photo-galvanic current}$$

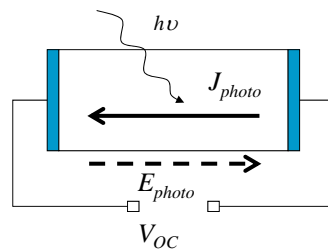
Example of asymmetric potential in pyroelectric crystal



10

Abnormal photovoltaic effect

- The abnormal photovoltaic effect or photogalvanic (photo-ferroelectric) effect



- In steady-state the photocurrent should be zero
- An internal field E_{photo} builds up to cancel the non-equilibrium carriers

Condition: $\Delta n \gg n_0$
(photo generated carrier density much higher than the thermally activated)

Anomalous Photovoltaic Effect

$$J^* = J + (\sigma_d + \sigma_{ph})E$$

- J^* is the transitional photocurrent density,
- J is the photovoltaic current density,
- σ_d and σ_{ph} are the dark and photoconductivities,
- E is the electric field formed due to the charging with photovoltaic current

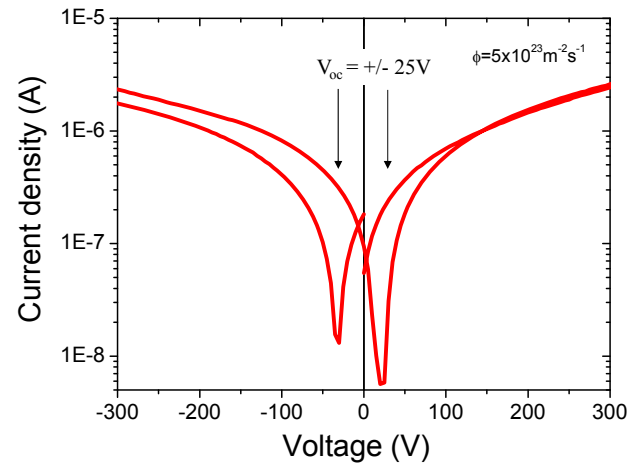
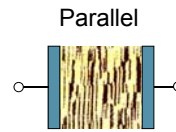
$$V_{oc} = \frac{J}{\sigma_d + \sigma_{ph}} l$$

- V_{oc} is the open circuit voltage
- l is the distance between electrodes

Fridkin, V. M., *Photoferroelectrics*,
Springer-Verlag Berlin Heidelberg New York, 1979

