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X-ray radiation effect on colloidal quantum dot  
based short-wavelength infrared photodiode

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# Introduction

# Introduction

Necessity of short wavelength infrared (SWIR) detectors – Basic applications

Tesla's autonomous vehicle system

Using visible camera

SWIR image sensor



<https://www.tesla.com/autopilot>

Risk of accidents at night and in bad weather

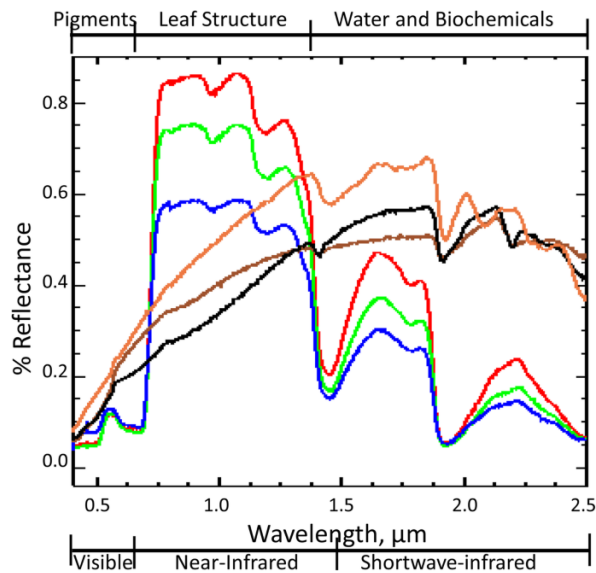


<https://www.sensorsinc.com/gallery/images>

Acquisition of invisible information

## Advantages for earth observation using SWIR imager

Ecological Processes 10, 1, 2021



## Low-reflectance in 1420 nm wavelength

- We believe that the monolithic CQD-based SWIR imager is a promising candidate for a cost-competitive observation system for earth observation



## ESA's earth observation program from 2010 to 2023

# Introduction

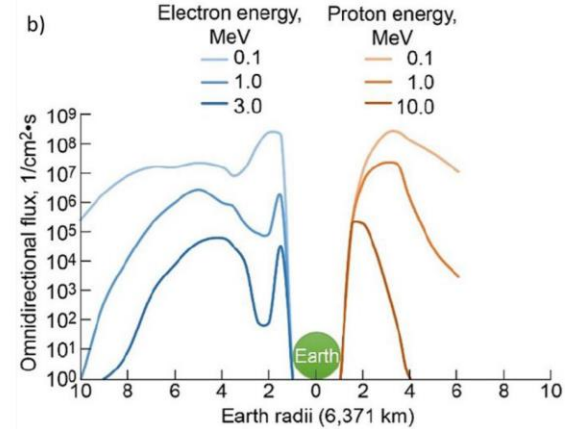
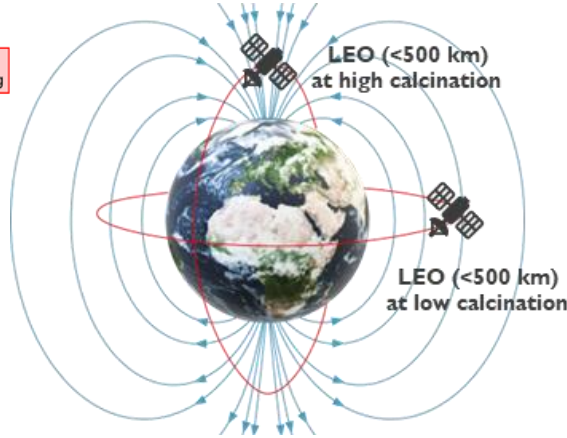
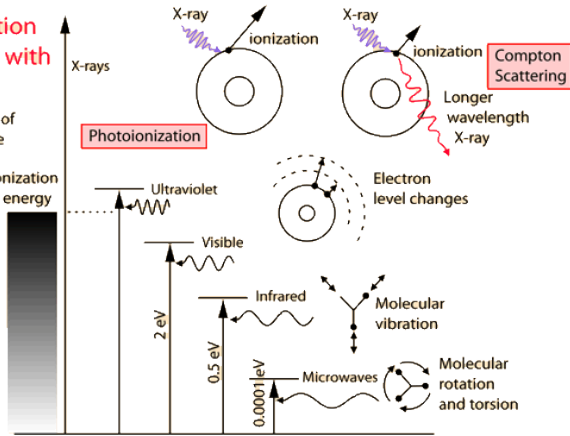
## Radiation effects on near-Earth orbit

