

Photoconductivity of metal oxide nanolayers

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Outline

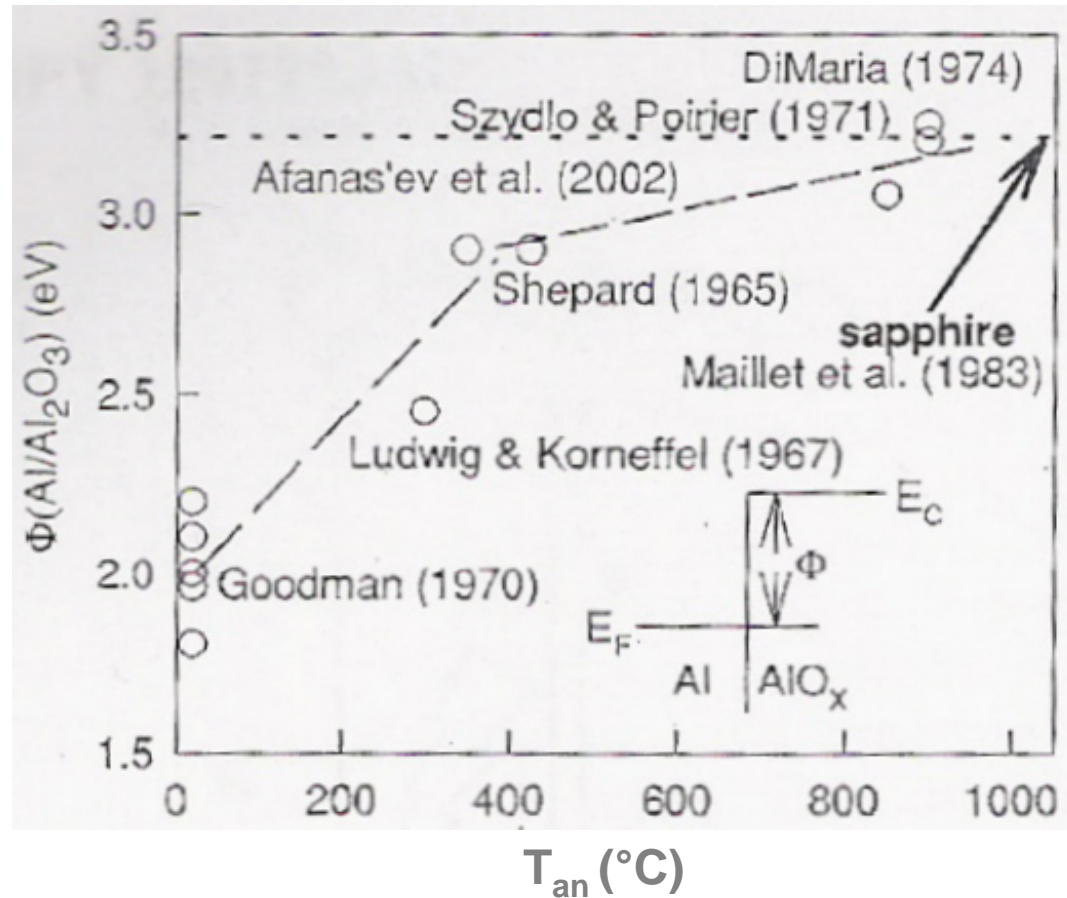
- Introduction
- Experimental method of photoconductivity (PC)
- Sample description
 - HfSiO_x
 - HfAlO_x
 - HfTiO_x
 - HfSrO_x
 - HfCeO_x
- Results of PC experiments
- Conclusions

Introduction

Properties of **metal oxide alloys**:

- A simple electron system with O-derived states in the oxide valence band (VB) (the top VB edge is unlikely to change its energy position with altering oxide composition) and unoccupied metal-derived states in the oxide conduction band (CB).
- Nanometer thin insulating films which are grown at low temperature (300 °C).
- Binary oxides offer the best of two worlds:
 - Combine the best of oxide qualities
 - Change the concentration to adapt the oxide to the substrate
- Cations of two sort form of subnetworks, which are diluted as compared to an elemental oxide. This dilution may affect the bandformation of the electron.

Introduction



-Electronic properties of the oxide are affected by growth temperature.

-Stoichiometry of thin oxide or metal-oxide alloy may not be the same as for bulk crystal.

-Stoichiometry, structure and thickness may effect the fundamental electronic properties.

