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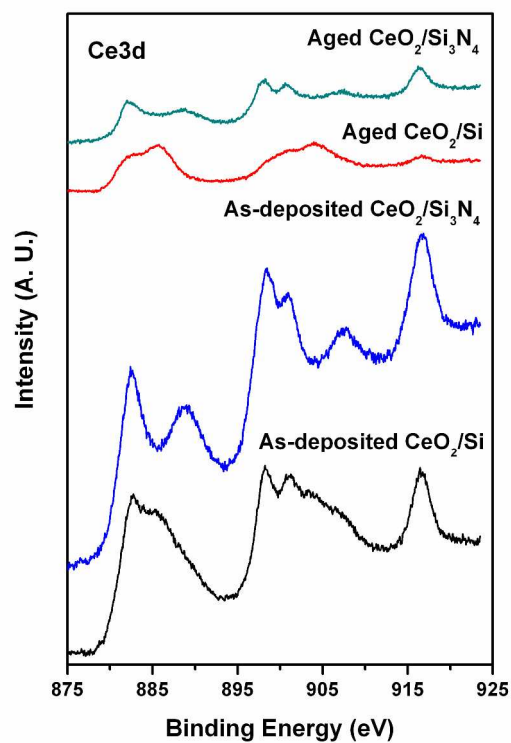
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# XRD and XPS studies of room temperature spontaneous interfacial reaction of CeO<sub>2</sub> thin films on Si and Si<sub>3</sub>N<sub>4</sub> substrates

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## Graphical Abstract



# XRD and XPS studies of room temperature spontaneous interfacial reaction of CeO<sub>2</sub> thin films on Si and Si<sub>3</sub>N<sub>4</sub> substrates

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## Abstract

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) investigations of interfacial reaction between Ce and Si have been carried out on the same set of as-deposited and 15 months aged films. XRD patterns demonstrate the presence of several peaks associated with CeO<sub>2</sub> planes in aged CeO<sub>2</sub>/ Si<sub>3</sub>N<sub>4</sub> thin film in comparison with as-deposited nanocrystalline film, whereas peak gets broadened in CeO<sub>2</sub>/Si film after aging. XPS studies show that interfacial reaction occurs spontaneously in CeO<sub>2</sub>/Si thin film at room temperature. Ce is present as both Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states in as-deposited CeO<sub>2</sub>/Si thin film, whereas Ce<sup>4+</sup> is the main species in CeO<sub>2</sub> thin film deposited on Si<sub>3</sub>N<sub>4</sub> substrate. When XPS has been recorded after 15 months, concentration of Ce<sup>3+</sup> species is observed to increase drastically in CeO<sub>2</sub>/Si thin film. In contrast, interfacial reaction between CeO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> substrate is not significant in the film even after 15 months of deposition. This shows that the initial room temperature spontaneous interfacial reaction observed in CeO<sub>2</sub>/Si film continues at much higher rate, whereas nature of CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interface remains the same after 15 months, proving its stability.

**Keywords:** Thin film; CeO<sub>2</sub>; Si; Si<sub>3</sub>N<sub>4</sub>; Interfacial reaction; XRD; XPS

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## 1. Introduction

In last several years, CeO<sub>2</sub> based materials have attracted much attention for their applications in catalysis, hydrogen production, H<sub>2</sub>-O<sub>2</sub> recombination in batteries and electrodes in fuel cells.<sup>1-5</sup>

In microelectronics, it has also been found to be a high  $\kappa$ -gate oxide material for its unique properties like moderate band gap (3–3.6 eV), high dielectric constant (23–52), high refractive index (2.2–2.8) and high dielectric strength ( $\sim 25 \text{ MV cm}^{-1}$ ).<sup>6</sup> It is also suitable for Si based metal oxide semiconductor (MOS) devices due to its small lattice mismatch ( $-0.35\%$ ) with Si that favors its epitaxial growth on different silicon surfaces.<sup>6,7</sup> In this regard, understanding of the growth, structure, nature of interface and long term stability between CeO<sub>2</sub> and substrates are very crucial for device applications.

