

Enhanced Hydrophobicity of CeO₂ Thin Films by Surface Engineering

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Abstract

Due to its advanced surface properties and many technologically important applications, cerium dioxide (CeO₂, ceria) has become the focus of extensive research. This work presents a study of factors influencing the wetting properties of ceria. For this, CeO₂ thin films were deposited on substrates with different morphologies and characterized by means of XRD, SEM, XPS and water contact angle (WCA) measurements. The obtained results on wetting behavior were expanded using different organic materials on top of the CeO₂ thin films to enhance their hydrophobicity. The achieved WCAs were compared with those from samples without ceria to find the effect of the material on the water repelling properties. The results revealed that all factors – the surface material, adsorbed organic molecules and surface texturization – modify the wetting properties of CeO₂ thin films independently. This indicates that to achieve a superhydrophobic condition it is necessary to assess all the parameters which may control water behavior on the surface.

Keywords

Cerium dioxide; Sputter deposition; Superhydrophobicity; Surface texturization.

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1. Introduction

In the current glass market, there is a great need for inorganic materials that are mechanically strong with respect to mechanical wearing, can withstand high temperature processing, and possess enhanced wettability with large water contact angles. Such materials are interesting for applications in photovoltaic panels installed in rainy or high humidity areas, windows of buildings, automobiles, etc.

Rare-Earth metal oxides (REOs) possess hydrophobic properties [1]. Cerium dioxide (ceria), which cation is the most abundant lanthanide in the Earth's crust [2], exhibits a large bandgap between 3.0–3.6 eV [3]–[5] which makes this material promising for the above-mentioned applications. The original explanation of the ceria wetting behavior was based on its electronic structure [1]. According to that explanation, valence electron orbitals of the cerium atoms in CeO_2 are protected by the electron octet $2s^22p^6$ of crystalline oxygen which makes it difficult for water molecules to build chemical bonds with the surface. Later studies found, however, that as-prepared REOs show intrinsic hydrophilicity, and attributed high water contact angles (WCA) to adsorption of hydrocarbons which often are present in indoor air and pump systems [6]–[10]. Surface cleaning with high temperature annealing or with plasma treatment [11] are able to switch the wetting behavior of REOs from hydrophobicity to hydrophilicity. The hydrocarbon adsorption usually occurs at surface defects such as oxygen vacancies and adsorbed -OH groups, or by physical adsorption on the locally ideal surface [11]. So, the nature of the hydrophobicity of CeO_2 still remains unclear.

The goal of the current study is to investigate which factors control the wetting behavior of CeO_2 . We report how to enhance hydrophobicity of CeO_2 by texturizing the substrate surface and depositing hydrocarbons. The clear understanding of the parameters governing hydrophobicity and their relationship might accelerate research and implementation of the material in real-life applications.

2. Experimental details

The principal way to achieve the superhydrophobic state with WCA above 150° is through the creation of surface roughness by surface texturization [12]. It should be mentioned that besides helping to achieve the superhydrophobic condition, the advanced surface morphology reduces reflection from the material and therefore makes it advantageous for use in PV applications. For the bulk material, the surface texturization can be performed within two different paradigms or their combinations [13]. The first one, “Top-Bottom”, implies selective removal of material from the surface by etching or laser ablation [14]. The second approach called “bottom-up” consists of deposition of new material on the surface, creating a new geometric pattern on top of it. For the thin films produced by the sputter deposition technique, the surface roughness can be related to the substrate texturization if the typical size of the texture element is much more or comparable with the film thickness. In this case the deposited thin film inherits the texturization of the substrate which helps to modify wetting properties of the material.

The procedure for producing CeO_2 -based superhydrophobic films utilized in this work consists of 3 consequent steps [Fig. 1]: 1) texturization of the substrate by chemical etching; 2) sputter deposition of the CeO_2 thin film; 3) controlled adsorption of organic molecules by placing the CeO_2 -coating in a saturated environment of organic materials.

The substrates used to obtain the superhydrophobic condition for CeO_2 were monocrystalline (100) *n*-type silicon wafers with initial thickness $d=100\text{ }\mu\text{m}$. In order to get even texturization of ceria thin films, the Si-wafers were chemically etched with a KOH wet process [15]. The KOH concentration was maintained at a level of 2 wt. % during etching. The etching was carried out at 80°C for 20 min. To terminate the etch and remove any etchant remaining on the Si-surface, the wafers were immersed in a 5% HCl solution for 120 seconds and subsequently rinsed and dried using N_2 gas. The mass loss from the wafers was found to be roughly 6% of the initial value. Before deposition of ceria, Si-substrates were cleaned by ultrasonication in isopropanol for 10 minutes, rinsed with deionized water and dried in N_2 gas at room temperature. For the reference samples, we utilized non-treated flat Si-wafers as substrates.