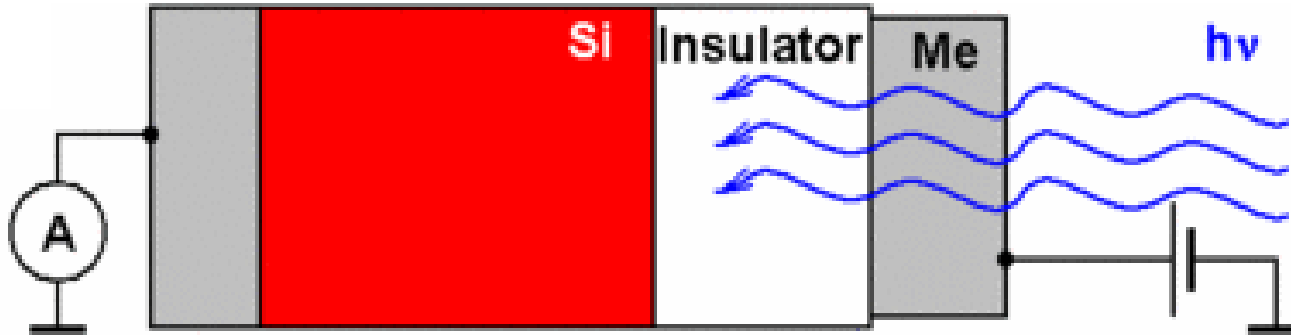
Goal of our study

- Analyze the impact of another cation on the electron structure of HfO_2 and its bandgap.
- Bandgap of these nanometer thin oxides is a fundamental parameter which has not been studied.
- Implementation of physically reliable procedure is needed:

PHOTOCONDUCTIVITY MEASUREMENTS

Experimental method: photoconductivity (PC)

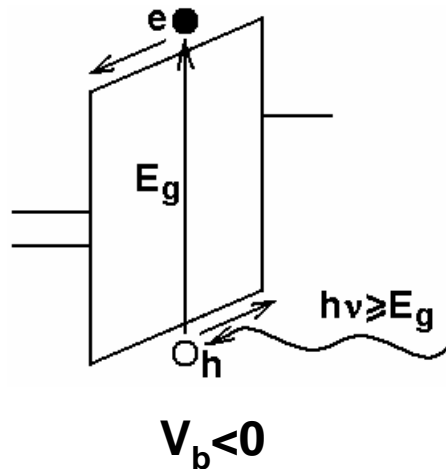
Silicon/Insulator/Metal heterostructure



Calculated value:

$$Yield = \frac{\text{Photocurrent}}{\text{Photon flux}}$$

Band diagram



- Photons of high energy are needed.
- Carrier **generation** and subsequent transport inside the insulator.
- The threshold of **intrinsic PC** directly corresponds to the band gap width.

Sample description

-Au/HfSiO/(100)Si

5-10 nm thick oxide

300-400 °C

Films have been prepared by MOCVD (metal-organic chemical vapour deposition) .

-Au/HfAlO/Si

Films have been prepared by MOCVD.

Au/HfTiO₂/Si

Films have been prepared by MOCVD.