### The interaction of radiation with matter.

Click on any type of radiation for more information.

Large number of available energy states, strongly absorbed.

Small number of available energy states, almost transparent.

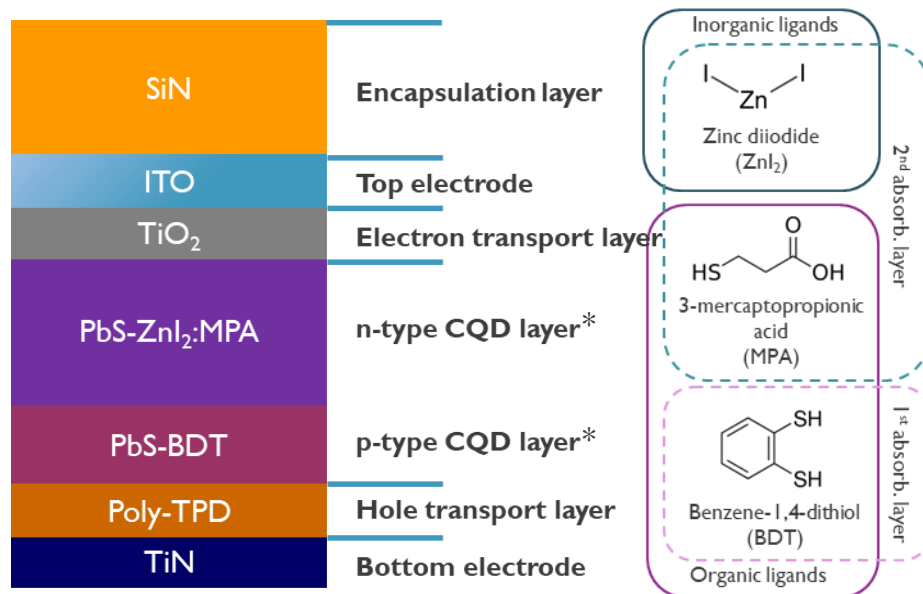


- X-rays have a high ionization energy, which is a suitable to test radiation effects.
- In near-Earth orbit (<500 km), the artificial satellites are exposed to 0.1-1 krad(Si)/year on low inclination and 1-10 krad(Si) on higher inclinations

# Our approaches

# Device structure (TFPD)

## Key issues under X-ray irradiation



\*CQDs are selected for 1420 nm detection

## ■ Issue

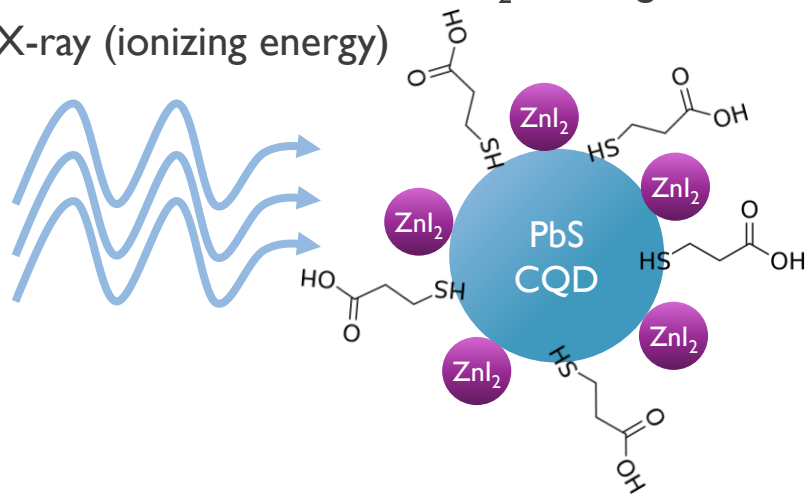
- How much is affected under X-ray (ionizing energy) radiation?
  - 220 krad(Si) is enough to understand the robustness of X-ray radiation in near-Earth space for 10 yrs.
- Which layer is a dominant layer in determining device performance?
  - Interface between ETL and CQD
  - Interface between HTL and CQD
  - Interface between n-type and p-type CQDs

