

Influence of Anodization Conditions on the Electronic Structure of TiO₂ Nanotubes

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The storage of solar energy is needed to overcome the inherent intermittencies of sunlight, and the photoelectrochemical conversion of light and water into storable hydrogen fuel is a route with great potential. TiO₂ nanotubes can be formed by the anodization of Ti foils in electrolytes containing F⁻ ions. Their high surface area, stability in solution and under irradiation, and 1D charge transport along the tube length makes them promising candidates for photoelectrochemical applications.¹ Despite considerable investigations that show that a variety of morphologies can be obtained from anodizing Ti foils in organic solutions with varying water content, the effect of the anodization conditions on the photoelectrochemistry and electronic structure of the TiO₂ nanotubes are not well understood. Recently, we have shown that TiO₂ nanotubes grown in 11 vol% water possess the highest photocurrent conversion efficiency among 1 μm nanotubes formed in the range of 2 - 45 vol% water, with the cause being a general improvement in crystallinity under these conditions.² A finer probing of the influence of the anodization conditions on the electronic structure of TiO₂ nanotubes is still needed. TiO₂ is known to contain a set of shallow level donor states located in an exponential distribution near the conduction band and a deep level trap,^{3,4} and these defect states may be examined by electrochemical impedance spectroscopy.

TiO₂ nanotubes of length 1 μm were anodized in solutions of ethylene glycol containing 0.3 wt% NH₄F + 2 vol% water and 0.5wt% + 11 vol% water. Electrochemical impedance spectroscopy was carried out in the dark and under illumination scanning at a potential range between 0.8V_{SCE} and -0.5V_{SCE} and a frequency range of 200 kHz to 1 mHz in a solution of 0.2M Na₂SO₄ and 0.1M NaCH₃COO (pH = 7). The capacitance as a function of potential at low frequency was used to determine a density of defect states.^{5,6}

In Figure 1, two peaks detected in these samples indicate the presence of two distinct defect states located at -0.2 V_{SCE} and 0.5 V_{SCE}. The first we assign to donor states near the conduction band; these have a density of approximately 10²⁰ cm⁻³. The latter we assign to the deep level trap states with densities of 6.5 x 10¹⁶ cm⁻³ and 2.4 x 10¹⁶ cm⁻³ for 2 and 11 vol % respectively. The lower level of deep trap states would contribute in part to the higher photocurrent conversion efficiency for nanotubes formed in anodization solutions containing 11 vol% water compared to 2 vol% water. These new results are consistent with our Mott-Schottky measurements of the doping density and the determination of the density of deep level states by photocurrent onset transients reported in ref 2.

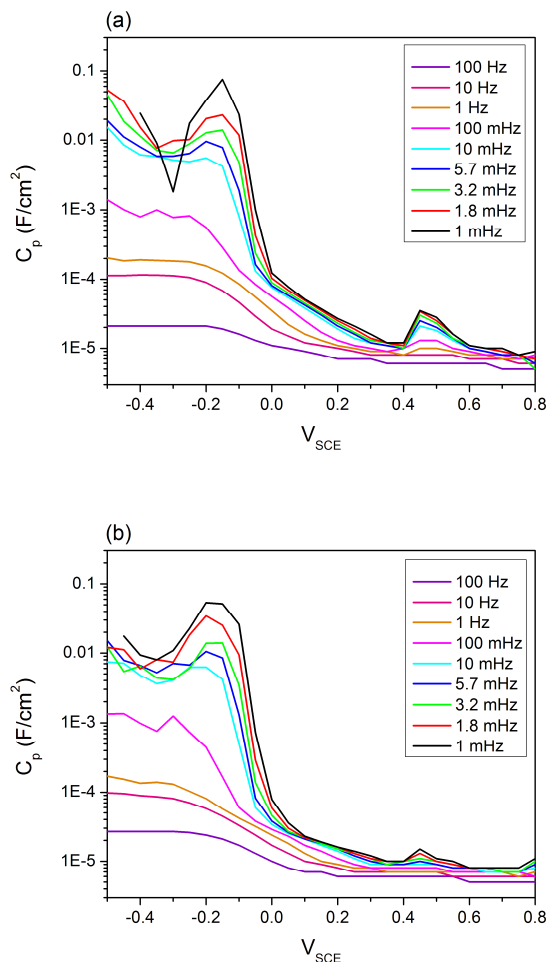


Figure 1. Capacitance as a function of applied potential for TiO₂ nanotubes anodized in (a) 2% water solution and (b) 11% water solution.

References

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