

BRIEF COMMUNICATIONS

Electron Beam Reduction of Cubic Y-Doped ZrO₂(100): A Study by X-Ray Photoelectron Spectroscopy

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Electron beam reduction of cubic Y(III)-doped ZrO₂(100) has been studied by X-ray photoelectron spectroscopy. In the initial stages of irradiation with 2-keV electrons oxygen loss is accompanied by specific reduction of Zr(IV) to Zr(0) without concomitant reduction of Y(III). The cross section for oxygen desorption is estimated to be 3.9×10^{-20} cm². Surface stoichiometry is restored by argon-ion bombardment. © 1987 Academic Press, Inc.

Yttria-doped cubic zirconia Zr_{1-2x}Y_{2x}O_{2-x} is a high-temperature ceramic material with a range of potentially useful properties including good mechanical toughness and high oxygen ion conductivity (1). Many applications of zirconia depend intimately upon its surface chemistry. Thus, when used as an oxygen sensing electrode the response rate is governed by the kinetics of oxygen exchange at the surface: considerable effort has been devoted to improvement of surface exchange rates by suitable surface pretreatments (2). In assessing the mechanical properties and electrical conductivity of polycrystalline material, due consideration must be given to the influence of segregation of Y³⁺ to grain boundaries (3). Here surface segregation provides a model for grain boundary segregation. In a quite different context Y-doped ZrO₂(100)

has been suggested as an optimal substrate for epitaxial growth of silicon on insulator layers, the lattice match being much better than with more conventional Al₂O₃ substrates (4). Against this background we are involved in the study of cubic zirconia by surface sensitive electron spectroscopic techniques and report here some results pertaining to the reduction of Y-doped zirconia under electron irradiation. The striking feature we wish to highlight in the present communication is that electron bombardment leads to selective reduction of host Zr(IV) without parallel reduction of the Y(III) dopant.

Experiments were conducted on slices of (100) oriented 16% Y₂O₃-doped ZrO₂ supplied by Ceres Inc. Material from this batch had previously been used in studies of oxygen-ion diffusion by dynamic secondary ion mass spectroscopy (5). Crystal slices gave weak but well-defined LEED patterns after annealing at elevated temperatures

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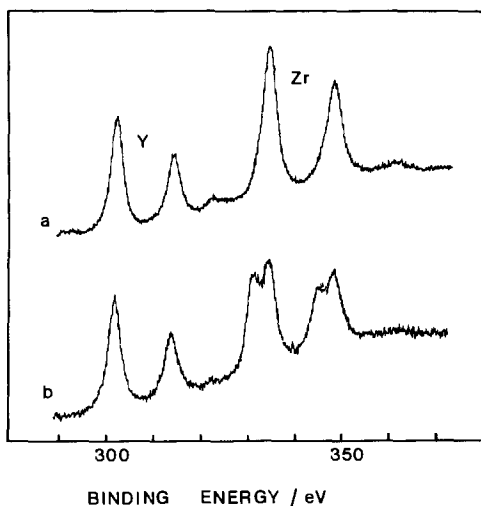


FIG. 1. $MgK\alpha$ X-ray photoelectron spectra of 16% Y_2O_3 doped ZrO_2 in the metal $3p$ region. (a) Cleaned annealed surface. (b) Following electron bombardment. Note additional structure in $Zr\ 3p$ spectrum to the low binding energy side of the original spin-orbit components.

(>600°C) in UHV, indicating that no major faceting of the polar (100) fluorite surface had taken place (4, 6). In the course of development of procedures for producing well-ordered $ZrO_2(100)$ surface in an ESCALAB X-ray photoelectron spectrometer (base pressure 10^{-10} Torr), crystal slices that had been cleaned by argon-ion bombardment and resistive annealing at temperatures below 600°C were subject to electron beam heating. There was no indication of reduction of the sample surface as a result of the initial argon bombardment from a Penning ion gun. However, even when the electron flux was nominally directed on the back of the sample holder, rapid desorption of oxygen by stray electrons was apparent. Figure 1 for example shows $3p$ region spectra before and after electron irradiation of this sort. Electron bombardment leads to the appearance of a second set of spin-orbit components overlapping the original $Zr\ 3p$ components on the low binding energy side: the new peaks

are associated with a reduced zirconium species. No corresponding changes are found in the $Y\ 3p$ region. Further experiments established that surface stoichiometry could be restored by 2-keV argon-ion bombardment: thus even for electron-damaged surfaces where the $O\ 1s$ signal had been reduced to 20% of its initial value, 2-keV ion bombardment at $20\ \mu A/cm^2$ for about 15 min led back to the original $O\ 1s$ intensity and a simple spin-orbit doublet in the $Zr\ 3p$ region.

