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Interfacial interaction between cerium oxide and silicon surfaces

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ABSTRACT

The interaction of cerium oxide films with Si substrates is investigated by means of X-ray photoelectron spectroscopy. Cerium oxide films of different thickness have been grown at room temperature by reactive deposition on different Si surfaces, namely Si(111), Si(100) and thermally oxidized Si(100). We show that cerium oxide and silicon form a silicate phase of subnanometric thickness and that the interfacial phase composition and thickness is similar on the (111) and (100) Si surfaces. The silicate phase formed at the interface contains cerium in the 3+ oxidation state, while silicon presents different oxidation states up to 4+. With a thermal annealing in O_2 at 1040 K the interface reaction proceeds and the silicate phase evolves in stoichiometry. We demonstrate the stability of the silicate phase towards oxidation after exposure to atomic or molecular oxygen or air. The presence of a thick thermal oxide layer on the Si surface partially limits the extent of the reaction.

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1. Introduction

Besides the widely recognized interest in cerium oxide for catalytic applications [1,2], CeO_2 is also important as a high dielectric constant material for electronic applications and it is a potential candidate as an alternative gate to SiO_2 in metal-oxide-semiconductor devices [3,4]. The small lattice mismatch (−0.35%) with silicon may favor in principle an epitaxial growth of CeO_2 on the different silicon surfaces, opening up the possibility to use cerium oxide also as a buffer layer for the epitaxial growth of other functional oxide films (e.g. superconducting or ferroelectric) on Si [5,6].

Several works, investigating the interaction between CeO_2 and different Si surfaces, report the formation of a reduced CeO_{2-x} phase and of a SiO_2 phase at the interface [7–9]. A deeper investigation of the structure and composition of the interface chemistry and structure evidenced the formation of a cerium silicate phase [10–13], in analogy with other rare earth oxide/Si systems [14,15]. Surprisingly, in some cases the presence of amorphous silicate and silicon oxide phases at the interface does not prevent to establish an epitaxial relation between ceria and silicon [7,16,17], however it is recognized that the preparation conditions are crucial in this respect. In some studies the interface was shown to be very sharp and SiO_2 free [11–13], while in some others the formation of a SiO_2 layer between Si and the silicate was observed [7]. To overcome the limitations due to the interfacial reactivity, growth procedures to reduce the formation of an amorphous layer between ceria and silicon have been identified. These include the use of a buffer layer of CaF_2 [18] and the growth on a Si surface passivated with a H [9,19] or Cl [20] layer.

On the other hand cerium silicates have been shown to be also interesting materials in themselves for applications in optoelectronics, in particular for silicon-based light emitting devices in view of their photoluminescence properties [13,21].

The aim of this work is to get more insight on the interaction between cerium oxide and silicon by comparing the results of X-ray photoelectron spectroscopy studies of cerium oxide layers of different thickness grown on different silicon surfaces, either clean or with a thermal oxide layer, before and after thermal treatments in O_2. The results allow to identify the chemical species present at the interface, to estimate the thickness of the interfacial phases and to have information on their stability under thermal and oxidizing treatments.

2. Experimental section

The samples described in this work were prepared and characterized using two experimental chambers connected in ultrahigh vacuum (UHV): one allows for the growth of the cerium oxide layers, the second one is equipped with facilities for characterization by Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Low Energy Electron Diffraction (LEED). The base pressure in the UHV apparatus is 1×10^{-10} Torr.

Three different Si substrates were used for the growth of cerium oxide films: a Si(111) surface, a Si(100) n-type surface and a Si(100) p-type surface with a 500 nm thick thermal oxide layer. All of the surfaces were degassed in UHV at 920 K for 1 h and prepared by repeated cycles of Ar^+ sputtering (1 keV, 1 μA) and annealing (1040 K) in UHV.

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At the end of the cleaning procedures the level of contaminants was below the sensitivity of AES. For the Si(111) surface LEED showed a bright (7×7) reconstruction, while for the Si(100) a (2×1) reconstruction was observed, confirming the complete removal of native oxides. As expected the surface with the thick thermal oxide did not show any LEED pattern.

Cerium oxide layers were grown by reactive evaporation of metallic cerium using molecular oxygen as the oxidizing gas. Cerium was supplied from an electron beam evaporator with an evaporation rate, measured by a quartz microbalance, of approximately 0.2 Å/min. O_2 was dosed through a nozzle close to the sample surface in O_2 background pressure of 1×10^{-7} Torr. The substrates were kept at RT during cerium oxide growth. The total amount of evaporated cerium oxide in each sample was estimated by substrate Si 2p XPS intensity attenuation, using an electron mean free path evaluated from ref. [22], and cross checked with the evaporation cell calibration performed using the quartz microbalance.

The evolution of the interface composition with thermal treatments in molecular and atomic oxygen was also investigated. Atomic oxygen was supplied through a thermal cracker with an O_2 background pressure of 1×10^{-7} Torr.

XPS is a suitable tool to get information on the reactivity at the interface between oxides and metals and on the extent of the interfacial intermixed phase [8,10,11,15,23].

