XPS studies on the interaction of CeO$_2$ with Silicon in magnetron sputtered CeO$_2$ thin films on Si and Si$_3$N$_4$ substrates

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Abstract

CeO$_2$ thin films were deposited on silicon and silicon nitride substrates by magnetron sputtering at room temperature and annealed at 400 and 600 °C in air and vacuum. Interaction between deposited CeO$_2$ and Si in CeO$_2$/Si and CeO$_2$/Si$_3$N$_4$ systems was investigated by XPS. The results show that Ce is present as both Ce$^{4+}$ and Ce$^{3+}$ oxidation states in CeO$_2$ film deposited on Si substrate, whereas Ce$^{4+}$ is the main species in as-deposited CeO$_2$/Si$_3$N$_4$ film. Detailed analyses of Ce3d, Si2p and O1s core level spectra demonstrate that Ce$_2$O$_3$ and SiO$_x$ or cerium silicate type of species are formed at the interface of CeO$_2$ and Si. Concentrations of Ce$^{3+}$ species increase drastically in CeO$_2$/Si thin films after annealing at 400 °C in vacuum due to enhanced interfacial reaction. On the other hand, interfacial reaction between CeO$_2$ and Si$_3$N$_4$ substrate is limited in as-deposited as well as 600 °C heat treated films.

Keywords: CeO$_2$; Thin film; Silicon; Silicon nitride; Interfacial reaction; XPS

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1. Introduction

In last several years, CeO$_2$ powders and thin films have become attractive materials for various catalytic, electrochemical, electronic, optical, electrical, gas sensor and corrosion resistant applications [1–8]. CeO$_2$ based materials are important for applications in auto exhaust catalysis, hydrogen production, electrodes in fuel cells [1,2,9,10]. In microelectronics, among various high-$\kappa$ gate oxide materials, CeO$_2$ is one of the attractive candidates due to its high dielectric constant (23–52), high refractive index (2.2–2.8), high dielectric strength ($\sim$25 MV cm$^{-1}$) and moderate band gap (3–3.6 eV) [11]. Small lattice mismatch as well as thermodynamic stability in contact with Si favors the epitaxial growth of CeO$_2$ on different Si surfaces [12,13]. Moreover, with its good adhesion on Si, high stability against mechanical abrasion and chemical attack it is more suitable for complementary metal–oxide–semiconductor (CMOS) devices. It has also been a potential alternative to standard SiO$_2$ based silicon-on-insulator (SOI) technology [14]. In this sense, many research groups have attempted to grow epitaxial thin films on Si substrates by different thin film deposition techniques such as electron beam evaporation, magnetron sputtering, flash evaporation, pulsed laser deposition, ion beam epitaxy, molecular beam epitaxy, plasma enhanced chemical vapor deposition, sol-gel, spray pyrolysis [12–24]. However, in most cases, an important issue is the nature of CeO$_2$–Si interface and its stability as potential applications depend on better understanding and controlling the quality of CeO$_2$/Si interface.

It has been found that Si can react with CeO$_2$ at the CeO$_2$/Si interface to form silicon oxides, cerium silicate [13,19,25–27]. In a recent study, Skála and Matolín have investigated the interaction of silicon and CeO$_2$ employing XPS where they have found the formation of cerium
silicate whose thickness has been limited by diffusion of silicon [28]. They have also found formation of sub oxides of silicon. When CeO$_2$ is directly deposited on Si, an interfacial layer is formed resulting in high interface state densities and in an increase of effective oxide thickness which is not desirable [18,25]. For example, silicate and silicide formed at the interface of high-$\kappa$ material, HfO$_2$ and Si during film deposition and subsequent annealing has been found to degrade the device performance [29–31]. However, Si$_3$N$_4$ layer has been used to minimize the formation of interfacial layers in case of HfO$_2$/Si film [32,33]. Interfacial reaction with HfO$_2$ has been controlled by nitridation and oxynitridation of Si [30]. Therefore, within this context, interaction between CeO$_2$ and Si$_3$N$_4$ is important. Hence, thermal stability and bonding nature at the interface of CeO$_2$ and Si in CeO$_2$/Si and CeO$_2$/Si$_3$N$_4$ has been explored in details in this work.