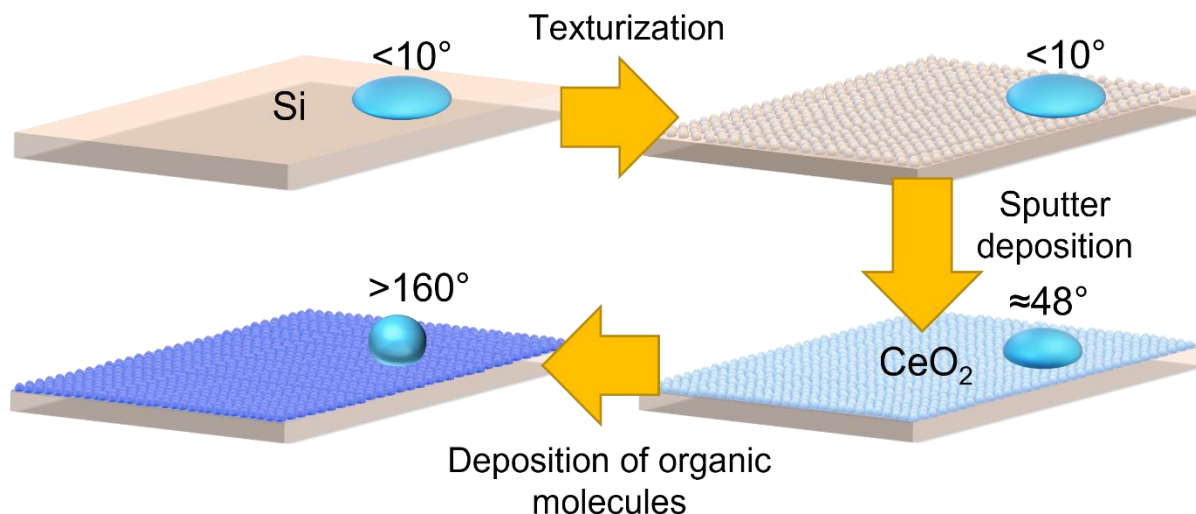


Fig. 1 – Production procedure for CeO_2 -based superhydrophobic coatings

The cerium dioxide thin films were deposited by DC reactive magnetron sputtering (Leybold A550V7 industrial type unit). The base pressure in the process chamber was maintained at 3×10^{-6} mbar. A cerium metal target of purity 99.5% was used in an argon-oxygen gas mixture with O/Ar inlet flow proportion at 31% and total pressure 0.5 Pa. The substrate and the target were both kept at room temperature during the deposition process. The power density during the deposition process was 1.06 W/cm^2 . The deposited thin films had a thickness of 200 nm for the flat substrate and was determined by a profilometer.

After CeO_2 deposition, the obtained thin films were covered with different organic materials by thermal evaporation performed in air. For this, samples were put in a polypropylene box with a liquid source of organic molecules before the closed and sealed box was placed in an oven at a temperature of 100°C for durations up to 17 hours. The organic materials used for the deposition were silicone oil (technical grade, type P20.275.50, Huber SilOil) and hydrocarbon 1-octadecene (technical grade 90%, Sigma-Aldrich).

The phase content of the obtained thin films was characterized by means of XRD (Bruker D2 Phaser, Cu-K α radiation). The scanning was conducted with Bragg-Brentano focusing, in the range of 2θ from 20° to 60° to estimate the contribution of the main planes to the surface crystallography. The surface images of the films were obtained with SEM (JEOL model JSM-7900F). The wettability characterization was carried out with the sessile droplet method. Droplets of Milli-Q water were placed on the thin film surface with a manually controlled mechanical syringe with varying droplet volume in the range 8-12 μL . The water droplets on the surface were photographed using a high-speed camera. Image analysis and calculations of the contact angles were performed with Attension Theta software. The final value of the contact angle for each sample was averaged over five independent measurements.

