Effect of UV Irradiation on Electrochemical Behavior of Zirconium Oxide at High Temperature Water Conditions

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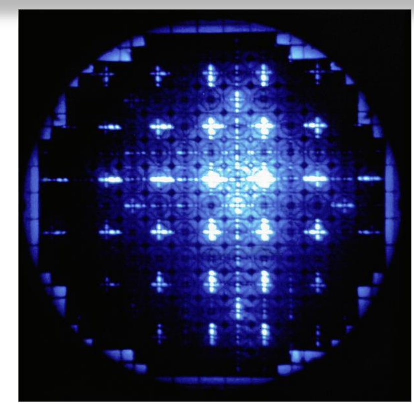
MOTIVATION AND OVERALL OBJECTIVES

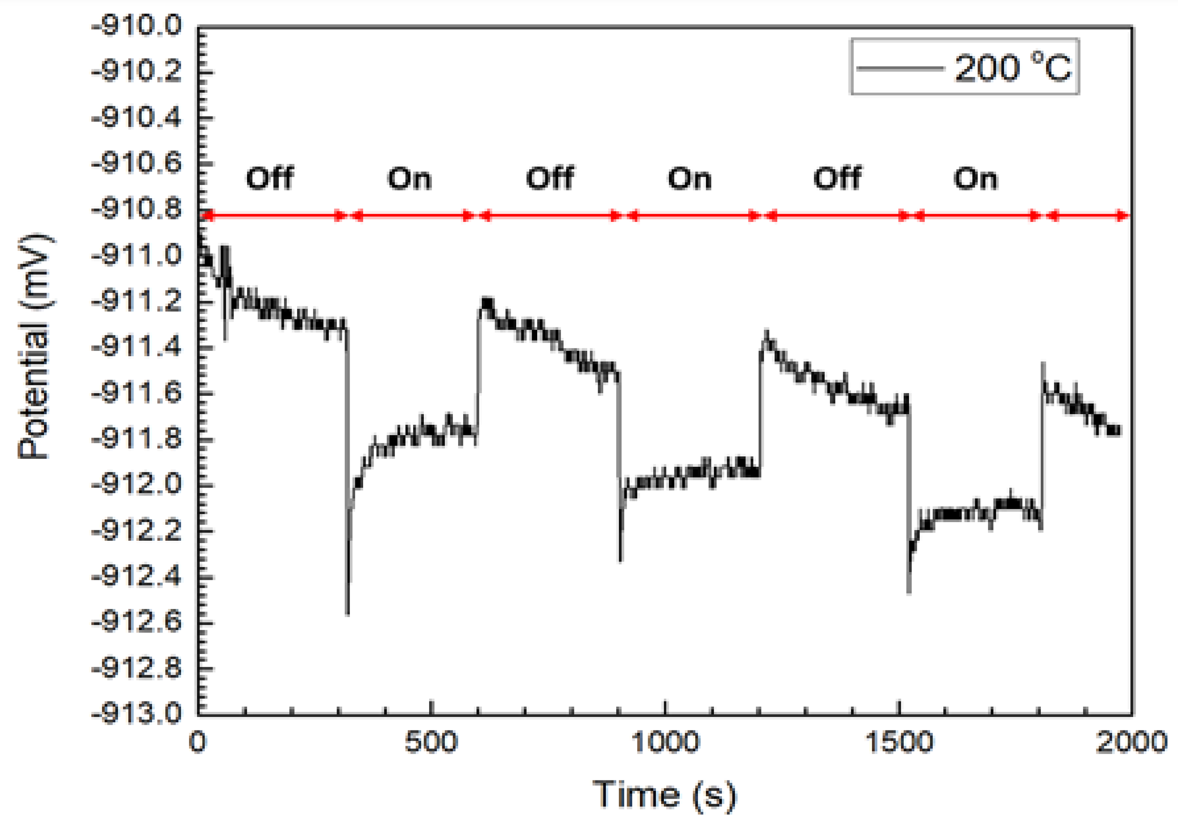
- Claddings experience **various types of irradiation sources** in reactor core such as neutron, gamma rays, beta ray, and especially **ultraviolet (UV) light comes from Cerenkov radiation with the average energy of 2.35 eV**.
- The objective of this study is to **investigate the effect of UV on Zircaloy-4 corrosion** through separate effects experiments.
- Our approach:
  - Using **in-situ EIS, SEM, TEM, and EDS** to analyze the oxide surface and cross section of corroded sample with UV-irradiated and non-UV irradiated Zircaloy-4 samples.