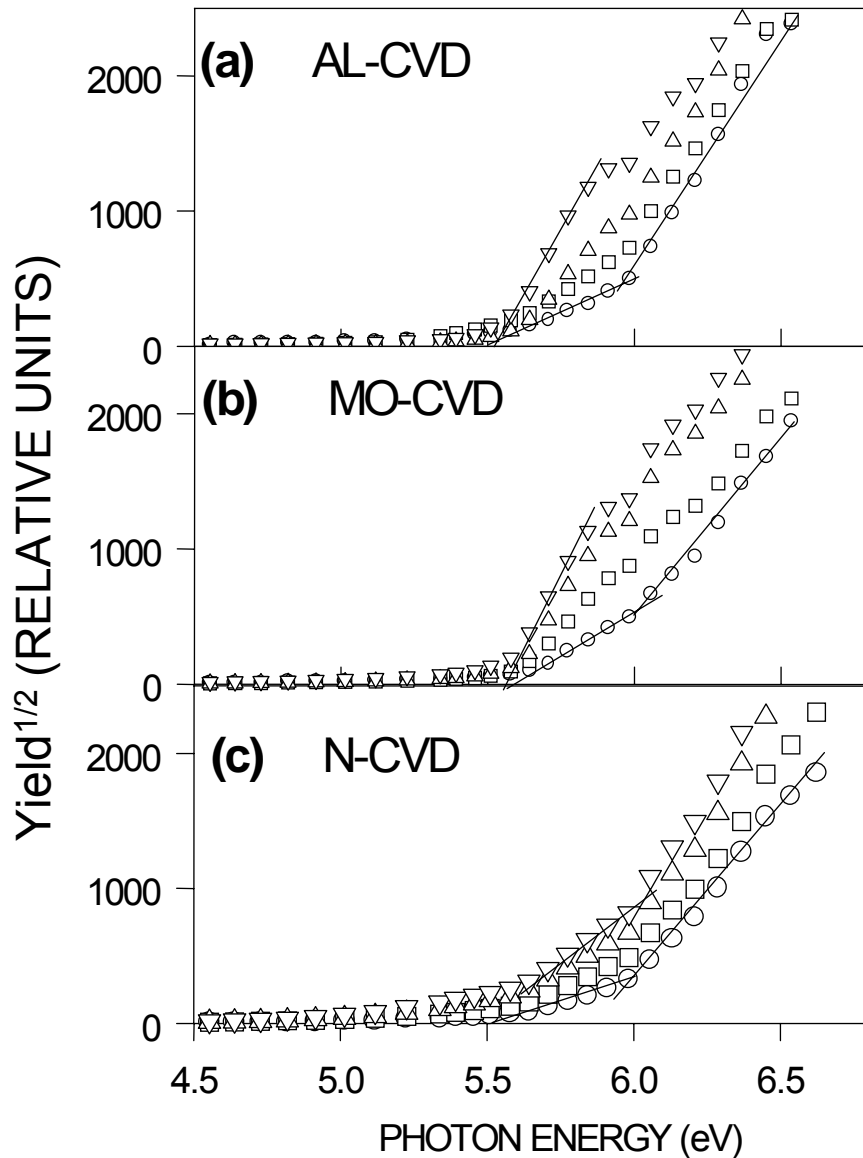
-Au/SrHfO₃/Si

Predicted to behave similar to strontium zirconate that has a κ -value of ~30, a bandgap of about 5 eV and is thermodynamically stable on Si. Thin films of strontium hafnate have been prepared by co-sputtering of Hf and SrO₂.

-Au/CeHfOx/Si

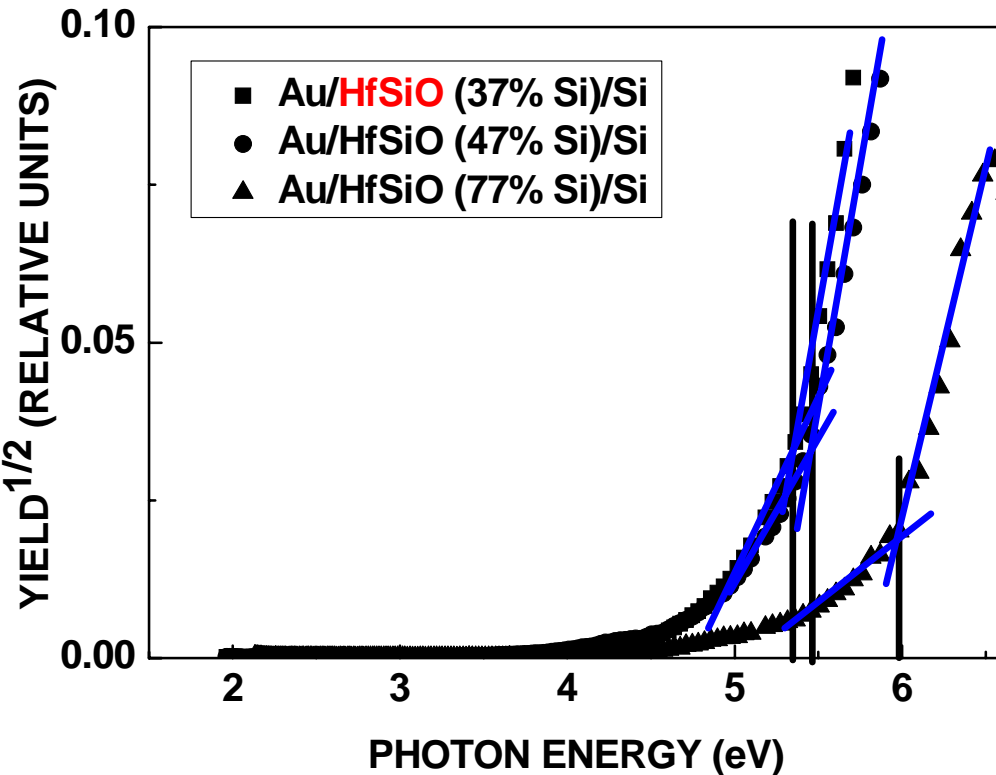
Films prepared by pulsed lased deposition (PLD).