To confirm the elemental composition, X-ray photoelectron spectroscopy (XPS) was performed on a CeO_2 sample at the AU-MATLINE beamline of the ASTRID2 synchrotron, Aarhus University, Denmark. To reduce the probability of charging effects due to the insulating nature of CeO_2 , a thinner film of 50 nm thickness was deposited on a flat Si substrate, without any consequent covering with organic materials. Measurements were performed in ultrahigh vacuum (pressure in the order of 10^{-10} mbar) and with photoexcitation energies 600 eV and 650 eV. The sample was measured as prepared, and after having been heated to 700°C in vacuum.

3. Results and Discussion

3.1 Wettability

Influence of organic material type on wettability

Dependences of the WCA for the CeO_2 deposited on the texturized and flat Si with deposited silicone oil (SiOil) and 1-octadecene are shown in Fig 2(a) and (b), respectively. The initial values of WCA for the as-deposited ceria stay below 60° , defining the surface as hydrophilic. Such wetting behavior corresponds well with numerous works [6]–[9], [16]–[19] and confirms the idea of the intrinsic hydrophilicity of CeO_2 . The obtained results demonstrate a significant increase of the hydrophobicity after deposition of the carbon containing molecules. For both types of the deposited organic materials, WCA exceeds 90° and transforms the ceria surface to the hydrophobic state. The saturation of the WCA values for the 1-octadecene occurs faster than that for the silicone oil, however the maximum achieved values remain lower for both the texturized and flat thin film. According to the Young equation, this indicates a lower surface energy for the silicone oil which stimulates reducing the total interface area between water and ceria. Texturization enhances the initial hydrophobicity of the CeO_2 surface no matter what contaminator was used. It should be noted that silicone oil deposition on the surface allows superhydrophobicity of the CeO_2 with contact angle 162° .

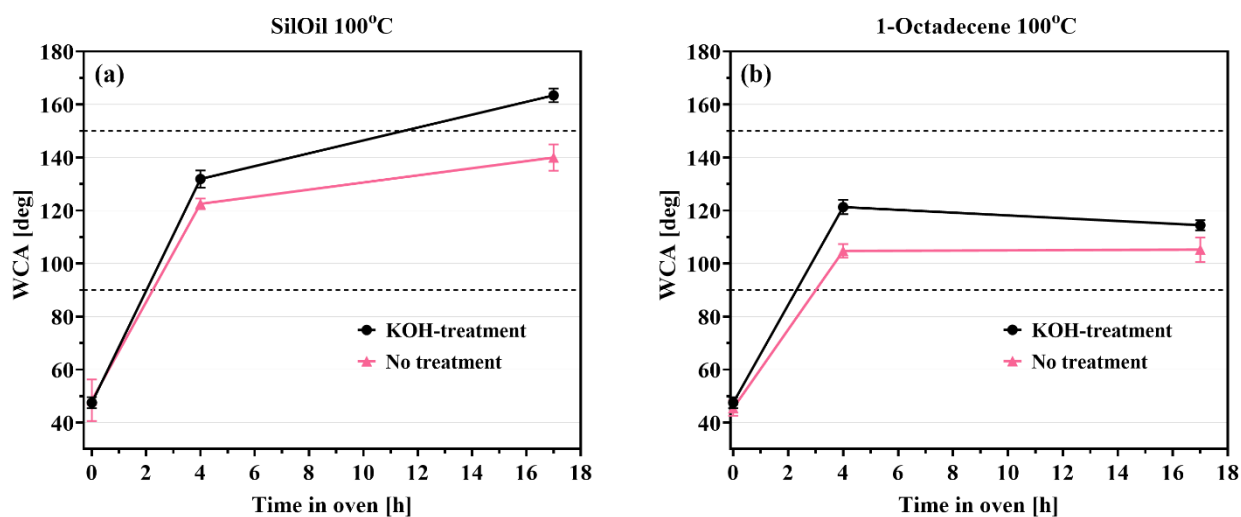


Fig 2. – Dependence of WCA on time of organic molecules deposition for (a) silicone oil and (b) 1-octadecene

Applying the adsorption process of the organic molecules allows us to achieve three different goals. The first one is related to the time of saturation for wetting properties. In various works [6]–[9], [18], the period of establishment for the hydrophobic state of CeO_2 and other REOs is found in the large range from days to months. Applying the deposition process in a saturated environment allows the completion time to be reduced from days to hours. This time might be controlled by the temperature of the process which governs the vapor pressure of the organic material. The second advantage is in the reproducibility of the results over different experiments since the deposition environment remains constant. The last advantage of using a controlled environment is the ability to modify the final wetting properties of the material using various substances, including those which cannot be found in atmosphere or vacuum chambers.

