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High-resolution depth profiling for passive anodized TiO2 ultra-thin films

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Titanium is used pervasively over a range of fields [1], e.g. Ti is ubiquitous in biomedical implants, due to its low reactivity with the surrounding tissues. When Ti is exposed to air or water the resultant oxide is strongly adherent and thermodynamically stable, which protects the underlying metal from further oxidation The ability of Ti to withstand corrosion depends on the quality and characteristics of its unique passive oxide [2] which in turn depend on oxidation parameters. For example, electrochemically formed oxide films on Ti can be amorphous or crystalline, depending on the final anodization potential and electrolyte involved [3]. This can directly affect the biocompatibility of Ti, as thickness and crystallinity (rutile vs. anatase) can affect the degree of adsorption from human blood plasma [4]. Thus understanding the oxidation at an atomistic level is necessary if one wishes to develop better protective films. Isotopic labeling is used in conjunction with high-resolution ion depth profiling methods, including medium energy backscattering (MEIS) and nuclear reaction profiling (NRP) to determine O depth profiles and elucidate the transport and reaction mechanisms of the oxidation [5]. Magnetron sputtering was used to deposit Ti on Si(001), then exposed to isotopic 18O water vapour in Ar atmosphere to form an ultra-thin TiO2 film. The TiO2/Ti/Si(001) film was then electrochemically oxidized in D216O water over a range of voltages from 0-10 V, resulting in ~40–295 Å thick oxide regions. As oxide thickness increases as a function of anodization voltage while the total concentration of 18O remains constant, the 18O is found at increasingly greater depths, while the 16O concentration rises monotonically at the oxide-electrolytle interface indicating O exchange reactions. New titanium oxide is created by 18O being diffusing towards the oxide-metal interface, all of which is consistent with O ions as a mobile species but additionally with the Ti ions will transported towards the oxide-oxidant interface resulting in growth at that interface as well.

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