HfO₂ Bandgap from PC



- Independent of deposition technique the derived bandgap from PC measurement is 5.5 eV.
- The impurities in the oxide do not change the observed band gap.

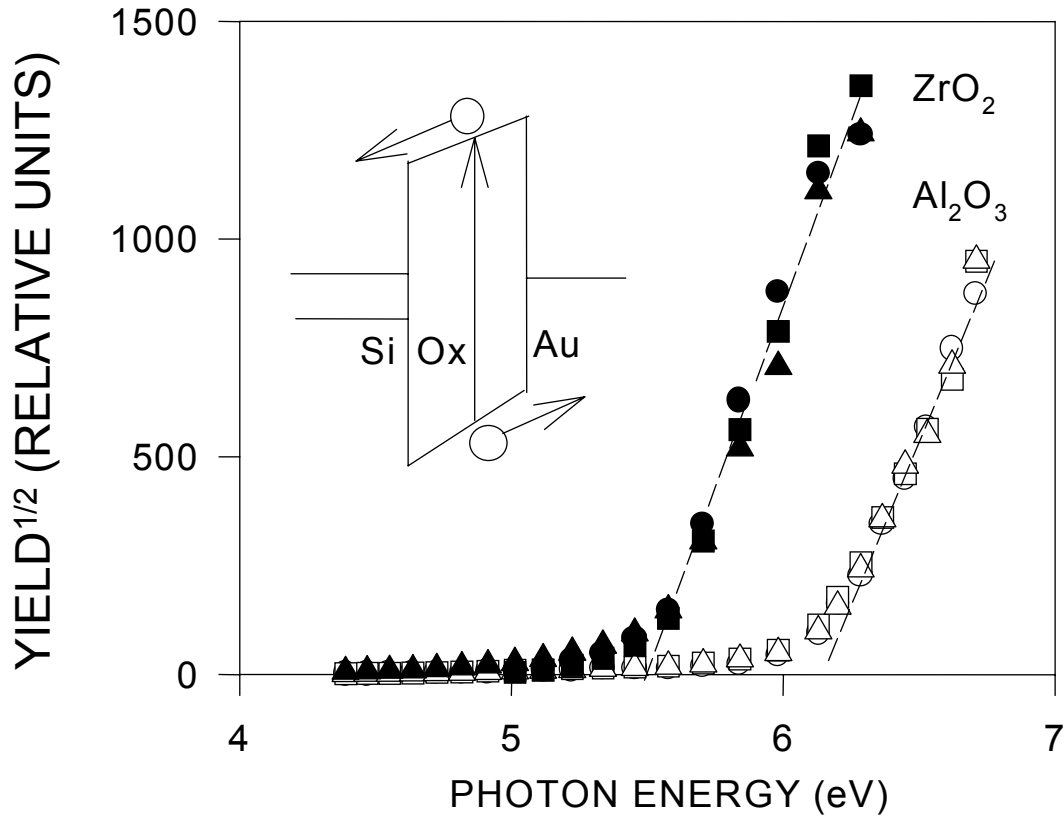
HfSiO Bandgap from PC



- When % of Si is less than 50, the band gap is determined by Hf-derived states and therefore has a value that is close to the value of pure HfO₂.
- For 77% Si the band gap widens to 5.9 ± 0.1 eV, but the PC subthreshold of 5.5 eV (cfr. HfO₂) is still present which suggests **phase separation**.
- Subthreshold PC suggests excitation of bandtail states of an amorphous oxide.