Influence of the different substrates

To summarize the influence of the different factors on the wetting properties of the surfaces, WCA for samples with and without deposited CeO_2 have been compared, with and without silicone oil present. The comparative diagram of the wetting properties for different types of surfaces is shown in Fig. 3. For each type of substrate topology, we considered 4 different situations: deposited ceria and SiOil (black bars), substrate without ceria but with SiOil (red), ceria without SiOil (blue) and bare substrate without SiOil (grey). All depositions of the silicone oil have been carried

out for 17 hours. Analysis shows that the presence of the ceria thin film increases WCA regardless of the presence of the attached organic molecules on the surface (black and red, blue and grey columns within one group for samples with and without SilOil, respectively). The surface of the substrate without ceria (red and grey bars in Fig. 3) consists of the non-stoichiometric SiO_x , naturally formed by oxidation of silicon in the atmospheric air. Silicon oxide possesses hydrophilic behavior with contact angle less than 10° , corresponding well with the studies on the wetting properties of silica [6]. Applying the SilOil significantly increases hydrophobicity for any type of surface, however, the presence of the organic molecules with low surface energy does not make different materials equally water repelling. This fact points out the importance of the surface material in achieving the superhydrophobic condition.

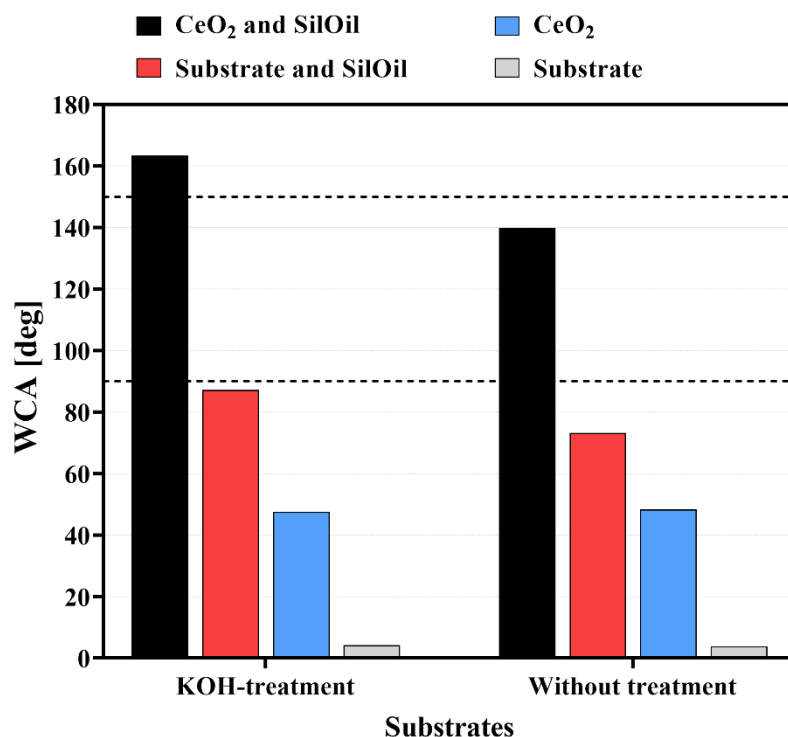


Fig 3 – Comparative diagram of the WCA for different substrates with and without adsorbed organic molecules. Dashed lines indicate thresholds for the hydrophobic (90°) and superhydrophobic (150°) conditions

3.2 XRD and SEM measurements

Results of the XRD measurement are shown in Fig. 4(a). The pattern obtained indicates presence of the *fcc* fluorite structure of CeO_2 . The peak at $2\theta \approx 33^\circ$ appears as combination of signals from CeO_2 (200) and Si (200) planes. The reflection from the latter is forbidden for the ideal Si-crystal, and when it occurs it may indicate lattice distortion of the substrate [20]. Analysis within the Debye-Scherrer equation applied to peaks (111), (220) and (331) reveals the average crystalline size equal to 15 nm. The lattice parameter is found according to the Bragg equation as $a=5.41\text{\AA}$ which corresponds well with the reported value of 5.411\AA (JCPDS No. 34-0394).

The SEM micrograph of the texturized thin film surface is shown in Fig. 4(b). Applying the KOH treatment to the monocrystalline Si-substrate creates a pyramidal morphology of the surface. This effect is a result of the selective etching where different crystallographic planes are etched at different rates. The surface of the pyramids is formed by Si-(111) planes. Deposition of the ceria thin film on top of the etched silicon does not change morphology of the surface. This occurs due to a relatively small thickness of the film compared with the typical size of the features on the substrate, allowing CeO_2 to inherit roughness.

