Ultra-high Vacuum Preparation and Characterization of Ultra-thin Layers of SiO_2 on ZrO_2 and TiO_2 by Chemical Vapour Deposition of $Si(OEt)_4$

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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[1,2] and coatings which protect pigments against photo-degradation and metals against corrosion.[3] In microelectronic devices, silica thin films are important constituents.[3] The chemistry involved in the formation of these coatings is largely unexplored. In one example, Roozeboom *et al.* analysed V_2O_5 thin films on various oxides by Raman spectroscopy.[4]

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^2 g^{-1}; obtained by calcination of $Zr(OH)_4$] and TiO_2 (50 m^2 g^{-1}; Degussa P-25). The oxide powders were pressed into very transparent Ta mesh to form a heatable and mechanically stable sample.[5] $Si(OEt)_4$ (6×10^{-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 $Si(OEt)_4$ was decomposed by heating up to 800 K at a rate of 2 K s^{-1}. The amount of SiO_2 deposited was controlled by repeating the above process.

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

A.e.s. data show the formation of SiO_2 on both ZrO_2 and TiO_2. On TiO_2 some carbon is retained but not on ZrO_2.[5] Typical i.s.s. spectra for SiO_2 overlayers on ZrO_2 and TiO_2 are shown in Figure 1. The peaks at *ca.* 870, 740, and 830 eV are due to Zr, Si, and Ti, respectively.[6,7] 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_2 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

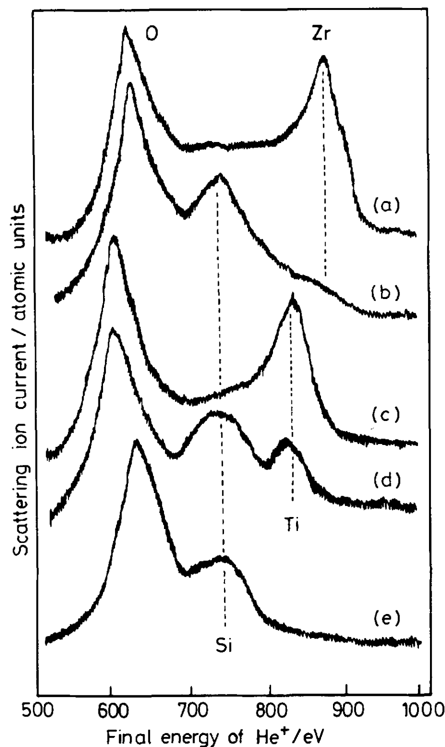

Figure 1. I.s.s. spectra of ZrO_2 and SiO_2 deposited on ZrO_2 obtained using a He^+ beam (0.95 eV, 0.5 μA). (a) ZrO_2, (b) SiO_2-covered ZrO_2 (exposure time; 100 min, SiO_2 content by a.e.s.; 40%), (c) TiO_2, (d) SiO_2-covered TiO_2 (exposure time; 100 min, SiO_2 content by a.e.s.; 50%), and (e) SiO_2.

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,[6,7] the results shown in Figure 2 indicate that the SiO_2 overlayer covered nearly fully the ZrO_2 surface. On the other hand, a.e.s. gives information on a few layers of the surface.[6,8] The attenuation length of a.e.s. electrons from Zr passing through SiO_2 is about 5 monolayers based on Seah's equation.[5,9] Since the Zr a.e.s. peak decreased to about one-half of its initial value by deposition of SiO_2 (after 100 min), the thickness of SiO_2 is estimated to be *ca.* 10 Å.[5,10]

The desorbing decomposition products from $Si(OEt)_4$ adsorbed on ZrO_2 and TiO_2 are exclusively ethene and water.[5] Changes of the decomposition activity of ZrO_2 and TiO_2 were monitored by the amount of ethene desorbed in t.p.d. experiments performed in a different u.h.v. system.[11] $Si(OEt)_4$ (6×10^{-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^{-1}. The decomposition activity changes (defined as the amount of ethene desorbed in the t.p.d.) of ZrO_2 and TiO_2 for $Si(OEt)_4$ are plotted in Figure 2. The decomposition activity of ZrO_2 decreased strongly and monotonically as the Si content increased. This result is consistent with the formation of a uniform ultra-thin film on ZrO_2 because SiO_2 itself is inert

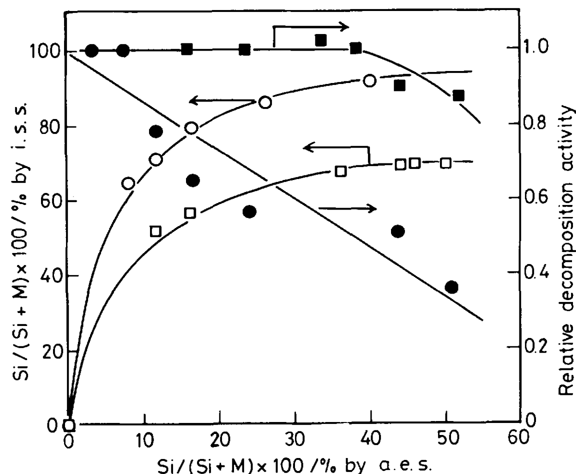

Figure 2. Changes in Si fraction measured by i.s.s. and decomposition activity for $Si(OEt)_4$ as a function of Si content measured by a.e.s. M = Ti or Zr. ○: Si fraction by i.s.s. for ZrO_2, ●: decomposition activity for ZrO_2, □: Si fraction by i.s.s. for TiO_2, ■: decomposition activity of TiO_2.

for the adsorption and the decomposition under these conditions.[5] 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.[12,13]

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