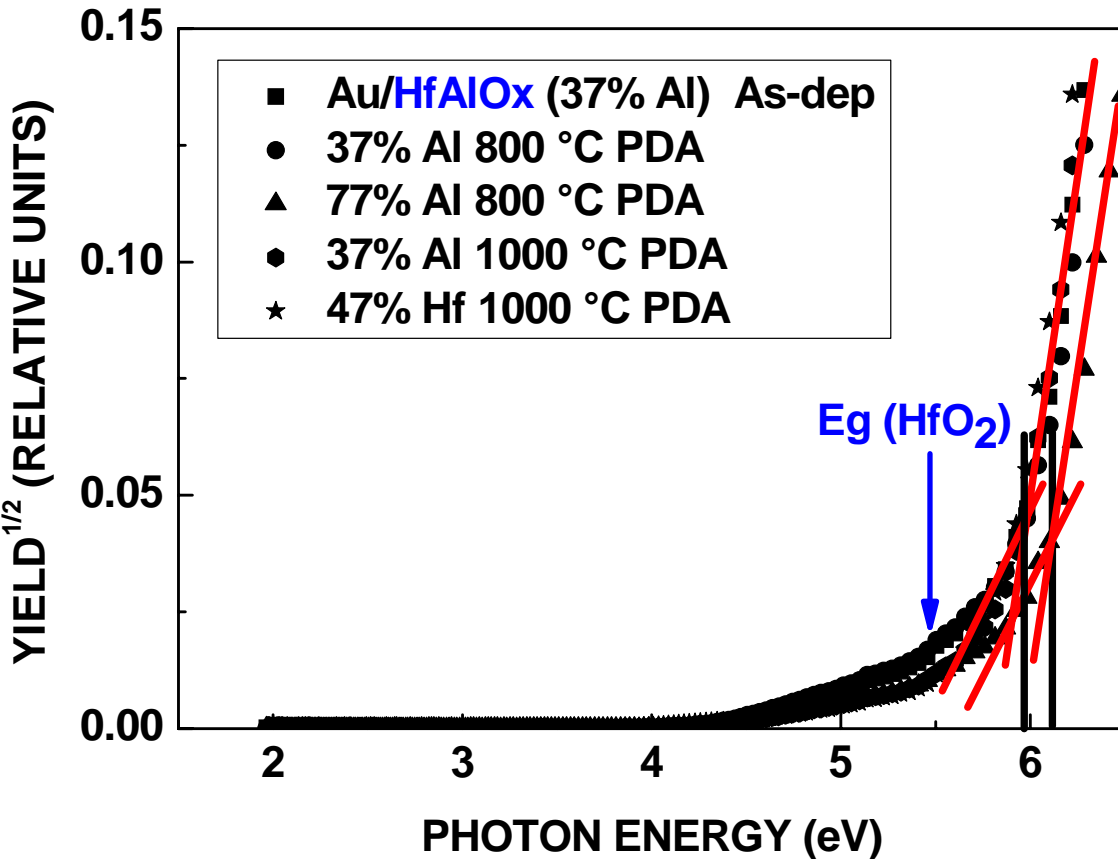
$$\begin{aligned} E_g (\text{HfSiO } 37\% \text{ Si}) &= 5.4 \pm 0.1 \text{ eV} \\ E_g (\text{HfSiO } 47\% \text{ Si}) &= 5.4 \pm 0.1 \text{ eV} \\ E_g (\text{HfSiO } 77\% \text{ Si}) &= 5.9 \pm 0.1 \text{ eV} \end{aligned}$$