Cerenkov Effect in NPP

EXPERIMENTAL SETUP AND PROCEDURE

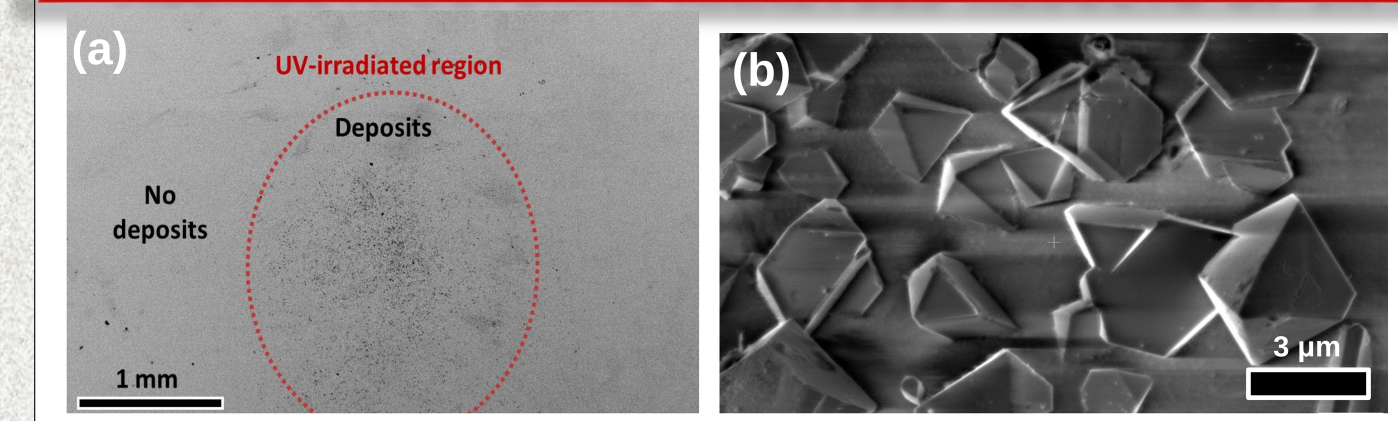
Schematic and pictures of in-situ EIS cell for sapphire window engineered autoclave



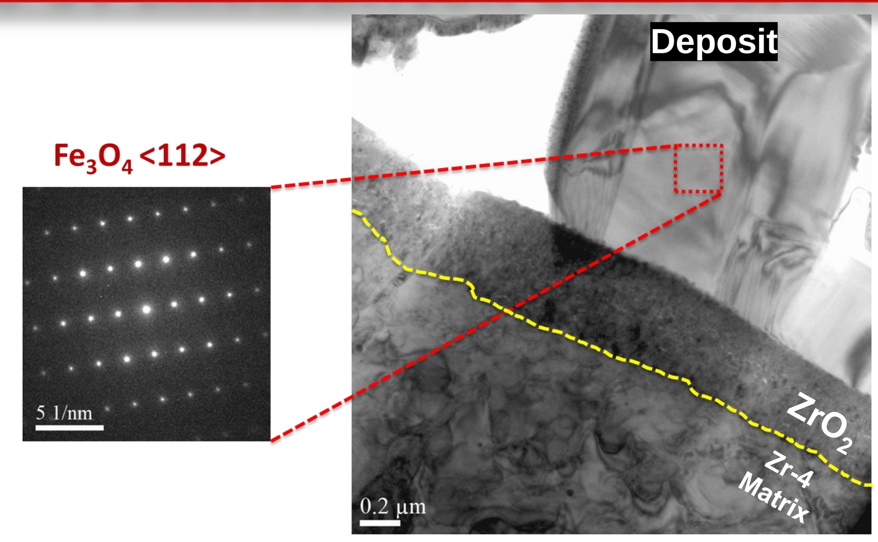
OCP change by UV irradiation at 200 °C DI water condition (UV source output with power density 8.62 W/cm²)

- **Corrosion experiment at two different temperature conditions, 260 °C and 320 °C with 2.5 ppm DH**
- **260 °C sample - UV Irradiation during whole experiment, 320 °C sample - EIS measurement without UV**