Growth of CeO$_2$ on Si substrate, their structure and interaction with Si under different conditions have been studied by XRD, TEM, SEM, RHEED, LEED, RBS, Raman, AES, XPS and XANES [15,16,18,20,34–38]. XPS particularly provides detailed information about the electronic nature of the interaction. There are several XPS studies about the interfacial reaction between CeO$_2$ and Si in the literature [13,25,26,38–42]. However, growth and structure of CeO$_2$ on Si$_3$N$_4$ substrate and their interaction is lacking in the literature. In the present study, we, for the first time report the growth of CeO$_2$ on Si$_3$N$_4$ substrate using magnetron sputtering and detailed XPS studies of interaction between CeO$_2$ and Si. Growth and interaction of CeO$_2$ with Si on Si substrate have also been investigated for comparison.

2. Experimental methods

CeO$_2$ thin films were deposited on Si and Si$_3$N$_4$ substrates using a CeO$_2$ 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 by sonication using acetone/isopropyl alcohol 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$_2$ 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$_2$ thin films is around 25 nm.

XPS of CeO$_2$ thin films were recorded with a SPECS spectrometer using non-monochromatic AlKα source (1486.6 eV) run at 150 W (12 kV and 12.5 mA). The binding energies reported here were calculated with reference to C1s peak at 284.6 eV with a precision of ± 0.1 eV. All the spectra were obtained with a pass energy of 25 eV and step increment of 0.05 eV. The experimental data were curve fitted into several components with Gaussian-Lorentzian peaks using Shirley background employing CasaXPS program. For component peaks, slightly different full width at half maximum (FWHM) was used for different chemical states. The spin-orbit splitting and doublet intensities were fixed as given in the literature [43].

3. Results and discussion

3.1. As-deposited films

Fig. 1 compares Ce3d core level spectra of CeO$_2$ films deposited on Si and Si$_3$N$_4$ substrates. The spectral envelop of Ce3d on Si substrate reveals that Ce is in both +4 and +3 oxidation states and it could be resolved into several Ce3d$_{5/2,3/2}$ spin-orbit doublet peaks with splitting of around 18 eV. In contrast, on Si$_3$N$_4$ substrate, the spectrum mostly resembles the +4 state in CeO$_2$. Fig. 2 presents deconvoluted Ce3d spectra of CeO$_2$ coated on Si and Si$_3$N$_4$ substrates. Binding energies, FWHMs and relative integrated peak areas of Ce3d$_{5/2,3/2}$ spin-orbit
doublets in CeO$_2$ films deposited on Si and Si$_3$N$_4$ are summarized in Tables 1 and 2, respectively. In Fig. 2 (a) related to CeO$_2$/Si film, peaks labeled as v are arising from 3d$_{5/2}$ photoemissions, whereas associated 3d$_{3/2}$ emissions are labeled as u. Spin-orbit peaks of v$''' \text{ and } u'''$ at $898.2$ and $916.5$ eV with $18.3$ eV separation are attributed to primary photoionization from Ce$^{4+}$ with Ce$^{3d\,4f\,O^2p^6}$ final state. Lower binding energy states of v$''-u''$ and v–u have been assigned to the Ce$^{3d\,4f\,O^2p^5}$ and Ce$^{3d\,4f^2\,O^2p^4}$ final states shake-down satellite features [38,44–47]. Satellites are caused by the facilitation of ligand (O2p) to metal (Ce4f) charge transfer by primary photoionization process. Peaks labeled as v$_o$, v$'$ and u$_o$, u$'$ at $881.1$, $885.5$ and $899.0$, $903.9$ eV are associated with Ce$^{3+}$ final states. In this sense, v$'-u'$ spin orbit doublet peaks are assigned to main photoionization from Ce$^{3d\,4f\,O^2p^6}$ final state, whereas lower binding energy v$_o$–u$_o$ peaks correspond to characteristic Ce$^{3d\,4f^2\,O^2p^5}$ final state shake-down satellites [26,38,44–48]. It has been proposed that fully oxidized CeO$_2$ layer grows on top of the interfacial phase and Ce$^{3+}$ containing phase is buried under CeO$_2$ layer [13]. Peak areas (A) of Ce$^{4+}$ and Ce$^{3+}$ components are commonly used to estimate their relative concentrations (C) in the films using the following equations [26,46]:

$$A_{\text{Ce}^{4+}} = A_{v_o} + A_{v'} + A_{u'} + A_{u'''}$$  \hspace{1cm} (1)

$$A_{\text{Ce}^{3+}} = A_{v'} + A_{u'} + A_{u'''} + A_{u''} + A_{v''} + A_{v'''}$$  \hspace{1cm} (2)

$$C_{\text{Ce}^{3+}} = \frac{A_{v'}}{A_{v'} + A_{u'} + A_{u'''} + A_{u''} + A_{v''} + A_{v'''}}$$  \hspace{1cm} (3).

According to the equation (3) the concentration of Ce$^{3+}$ in CeO$_2$ deposited on Si is estimated to be 32% with respect to the total amount of Ce species. On the other hand, mainly Ce$^{4+}$ related peaks along with a small amount of Ce$^{3+}$ can be seen in CeO$_2$ deposited on Si$_3$N$_4$ substrate which
is displayed in Fig. 2 (b). Here estimated amount of Ce\(^{3+}\) is 11% only. It is worth noting that Ce is in +3 oxidation state in all cerium silicates and therefore, observation of Ce\(^{3+}\) in CeO\(_2\) films deposited on both Si and Si\(_3\)N\(_4\) substrates can be associated with formation of cerium silicate as observed in similar CeO\(_2\) films or Ce\(_2\)O\(_3\) at the interface [13]. It is to be noted that amount of Ce\(^{3+}\) is less on Si\(_3\)N\(_4\) substrate in comparison with Si substrate indicating that interfacial reaction between CeO\(_2\) and Si is low when CeO\(_2\) is deposited on Si\(_3\)N\(_4\) substrate.

In Fig. 3, Si2p core level spectra from Si substrate coated with CeO\(_2\) film is shown. Si2p in pure Si substrate is also given for comparison. A sharp peak at 99.4 eV observed in pure Si substrate corresponds to elemental Si. In contrast, broad nature of Si2p core level spectrum in CeO\(_2\) coated Si substrate indicates the presence of several Si species which can be deconvoluted into component peaks. Component peak at 99.3 eV corresponds to elemental Si present in Si substrate, whereas peaks observed at 101.2 and 102.4 eV could be attributed to Si\(^{2+}\) and Si\(^{3+}\) species [49,50]. The appearance of these species at the interface of CeO\(_2\) and Si shows the interaction between them where it can be expected to bond in a Si–Ce–O matrix in the form of silicate [27]. On the other hand, single peak at 101.5 eV found in Si2p core level spectrum in CeO\(_2\)/Si\(_3\)N\(_4\) film can be assigned for Si–N bond in Si\(_3\)N\(_4\) [51].

O1s core level spectra can be used as another source of information on oxidation states of Ce. Deconvoluted O1s core level spectra from as-deposited film on Si and Si\(_3\)N\(_4\) substrates are shown in Fig. 4. O1s core level spectrum in as-deposited film on Si shows four peaks at 529.9, 531.6, 532.1 and 533.8 eV (Fig. 4a). Peak at 529.9 eV can be attributed to O\(^{2-}\) species in CeO\(_2\), whereas observed peak at 532.1 eV corresponds to O in Si–O bonded species that compares well with the literature [13,40,41]. Intermediate peak at 531.6 eV is related to Ce\(^{3+}\) species originated from silicate or Ce\(_2\)O\(_3\) species [13]. Amount of Ce\(^{3+}\) has been estimated from areas of O1s
component peaks related to Ce$^{4+}$ and Ce$^{3+}$ species and it is found to be 28% which is close to the estimation from corresponding Ce3d peak. A higher binding energy component at 533.8 eV is associated with adsorbed H$_2$O species. In contrast, CeO$_2$ film deposited on Si$_3$N$_4$ substrate contains an intense peak at 529.8 eV that is related to O$^{2-}$ species in CeO$_2$ (Fig. 4b). Two weak peaks at 531.4 and 532.5 eV are assigned for oxygen species in silicate or Ce$_2$O$_3$ and Si–O network, respectively. Thus, O1s core levels demonstrate that the relative concentration of Ce$^{3+}$ related oxygen species is less in the film deposited on Si$_3$N$_4$ substrate compared with Si counterpart.