# Hypotheses – Materials(I)

Investigation of influence under X-ray irradiation

## Hypotheses

X-ray (ionizing energy)



1. Ionizing radiation generates electron from PbS CQDs to ligands
  1. PbS CQD loses the electrons (loss electron)
  2.  $\text{ZnI}_2$  becomes  $\text{ZnI}_3^-$
2. Ionizing radiation generates electron from ligands
  1.  $\text{ZnI}_2$  loses electrons and separates as  $\text{ZnI}^+$  and the oxidized iodide
  2. Hydroxyl group in MPA loose electron and Hydrogen becomes free



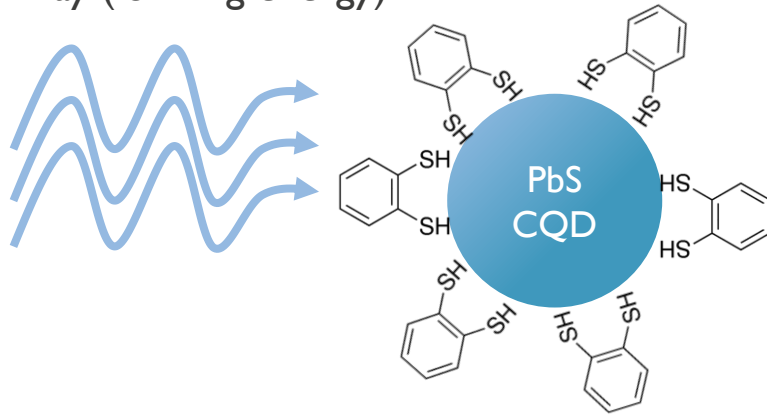
# Hypotheses – Materials(II)

Investigation of influence under X-ray irradiation

## Hypotheses

PbS-BDT ligands

X-ray (ionizing energy)



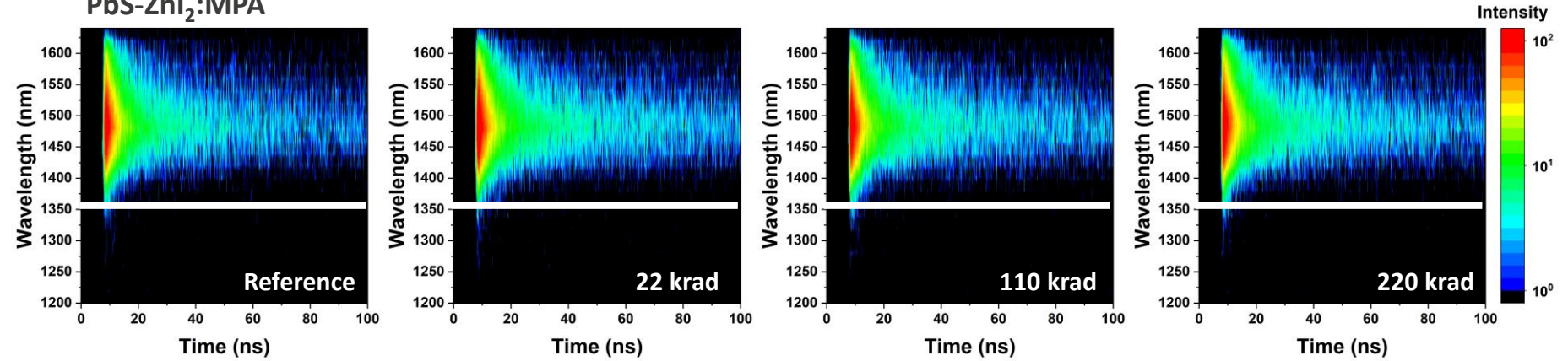
- I. Ionizing radiation generates electron from ligands
  1. BDT loses electrons and separates as  $\text{BDT}^+$
  2. And BDT will be delaminated from PbS CQD layer

