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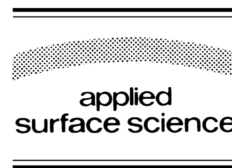

Preparation and characterisation of mixed oxide $(Ce,Zr)O_2$ thin films on Si (111) substrates

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Abstract

We have grown thin films of mixed oxides on Si (111) substrates by electron beam evaporation of pressed $Ce_xZr_{1-x}O_2$ pellets. The growth was initiated under UHV environment, and proceeded then under O_2 atmosphere. A multitechnique approach (XPS, AES, LEED, XRD, RBS) was used to characterise the chemical and structural composition of the film as well as their interface with the substrate. The films are about 100 Å thick and present at least two phases corresponding to ZrO_2 and CeO_2. XPS depth profiles showed the following structure, starting from the substrate: a region of interdiffused Zr and Si, a $CeSiO_x$ layer mixed with ZrO_2 and finally the homogeneous $(Ce,Zr)O_2$ film, enriched in Ce with respect to the pellet. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ceria–zirconia mixed oxide; Thin film; XPS; Interface; Solid solution

1. Introduction

Cerium oxide is widely employed as a promoter for noble metal/alumina automotive exhaust catalysts (three way catalysts). Adding ZrO_2 to CeO_2 significantly increases its thermal stability and improves its ability to store and release oxygen (oxygen storage capacity) under reaction conditions [1]. As far as thin films are concerned, the growth of cerium oxide films on various substrates has been reported by several groups, with several techniques as this system has many potential applications: buffer layer on sapphire (Al_2O_3) for chemically isolating $YBa_2Cu_3O_{7-\delta}$ (YBCO) films [2–4], interface material for silicon-on-insulator (SOI) applications, and stable capacitor devices [2]. The interesting point in using Si (111) as a substrate is its good lattice match with CeO_2 ($< 0.35\%$ mismatch). Our purpose is to prepare oriented model surfaces of ceria-based mixed oxides grown on Si (111) substrates, starting from pressed mixed oxides: this article describes these films as well as their interface with silicon.

2. Experimental

2.1. Materials

The source materials are solid solutions of cerium and zirconium mixed oxides with CeO_2 molar content x ranging from 15 to 68% (referred to as

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CZ-x/100-x) as well as the reference oxide of pure CeO_2 (CZ-100/0). All these materials were prepared by Rhodia. (111)-oriented silicon substrates, 0.40 mm thick, were cut into 80 mm × 80 mm squares and chemically cleaned according to a procedure established by Kern and Puotinen [5], including three different baths based on NH_4OH:H_2O_2, pure HF, and HCl:H_2O_2 solutions. During the evaporations, pure O_2 (purity > 99.9995%) was used.

2.2. Thin film preparation

The oxide targets were pressed into pellets before loading into the evaporator. The clean Si (111) substrates were introduced into ultra-high vacuum (UHV) after rinsing and drying and flashed to remove the oxide layer before evaporation. The films were prepared using a Varian evaporator (VT112) equipped with a water-cooled Varian electron gun (989-0003). The base pressure was 4×10^{-9} Torr and the substrate-to-target distance about 20 cm. After careful preliminary outgassing of the targets to 10^{-8} Torr, the evaporation proceeded under vacuum during the first 50 Å, then under 5.10^{-7}–5.10^{-6} Torr O_2 with a substrate heated at about 500°C during evaporation. The samples were then ex situ analysed by several techniques.

2.3. Techniques

The XPS spectra were measured with an SSX-100 spectrometer equipped with a focused (spot size 600 Å) and monochromatised Al K_α anode ($h\nu = 1486.6$ eV). The X-ray source power was kept around 150 W. The thin films were sufficiently conducting, so that no charge-stabilising technique was needed. The energy resolution corresponds to a FWHM (full width at half maximum) of 1.1 eV for the Au $4f_{7/2}$ peak. Binding energies are referred to the C 1s peak at 284.6 eV (hydrocarbon form contamination) and given within an accuracy of ± 0.2 eV. Depth profiles were also recorded using argon sputtering (4 keV, 8×10^{-8} Torr) in order to get information on the substrate/film interface. Ce 3d, Ce 4d, Zr 3d, O 1s, and C 1s core levels have been recorded at each steps, as well as the Si 2p peak when needed.

Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) facilities were used to obtain information about the surface chemical state and the structure of the outermost layer. X-ray diffraction (XRD) with a Cu K_α anode (1.5413 Å), Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) using a $^3He^+$ beam of 2.4 MeV have been performed to complete the characterisation of the bulk.

