An attempt to correlate surface physics and chemical properties : Molecular beam and Kelvin probe investigations of $Ce_{1-x}Zr_xO_2$ thin films

Electronic Supplementary information (ESI)

SI-1: Sample preparation: *Preparation of $Ce_{1-x}Zr_xO_2$ thin films.*

Precursors for the sol-gel synthesis of CZ are cerium (III) nitrate (Ce $(NO_3)_3.6H_2O$, LobaChemie), zirconium oxychloride ($ZrOCl_2.8H_2O$, Thomas Backer) and ethanol (C_2H_5OH 99.9%, Thomas backer). 0.1 M solution of CZ is made by adding cerium (III) nitrate with zirconium oxychloride in required stoichiometric proportion in ethanol to form $Ce_{1-x}Zr_xO_2$.[1] 0.434 g of cerium nitrate and 0.322 g of the zirconium oxychloride was added to 20 ml of ethanol to prepare $Ce_{0.5}Zr_{0.5}O_2$. The solution was stirred for 3 h. The clear transparent sol has been utilized for spin coating on Si wafer (99.9999% pure and 0.625 mm thick - MaTeck, Germany), before it is converted into gel. 5 µl of the above solution was taken in a micropipette and it was spun coated on 12 or 25 mm^2 area of Si wafer at a spinning speed of 8500 rpm for 120 s. Thin film was dried in an air oven at 100° C for 12 h. Finally, the CZ films were heated to 500° C in a muffle furnace at a heating rate of 2° C/min in air, and calcined at 500° C for 1 h.[1]

SI-2: KPM Principle

When two metals of different (electro-chemical potentials) work-functions are electrically connected, the electron flow takes place from a metal of a higher work-function to that of a lower work-function; electrons flow only if there is a potential. This potential is created by the electrical contact, and hence it is also known as contact potential difference (CPD) method. Alternately, if a metal probe (or tip) is brought into the electrical vicinity of the metal or semiconductor surface under investigation, the capacitance is formed between the tip and the surface which has all the information of the surface under evaluation. Surface potential measurement by this method is known as non-contact method. Since work-function is defined as the energy required to remove electron from Fermi level to the vacuum level, any change in the Fermi level can be measured through change in CPD. The basic principles of KPM have been described in detail elsewhere.[2] KPM tip remains intact during and after KPM measurements and it was ensured from SEM measurements. SEM measurement of a tip is given after the KPM measurement below.