CeO<sub>2</sub> thin films have mainly been grown on Si, Si<sub>3</sub>N<sub>4</sub>, sapphire, LaAlO<sub>3</sub>, SrTiO<sub>3</sub>, glass, alloy and yttria-stabilized zirconia (YSZ) substrates using different thin film deposition techniques such as magnetron sputtering, electron beam evaporation, flash evaporation, pulsed laser deposition, ion beam epitaxy, molecular beam epitaxy, plasma enhanced chemical vapor deposition, sol-gel, spray pyrolysis have been employed to deposit CeO<sub>2</sub> films.<sup>7-20</sup> Recently, we have investigated interfacial reactions between CeO<sub>2</sub> and substrates like Si, Al, Ti-6Al-4V alloy, Si<sub>3</sub>N<sub>4</sub> and glass using XPS.<sup>8,9</sup> It has been observed that significant interfacial reaction occurs between CeO<sub>2</sub> and Si leading to the formation of Ce<sub>2</sub>O<sub>3</sub> and silicate in CeO<sub>2</sub>/Si film, whereas reaction is limited in CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>.<sup>8</sup> Extent of interfacial reactions of CeO<sub>2</sub> in different types of substrates are found as follows: Si > Al > Ti-6Al-4V alloy > Si<sub>3</sub>N<sub>4</sub> > glass.<sup>9</sup> However, reports on long term stability of CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> interfaces lack in the literature. In this communication, we compare the structural changes and reaction at the interfaces of CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> films after 15 months of deposition employing XRD and XPS.

## 2. Experimental methods

Details of growth and characterization of sputter deposited CeO<sub>2</sub> thin films on Si and Si<sub>3</sub>N<sub>4</sub> substrates are given in our previous publications.<sup>8,9</sup> CeO<sub>2</sub> thin films were deposited on Si and Si<sub>3</sub>N<sub>4</sub> substrates of 10 mm × 10 mm dimensions using a CeO<sub>2</sub> target (Allvac, 99.9%) employing magnetron sputtering assisted by inductively coupled plasma generated with 50 W RF power at 13.56 MHz. The substrates were cleaned with acetone and isopropyl alcohol with sonication prior to loading into the vacuum chamber. The chamber was pumped down to a base pressure of  $3 \times 10^{-6}$  mbar. The substrates were etched with H<sub>2</sub> plasma prior to deposition of thin films. Sputter deposition was carried out at room temperature with Ar atmosphere at a pressure of 8 μbar. The substrate was biased to a constant negative voltage of 150 V and the target was biased with bipolar pulses of 300 V using a pulse generator. Thickness of obtained CeO<sub>2</sub> thin films is around 25 nm. CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> thin films were kept in small plastic boxes in ambient conditions.

The structure of as-deposited and aged CeO<sub>2</sub> films was determined by XRD employing a PANalytical X'Pert PRO X-Ray diffractometer operated with CuKα radiation of 1.5418 Å wavelength at 40 kV and 30 mA in the 2θ range 20–60° with step size of 0.033°. XPS of CeO<sub>2</sub> thin films were recorded with a SPECS spectrometer using non-monochromatic AlKα radiation (1486.6 eV) as an X-ray source operated at 150 W (12.5 kV and 12 mA). The binding energies reported here were calculated with reference to C1s peak at 284.6 eV. All the spectra were obtained with pass energy of 25 eV and step increment of 0.05 eV. CasaXPS program was employed for curve-fitting of Ce3d core levels spectra into several components with Gaussian-Lorentzian peaks after Shirley background subtraction. Peak positions, spin-orbit splitting,

doublet intensity ratios and full width at half maximum (FWHM) were allowed to vary slightly as followed in the literature.

### 3. Results and discussion

XRD patterns of as-deposited and aged  $\text{CeO}_2$  thin films on Si and  $\text{Si}_3\text{N}_4$  substrates are displayed in Fig. 1. Main diffraction peaks associated with substrates that appear after  $60^\circ$  are not shown here. In both as-deposited films, a broad peak observed at  $33.4^\circ$  corresponds to  $\text{CeO}_2(200)$  reflection (JCPDS No. 81-0792) indicating the nanocrystalline nature of the films.<sup>21</sup> It is clear from the XRD patterns that  $\text{CeO}_2$  films grow preferentially to its (200) plane on Si and  $\text{Si}_3\text{N}_4$  substrates. There is a significant change in the XRD pattern of aged  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film. Intense diffraction peaks associated with (111), (200), (220) and (311) planes of  $\text{CeO}_2$  can be seen in the pattern of aged film. However, diffraction peak observed at  $33.4^\circ$  in as-deposited  $\text{CeO}_2/\text{Si}$  film appears to be broad after 15 months of deposition.