3.2. Heat treated films

CeO$_2$ films on Si and Si$_3$N$_4$ substrates were heat treated at 400 and 600 °C under a vacuum of $10^{-5}$ mbar for 30 min to know about the stability of the interface. Films coated on Si$_3$N$_4$ substrate were also heated at the same temperatures in air, but in case of films on Si, only vacuum annealing was carried out to avoid effect of atmospheric oxygen. Fig. 5 compares Ce3d core level spectra from CeO$_2$ deposited on Si and Si$_3$N$_4$ after annealing at different conditions. It can be observed from the figure that Ce3d spectral nature on Si substrate heated at 400 and 600 °C in vacuum are different from that on Si$_3$N$_4$ substrate. Amount of Ce$^{4+}$ species in CeO$_2$ films deposited on Si substrate decreases when films are heat treated at higher temperatures indicating the reduction of Ce$^{4+}$ species. This can be clearly understood from the intensity of u”” peak that decreases on annealing. After annealing the film at 600 °C in vacuum, u”” peak nearly disappears in the Ce3d spectrum shown in Fig. 5. Typical deconvoluted Ce3d core level spectra from 400 and 600 °C heat treated CeO$_2$ coated on Si and Si$_3$N$_4$ substrates, respectively are given in Fig. 6. Deconvoluted spectrum of the CeO$_2$/Si film heated at 400 °C in vacuum shown in Fig. 6 (a)
demonstrates the presence of mainly Ce\textsuperscript{3+} species in heat treated film and its amount is 54% calculated using equation (3). Peaks labeled as \( v_o, v' \) and \( u_o, u' \) at 881.5, 885.6 and 899.4, 904.2 eV are assigned to Ce\textsuperscript{3+} final states along with small contributions from Ce\textsuperscript{4+} species at 883.2, 888.5, 898.4, 901.6, 906.7 and 916.8 eV. Ce\textsuperscript{3+} species can be related to the formation of silicate or Ce\textsubscript{2}O\textsubscript{3} like phases. Intensities of peaks associated with Ce\textsuperscript{4+} species further decrease when sample is vacuum heated at 600 °C and from Fig. 5 it is clear that film predominately contains Ce\textsuperscript{3+} species. Amount of Ce\textsuperscript{3+} is 74% as evaluated from deconvoluted spectrum. In contrast, Ce\textsuperscript{4+} species predominates in CeO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} films heated at 400 and 600 °C in vacuum and also in air as can be seen from the intensity of \( u'' \) peak in Fig. 5 as well as the deconvoluted Ce3d spectrum in Fig. 6 (b) related to CeO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} film heated at 600 °C. Though concentration of Ce\textsuperscript{3+} species increases slightly in CeO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} film when heat treatment temperature increases from 400 to 600 °C in vacuum, but overall predominant species is Ce\textsuperscript{4+}. Similarly, Ce\textsuperscript{4+} is the main species in CeO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} films heated at 400 and 600 °C in air along with trace amount of Ce\textsuperscript{3+} components that could be seen from Tables 3 and 4, respectively where binding energies and relative integrated peak areas of Ce3d\textsubscript{5/2,3/2} spin-orbit doublets are given. This shows that CeO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} film is stable even after high temperature heat treatment in air. Similar characteristic behavior has also been reflected in the Ce4d core level spectra of as-deposited and heat treated films which are shown in Fig. 7. Ce4d core level of as-deposited CeO\textsubscript{2}/Si thin film shows several peaks at 108.5, 111.8, 114.8, 121.7 and 125.0 eV. According to the literature, peaks at 121.7 and 125.0 eV with spin-orbit splitting of 3.3 eV correspond to Ce4d\textsubscript{5/2,3/2} components of Ce\textsuperscript{4+} [52,53]. It is clear from the Fig. 7 that as-deposited CeO\textsubscript{2} film on Si substrate contains lower amount of Ce\textsuperscript{4+} species and it further decreases with increase in heat treatment temperature. On the other hand, intense higher binding energy Ce\textsuperscript{4+} component peaks are observed in the spectra obtained
from as-deposited as well as heat treated CeO₂ films deposited on Si₃N₄ substrate. Thus, XPS results demonstrate that heat treatment of CeO₂ films deposited on Si substrate facilitates the interfacial reaction between CeO₂ and Si resulting cerium silicate or Ce₂O₃. In contrast, the interface between CeO₂ and Si₃N₄ is stable even after high temperature treatment in air and vacuum.