Thin film vs single crystal

Open circuit voltage – Thin film

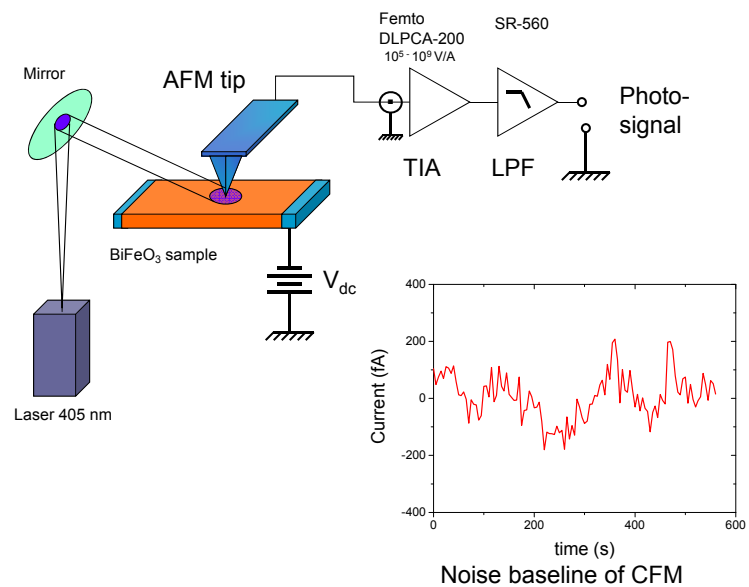


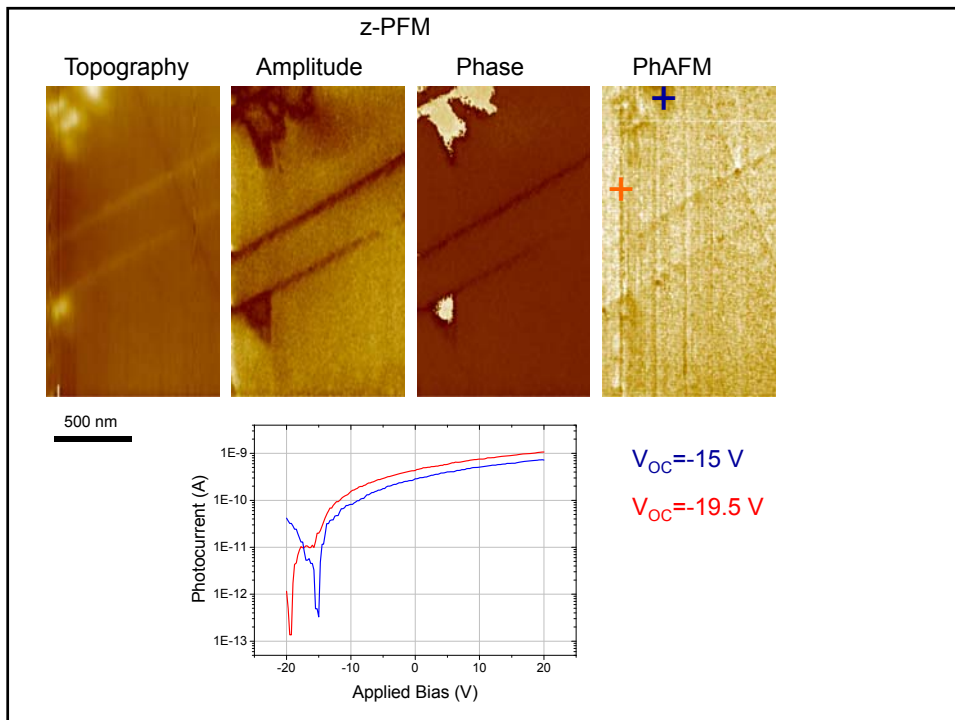
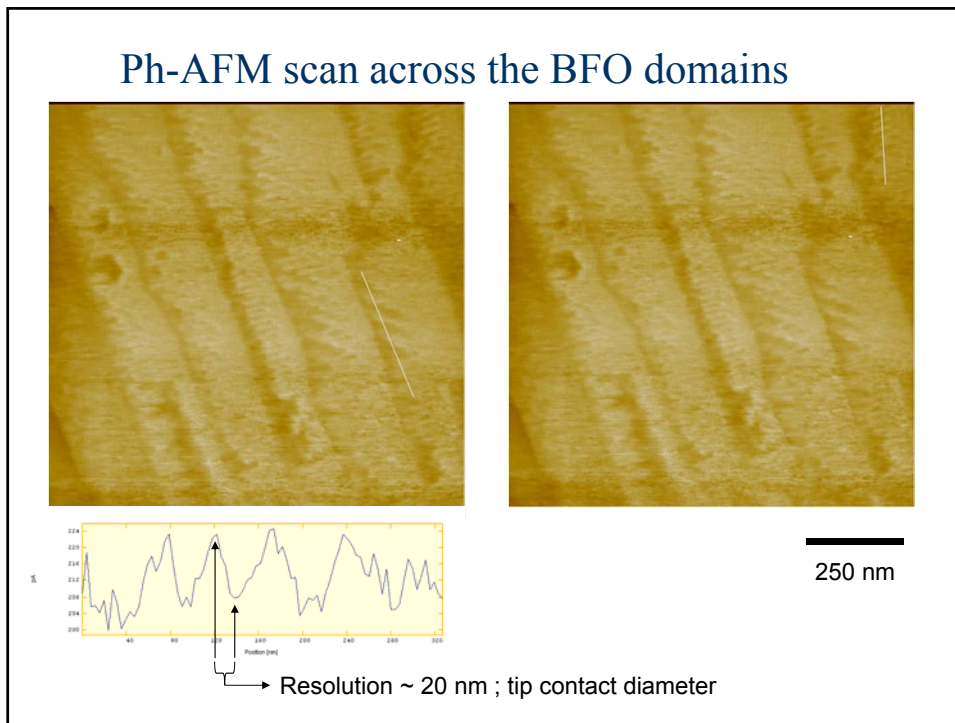
APV effect

- The abnormal photovoltaic effect in BFO is solely due to photogalvanic (photo-ferroelectric) effect or bulk PVE
- The BPV photocurrent is tensorial in nature
- It depends solely by the crystalline structure

Time-resolved photoelectric force microscopy for high resolution mapping of recombination centers