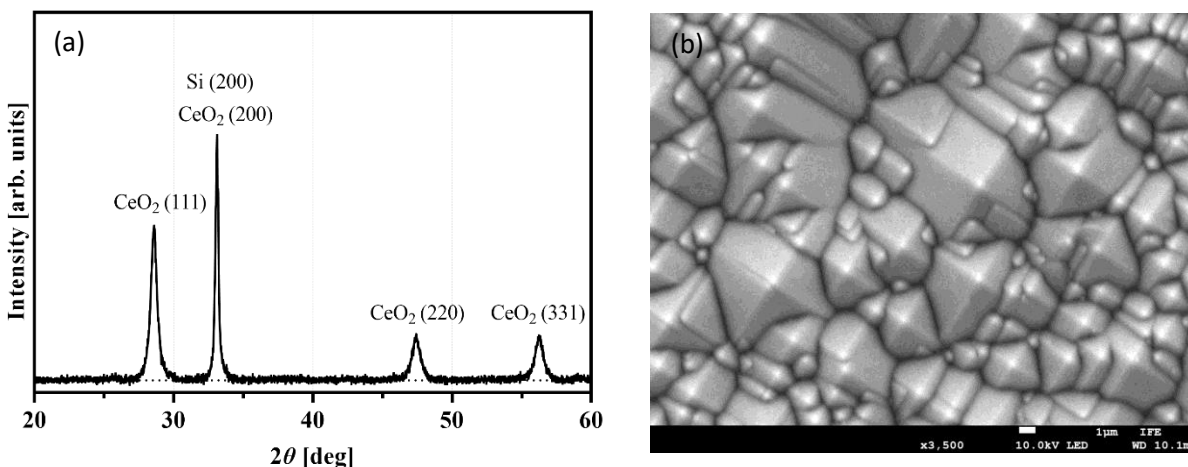


Fig 4 – XRD pattern (a) and SEM micrograph (b) of the CeO₂ thin film deposited on the texturized substrate

3.3 XPS measurements

XPS spectra for the CeO₂ films are presented in Fig. 5. From the widescan [Fig. 5(a)], Ce and O peaks are observed, together with C and some Si from the substrate. Before the sample was heated in vacuum, the relative intensities of Ce4p:O1s:C1s were found to be 1:2:4, and after heating the ratios were 1:2:2. Hence, the intensity of the O 1s and Ce peaks increases and the C 1s peak decreases upon heating, indicating that some of the carbon contamination on the surface is released and more of the CeO₂ is seen. The spectra shift 1-3 eV towards lower binding energies after heating. When the thin film is heated in vacuum, oxygen may be emitted from the surface. This in turn may change the potential at the surface, possibly causing the observed shift in binding energy [21]. The binding energies given in previous work [22]–[25] are closer to those of the sample after it has been heated in vacuum, and the following discussion will hence be based on those values.

Figure 5 (b)-(d) shows spectra of the O 1s, C 1s and Ce 4p peaks. The O 1s spectra can be decomposed into three peaks with binding energy 530.2 eV (531.5 eV), 531.6 eV (533.5 eV) and 532.5 eV (534.6 eV) after (before) heating. The largest component at $E_B=530.2$ eV is oxygen from the CeO₂ lattice, and this is the component increasing upon heating. The component at 531.6 eV has previously been assigned to hydroxyls or carbonates [22]–[24], and the peak at 532.5 eV may be from O bound to the Si-substrate or molecular water [23]–[25]. Since the Si 2p peak can be seen [Fig. 5(a)] even with a relatively thick film of CeO₂, the film is probably not uniform. It is likely that the substrate has reacted with oxygen to form SiO₂ during the preparation of the sample, and that some of this SiO₂ gives rise to the peak at 532.5 eV. The peak decreases upon heating, as is expected for both SiO₂ and adsorbed water. Heating may make the film more uniform, such that less of the SiO₂ is seen, or make water evaporate from the surface.