## Results - Materials characterization

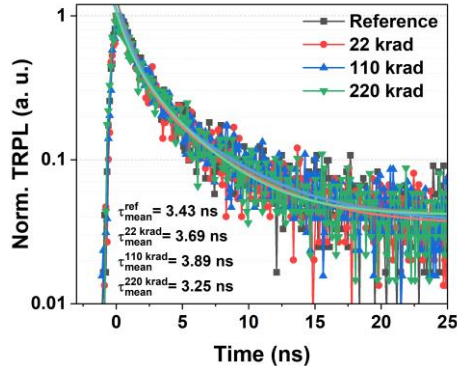
# Materials characterisation - I

## Time-resolved photoluminescence (TRPL)

PbS-ZnI<sub>2</sub>:MPA



Pump wavelength: 1460 nm



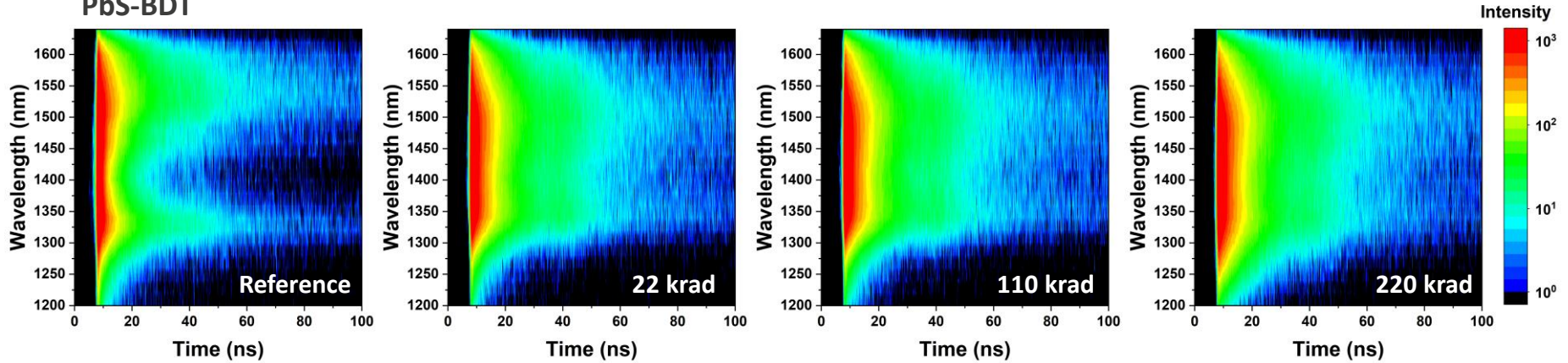
### ■ Biexponential treatment to extract the mean carrier lifetime

- $I_{PL}(t) = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}})$
- $\tau_{\text{mean}} = [A_{\text{fast}} \tau_{\text{fast}}^2 / (A_{\text{fast}} \tau_{\text{fast}} + A_{\text{slow}} \tau_{\text{slow}})] + [A_{\text{slow}} \tau_{\text{slow}}^2 / (A_{\text{fast}} \tau_{\text{fast}} + A_{\text{slow}} \tau_{\text{slow}})]$
- $\tau_{\text{mean}}^{\text{ref}} = 3.43 \text{ ns}, \tau_{\text{mean}}^{22 \text{ krad}} = 3.69 \text{ ns}, \tau_{\text{mean}}^{110 \text{ krad}} = 3.89 \text{ ns}, \tau_{\text{mean}}^{220 \text{ krad}} = 3.25 \text{ ns}$