Ce3d core level spectra of  $\text{CeO}_2/\text{Si}$  and  $\text{CeO}_2/\text{Si}_3\text{N}_4$  films at different conditions are shown in Fig. 2. It is clear from the figure that Ce3d spectral envelop of as-deposited  $\text{CeO}_2/\text{Si}$  film is significantly different from the film after 15 months of deposition. Spectral envelopes of the film deposited on Si substrate indicate that Ce is in both +4 and +3 oxidation states and it can be resolved into several  $\text{Ce}3d_{5/2,3/2}$  spin-orbit doublet peaks related to  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  species along with satellites. Satellite peaks are associated with the charge transfer from ligand ( $\text{O}2p$ ) to metal ( $\text{Ce}4f$ ) during photoionization processes. Appreciable change in Ce3d core level spectrum is observed in the aged  $\text{CeO}_2/\text{Si}$  film. Comparison of spectral envelopes indicates that most of  $\text{Ce}^{4+}$  species present in as-deposited film is transformed into  $\text{Ce}^{3+}$  species during this time span. In contrast, there is no appreciable change in the spectrum of  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film after 15 months of deposition demonstrating that Ce is mostly present in +4 oxidation state. Fig. 3 presents typical

curve-fitted Ce3d spectra of CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> films after 15 months of deposition. In both the figures, Ce3d spectra consist of 10 peaks that are curve fitted in 5 doublets corresponding to 3d<sub>5/2</sub> (labeled as v) and 3d<sub>3/2</sub> (labeled as u) components. In curve-fitted Ce3d spectrum of CeO<sub>2</sub>/Si film, three doublet peaks labeled as v–u (882.7 and 901.2 eV), v''–u'' (888.8 and 907.1 eV) and v'''–u''' (898.1 and 916.5 eV) with spin-orbit separation of 18.5, 18.3 and 18.4 eV, respectively are assigned for the Ce<sup>4+</sup> species, whereas peaks labeled as v<sub>0</sub>–u<sub>0</sub> (881.6 and 899.6 eV) and v'–u' (885.5 and 903.9 eV) are associated with Ce<sup>3+</sup> species.<sup>8,9,22</sup> The u''' peak is relatively well separated from the rest of the spectrum and is the characteristic of the presence of tetravalent Ce (Ce<sup>4+</sup>) in Ce compounds. It is to be noted that v''' and u''' spin-orbit peaks are attributed to the primary photoionization from Ce<sup>4+</sup> with Ce3d<sup>9</sup>4f<sup>0</sup>O2p<sup>6</sup> final state, whereas lower binding energy peaks of v''–u'' and v–u correspond to the shake-down satellite features of Ce3d<sup>9</sup>4f<sup>1</sup>O2p<sup>5</sup> and Ce3d<sup>9</sup>4f<sup>2</sup>O2p<sup>4</sup> final states of Ce<sup>4+</sup>. Spin-orbit doublet peaks of v'–u' are related to Ce3d<sup>9</sup>4f<sup>1</sup>O2p<sup>6</sup> final state of main photoionization from Ce<sup>3+</sup> and associated lower binding energy v<sub>0</sub>–u<sub>0</sub> peaks are characteristic shake-down satellites of Ce3d<sup>9</sup>4f<sup>2</sup>O2p<sup>5</sup> final state. Peak areas (A) of Ce<sup>4+</sup> and Ce<sup>3+</sup> components are commonly used to estimate their relative concentrations (C) in the films using the following equations:<sup>8,23</sup>

$$A_{\text{Ce}^{3+}} = A_{v_0} + A_{u_0} + A_{v'} + A_{u'} \quad (1)$$

$$A_{\text{Ce}^{4+}} = A_v + A_u + A_{v''} + A_{u''} + A_{v'''} + A_{u'''} \quad (2)$$

$$C_{\text{Ce}^{3+}} = \frac{A_{\text{Ce}^{3+}}}{A_{\text{Ce}^{3+}} + A_{\text{Ce}^{4+}}} \quad (3).$$

Concentration of Ce<sup>3+</sup> in as-deposited CeO<sub>2</sub>/Si film is evaluated to be 32% with respect to the total amount of Ce species.<sup>8</sup> On the other hand, mainly Ce<sup>3+</sup> related peaks along with a small

amount of  $\text{Ce}^{4+}$  can be seen in the film after 15 months of deposition and its concentration is 67% which is more than double in comparison with as-deposited film. In case of  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film,  $\text{Ce}^{4+}$  species is predominant after 15 months of deposition. A comparison of concentrations of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  evaluated from Ce3d spectra in  $\text{CeO}_2/\text{Si}$  and  $\text{CeO}_2/\text{Si}_3\text{N}_4$  thin films at different conditions are given in Table 1. It is important to note that  $\text{Ce}^{3+}$  in  $\text{CeO}_2/\text{Si}$  film can be related to the formation of cerium silicate or  $\text{Ce}_2\text{O}_3$  at the interface.<sup>7</sup> Drastic increase in the concentration of  $\text{Ce}^{3+}$  in  $\text{CeO}_2/\text{Si}$  film compared to  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film after 15 months of deposition indicates that interfacial reaction between  $\text{CeO}_2$  and Si occurs continuously in  $\text{CeO}_2/\text{Si}$  film at room temperature.