Al₂O₃ Bandgap from PC



$E_g(\text{Al}_2\text{O}_3) = 6.1 \pm 0.1 \text{ eV}$

HfAlOx Bandgap from PC

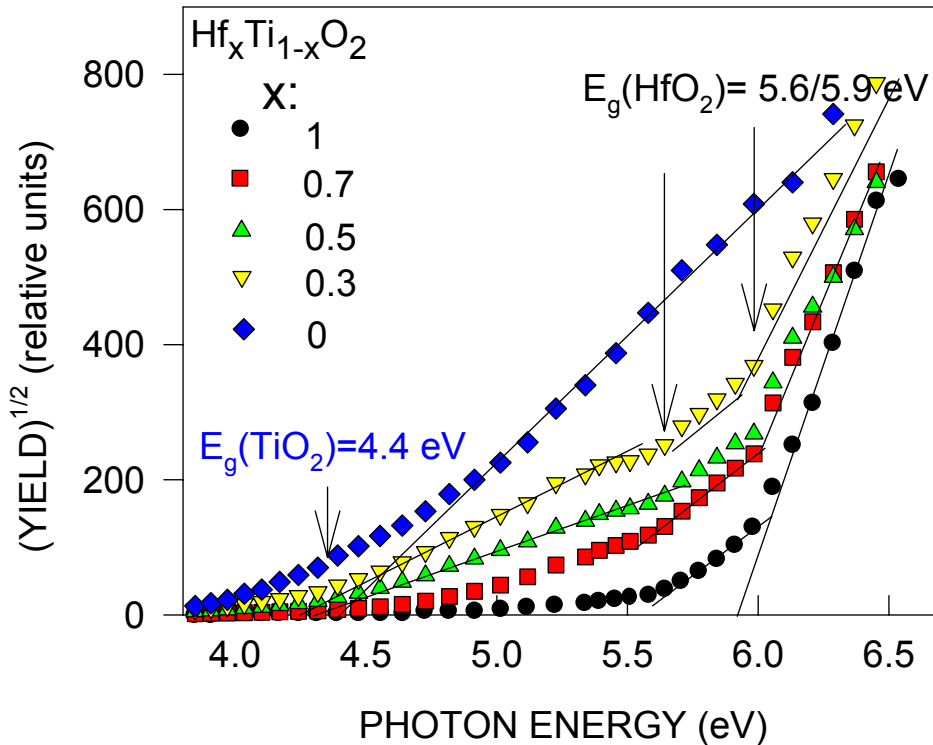


- No influence of annealing.
- Change in oxide composition is not reflected in a change of band gap width.
- PC excitation from O-derived states in oxide VB to unoccupied Hf-derived states in CB (very weak).
- Bandgap of (HfAlOx) is close to the bandgap of Al₂O₃ regardless to the composition indicating that the subnetwork with the largest band-gap preserves its electron state spectrum.

$E_g(\text{HfAlOx}) = 6.0 \pm 0.1 \text{ eV}$

**NO PHASE SEPERATION BUT
DILUTION OF HF NETWORK**

HfTiO_x Bandgap from PC



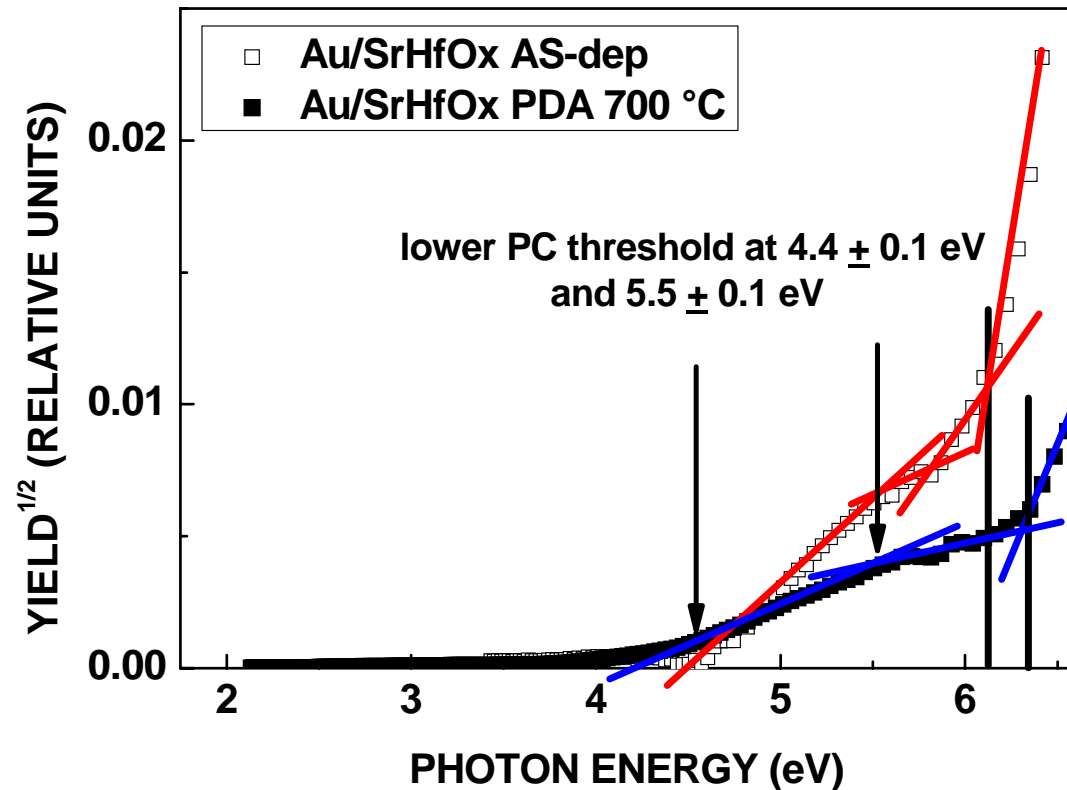
- E_g is reduced from 5.6 eV to 4.4 eV with increasing Ti content, but the 5.6 eV threshold is still observed in all Hf-containing samples.