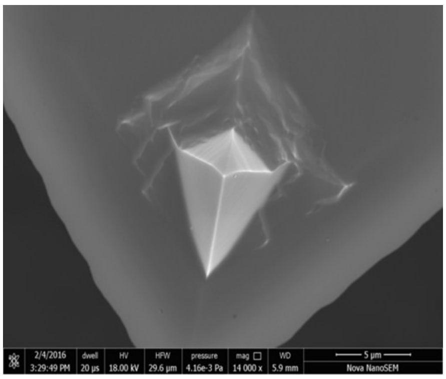
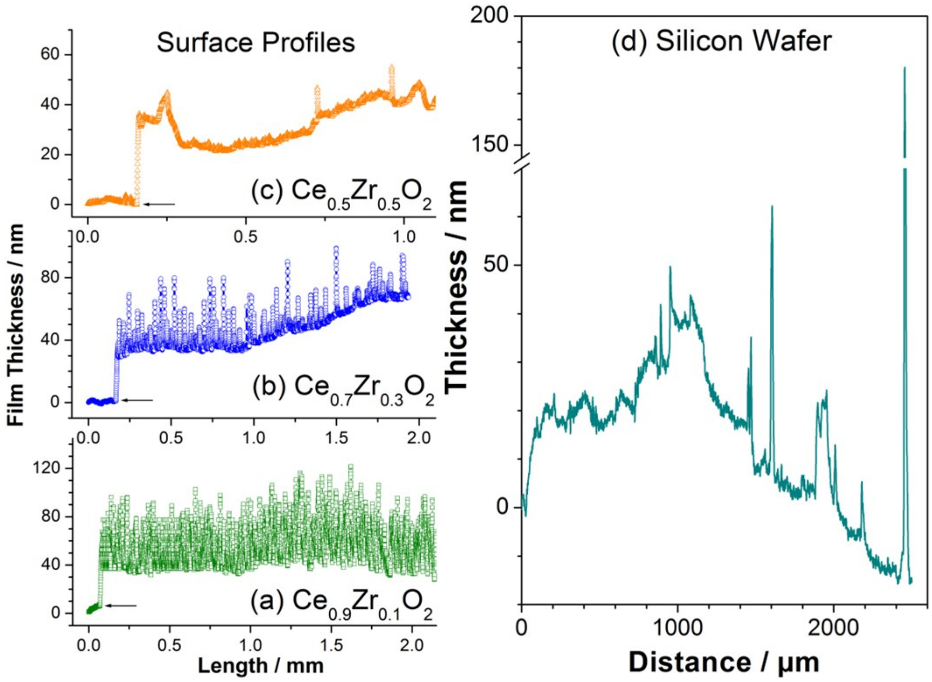
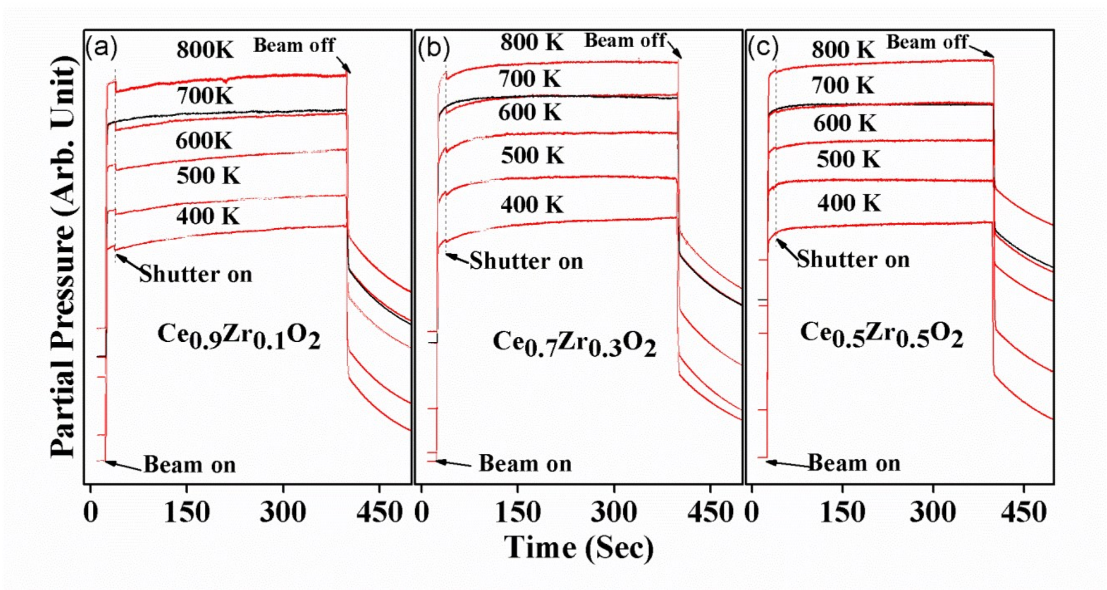


Fig. SI2: SEM measurement made with KPM tip, after the measurements.



SI-3: Surface profiles measured with profilometer for surface roughness. Arrow mark indicates the Si substrate surface. Sudden spikes in height observed at certain area are due to the Si-wafer substrate, and it is confirmed from the surface profile of Si wafers, shown in (d). Film thickness and surface roughness is similar with $Ce_{0.9}Zr_{0.1}O_2$ composition; however, roughness decreases dramatically with increasing Zr-content.



SI-4. *O_2 uptake as a function of time and temperature on a) $Ce_{0.9}Zr_{0.1}O_2$, b) $Ce_{0.7}Zr_{0.3}O_2$, and c) $Ce_{0.5}Zr_{0.5}O_2$ thin films. Reference experiments shown for 700 K (dotted line) is helpful to calculate the oxygen uptake and by a simple subtraction with the experimental trace.*

SI-5: Topography rms roughness, surface potential from potential image, and activation energy calculated from sticking probability of $Ce_{0.9}Zr_{0.1}O_2$, $Ce_{0.7}Zr_{0.3}O_2$, and $Ce_{0.5}Zr_{0.5}O_2$.

Sample/roughness	R_{rms} (topography)	Surface Potential	Activation energy
$Ce_{0.9}Zr_{0.1}O_2$	31.43 nm	80 mV	11.26 KJ/mol
$Ce_{0.7}Zr_{0.3}O_2$	20 nm	21 mV	17.69 KJ/mol
$Ce_{0.5}Zr_{0.5}O_2$	1.36 nm	6 mV	25.53 KJ/mol

Reference:

1. Dubey A. J.; Kolekar, S. K.; Gnanakumar, E. S.; Roy, K.; Vinod, C. P.; Gopinath, C. S. *Catal. Str. React.*, **2016**, *2*, 1-12. (DOI: 10.1080/2055074X.2015.1133269).
2. Kitamura, S.; Iwatsuki, M. *Appl. Phys. Lett.* **1998**, *72*, 3154.