O1s core level spectrum of respective  $\text{CeO}_2$  thin film can also reveal the oxidation states of Ce in the film. In Fig. 4, O1s core level spectra of  $\text{CeO}_2/\text{Si}$  and  $\text{CeO}_2/\text{Si}_3\text{N}_4$  films at different conditions are shown. It is to be mentioned that O1s core level spectral envelop of as-deposited  $\text{CeO}_2/\text{Si}$  film is different from that of aged film, whereas both spectra look similar in  $\text{CeO}_2/\text{Si}_3\text{N}_4$  films. Peak at 529.9 eV corresponds to  $\text{O}^{2-}$  species in  $\text{CeO}_2$ , whereas peak at 531.6 eV is associated with  $\text{Ce}^{3+}$  species originated from silicate or  $\text{Ce}_2\text{O}_3$  species.<sup>8</sup> It has been found from the figure that  $\text{Ce}^{4+}$  related peak along with strong peak associated with  $\text{Ce}^{3+}$  species are present in as-deposited  $\text{CeO}_2/\text{Si}$  film. Intensity of the peak related to  $\text{Ce}^{4+}$  decreases drastically in the film after 15 months of deposition. On the other hand, intensity of the peak corresponding to  $\text{Ce}^{4+}$  remains unchanged in  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film after 15 months of deposition.

High resolution Si2p core level spectra of  $\text{CeO}_2/\text{Si}$  and  $\text{CeO}_2/\text{Si}_3\text{N}_4$  films at different conditions are shown in Fig. 5. Broad envelopes of Si2p core level spectra in  $\text{CeO}_2/\text{Si}$  films indicate the presence of elemental Si as well as oxidized Si species that can be curve fitted into several component peaks. A peak at 99.3 eV is related to the contribution from elemental Si



present in Si substrate. On the other hand, observed peaks at 101.2 and 102.4 eV correspond to  $\text{Si}^{2+}$  and  $\text{Si}^{3+}$  species, respectively.<sup>24,25</sup> The appearance of these species at the interface of  $\text{CeO}_2$  and Si indicates the interaction between them resulting the formation of cerium silicate species.<sup>6,7</sup> and concentrations of different oxide species increase in the film to some extent after 15 months of deposition demonstrating the continuous interfacial reaction over time. In contrast, a weak single peak at 101.5 eV in Si2p core level spectrum in  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film is attributed to Si–N bond in  $\text{Si}_3\text{N}_4$  and it remains same after 15 months of deposition.<sup>26</sup>

It has been observed from XPS studies that concentration of  $\text{Ce}^{4+}$  species in  $\text{CeO}_2/\text{Si}$  film decreases after 15 months of deposition indicating the continuous reduction of  $\text{Ce}^{4+}$  species to  $\text{Ce}^{3+}$  at room temperature. Decrease in the  $u'''$  peak intensity and increase in  $v'$  and  $u'$  intensities in the film after 15 months of deposition confirms the  $\text{Ce}^{4+}$  reduction. On the other hand,  $\text{Ce}^{4+}$  species predominates in  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film after 15 months of deposition demonstrating that  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film is stable even after 15 months of deposition at room temperature. XRD results also support this finding as intense peaks related to  $\text{CeO}_2$  are observed only in  $\text{CeO}_2/\text{Si}_3\text{N}_4$  film indicating the lack of intermixing between  $\text{CeO}_2$  and Si in this system. Thus, spontaneous interfacial reaction at room temperature increases  $\text{CeO}_2$  reduction in  $\text{CeO}_2/\text{Si}$  film. It has also been demonstrated earlier that interfacial reaction in  $\text{CeO}_2/\text{Si}$  film can occur as change in standard molar free energy of formation of products and reactants ( $\Delta G^\circ$ ) is negative ( $3\text{Si} + 8\text{CeO}_2 \rightarrow \text{SiO} + \text{Si}_2\text{O}_3 + 4\text{Ce}_2\text{O}_3$ ,  $\Delta G^\circ = -340.8 \text{ kJ mol}^{-1}$ ) indicating that reaction is thermodynamically favorable to proceed to their products.<sup>9</sup> Therefore, this reaction continuously goes on at room temperature over the time.