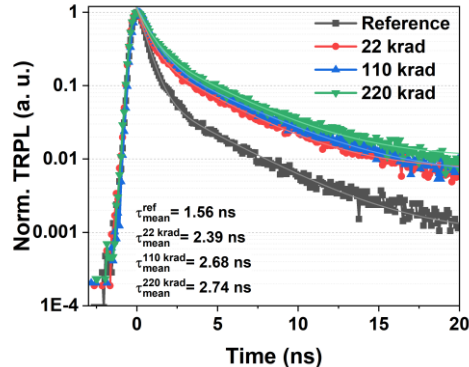
# Materials characterisation - I

## Time-resolved photoluminescence (TRPL)

PbS-BDT



Pump wavelength: 1460 nm



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- $\tau_{\text{mean}}^{\text{ref}} = 1.56 \text{ ns}, \tau_{\text{mean}}^{22 \text{ krad}} = 2.39 \text{ ns}, \tau_{\text{mean}}^{110 \text{ krad}} = 2.68 \text{ ns}, \tau_{\text{mean}}^{220 \text{ krad}} = 2.74 \text{ ns}$

# Hypotheses – Materials(I)

Investigation of influence under X-ray irradiation

## Hypotheses

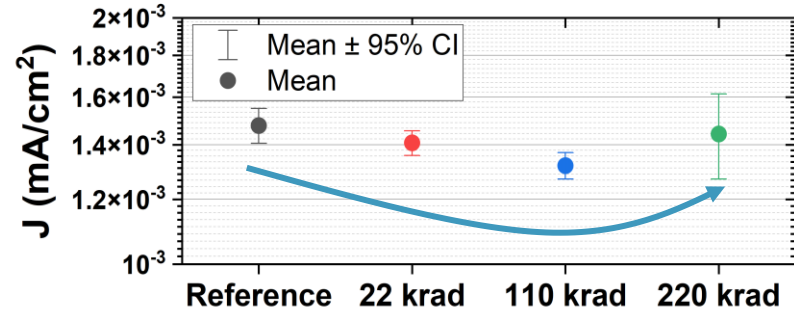
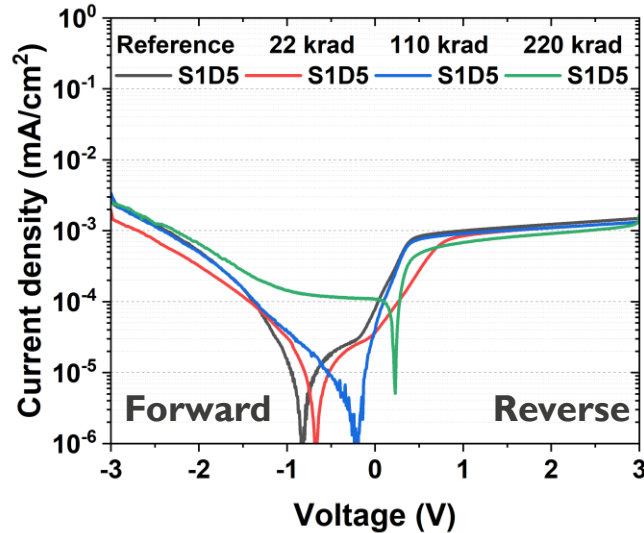
PbS-ZnI<sub>2</sub>-MPA ligands