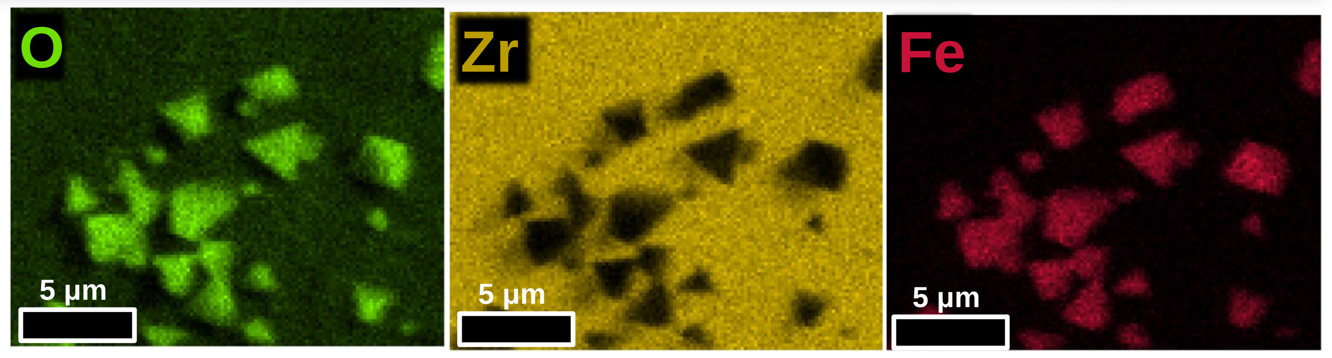
MICROSTRUCTURAL ANALYSIS RESULTS OF IN-SITU UV IRRADIATION CORROSION



(a) Surface image of UV-irradiated sample after 7 d corrosion test with flowing loop, (b) SEM images of deposits formed at UV-irradiated region on ZrO_2