#### 4. Conclusions

CeO<sub>2</sub> related prominent peaks are observed in XRD pattern of aged CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> film with respect to as-deposited film, whereas only peak observed in as-deposited film becomes broad in aged CeO<sub>2</sub>/Si film. XPS studies show that most of Ce<sup>4+</sup> species gets reduced to Ce<sup>3+</sup> in CeO<sub>2</sub>/Si film after 15 months of deposition, whereas mainly Ce<sup>4+</sup> species is present in CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> film of same time period. Extent of spontaneous interfacial interaction at room temperature over time is found to be very high in CeO<sub>2</sub>/Si film, whereas it is significantly less in CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> film in the same condition. Thus, CeO<sub>2</sub> film deposited on Si<sub>3</sub>N<sub>4</sub> is stable in comparison with CeO<sub>2</sub>/Si film over time.

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### Figure captions

Fig. 1 XRD patterns of (a) as-deposited CeO<sub>2</sub>/Si, (b) as-deposited CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>, (c) aged CeO<sub>2</sub>/Si and (d) aged CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>.

Fig. 2 XPS of Ce3d core levels in CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> films: (a) as-deposited and (b) aged.

Fig. 3 Curve-fitted XPS of Ce3d core levels in aged CeO<sub>2</sub> films deposited on (a) Si and (b) Si<sub>3</sub>N<sub>4</sub> substrates [ $v_0$ – Ce<sup>3+</sup>3d<sub>5/2</sub>,  $v$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $v'$ – Ce<sup>3+</sup>3d<sub>5/2</sub>,  $v''$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $v'''$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $u_0$ – Ce<sup>3+</sup>3d<sub>3/2</sub>,  $u$ – Ce<sup>4+</sup>3d<sub>3/2</sub>,  $u'$ – Ce<sup>3+</sup>3d<sub>3/2</sub>,  $u''$ – Ce<sup>4+</sup>3d<sub>3/2</sub>,  $u'''$ – Ce<sup>4+</sup>3d<sub>3/2</sub>].

Fig. 4 XPS of O1s core levels in CeO<sub>2</sub> films deposited on Si and Si<sub>3</sub>N<sub>4</sub> substrates: (a) as-deposited and (b) aged.

Fig. 5 XPS of Si2p core levels in CeO<sub>2</sub> films deposited on Si and Si<sub>3</sub>N<sub>4</sub> substrates: (a) as-deposited and (b) aged.

**Table 1.** Relative surface concentrations of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  species in as-deposited and aged  $\text{CeO}_2/\text{Si}$  and  $\text{CeO}_2/\text{Si}_3\text{N}_4$  thin films as evaluated from XPS

Ce species	As-deposited		Aged	
	$\text{CeO}_2/\text{Si}$	$\text{CeO}_2/\text{Si}_3\text{N}_4$	$\text{CeO}_2/\text{Si}$	$\text{CeO}_2/\text{Si}_3\text{N}_4$
$\text{Ce}^{4+}$	$68 \pm 1.73$	$89 \pm 0.95$	$33 \pm 4.4$	$82 \pm 1.93$
$\text{Ce}^{3+}$	$32 \pm 1.73$	$11 \pm 0.95$	$67 \pm 4.4$	$18 \pm 1.93$