Deconvoluted Si2p core level spectra from Si substrate obtained after heat treatment at 400 and 600 °C in vacuum are shown in Fig. 8. Envelop of Si2p core level peak in heat treated films on Si in the figure indicates an increase in spectral intensities of oxide related peaks already present in the as-deposited condition. Peaks at 99.3, 101.2 and 102.3 eV are assigned for elemental Si⁰, Si²⁺ and Si³⁺ species, respectively. A new peak at 103.3 eV is also seen along with the other three peaks in the film heated at 600 °C that is related to Si⁴⁺ species [49,50]. New species are formed at the interface of CeO₂ and Si due to enhanced interaction between them at higher temperatures. On the other hand, Si2p core level spectral features in CeO₂/Si₃N₄ films with various heat treatment conditions shown in Fig. 9 are different from CeO₂/Si films. Si2p spectrum from pure Si₃N₄ substrate is also shown in the figure for comparison. In Si₃N₄ substrate, Si2p peak at 101.5 eV is assigned for Si–N bond in Si₃N₄ which agrees well with the literature [51]. A single peak at 101.7 eV corresponding to Si2p is observed in as-deposited as well as vacuum annealed CeO₂/Si₃N₄ films. The intensity of this peak is very low in air annealed CeO₂/Si₃N₄ films.

O1s spectral features have changed due to annealing of CeO₂ films on both substrates and they are shown in Fig. 10. It is clear from Fig. 10 (a) that intensity of O1s component associated with CeO₂ in CeO₂/Si film is reduced after heat treatment at 400 °C in vacuum, whereas intensity of Ce₂O₃ related peak at 532 eV increases. Concentration of Ce³⁺ species evaluated from the
deconvoluted O1s core level spectrum increases to 56% after annealing at 400 °C in vacuum which is close to the value of 54% obtained from Ce3d spectrum. On the other hand, CeO₂ film deposited on Si₃N₄ substrate shows an intense peak at 529.9 eV corresponding to O²⁻ species in CeO₂ after heat treatment at 400 °C in vacuum as displayed in Fig. 10 (b). Two low intensity peaks at 531.7 and 532.9 eV are attributed to oxygen species in silicate or Ce₂O₃ and Si–O network, respectively. Relative concentration of Ce³⁺ from O1s core level peak of CeO₂/Si₃N₄ heat treated at 400 °C in vacuum is 14% which is close to the value of 15% obtained from Ce3d spectrum. Ce³⁺ concentration increases slightly upon heat treatment at 600 °C. However, concentrations of Ce⁴⁺ and Ce³⁺ in CeO₂/Si₃N₄ films after heat treatment in air are more or less same with as-deposited film. Thus, XPS studies demonstrate the stability of CeO₂/Si₃N₄ interface and that there is no significant change in concentrations of Ce⁴⁺ and Ce³⁺ in CeO₂ films on Si₃N₄ substrate after heat treatment in air or vacuum.