In order to quantify the reduction behavior under electron irradiation, a cleaned and annealed crystal slice was subject to front face 2-keV electron bombardment from a tungsten filament at an electron flux of $5\ mA/cm^2$ for periods up to 500 sec. Figure 2 shows the progressive growth of peaks to

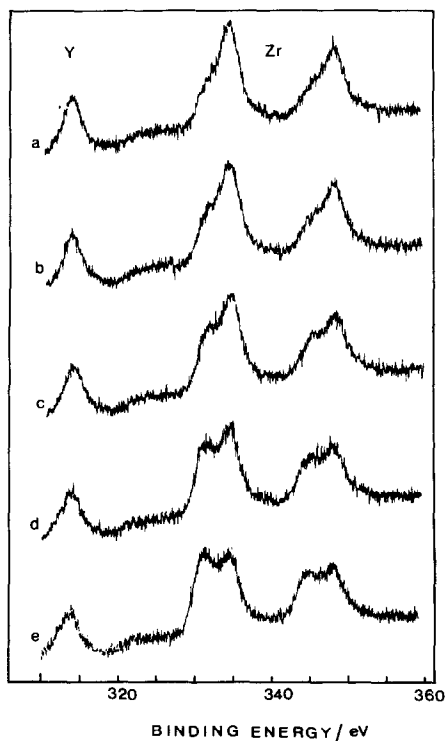


FIG. 2. Variation with time in the $Zr\ 3p$ and $Y\ 3p_{1/2}$ signals in the $MgK\alpha$ spectrum of 16% Y_2O_3 doped ZrO_2 under 2-keV electron irradiation at $5\ mA/cm^2$. (a) 82 sec, (b) 140 sec, (c) 200 sec, (d) 300 sec, (e) 460 sec.

the low binding energy side of the original Zr 3*p* peaks with a constant chemical shift difference of 2.8 eV between the two. In Fig. 3 we show the corresponding changes as a function of time in the intensity of the high and low binding energy (HBE and LBE) Zr3*p*_{3/2} features, together with a plot of the variation of the logarithm of the intensity ratio between the O 1*s* and Zr3*p*_{3/2} peaks. The initial decay of the intensity ratio conforms to first order behavior:

$$R(t) = R(0) \exp(-\sigma\phi t/e)$$

where $R(t)$ is the intensity ratio at time t , $R(0)$ its initial value, ϕ the electron flux, σ the cross section for oxygen desorption, and e the electron charge. From this relationship we estimate that the desorption cross section is 3.9×10^{-20} cm². This is smaller than the cross section 1.3×10^{-19} cm² for desorption of oxygen from the W(100) surface by 2.5-keV electrons (7), but we believe it is the correct order for a d^0 oxide. The corresponding cross section for decomposition of Na_{0.72}WO₃ with 3-keV electrons is 6.0×10^{-21} cm² (8). This lower value presumably reflects the efficient operation of the Knotek-Feibelman interatomic decay mechanism (9) for only the d^0 systems.

Further consideration of the oxygen decay curve allows us to gain some insight into the oxidation state of the zirconium species responsible for the low binding energy peaks. The bulk stoichiometry of the crystal Zr_{0.72}Y_{0.28}O_{1.86} gives a Y/Zr ratio of 0.39. However, the ratio of Y/Zr peak intensities in XPS (with due allowance for photoionization cross-section effects (10)) is 0.6, corresponding to a surface stoichiometry of Zr_{0.63}Y_{0.37}O_{1.81}. The surface segregation of Y(III) in cubic zirconia implied by these data has been noted previously (3, 4, 11), but it is particularly striking at our single-crystal surfaces, the O/Zr ratio inferred from consideration of O 1*s* and Zr 3*p*_{3/2} peaks is 3.1, in reasonable agreement

with our proposed surface stoichiometry where O/Zr = 2.9. Assuming exclusive reduction of Zr(IV) under electron irradiation, it is possible to estimate the diminution in the O/Zr intensity ratio necessary to effect complete reduction of the Zr(IV). If the LBE peak corresponded to Zr(III), the oxygen loss curve of Fig. 3a suggests that about 200 sec electron bombardment should be sufficient to ensure complete conversion to the LBE species. However, it is obvious from Figs. 3a and b that both LBE and HBE species coexist after this time, precluding the possibility of reduction to Zr(III). In fact, our intensity data are consistent only with Zr(0) as the product of electron reduction, and electron beam exposures of around 1000 sec are necessary