PbS-ZnI<sub>2</sub>:MPA has a robustness under X-ray radiation

## Results - Device characterization

# J-V measurement

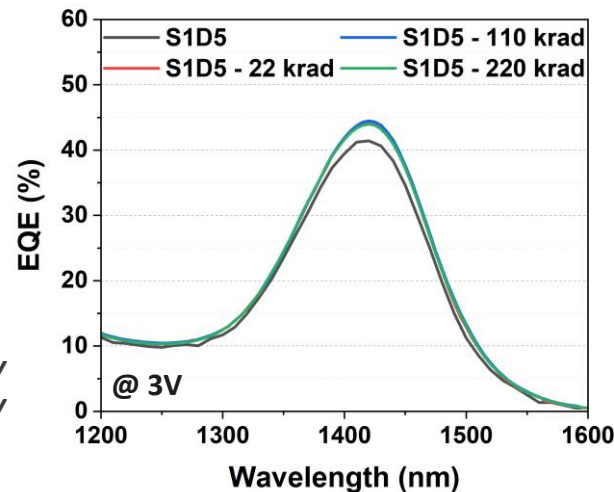
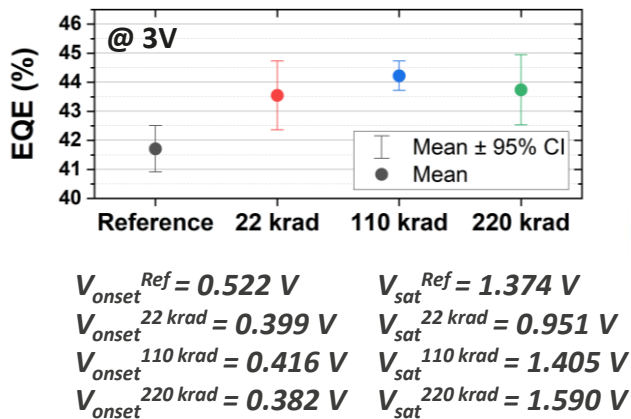
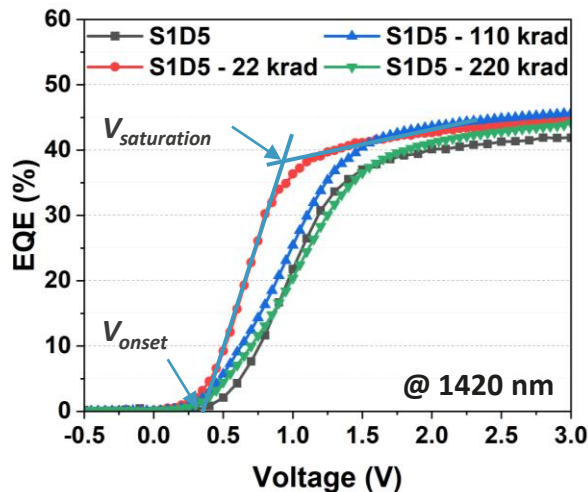
TFPD



- According to the increase in X-ray radiation dose (Total ionizing dose, TID), the leakage current was decreased slightly until 110 krad, after that was recovered.

# EQE measurement

## EQE vs Voltage / EQE vs Wavelength

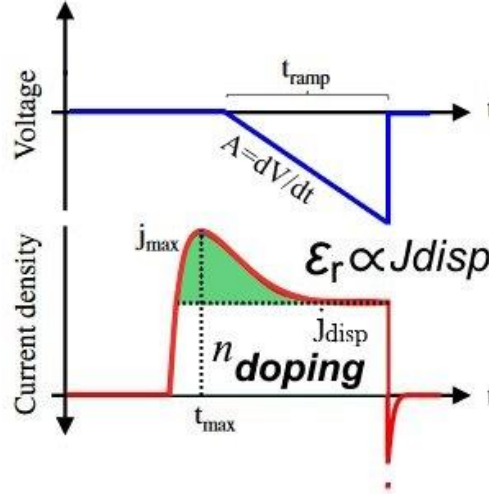
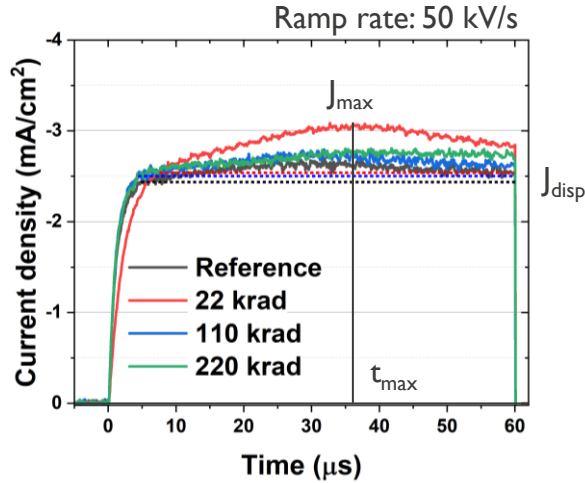