- The subnetwork of the largest bandgap preserves its electronic structure.

- Ti subnetwork yields a concentration independent bandgap (suggesting that the Ti and Hf states do not interact)

PHASE SEPERATION

SrHfOx Bandgap from PC



- E_g (as-dep SrHfOx) = 5.7 ± 0.1 eV, which is close to the bandgap of pure HfO₂.

-PC excitation from O-derived states in oxide VB to unoccupied Hf-derived states in CB.

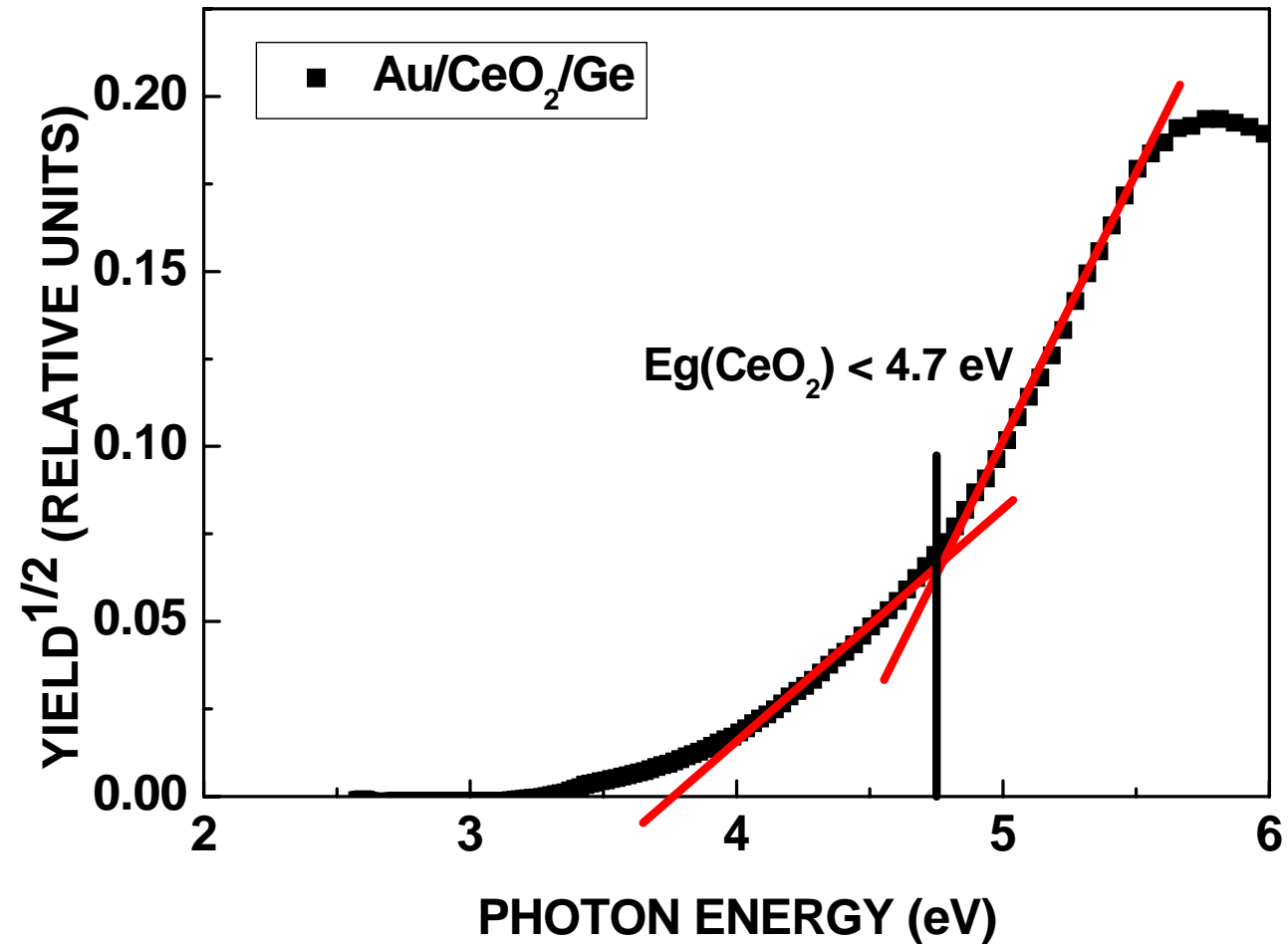
-The lower PC threshold of 4.4 eV can be explained by e⁻ excitation to CB states derived from Sr²⁺.

