Anodically Grown TiO_2 Thin-Films: Structure and Dielectric Properties

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TiO_2 (titanium oxide) thin-films grown by anodic oxidation of Ti in an electrolyte possess promising properties for using them as dielectric layers in nanocapacitor applications. The films we fabricated to date have a dielectric constant between $\varepsilon = 60$ and 150 and a breakdown voltage of $U_b > 400\,V$). In order to optimize the performance of TiO_2 dielectric layers, we investigate their microscopic structure and study the correlation between structural defects and electrical properties. Electro-polished samples of high-purity Ti and, for comparison with a “well-behaved” dielectric, high-purity Ta were anodized in dilute aqueous H_3PO_4 and HNO_3 electrolytes, respectively. The anodizing voltages ranged from $U_a = 5$ to 400 V. The resulting film thickness t was found to increase linearly with U_a: $t = k \cdot U_a$, with $k = 1.33\,nm/V$ for TiO_2 and 1.42 nm/V for Ta_2O_5. The atomistic structure and the defects in the oxide films may give clues to the growth mechanisms and electrical performance.

Table 1 compiles the charge densities and the leakage currents we measured on TiO_2 and Ta_2O_5 thin-films grown by applying identical anodization voltages U_a. The surface topographies of these films were imaged by SEM (scanning electron microscopy), Fig. 1, and AFM (atomic force microscopy). The internal structure was investigated by transmission electron microscopy (TEM). TEM specimens were prepared for by ion-beam thinning as well as by electrolytic back-thinning. Plan-view specimens were made by both methods, while cross-section specimens could only be prepared by the sputtering method.

Fig. 2A shows a cross-section through a TiO_2 film grown at 30 V in 1% H_3PO_4. The film thickness ranges from 35 to 70 nm. The micro-diffraction pattern (insert) has a diffuse background and faint diffraction rings/spots. These features indicate that the oxide is basically amorphous, but contains TiO_2 nanocrystals and voids.

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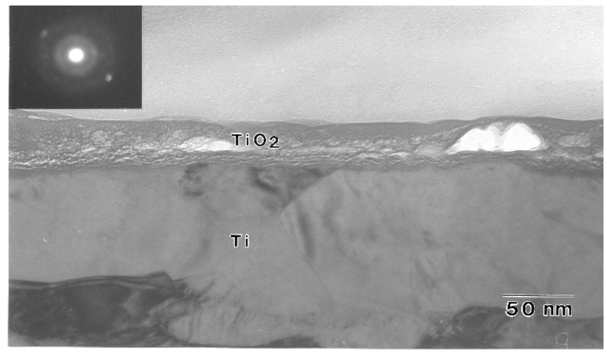
Table 1. Comparison of capacitance (per unit area) of anodized Ti and Ta. (Area of the Ti-capacitor: 2.000 cm^2, area of the Ta-capacitor: 0.226 cm^2)

		Ti/TiO_2	Ta/Ta_2O_5
Anodizing Voltage	Measuring Voltage (V)	Capacitance ($\mu F/cm^2$)	Capacitance ($\mu F/cm^2$)
10	10	1.01	1.19
	5	1.03	1.23
20	20	0.45	0.64
	10	0.86	0.65
	5	1.22	0.64
30	30	0.40	0.40
	20	0.54	0.39
	10	2.52	0.40
	5	4.00	0.39

$U_a = 15\,V$ $U_a = 20\,V$

Figure 1. SEM micrographs of the surfaces of TiO_2 thin-film obtained by anodization of Ti. Anodization voltages $U_a \leq 15\,V$ yield a smooth surface and a low leakage current. Above 15 V, defects (protrusions) form on the film.



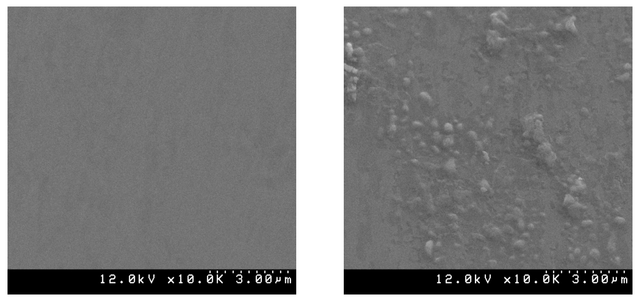


Figure 2. Cross-section TEM micrograph of an anodically grown TiO_2 film on Ti (anodizing voltage: 30 V).