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## Ultra-high Vacuum Preparation and Characterization of Ultra-thin Layers of SiO<sub>2</sub> on $ZrO_2$ and TiO<sub>2</sub> by Chemical Vapour Deposition of Si(OEt)<sub>4</sub>

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 $SiO_2$  overlayers, prepared by chemical vapour deposition of  $Si(OEt)_4$ , were identified by ion scattering spectroscopy and Auger electron spectroscopy to be ultra-thin films uniformly coating  $ZrO_2$ , but this was not the case for  $TiO_2$ .

 $SiO_2$  thin films on metals and metal oxides form useful materials such as anti-reflection coatings<sup>1,2</sup> and coatings which protect pigments against photo-degradation and metals against corrosion.<sup>3</sup> In microelectronic devices, silica thin films are important constituents.<sup>3</sup> The chemistry involved in the formation of these coatings is largely unexplored. In one example, Roozeboom *et al.* analysed V<sub>2</sub>O<sub>5</sub> thin films on various oxides by Raman spectroscopy.<sup>4</sup>

In this communication we report that  $SiO_2$  overlayers prepared by chemical vapour deposition (c.v.d.) of  $Si(OEt)_4$ on  $ZrO_2$  are present as a relatively uniform ultra-thin film whereas on  $TiO_2$  the overlayer did not uniformly cover the substrate. The decomposition of  $Si(OEt)_4$  was followed in ultra-high vacuum (u.h.v.) using Auger electron spectroscopy (a.e.s.), ion scattering spectroscopy (i.s.s.), and temperature programmed desorption (t.p.d.).  $SiO_2$  overlayers were prepared *in situ* by decomposition of  $Si(OEt)_4$  in a u.h.v. system onto  $ZrO_2$  [50 m<sup>2</sup> g<sup>-1</sup>; obtained by calcination of  $Zr(OH)_4$ ] and  $TiO_2$  (50 m<sup>2</sup> g<sup>-1</sup>; Degussa P-25). The oxide powders were pressed into very transparent Ta mesh to form a heatable and mechanically stable sample.<sup>5</sup> Si(OEt)<sub>4</sub> ( $6 \times 10^{-6}$  Torr) (Alfa Products; 99.9999% on a metal basis) was dosed on to the oxides (pre-evacuated at 773 K) at 300 K for selected times, then adsorbed Si(OEt)<sub>4</sub> was decomposed by heating up to 800 K at a rate of 2 K s<sup>-1</sup>. The amount of SiO<sub>2</sub> deposited was controlled by repeating the above process.

A.e.s. spectra were obtained in the derivative mode (2 keV, 16  $\mu$ A). In ion scattering spectroscopy (i.s.s.), a defocussed helium ion beam was used (0.95 keV, 0.5  $\mu$ A, laboratory scattering angle was 90 °).

A.e.s. data show the formation of SiO<sub>2</sub> on both ZrO<sub>2</sub> and TiO<sub>2</sub>. On TiO<sub>2</sub> some carbon is retained but not on ZrO<sub>2</sub>.<sup>5</sup> Typical i.s.s. spectra for SiO<sub>2</sub> overlayers on ZrO<sub>2</sub> and TiO<sub>2</sub> are shown in Figure 1. The peaks at *ca*. 870, 740, and 830 eV are due to Zr, Si, and Ti, respectively.<sup>6,7</sup> The oxygen peak is located in the range of 610—640 eV and varies because of small charging effects. Obviously, the peaks for Zr and Ti decreased when SiO<sub>2</sub> was deposited. After a 100 min dose, the Zr peak was quite small, but the Ti peak still remained.