3. Results and discussion

We have made different mixed oxide thin films by evaporating pellets made from CZ-15/85, CZ-50/50, and CZ-68/32 powders, chosen from the first evaporation attempts on polycrystalline Ta substrates [6]. All samples have been analysed after transfer in air, which systematically creates a contamination layer detected by both AES and XPS on the as-received samples. The surface composition deduced from the XPS analysis of the films has been used to label them: Film-x/(100-x), by reference to the powder label CZ-x/100-x. First, the XPS Ce/Zr atomic surface ratios point out a zirconium surface enrichment in the contamination layer compared to the bulk of the film (Table 1): the zirconium surface segregation is most probably associated with carbon and oxygen contamination because the higher O/cations and C/cations ratios, the higher the Zr/cations proportion compared to the bulk of the film. As for any oxide exposed to the atmosphere, both undissociated and dissociated H_2O molecules can contribute to the saturation of the cationic and anionic terminations in the outer layer [7], here it seems that zirconium oxide is more sensitive to hydroxylation than

Table 1
XPS atomic ratios calculated with the O 1s, C 1s, Ce 4d and Zr 3d core levels

Source materials	O/Ce +Zr	C/Ce +Zr	Film-x/ 100-x (a)	Film-x/ 100-x (b)	Film-x/ 100-x (c)
CZ-15/85	2.80	1.88	F-5/95	F-39/61	–
CZ-50/50	2.57	1.62	F-47/53	–	–
CZ-50/50	2.31	1.04	F-58/42	F-75/25	F-80/20
CZ-68/32	2.25	1.44	F-63/37	F-80/20	–

Surface cation distribution F-x/100-x is obtained: (a) from XPS analysis of the as-received surface film; (b) average value over the XPS depth-profile analysis of the film; (c) average value from RBS/NRA analysis over the full thickness of the film.

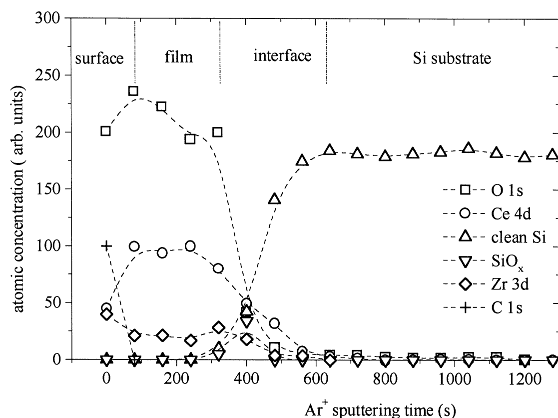

Fig. 1. XPS depth profile (Ar^+ sputtering) of a film obtained from CZ-50/50 source and labelled $Film_{XPS}$-75/25 based on the composition determination by XPS. The film is 86 Å thick according to quartz oscillator.

cerium oxide. Then, in addition to the contamination layer, the XPS depth profiles allow us to divide the thickness of the obtained films into three other regions, referred to as: film, interface and substrate (Fig. 1). The following paragraphs describe the corresponding chemical information deduced from XPS.

We have been able to obtain homogeneous mixed films with no detectable impurities in all attempts. From the point of view of cation distribution, zirconium seems to present some difficulty to be evaporated by the electron bombardment of the powder. If we compare the distribution in the films and in the source (Table 1), there is at least a 30% Ce increase in the films compared to the mixed oxide powder. This was already observed in the case of films prepared on polycrystalline Ta [6], in similar conditions. As an element of comparison, Tomaszewski et al. [8] observe that the deposition speed is about 10 times lower in the reactive sputtering of ZrO_2 than of a metallic Zr target. We had some difficulty comparing our results with data from other ceria–zirconia thin films available in the literature as they were prepared by completely different methods (laser ablation [9] or sol–gel dip coating [10]): in both cases, no cerium enrichment was detected by AES and RBS.

To complete the film characterisation, one of our sample ($Film_{XPS}$-75/25 from a CZ-50/50 source) was characterised by RBS and NRA. These techniques allow us to determine the average composition of the film as well as its thickness. The composition is given in Table 1, it is very close to the value obtained by XPS ($Film_{RBS}$-80/20 vs. $Film_{XPS}$-75/25). The thickness is 130 Å which is reasonably close to the value indicated by quartz oscillator (90 Å). Fig. 2 shows the corresponding RBS spectrum. From a theoretical fit of this spectrum, we conclude that the interface between the mixed oxide layer and the substrate is not sharp. This is confirmed by XPS results which show that the interface is rather complicated indeed, as we will see next.