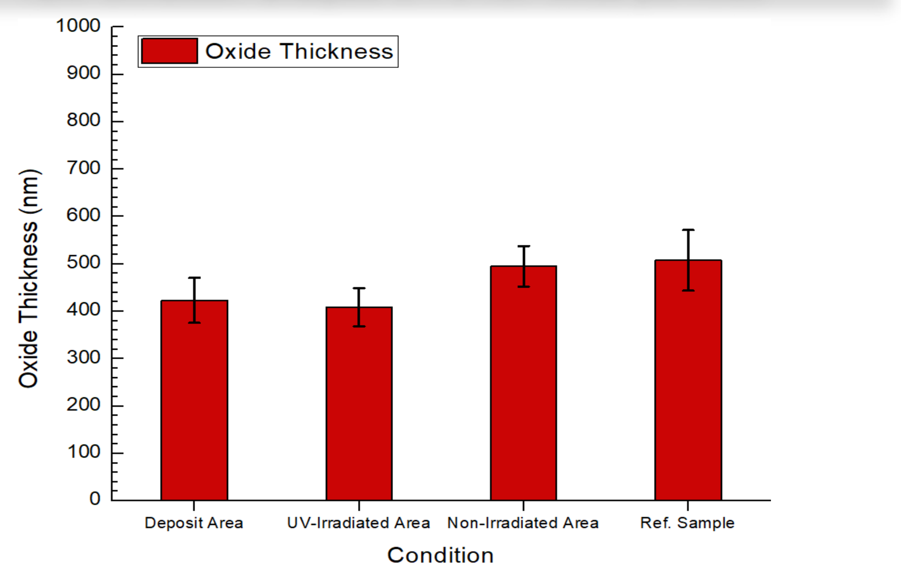


TEM diffraction analysis of Fe rich oxide particles



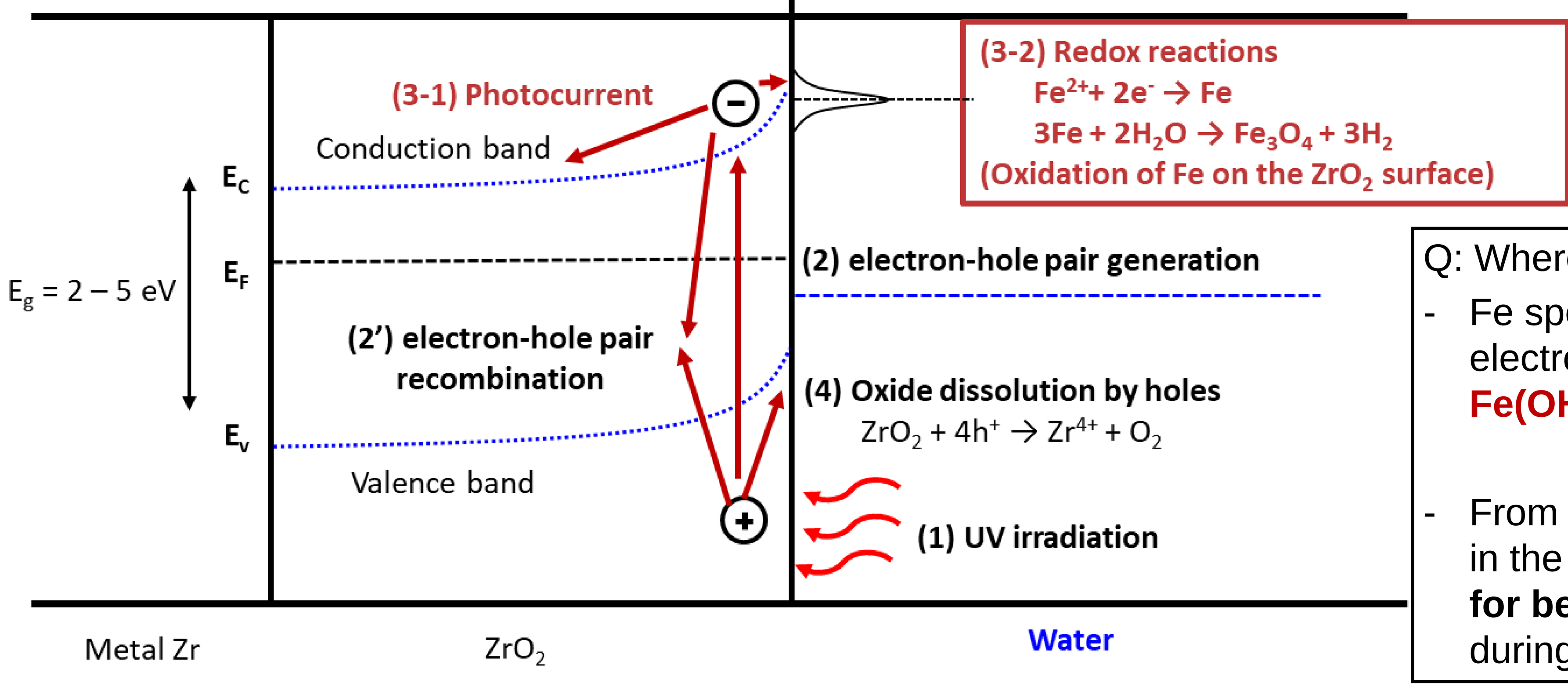
EDS analysis results of (a) oxygen, (b) zirconium, and (c) iron for the deposits in the deposit region.

- **Fe-enriched oxide deposits** are observed only at **UV-irradiated region** on ZrO_2 surface.
- **It can be concluded that UV irradiation may slightly reduce the growth of oxide film on zirconium alloy in high temperature water, although more data is needed to confirm this trend.**