- In EQE vs Voltage graph, the initial X-ray dose (22 krad) helped to enhance of onset voltage.
  - thereafter, it tends to return to its initial performance. That is, performance decreased.
- In EQE vs Wavelength graph, X-ray radiation seemed to affect the enhancement of EQE performance



# Data physics - I

## Dark Charge Extraction by Linearly Increasing Voltage (Dark-CELIV)



ramp rate  $\rightarrow$  relative permittivity  $\rightarrow$  thickness

$$j_{\text{disp}} = \frac{A \epsilon_0 \epsilon_r}{d}$$

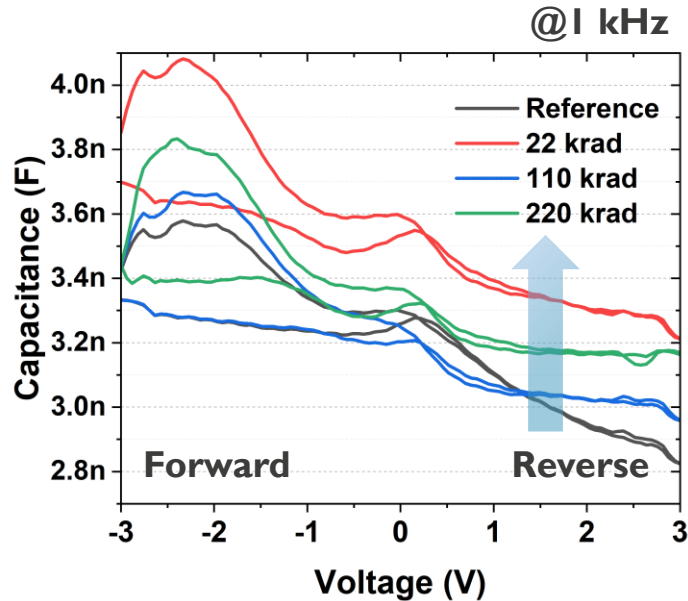
$$\mu = \frac{2d^2}{3At_{\max}^2 \left[ 1 + 0.36 \frac{\Delta j}{j(0)} \right]} \quad \text{if } \Delta j \leq j(0). \quad (1)$$

$$n_{\text{doping}} = \frac{1}{dq} \left( - \int_0^{t_{\text{ramp}}} j(t) dt - \frac{C_{\text{geom}} V(t_{\text{ramp}})}{S} \right)$$

	$J_{\text{disp}}$ (mA/cm <sup>2</sup> )	$J_{\max}$ (mA/cm <sup>2</sup> )	$t_{\max}$ (µs)	$\mu$ (cm <sup>2</sup> /V*s)	$n$ (1/cm <sup>3</sup> )
Reference	2.434	2.700	31.901	3.151e-5	2.068e+15
22 krad	2.545	3.086	32.704	2.895e-5	2.267e+15
110 krad	2.502	2.803	38.767	2.128e-5	2.136e+15
220 krad	2.502	2.808	50.324	1.261e-5	2.163e+15