The XPS measurements for the present study were performed at normal emission using Al K_α photons as the exciting probe. Si 2p, O 1s and Ce 3d photoemission lines of the different samples after the different preparation procedures are analyzed and compared. The analysis of Ce 3d photoemission spectra is quite complex because the peaks extend over a binding energy (BE) region of 40 eV in which, in general, three Ce^{4+}-related doublets and two Ce^{3+}-related doublets are present [24]. However, it is possible to separate the Ce^{3+} and Ce^{4+} contributions to the spectra to get the relative intensity of the features related to the two oxidation states (see Fig. 1). We performed the fitting following the procedure introduced by Skala et al. [25,26]. A Shirley-type background was used. Three Voigt-shaped doublets (spin-orbit splitting of 18.5 eV) were used to fit the Ce^{4+} ions signal and two doublets, with the same Voigt shape and spin-orbit, for Ce^{3+} ions. The Lorentzian width used and the binding energy values are fixed to the values of Skala et al. [25], while the Gaussian width was left as a free fitting parameter. The accuracy of the weight of the signal related to the single ionic species in the Ce 3d spectra is estimated to be ±2%, given the still open discussion about the origin and shape of the different contributions to the XPS lines [27] and their background which are not unique. Using the same fitting procedure for all of the spectra investigated, we can distinguish between spectra with Ce^{3+} contributions which differ by approximately ±0.5%. We have previously shown that this procedure is able to detect small changes in the oxidation state of cerium oxide [28] also at the interface with metals [29]. Four Voigt-shaped doublets (spin-orbit splitting of 0.6 eV) were used to fit the Si 2p spectra, while the fitting of O 1s core levels required four Voigt-shaped functions. The Lorentzian widths of these peaks were fixed to the values found in literature, while the Gaussian widths were set as free fitting parameters. A Shirley-type background was introduced in the fitting procedure for all of the analyzed spectra. All the binding energies of the peaks were constrained, although in some cases in order to optimize the shape of the fits some variations within 0.1–0.2 eV were introduced.

For all the XPS spectra we took into account the experimental broadening of our apparatus by convolving the sum of the Voigt peaks with a further Gaussian broadening of 1 eV. The figures report the Voigt-shaped components used for the fitting without experimental broadening to allow for a better identification of the different components used. The XPS spectra of samples of different thickness shown in the figures have been normalized in intensity in order to allow for a better comparison of their shape.

3. Results and discussion

3.1. Cerium oxide/Si(111) interaction

In order to understand the interaction between CeO_2 and silicon we deposited cerium oxide films of two different thicknesses, 0.7 and 3 nm, on Si(111) 7×7-reconstructed surfaces at room temperature. Fig. 1 shows the Ce 3d spectra of both films and the corresponding fits. The spectra of the as grown samples show the presence of both Ce^{3+} and Ce^{4+} ionic species. The relative intensity of the Ce^{3+}-related features, evaluated from the fitting, is much larger for the 0.7 nm film than for the 3 nm one (30% and 5% respectively, see Table 1). The presence of Ce^{3+} can be due to the formation of a cerium silicate at the interface, as already identified in similar growth conditions [11,12] and/or to the presence of the Ce_2O_3 phase [7,12]. The fact that the Ce 3d spectrum of the 0.7 nm sample contains a 70% contribution also from Ce^{4+}, which is the most stable valence state in cerium oxide, is an indication that a fully oxidized CeO_2 layer grows on top of the interfacial phase. Under the hypothesis that this phase containing Ce^{3+} ions is buried under the CeO_2 layer, the amount of cerium oxide which interacts with the silicon surface is actually more than 30% in the 0.7 nm sample, and it can be quantified as being approximately 0.3 nm thick from a simple attenuation model, using an electron mean free path evaluated from reference [22] and assuming a uniform morphology of the films, assumption justified by the observed strength of the interaction between Ce and Si.

To prove that the Ce^{3+} ions are not related to a non stoichiometric CeO_{2-x} phase, the samples were annealed at 1040 K in O_2 background pressure of 1×10^{-7} Torr. The same thermal treatment was shown to be effective in oxidizing the Ce^{3+} ionic species into Ce^{4+} in cerium oxide films of similar thickness on Pt(111) substrates [28]. After the treatment the Ce 3d spectrum of the 0.7 nm sample showed only Ce^{3+}-related features, while an increase in relative intensity (from 5 to 13%) of Ce^{3+}-related features was observed for the 3 nm sample (Fig. 1, Table 1). The increase in Ce^{3+} concentration allows to exclude that the observed Ce^{3+} signal is related to a Ce_2O_3-like phase or to defective sites of a CeO_2 phase. Furthermore, the observed behavior

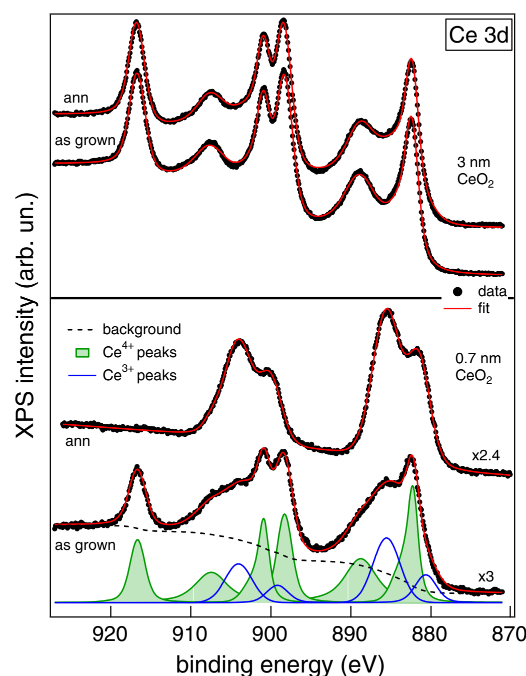

Fig. 1. Ce 3d XPS spectra and corresponding fits of 0.7 nm (bottom panel) and 3 nm (top panel) of cerium oxide on a Si(111) surface, as grown and after annealing in O_2 at 1040 K. The fitting components related to Ce^{4+} (filled peaks) and Ce^{3+} (empty peaks) species are also shown for one of the spectra. The spectra are normalized in intensity to compare their shapes.

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