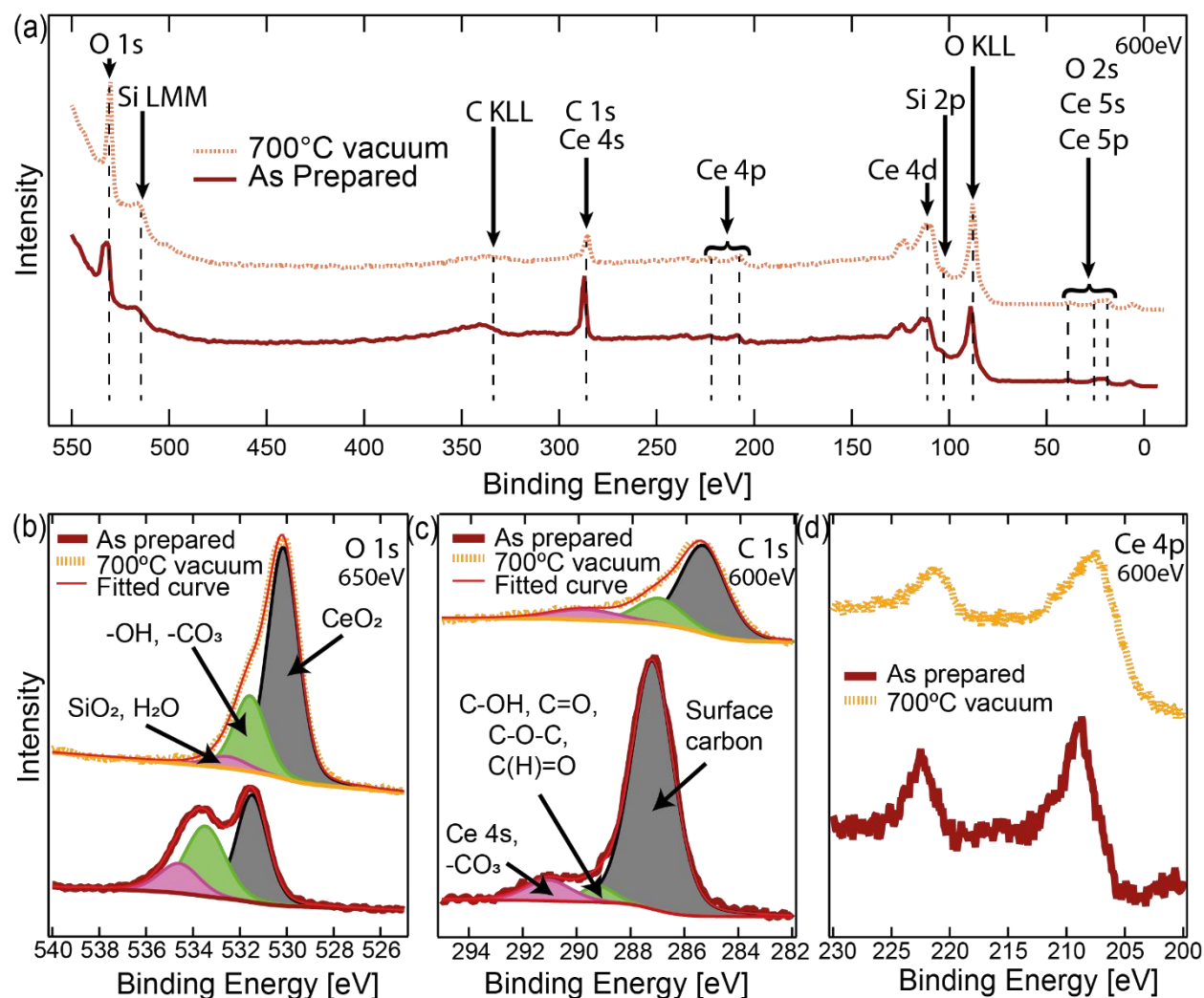


Fig. 5 – XPS results from as prepared and annealed samples: (a) Widescan measured with photon energy 600 eV. (b)-(d) Narrow scans of O 1s (b), C 1s (c) and Ce 4p (d) core levels. The dark red line is the sample as it was loaded, and the orange dotted line after it had been heated to 700°C in vacuum. The O 1s (b) and C 1s (c) spectra have been decomposed into peaks corresponding to different groups of molecules containing oxygen or carbon.

For the C 1s peak, the major component at binding energy 285.3 eV (287.2 eV) stems from a variety of hydrocarbons on the surface, as is expected for most samples exposed to air [26]. The peak at 287.0 eV (289.2 eV) is likely from carbon bound to oxygen in alcohols, ethers, ketones or aldehydes [23], [26]. Ce 4s is expected to be at a binding energy of 289 eV [25]. The peak at 289.7 eV (291.0 eV) in the C 1s spectrum is therefore thought to be Ce 4s, but it could also be carbonates [23].