In this work, XPS studies of CeO₂ films coated on Si and Si₃N₄ substrates demonstrate the presence of Ce₂O₃ and silicate phase at the interface between CeO₂ and Si at room temperature. Reactivity at the interface appears to be absent when CeO₂ is deposited on Si₃N₄ substrate. Extent of interfacial reaction increases with Si after heat treatment but it is minimum in case of Si₃N₄. Si has unfilled p level, whereas Si₃N₄ is an insulator with a large band gap of 5.1 eV having filled p levels of Si. In this sense, Si present on the silicon surface reacts with deposited CeO₂ layer in CeO₂/Si film and the interfacial reactions can be written as follows:

$$3\text{Si} + 8\text{CeO}_2 \rightarrow \text{SiO} + \text{Si}_2\text{O}_3 + 4\text{Ce}_2\text{O}_3 + 283.2 \text{ kJ mol}^{-1} \quad (4).$$

Thus, from thermodynamic point of view, the interfacial reaction given above can occur in the forward direction if we consider standard molar enthalpy of formation of different compounds.

Another type of reaction between Si and CeO₂ is also possible which is given below.
\[ x\text{Si} + \text{CeO}_2 \rightarrow \text{CeSi}_x\text{O}_{y} + \text{CeO}_{2-y} \] (5).

A similar type of silicate phase has also been found at HfO$_2$/Si interface [29,33]. Another way of understanding the results would be position of valence bands. Si$^0$ and Si$_3$N$_4$ have valence bands starting at 0.95 and 3.7 eV, respectively with respect to Fermi level, whereas empty Ce4f band in CeO$_2$ is located at 2 eV [54,55,2]. Therefore, Si$^0$ can transfer its electron easily to CeO$_2$ in CeO$_2$/Si film that facilitates reduction of Ce$^{4+}$ to Ce$^{3+}$. On the other hand, possibility of this kind of electron transfer in CeO$_2$/Si$_3$N$_4$ film is much less as valence band of Si$_3$N$_4$ is situated on the lower energy side compared to empty Ce4f band according to Fermi level. Therefore, interfacial reaction is absent in CeO$_2$/Si$_3$N$_4$ film.

**Conclusions**

CeO$_2$ films were deposited on Si and Si$_3$N$_4$ substrates by magnetron sputtering. XPS studies show that significant amount of Ce$^{3+}$ is present in addition to Ce$^{4+}$ in CeO$_2$/Si films due to interaction between CeO$_2$ and silicon on silicon substrate. Mainly Ce$^{4+}$ species are observed in as-deposited CeO$_2$/Si$_3$N$_4$ films. Interfacial reaction between CeO$_2$ and Si leads to the silicate formation. Heat treatment enhances the interfacial reaction in CeO$_2$/Si films. On the other hand, Ce$^{4+}$ species predominates in CeO$_2$/Si$_3$N$_4$ films even after heat treatment at high temperatures in vacuum and air demonstrating the stability of the interface.

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References


Table 1 Binding energies and integrated peak areas of Ce3d$_{5/2,3/2}$ spin-orbit doublets in CeO$_2$ film deposited on Si.

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Table 2 Binding energies and integrated peak areas of Ce3d\textsubscript{5/2,3/2} spin-orbit doublets in CeO\textsubscript{2} film deposited on Si\textsubscript{3}N\textsubscript{4}.

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Table 3 Binding energies and integrated peak areas of Ce3d$_{5/2,3/2}$ spin-orbit doublets in CeO$_2$ film deposited on Si$_3$N$_4$ and heat treated at 400 °C in air.

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Table 4 Binding energies and integrated peak areas of Ce3d$_{5/2,3/2}$ spin-orbit doublets in CeO$_2$ film deposited on Si$_3$N$_4$ and heat treated at 600 °C in air.