Photoelectric force microscopy





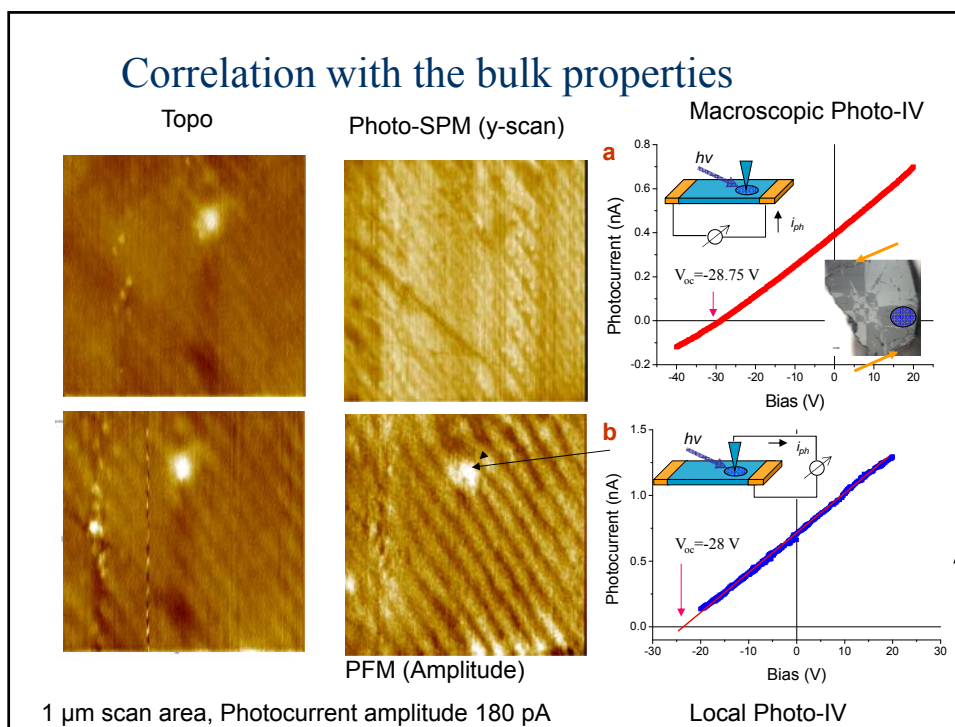


Photo-induced transient spectroscopy*

Nanoscale mapping of generation and recombination lifetimes

*M. Alexe, Nano Letters 12, 2193 (2012)

Photo-induced transient spectroscopy – PITS

Determination of deep levels in Cu-doped GaP using transient-current spectroscopy

Bruce W. Wessels

General Electric Corporate Research and Development, Schenectady, New York 12301
(Received 19 May 1975)

A method of determining deep levels in semiconductor junctions by observation of the temperature dependence of transient-current decay is described and applied to Cu-doped GaP. It is shown that the important deep-level parameters including trap energy, capture cross section, concentration, and recombination rate can be obtained. For Cu-doped GaP, several trapping levels were observed with energies of 0.50, 0.62, and 0.82 eV. Capture cross sections of these levels were of the order of $1 \times 10^{-16} \text{ cm}^2$.

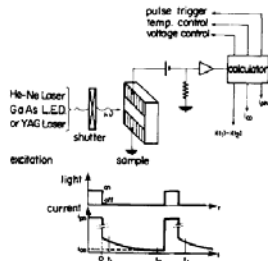
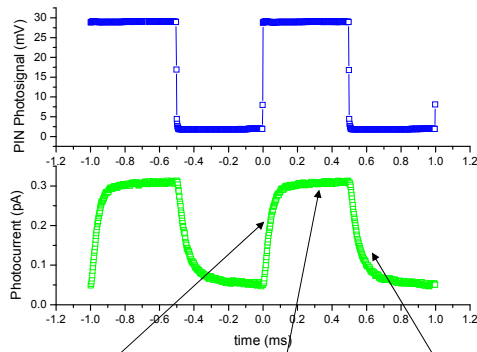


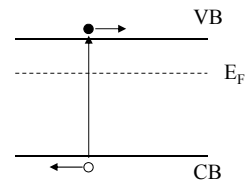
FIG. 1. Principle of the experiment.

Appl. Phys. Lett. 32(12), 15 June 1978

Laser 405 nm (3.08 eV)