Figure 2 shows plots of the Si surface fraction measured by



Figure 1. I.s.s. spectra of  $ZrO_2$  and  $SiO_2$  deposited on  $ZrO_2$  obtained using a He<sup>+</sup> beam (0.95 eV, 0.5  $\mu$ A). (a)  $ZrO_2$ , (b)  $SiO_2$ -covered  $ZrO_2$ (exposure time; 100 min,  $SiO_2$  content by a.e.s.; 40%), (c)  $TiO_2$ , (d)  $SiO_2$ -covered  $TiO_2$  (exposure time; 100 min,  $SiO_2$  content by a.e.s.; 50%), and (e)  $SiO_2$ .

i.s.s. (left vertical axis) as a function of Si content measured by a.e.s. The quantitative determination of Si fraction by i.s.s. was obtained by normalizing the peak area with those recorded under the same conditions on reference samples of  $ZrO_2$ ,  $TiO_2$ , and  $SiO_2$ , assuming that the ratio of metal cations to oxygen on the surface is 1:2 in all these oxides. The Si fraction for  $ZrO_2$  reached more than 90% when the Si content determined by a.e.s. was *ca*. 40%. In contrast with  $ZrO_2$ , the Si fraction on  $TiO_2$  was limited to 70% while the Si content increased to 50%.

Since i.s.s. is sensitive to only the top atomic layer of the surface,<sup>6,7</sup> the results shown in Figure 2 indicate that the SiO<sub>2</sub> overlayer covered nearly fully the  $ZrO_2$  surface. On the other hand, a.e.s. gives information on a few layers of the surface.<sup>6,8</sup> The attenuation length of a.e.s. electrons from Zr passing through SiO<sub>2</sub> is about 5 monolayers based on Seah's equation.<sup>5,9</sup> Since the Zr a.e.s. peak decreased to about one-half of its initial value by deposition of SiO<sub>2</sub> (after 100 min), the thickness of SiO<sub>2</sub> is estimated to be *ca*. 10 Å.<sup>5,10</sup>

The desorbing decomposition products from Si(OEt)<sub>4</sub> adsorbed on ZrO<sub>2</sub> and TiO<sub>2</sub> are exclusively ethene and water.<sup>5</sup> Changes of the decomposition activity of ZrO<sub>2</sub> and TiO<sub>2</sub> were monitored by the amount of ethene desorbed in t.p.d. experiments performed in a different u.h.v. system.<sup>11</sup> Si(OEt)<sub>4</sub> ( $6 \times 10^{-6}$  Torr) was introduced at 300 K for 1 min, and the temperature was increased to 800 K at a rate of 2 K s<sup>-1</sup>. The decomposition activity changes (defined as the amount of ethene desorbed in the t.p.d.) of ZrO<sub>2</sub> and TiO<sub>2</sub> for Si(OEt)<sub>4</sub> are plotted in Figure 2. The decomposition activity of ZrO<sub>2</sub> decreased strongly and monotonically as the Si content increased. This result is consistent with the formation of a uniform ultra-thin film on ZrO<sub>2</sub> because SiO<sub>2</sub> itself is inert



**Figure 2.** Changes in Si fraction measured by i.s.s. and decomposition activity for Si(OEt)<sub>4</sub> as a function of Si content measured by a.e.s. M = Ti or Zr.  $\bigcirc$ : Si fraction by i.s.s. for ZrO<sub>2</sub>,  $\bigcirc$ : decomposition activity for ZrO<sub>2</sub>,  $\Box$ : Si fraction by i.s.s. for TiO<sub>2</sub>,  $\blacksquare$ : decomposition activity of TiO<sub>2</sub>.

for the adsorption and the decomposition under these conditions.<sup>5</sup> Thus, the deposition process is self-terminating.

Unlike  $ZrO_2$ ,  $SiO_2$  deposited on  $TiO_2$  does not uniformly cover the  $TiO_2$ ; rather, small clusters of mixed oxides are probably formed which leave active  $TiO_2$  on the surface. The lower saturated value for the Si fraction on  $TiO_2$  (70%) by i.s.s. (Figure 2) is compatible with this model. Furthermore, the fact that the decomposition activity of  $TiO_2$  for  $Si(OEt)_4$ did not decrease strongly as Si deposition proceeded (Figure 2) can be explained by generation of new acid sites at the interface of  $TiO_2$  and  $SiO_2$ .<sup>12,13</sup>

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