The decomposition of the Ce 4p peak is under further investigation, but its general shape resembles that found in literature [25]. If a surface layer of carbon is removed when heating, the cerium intensity is expected to increase. However, from the narrow scan in Fig. 5(d), the intensity of the Ce 4p peak seems to not increase upon heating, and neither does the Ce 4s peak in Fig. 5(c). This is probably because of uncertainty in the intensities for these scans. Due to low intensities, a higher pass energy (100 eV, instead of 40 eV) was used when acquiring spectra Ce 4p and C 1s after heating. In Fig. 5(c) and (d), a scaling factor was utilized to obtain equivalent intensities before and after heating, but the uncertainty when comparing the intensity for these curves are greater than for the O 1s spectra. When looking at the Ce 4p peaks before and after heating from the widescan in Fig. 5(a), the intensity of Ce 4p seems to have doubled after heating.

4. Conclusions

In the current research effort, the different factors influencing the wettability of CeO₂ were studied. For this, magnetron sputtering deposition of CeO₂ thin films was carried out on texturized silicon. The chemical composition of the coatings was found as CeO₂ by means of XRD and XPS measurements and the texturization of the films was confirmed with SEM. We found that water contact angle of the films can drastically be enhanced by surface texturization. It was shown that hydrophobicity of the magnetron sputtered films can further be enhanced by depositing silicone oil and 1-octadecene. Our results indicate that different organic molecules adsorbed on the CeO₂ surface have a divergent effect on modification of the wetting properties. Despite the presence of adsorbed molecules, the surface material still has a significant effect on the general hydrophobicity that was shown for CeO₂ and naturally oxidized SiO_x. Control of all mentioned parameters – surface texturization, surface material and adsorbed organic molecules – allows variation of the water contact angle in a wide range, including the superhydrophobic state.

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References

- [1] G. Azimi, R. Dhiman, H. M. Kwon, A. T. Paxson, and K. K. Varanasi, “Hydrophobicity of rare-earth oxide ceramics,” *Nat. Mater.*, vol. 12, no. 4, pp. 315–320, 2013.
- [2] G. Gaustad, E. Williams, and A. Leader, “Rare earth metals from secondary sources: Review of potential supply from waste and byproducts,” *Resour. Conserv. Recycl.*, vol. 167, no. February 2020, p. 105213, 2021.
- [3] S. Guo, H. Arwin, S. N. Jacobsen, K. Järrendahl, and U. Helmersson, “A spectroscopic ellipsometry study of cerium dioxide thin films grown on sapphire by rf magnetron sputtering,” *J. Appl. Phys.*, vol. 77, no. 10, pp. 5369–5376, 1995.
- [4] S. Colis *et al.*, “Extrinsic ferromagnetism in epitaxial Co-doped CeO₂ pulsed laser deposited films,” *J. Appl. Phys.*, vol. 108, no. 5, 2010.
- [5] R. M. Bueno, J. M. Martinez-Duart, M. Hernández-Vélez, and L. Vázquez, “Optical and structural characterization of r.f. sputtered CeO₂ thin films,” *J. Mater. Sci.*, vol. 32, no. 7, pp. 1861–1865, 1997.
- [6] D. J. Preston, N. Miljkovic, J. Sack, R. Enright, J. Queeney, and E. N. Wang, “Effect of hydrocarbon adsorption on the wettability of rare earth oxide ceramics,” *Appl. Phys. Lett.*, vol. 105, no. 1, pp. 1–8, 2014.
- [7] S. Prakash *et al.*, “Intrinsic hydrophilic nature of epitaxial thin-film of rare-earth oxide grown by pulsed laser deposition,” *Nanoscale*, vol. 10, no. 7, pp. 3356–3361, 2018.
- [8] S. P. Fu, J. Rossero, C. Chen, D. Li, C. G. Takoudis, and J. T. Abiade, “On the wetting behavior of ceria thin films grown by pulsed laser deposition,” *Appl. Phys. Lett.*, vol. 110, no. 8, pp. 1–6, 2017.
- [9] R. Lundy *et al.*, “Exploring the Role of Adsorption and Surface State on the Hydrophobicity of Rare Earth Oxides,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 15, pp. 13751–13760, 2017.
- [10] Z. Shi, Z. Zhou, P. Shum, and L. K. Y. Li, “Thermal stability, wettability and corrosion resistance of sputtered ceria films on 316 stainless steel,” *Appl. Surf. Sci.*, vol. 477, pp. 166–171, 2019.
- [11] P. Xu, G. Meng, L. Pershin, J. Mostaghimi, and T. W. Coyle, “Control of the hydrophobicity of rare earth oxide coatings deposited by solution precursor plasma spray by hydrocarbon adsorption,” *J. Mater. Sci. Technol.*, vol. 62, pp. 107–118, 2021.