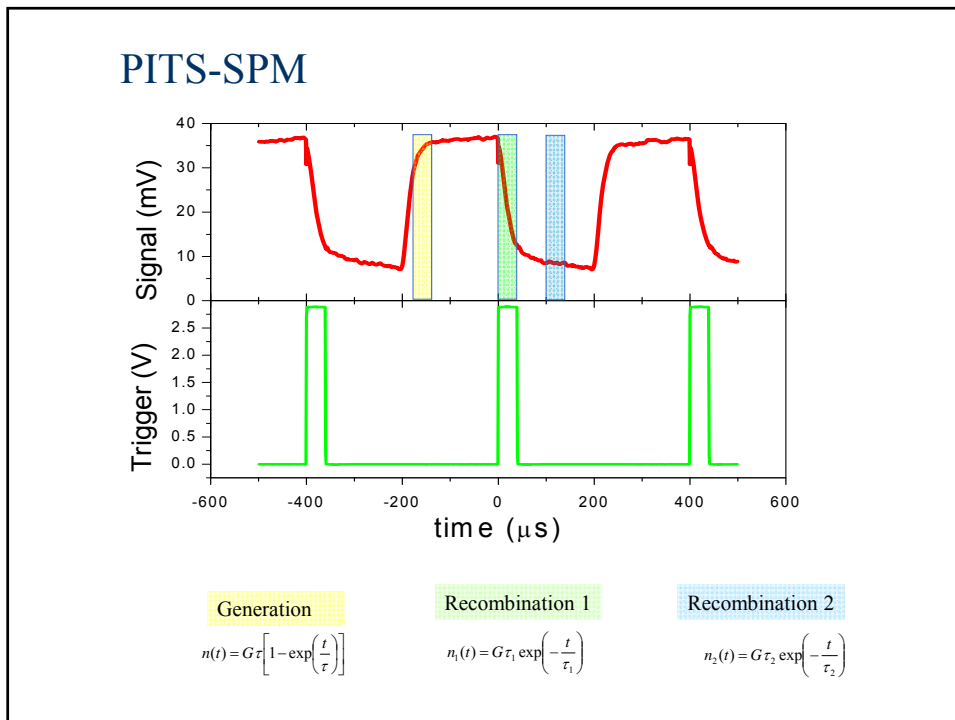
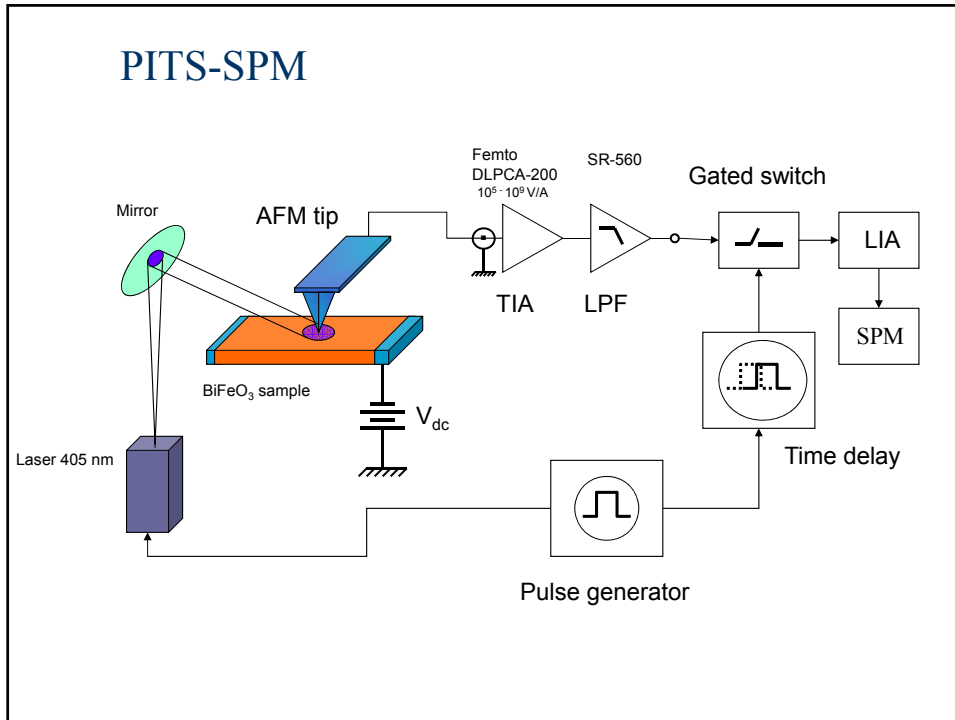
$E_g = 2.7 \text{ eV}$