Fig. 3a shows the region of the Ce 4d and Si 2p core levels in the XPS spectra, recorded at various stages during the depth profile. As one approaches the interface, the Ce 4d signal starts to decrease and new feature appear in the Si 2p core levels, at a binding energy (B.E.) of 102.3 eV. Simultaneously, the O 1s signal decreases (see Fig. 1). Eventually, only the Si 2p peak corresponding to pure Si is seen at 99 eV, with a feature near 117 eV due to a plasmon loss in Si.

The B.E. of Si 2p at 102.3 eV does not correspond to silicon in a SiO_2 environment which would be expected at 103.4 eV, but rather to another form of oxidised silicon. This may be because another type of oxide, involving Ce and/or Zr forms during the growth, or because Ar^+ sputtering changes the oxide to a form where most of the Si is in a Si^{3+} stage. In the case of pure CeO_2 films, the presence of oxidised silicon has been abundantly described in

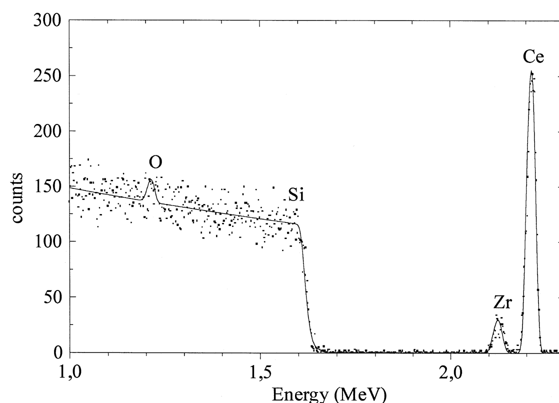

Fig. 2. RBS spectra of $Film_{XPS}$-75/25 obtained from CZ-50/50 source.

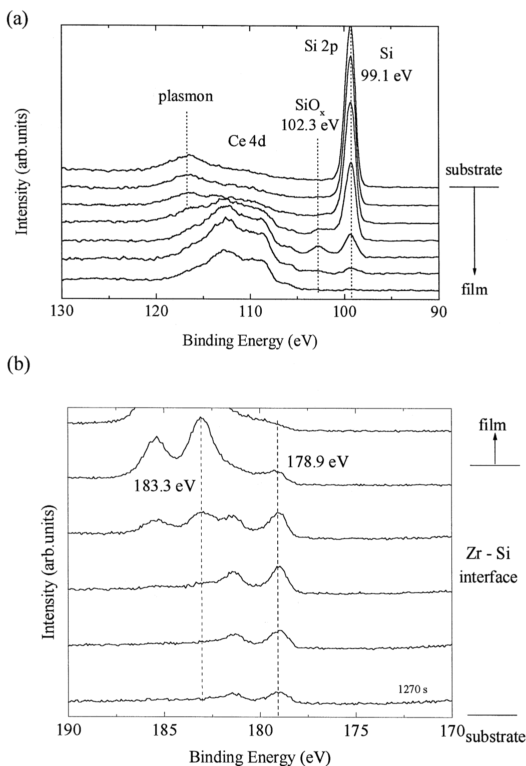

Fig. 3. (a) Ce 4d and Si 2p core levels from XPS depth profile of $Film_{XPS}$-75/25 zoomed at the interface with the substrate. (b) Zr 3d core level from XPS depth profile of $Film_{XPS}$-39/61 zoomed at the interface with the substrate.

the literature, sometimes as CeO_{2-x}/SiO_x [11,12], or as an amorphous silicate layer [13,14], where partial reduction of Ce^{4+} to Ce^{3+} occurs together with partial oxidation of Si.

This growth behaviour of oxides on Si has been tentatively explained by Nagata [15]. Based on standard free energies of formation ($\Delta G_f°$), they have shown that $CeSiO_4$ is more stable than CeO_2 during the early stages of growth of CeO_2 on Si. Our data suggest that a similar phenomenon may occur during the growth of mixed oxides.

The thickness of the interface layer can be estimated based on the area of the SiO_x and Si peaks in the Si 2p spectra. In this way, we find a range of 10–15 Å, equivalent to two to three initial $CeSiO_x$ planes.