-The lower PC threshold are insensitive to annealing:

PHASE SEPERATION

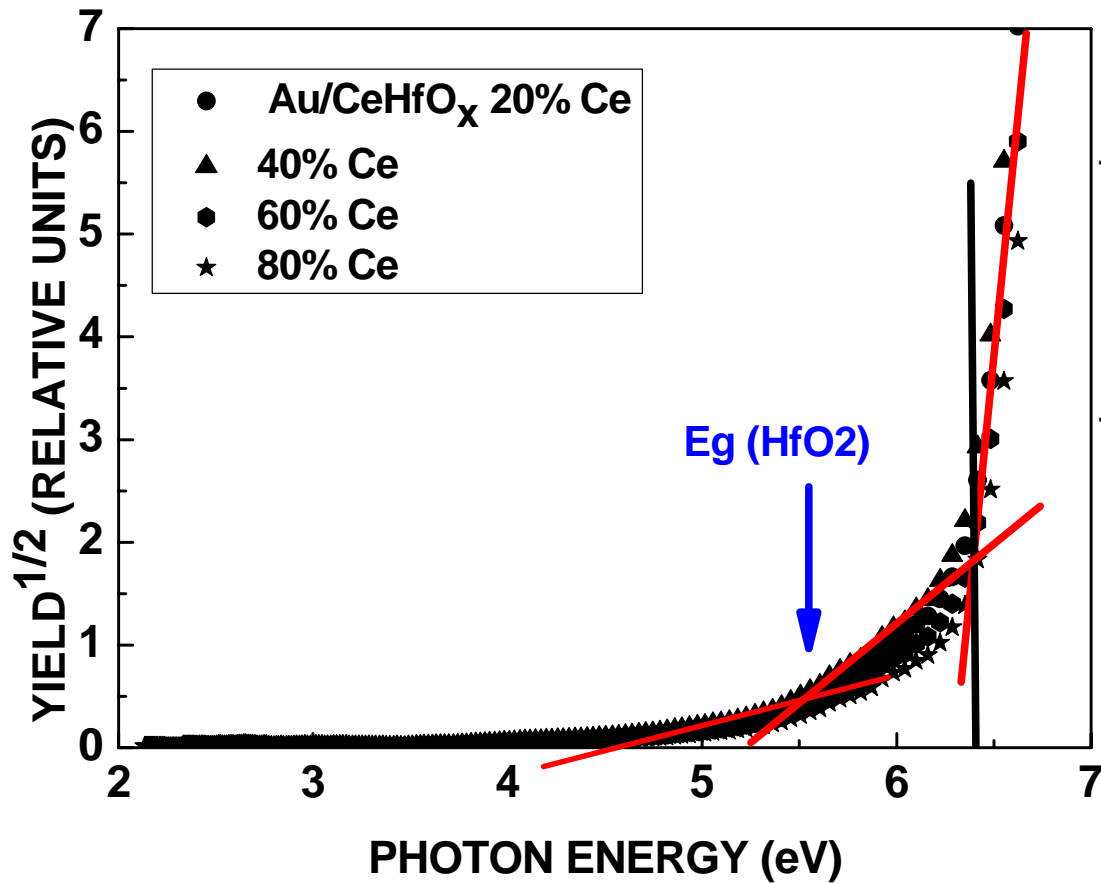
The lower PC threshold does not disappear after annealing, but the bandgap widens to 6.3 ± 0.1 eV which is due to structural transformation of the oxide.

CeO₂ Bandgap from PC



Eg (CeO) = 4.7 ± 0.1 eV

CeHfO_x Bandgap from PC



- Change in oxide composition is not reflected in a change of band gap.

- Subthreshold PC of 5.5 eV: excitation from O-derived states in oxide VB to unoccupied Hf-derived states in CB (seen for % of Ce > 20)

DILUTION OF NETWORK BY HF.

$$E_g(\text{CeHfO}_x) = 6.4 \pm 0.1 \text{ eV}$$

Conclusions

1. TWO OBSERVATIONS FROM SPECTRA:

- **PHASE SEPERATION:**

Bandgap of **elemental oxide** is preserved even in nanometer thick binary insulating films.

- **NO PHASE SEPARATION:**

Bandgap is affected by cation network **dilution**.

2. PC offers a method to trace phase separation in nanometer thin insulating films.