- [12] A. Marmur, "The Lotus Effect: Superhydrophobicity and Metastability," *Langmuir*, vol. 20, no. 9, pp. 3517–3519, Apr. 2004.
- [13] J. Jeevahan, M. Chandrasekaran, G. Britto Joseph, R. B. Durairaj, and G. Mageshwaran, "Superhydrophobic surfaces: a review on fundamentals, applications, and challenges," *J. Coatings Technol. Res.*, vol. 15, no. 2, pp. 231–250, 2018.
- [14] S. F. Toosi, S. Moradi, and S. G. Hatzikiriakos, "Fabrication of micro/nano patterns on polymeric substrates using laser ablation methods to control wettability behaviour: A critical review," *Rev. Adhes. Adhes.*, vol. 5, no. 1, pp. 55–78, 2017.
- [15] P. K. Basu, D. Sarangi, K. D. Shetty, and M. B. Boreland, "Liquid silicate additive for alkaline texturing of mono-Si wafers to improve process bath lifetime and reduce IPA consumption," *Sol. Energy Mater. Sol. Cells*, vol. 113, pp. 37–43, 2013.
- [16] J. Oh *et al.*, "The Apparent Surface Free Energy of Rare Earth Oxides is Governed by Hydrocarbon Adsorption," *iScience*, vol. 25, no. 1, p. 103691, 2021.
- [17] J. Tam, B. Feng, Y. Ikuhara, H. Ohta, and U. Erb, "Crystallographic orientation–surface energy–wetting property relationships of rare earth oxides," *J. Mater. Chem. A*, vol. 6, no. 38, pp. 18384–18388, 2018.
- [18] K. Nakayama, T. Hiraga, C. Zhu, E. Tsuji, Y. Aoki, and H. Habazaki, "Facile preparation of self-healing superhydrophobic CeO₂ surface by electrochemical processes," *Appl. Surf. Sci.*, vol. 423, pp. 968–976, 2017.
- [19] J. Bae, I. A. Samek, P. C. Stair, and R. Q. Snurr, "Investigation of the Hydrophobic Nature of Metal Oxide Surfaces Created by Atomic Layer Deposition," *Langmuir*, vol. 35, no. 17, pp. 5762–5769, 2019.
- [20] L. Zhao *et al.*, "Lithium niobate microtubes within ordered macroporous silicon by templated thermolysis of a single source precursor," *Chem. Mater.*, vol. 17, no. 1, pp. 3–5, 2005.
- [21] M. Jorge *et al.*, "Accelerated ageing of molybdenum oxide," *Mater. Res. Express*, vol. 4, no. 11, p. 115502, Nov. 2017.
- [22] S. Khan, G. Azimi, B. Yildiz, and K. K. Varanasi, "Role of surface oxygen-to-metal ratio on the wettability of rare-earth oxides," *Appl. Phys. Lett.*, vol. 106, no. 6, pp. 2–7, 2015.
- [23] L. Martínez, E. Román, J. L. de Segovia, S. Poupard, J. Creus, and F. Pedraza, "Surface study of cerium oxide based coatings obtained by cathodic electrodeposition on zinc," *Appl. Surf. Sci.*, vol. 257, no. 14, pp. 6202–6207, 2011.
- [24] E. J. Preisler, O. J. Marsh, R. A. Beach, and T. C. McGill, "Stability of cerium oxide on silicon studied by x-ray photoelectron spectroscopy," *J. Vac. Sci. & Technol. B Microelectron. Nanom. Struct. Process. Meas. Phenom.*, vol. 19, no. 4, pp. 1611–1618, 2001.
- [25] K. I. Maslakov *et al.*, "XPS study of ion irradiated and unirradiated CeO₂ bulk and thin film samples," *Appl. Surf. Sci.*, vol. 448, pp. 154–162, 2018.
- [26] T. L. Barr and S. Seal, "Nature of the use of adventitious carbon as a binding energy standard," *J. Vac. Sci. & Technol. A*, vol. 13, no. 3, pp. 1239–1246, 1995.