Oxide thickness after 260 °C 30 d corrosion with UV and non-UV conditions

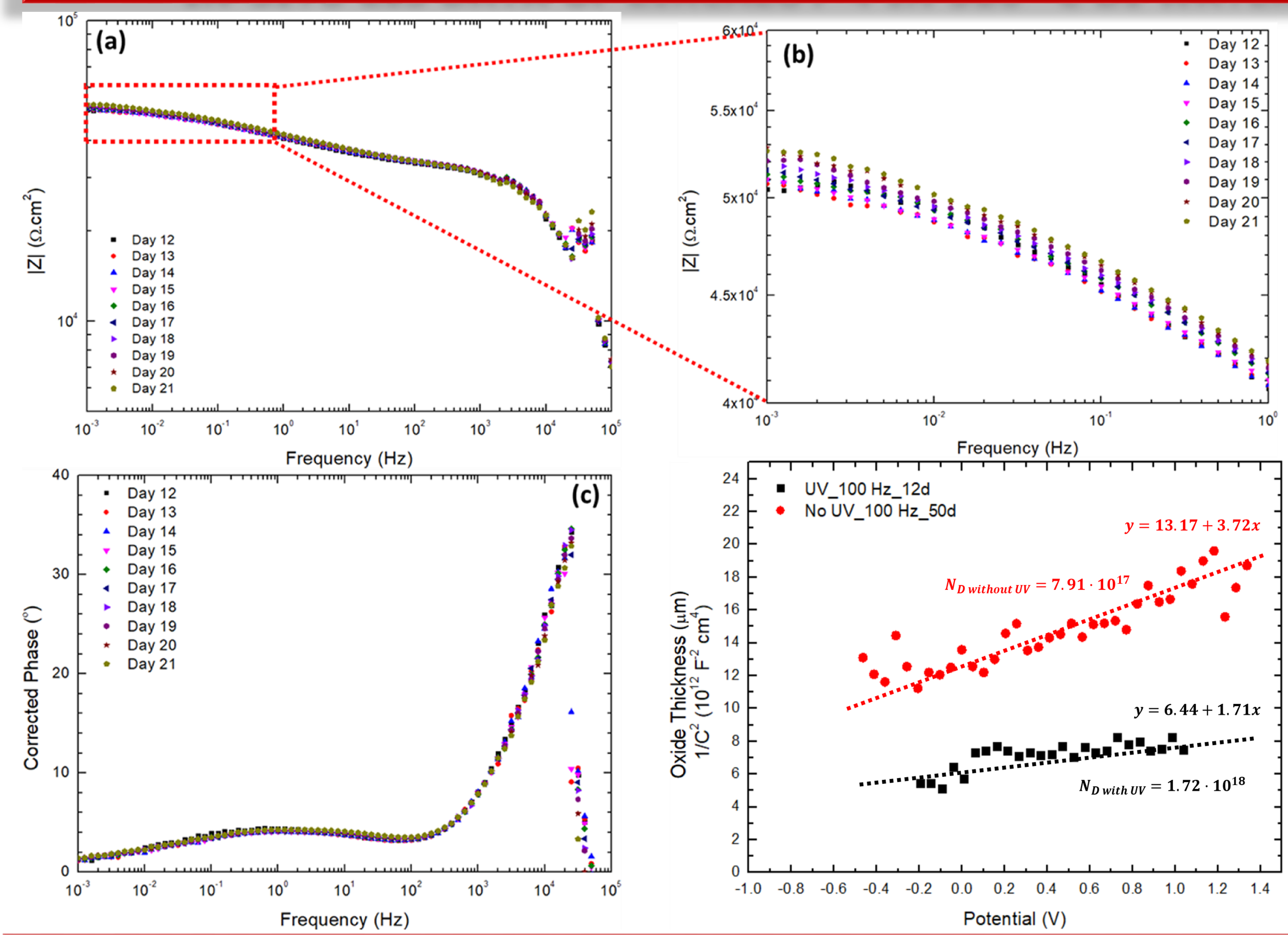
MECHANISM OF UV INDUCED DEPOSITS FORMATION ON ZrO_2



Q: Where is the source of Fe ion?

- Fe species dissolved in the electrolyte are **4 species, $Fe(OH)_2$, $Fe(OH)^{3-}$, Fe^{2+}, and $FeOH^{+}$**.
- From **MULTEQ simulation**, Fe ion in the electrolyte is **enough amount for being the source of Fe_3O_4** during corrosion with UV irradiation.

IN-SITU EIS DATA OF ZIRCALOY-4 IN 320 °C DI WATER CONDITION



In-situ EIS data of Zircaloy-4 in 320 °C DI water condition (a and b) Impedance-frequency plot (c) Phase-frequency plot (d) In-situ Mott-Schottky Analysis with and without UV irradiation

$$T = A\frac{\varepsilon(\omega)\epsilon_0}{C(\omega)}$$

- *T: Oxide thickness*
- *A: Cell area*
- *ε: Dielectric constant of the ZrO_2*
- *ϵ_0: Vacuum permittivity*
- *C: Capacitance value of ZrO_2*
- *ω: Angular frequency*

- **In-situ EIS data at 320 °C shows a gradual increase of impedance value of ZrO_2, indicating oxide growth.**
- **Oxide thickness can be calculated by the equation with a reciprocal capacitance value of ZrO_2.**

CONCLUSIONS

- In-situ UV irradiation at 320 °C for 21 days under reducing conditions reveals that UV irradiation induces the nucleation of deposits on the top of the zirconium oxide. The deposits are mostly iron oxide.
- The oxide deposits are located exactly in the UV irradiated surface on the sample. However, the deposits distribution inside of the UV irradiated surface is not homogeneous.
- Mott-Schottky analysis shows that the flat band potential decreases -0.2 V with UV irradiation on the oxide and that the donor density at the oxide surface increases under UV (x2)