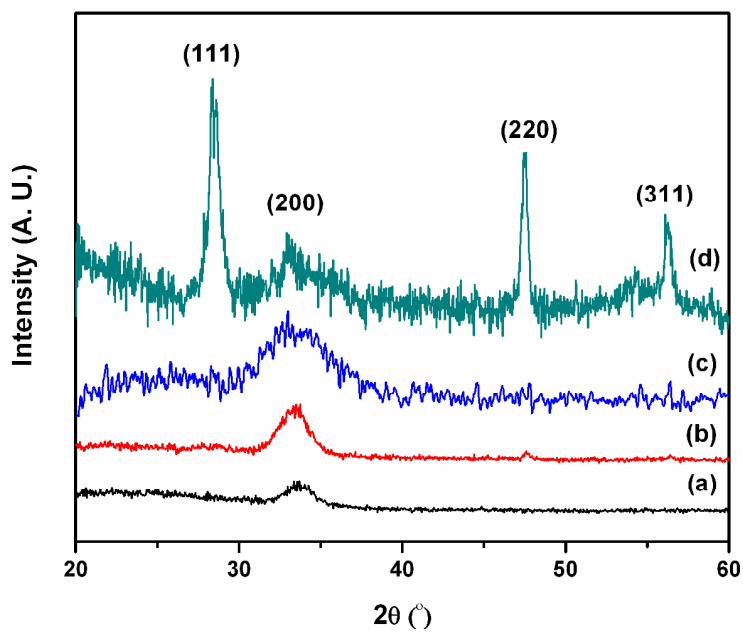


Fig. 1 XRD patterns of (a) as-deposited  $\text{CeO}_2/\text{Si}$ , (b) as-deposited  $\text{CeO}_2/\text{Si}_3\text{N}_4$ , (c) aged  $\text{CeO}_2/\text{Si}$  and (d) aged  $\text{CeO}_2/\text{Si}_3\text{N}_4$ .

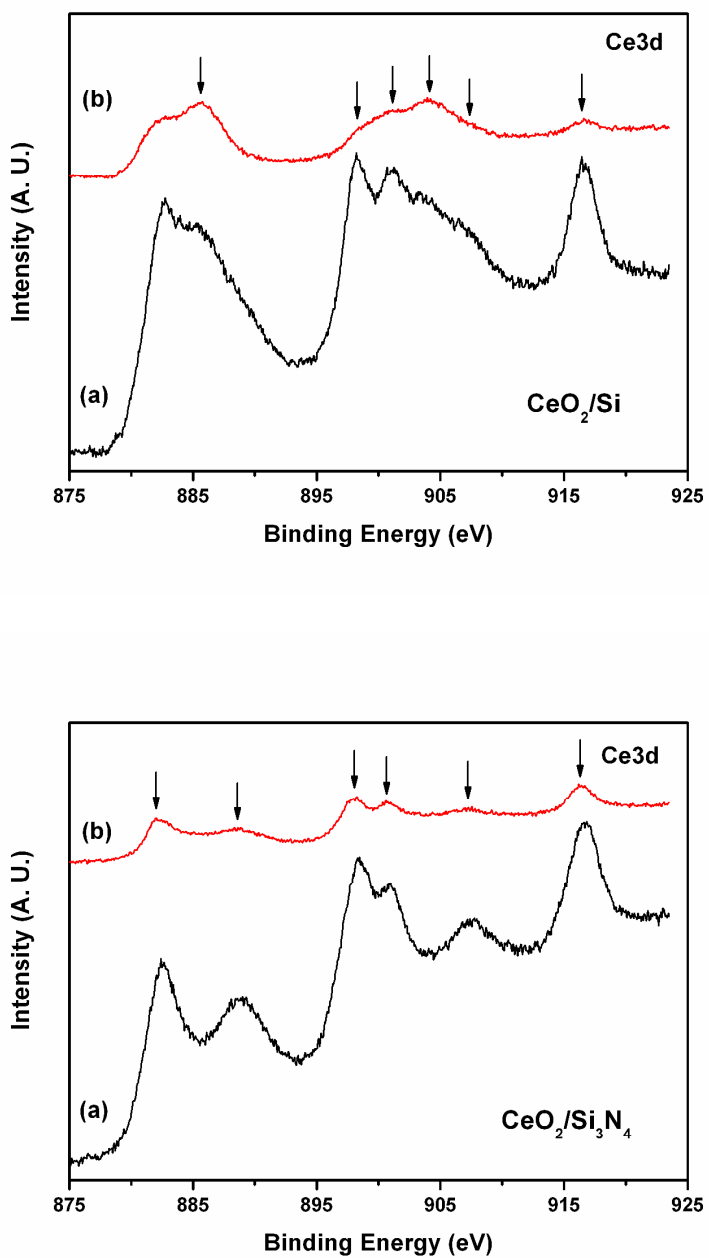


Fig. 2 XPS of Ce3d core levels in CeO<sub>2</sub>/Si and CeO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> films: (a) as-deposited and (b) aged.