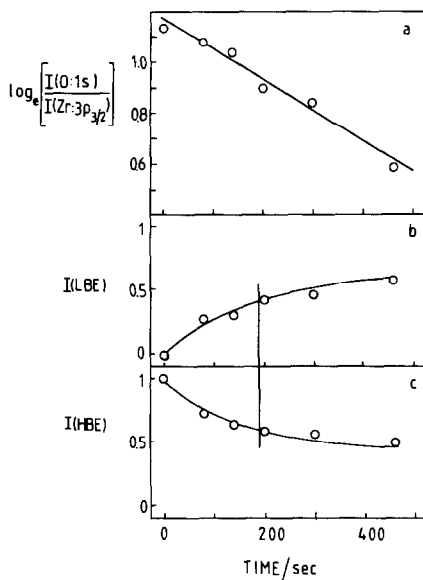


FIG. 3. (a) Variation with time in the O 1*s*/Zr 3*p*_{3/2} intensity ratio under electron irradiation as in Fig. 3 after correction for cross-section effects. The decay of the oxygen intensity is seen to conform to first order kinetic behavior. (b) Variation with time in the intensity of the low binding energy (LBE) Zr 3*p*_{3/2} component. (c) Variation with time in the intensity of the high binding energy (HBE) Zr 3*p*_{3/2} component. In (b) and (c) the vertical line marks the time at which complete conversion to a Zr(III) LBE species would be expected.

for complete reduction of Zr(IV). After prolonged electron irradiation of this sort some reduction of Y(III) is also evident. Finally, note that the chemical shift difference of 2.8 eV between the LBE and HBE components of the $Zr3p_{3/2}$ signal in reduced cubic zirconia is very close to the value of 2.6 eV measured in our spectrometer between zirconium foil and an oxidic overlayer grown by exposure of the foil to molecular oxygen at $p = 5 \times 10^{-6}$ mbar. Oxidation of Zr foil is known to produce a ZrO_2 overlayer (4, 12).

It is interesting to compare the reduction behavior of Y-doped ZrO_2 with that of other transition metal oxides. Many d^0 oxides including TiO_2 , MoO_3 , and WO_3 undergo facile reduction under either electron or ion bombardment. In the initial stages of reduction, d^1 states are introduced into the lattice. Thus argon-bombarded TiO_2 shows strikingly similar electronic properties to Ti_2O_3 (14). However, Kim and Winograd (15) noted that oxides such as Ta_2O_5 with free energies of formation above about 500 kJ/mole did not undergo reduction under bombardment by 400-eV argon ions: ZrO_2 with a free energy of formation of 1037 kJ/mole (16) falls naturally into this group. Nonetheless ZrO_2 thin films on Zr metal are reduced by 5-keV argon ions (12). Electron bombardment reduces most oxides including Ta_2O_5 , Al_2O_3 , and SiO_2 (17). In this sense the resilience of the Y(III) dopant in ZrO_2 to reduction under 2-keV electron bombardment must be considered remarkable. Note in particular that the enthalpy of formation per metal atom is lower for Y_2O_3 (879 kJ/mole) than for ZrO_2 (1101 kJ/mole) (16): we thus expect that the Y–O bond in cubic doped zirconia should be intrinsically weaker than the Zr–O bond. However, the smaller covalency of Y–O bonds as compared with Zr–O bonds will be one factor favoring selective desorption of oxygen ions surrounded dominantly by Zr through the interatomic Auger decay mechanism. We can also envisage that electrons left be-

hind after oxygen desorption will be trapped preferentially in Zr $4d$ (rather than Y $4d$) states. Disproportionation of these states must then occur to generate Zr(0). Of course the failure to observe reduced oxide phases in our experiments on ZrO_2 accords with the fact that well-defined bulk M_2O_3 and MO oxides phases are unknown for zirconium (18).

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