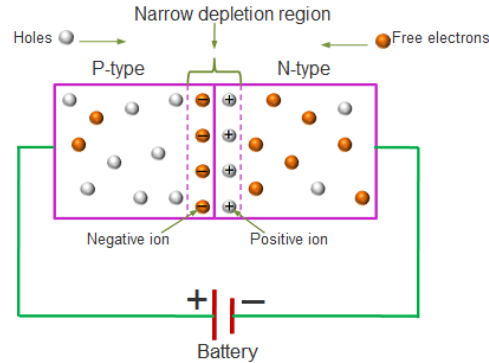
# Device physics - 2

## Capacitance – Voltage measurement



- In p-n junction diode, two types of capacitance take place

### Diffusion capacitance ( $C_D$ )

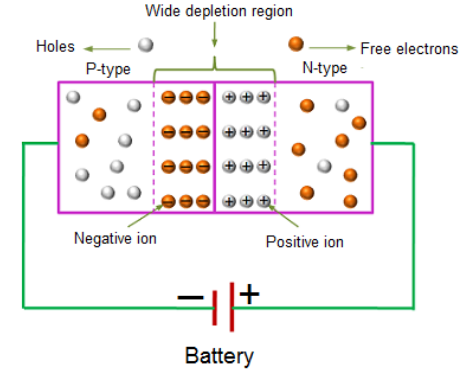


Forward bias

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$$C_D = dQ / dV$$

### Transition capacitance ( $C_T$ )



Reverse bias

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$$C_T = \epsilon A / W$$

Comparing single device to imager

# Future work plan - SWIR image sensor

## Experimental plan

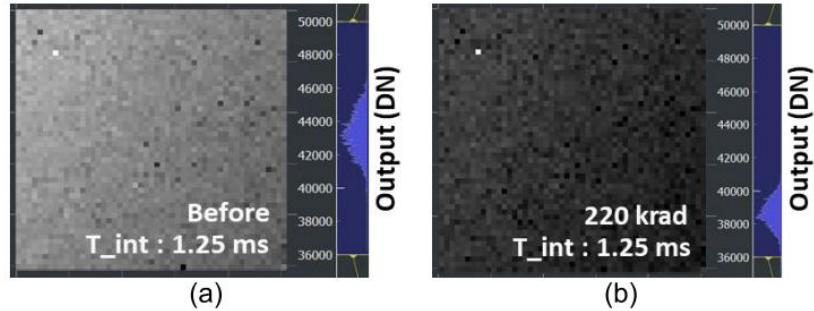


Fig. 11. Comparison of images (a) before and (b) after irradiation under dark conditions taken with QD-CIS.

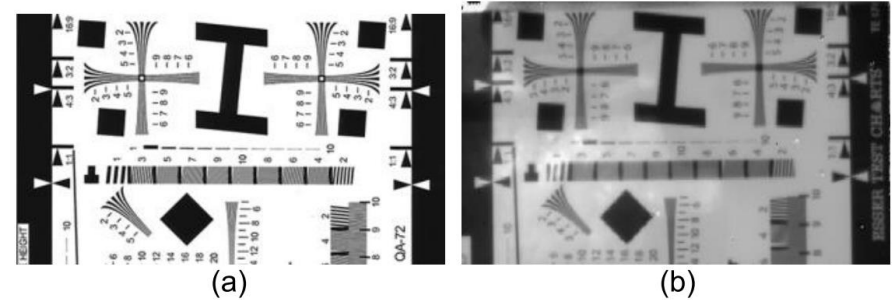


Fig. 12. Image quality test chart of (a) original image and (b) image captured using QD-CIS after 220 krad TID.

- I suspect how the thin film photodetector can protect Si-ROIC under X-ray radiation?
- We need more investigation of imager under X-ray radiation

# Conclusion

# X-ray radiation effects on CQD thin-film photodiode

## Summary

- Materials characterization
  - we recognized the organic ligands were detortion points under X-ray radiation.
  - The degradation of BDT ligands induced the oxidation of CQD surface.
  - This red shift phenomenon of PL spectra.
  - However, we covered the encapsulation layer in the actual device. Thus, the oxidation may not happen at the device level.
- Device characterization
  - Dark current and EQE are enhanced until TID of 22 krad(Si) and slightly degraded upon the TID.
  - X-ray radiation generates the increased doping concentration in TFPDs
    - From the C-V curves, the depletion region has a rigid (reducing trap states) than un-irradiated samples
  - Through the imager demonstration, we prove that this phenomenon is reliable.



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