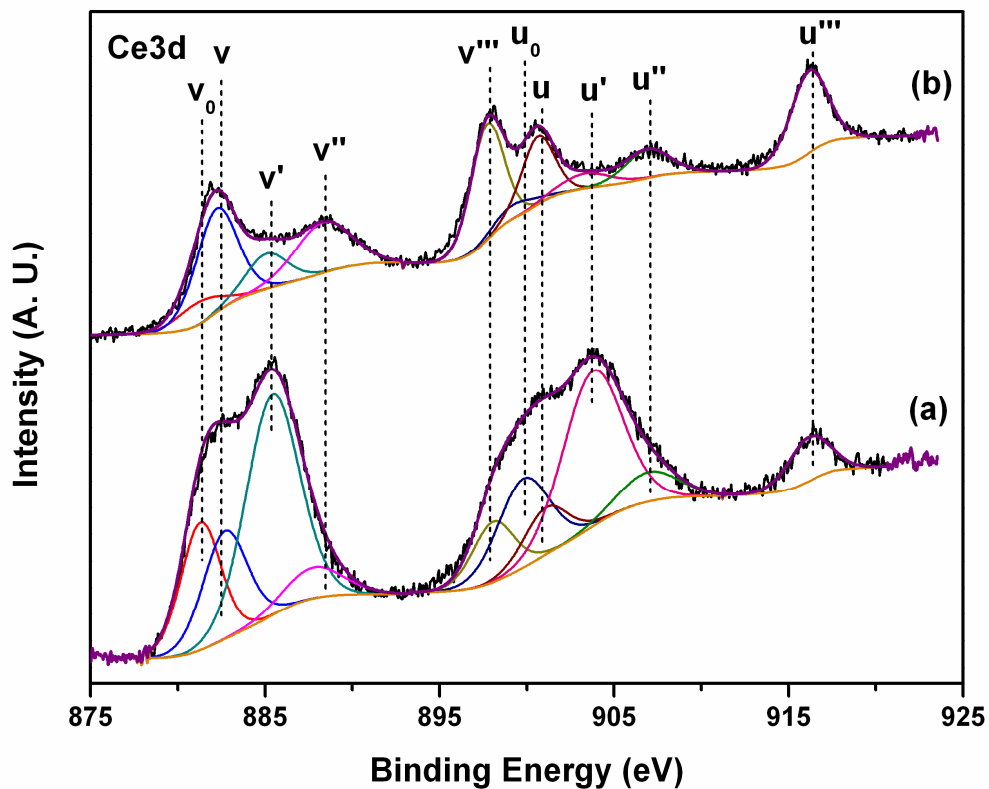


Fig. 3 Curve-fitted XPS of Ce3d core levels in aged CeO<sub>2</sub> films deposited on (a) Si and (b) Si<sub>3</sub>N<sub>4</sub> substrates [ $v_0$ – Ce<sup>3+</sup>3d<sub>5/2</sub>,  $v$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $v'$ – Ce<sup>3+</sup>3d<sub>5/2</sub>,  $v''$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $v'''$ – Ce<sup>4+</sup>3d<sub>5/2</sub>,  $u_0$ – Ce<sup>3+</sup>3d<sub>3/2</sub>,  $u$ – Ce<sup>4+</sup>3d<sub>3/2</sub>,  $u'$ – Ce<sup>3+</sup>3d<sub>3/2</sub>,  $u''$ – Ce<sup>4+</sup>3d<sub>3/2</sub>,  $u'''$ – Ce<sup>4+</sup>3d<sub>3/2</sub>].