The Zr 3d core level spectra (Fig. 3b) provide us with some information on the role of Zr at the beginning of the growth. All films obtained during the evaporations of CZ-15/85, CZ-50/50 and CZ-68/32 present the doublet of reduced zirconium at 178.9 eV near the Si substrate. The literature dealing with zirconia thin film mentions formation of a Zr-silicide [16] during the epitaxial growth of yttria-stabilised zirconia (YSZ) on Si(100) by ion beam sputtering of a target of ZrO_2 with 10 mol.% Y_2O_3 target. In particular, if the oxygen pressure is too low ($< 2 \times 10^{-6}$ Torr) during the growth of the films at 750°C, formation of (possibly epitaxial) $ZrSi_2$ is detected by Auger electron spectroscopy. Two reaction pathways can be identified which strongly depend on the O_2 pressure and on temperature of the substrate under vacuum: an arriving Zr atom may react with the silicon substrate to form Zr-silicide or will be oxidised if there are oxygen atoms available. The latter process is energetically more favourable ($\Delta G_f°(ZrO_2) \ll \Delta G_f°(ZrSi_2)$), but if a silicide nucleus has been formed it remains stable even under oxygen exposure. XPS characterisations of epitaxial growth of YSZ/Si(100) confirm this interpretation [17]. In our experiment, oxygen is added up to a pressure of 5×10^{-6} Torr only after a few minutes of evaporation to avoid oxidising the substrate. Therefore, the nucleation conditions are favourable for zirconium silicide formation. Reduced zirconium was not observed in the depth profiles of mixed films grown on Ta [6] ruling out the hypothesis of reduction of Zr under Ar^+ sputtering during XPS profiles. Away from the interface, the Zr 3d core level shifts gradually towards higher B. E. (183.3 eV) and a strong signal from cerium oxide is detected (Fig. 3a,b). The hypothesis of a $ZrSiO_4$ compound formed at the interface by analogy with the $CeSiO_x$ already described cannot be neglected, though in this case the B.E. of Si 2p would be observed at 101 eV [17], which we do not detect. To summarise: at the interface with silicon, we detect first reduced zirconium then oxidised cerium, silicon and zirconium. Early admission of oxygen would avoid forming reduced zirconium but would favour formation of silicon oxide which can induce the undesired complete amorphisation of the ceria-containing mixed oxide film.

Finally, we investigated the mixed oxide solid solution character of the film, as well as its structural properties. We chose Si (111) substrates because

epitaxial growth of CeO_2 (111) on Si (111) has been reported in the past for similar conditions [3,11–14,18]. Presently, the e-beam evaporation is not coupled to any analytical facilities. Therefore, LEED was not used to characterised the films structure, as it is too difficult to restore atomically clean and well ordered surfaces after transfer through air. To look for preferential growth orientations, XRD measurements were made on a pure CeO_2 film and on Film-39/61 obtained from CZ-15/85. XRD reference data on CZ-68/32, CZ-50/50 and CZ-15/85 powders have been characterised by XRD at another laboratory [19] and present the X-ray diffraction patterns of $Ce_{1-x}Zr_xO_2$ solid solution as expected. The structure of this solid solution is cubic for $x < 0.5$, and tetragonal for $x >= 0.5$. Only in the case of the CZ-15/85 sample, does the presence of peaks due to monoclinic–ZrO_2 indicate a partial segregation of ZrO_2 from the solid solution. In our XRD pattern coming from the mixed oxide film, we detect the presence of the (101) diffraction peak of monoclinic ZrO_2, and the (111) diffraction peak of cubic CeO_2 in addition to the signal coming from the substrate and little evidence of the formation of a solid solution. More work is still needed to characterise the structure of these films, probably using grazing incidence X-ray diffraction in order to minimise the signal from the substrate, since the films are very thin. However, these preliminary experiments are compatible with dual growth of both ZrO_2 and CeO_2 starting from the interface after bombarding the pellet.

4. Conclusion

We have obtained thin mixed ceria–zirconia films on silicon substrates by electron beam evaporation of mixed oxide solid solution pellets. The films show a ceria enrichment compared to the source material, regardless of composition of the source material. The interface of the oxide film with its substrate presents first a Zr-silicide layer and then the simultaneous presence of silicon, cerium and zirconium oxide. In the film, only zirconium and cerium in ZrO_2 and CeO_{2-x} environment are detected. Preliminary characterisations suggest to prove that the solid solution properties of the mixed oxides have been lost during evaporation to the benefit of oriented ZrO_2 and CeO_2.

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