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<th>Peak assignment</th>
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<th>Relative area (%)</th>
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Figure captions

Fig. 1. XPS of Ce3d core levels in as-deposited CeO$_2$ thin films on (a) Si and (b) Si$_3$N$_4$ substrates.

Fig. 2. Deconvoluted XPS of Ce3d core levels in as-deposited CeO$_2$ thin films on (a) Si and Si$_3$N$_4$ substrates.

Fig. 3. XPS of Si2p core levels in (a) CeO$_2$ deposited on Si substrate and (b) pure Si substrate.

Fig. 4. Deconvoluted XPS of O1s core levels in as-deposited CeO$_2$ thin films on (a) Si and (b) Si$_3$N$_4$ substrates.

Fig. 5. XPS of Ce3d core levels in CeO$_2$ thin films with different conditions: (a) deposited on Si and heat treated at 400 °C in vacuum, (b) deposited on Si and heat treated at 600 °C in vacuum, (c) deposited on Si$_3$N$_4$ and heat treated at 400 °C in vacuum, (d) deposited on Si$_3$N$_4$ and heat treated at 400 °C in air, (e) deposited on Si$_3$N$_4$ and heat treated at 600 °C in vacuum, and (f) deposited on Si$_3$N$_4$ and heat treated at 600 °C in air.

Fig. 6. Deconvoluted XPS of Ce3d core levels in CeO$_2$ thin films deposited on (a) Si substrate and heat treated at 400 in vacuum and (b) Si$_3$N$_4$ substrate and heat treated at 600 °C in vacuum.

Fig. 7. XPS of Ce4d core levels in CeO$_2$ thin films with different conditions: (a) as-deposited on Si, (b) as-deposited on Si$_3$N$_4$, (c) deposited on Si and heat treated at 400 °C in vacuum, (d) deposited on Si and heat treated at 600 °C in vacuum, (e) deposited on Si$_3$N$_4$ and heat treated at 400 °C in vacuum, (f) deposited on Si$_3$N$_4$ and heat treated at 400 °C in air, (g) deposited on Si$_3$N$_4$ and heat treated at 600 °C in vacuum, and (h) deposited on Si$_3$N$_4$ and heat treated at 600 °C in air.

Fig. 8. Deconvoluted XPS of Si2p core levels in CeO$_2$ thin films on Si substrate heat treated at (a) 400 and (b) 600 °C in vacuum.
Fig. 9. XPS of Si2p core levels in CeO$_2$/Si$_3$N$_4$ thin films with different conditions: (a) pure Si$_3$N$_4$, (b) as-deposited, (c) heat treated at 400 °C in vacuum, (d) heat treated at 400 °C in air, (e) heat treated at 600 °C in vacuum, and (f) heat treated at 600 °C in air.

Fig. 10. Deconvoluted XPS of O1s core levels in (a) CeO$_2$/Si and (b) CeO$_2$/Si$_3$N$_4$ thin films after heat treatment at 400 °C in vacuum.
Fig. 1. XPS of Ce3d core levels in as-deposited CeO₂ thin films on (a) Si and (b) Si₃N₄ substrates.
Fig. 2. Deconvoluted XPS of Ce3d core levels in as-deposited CeO₂ thin films on (a) Si and Si₃N₄ substrates.
Fig. 3. Deconvoluted XPS of Si2p core levels in (a) CeO₂ deposited on Si substrate and (b) pure Si substrate.
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Fig. 7. XPS of Ce4d core levels in CeO$_2$ thin films with different conditions: (a) as-deposited on Si, (b) as-deposited on Si$_3$N$_4$, (c) deposited on Si and heat treated at 400 °C in vacuum, (d) deposited on Si and heat treated at 600 °C in vacuum, (e) deposited on Si$_3$N$_4$ and heat treated at 400 °C in vacuum, (f) deposited on Si$_3$N$_4$ and heat treated at 400 °C in air, (g) deposited on Si$_3$N$_4$ and heat treated at 600 °C in vacuum, and (h) deposited on Si$_3$N$_4$ and heat treated at 600 °C in air.
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