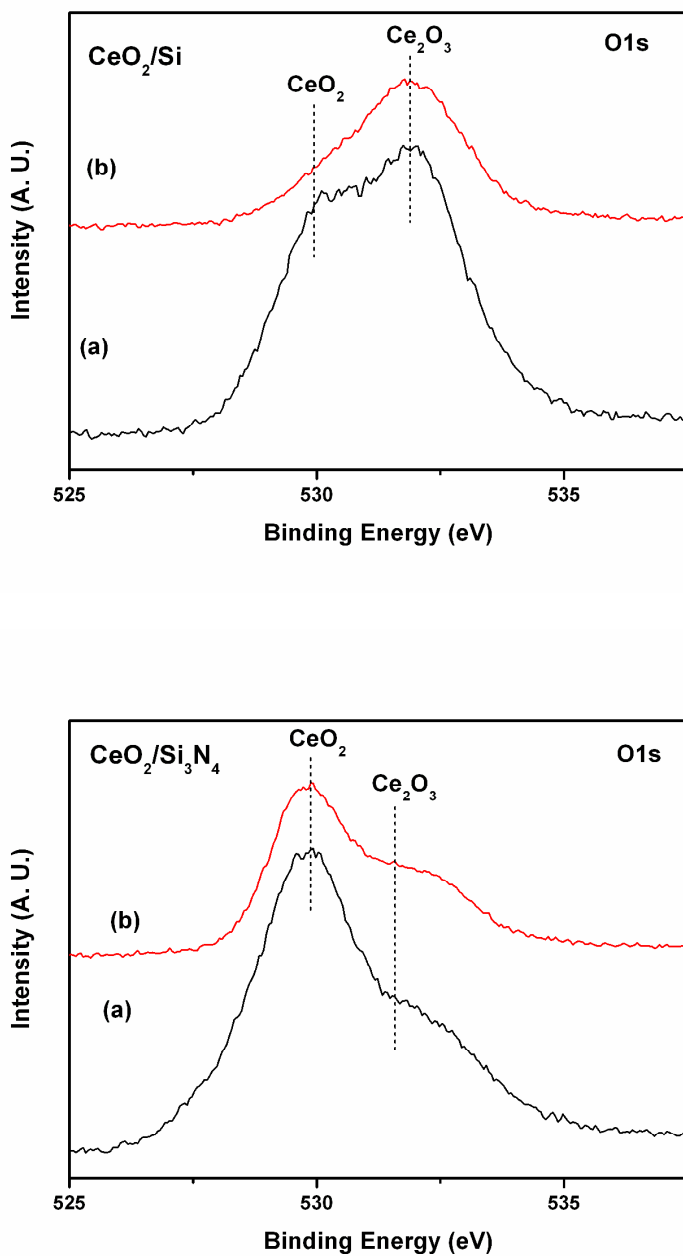


Fig. 4 XPS of O1s core levels in  $\text{CeO}_2$  films deposited on Si and  $\text{Si}_3\text{N}_4$  substrates: (a) as-deposited and (b) aged.

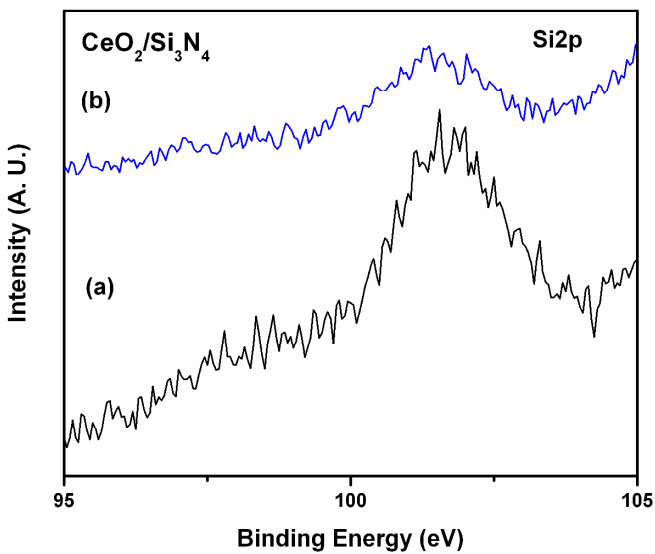
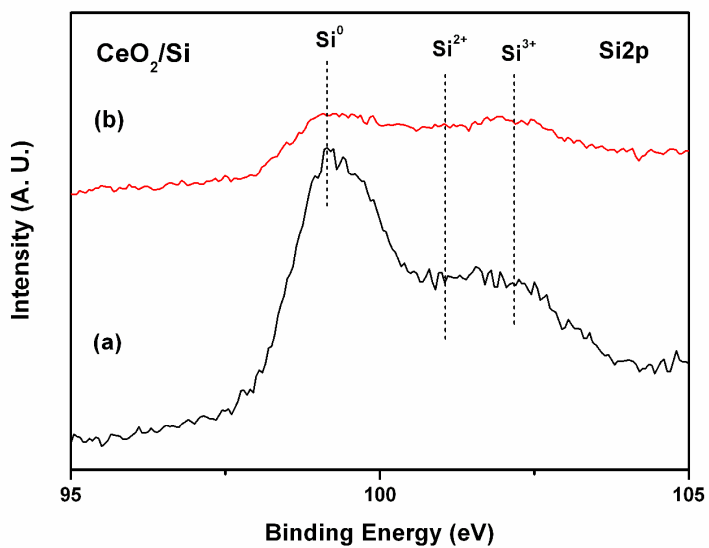


Fig. 5 XPS of Si2p core levels in CeO<sub>2</sub> films deposited on Si and Si<sub>3</sub>N<sub>4</sub> substrates: (a) as-deposited and (b) aged.