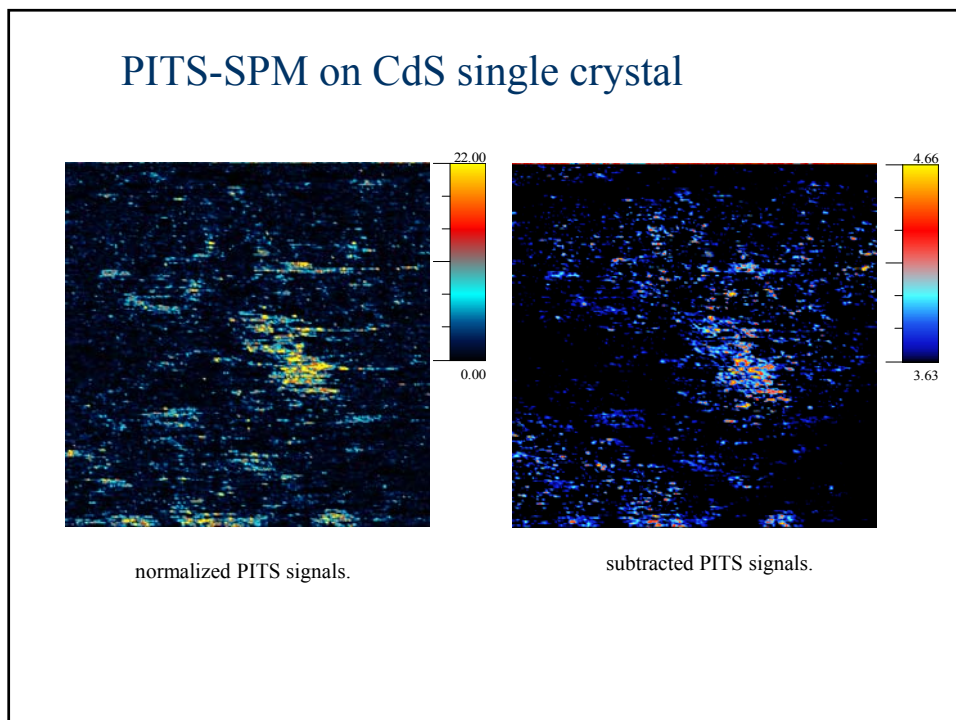
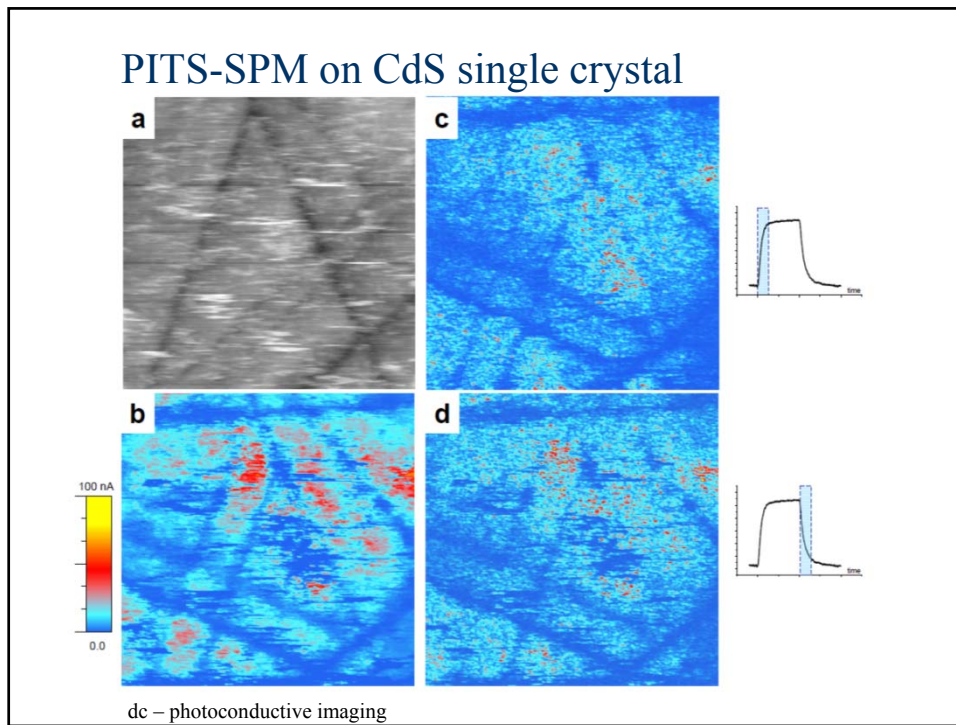


$$\text{Rate equation: } \frac{\partial n(t)}{\partial t} = G - R = G - \frac{n(t)}{\tau_{\text{eff}}}$$

G - rate of excitation
R - recombination rate
n - photoinduced carrier density
 τ - carrier (effective) lifetime

Rise curve: $n(t) = G\tau \left[1 - \exp\left(-\frac{t}{\tau}\right) \right]$ Steady state: $n(t) = G\tau$ Decay curve: $n(t) = G\tau \exp\left(-\frac{t}{\tau}\right)$





Conclusion

- PITS-SPM is a powerful technique to map the defects and recombination centers
- Lateral resolution in the range of tip-surface contact diameter (20 nm)
- Temperature dependence will add energy resolution