# Characterization of Thin Film $TiO_2$ Photoelectrodes Prepared by Various ALD Procedures

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## INTRODUCTION

Surface coverage by thin films is of great technological importance, because it improves mechanical, optical, and electrochemical properties of solid surfaces. We have shown, that atomic layer deposition (ALD) of titanium dioxide protects a semiconducting hematite electrode against corrosion and photocorrosion[1]. The present work studies in detail the properties of ALD-$TiO_2$ layers deposited on FTO substrates.

## EXPERIMENTAL/THEORETICAL STUDY

$TiO_2$ thin films (8, 20 and 50 nm) were deposited by various ALD procedures on FTO substrates. The structural and morphological properties of $TiO_2$ films were determined by X-ray diffraction (XRD) and atomic force microscopy (AFM). The conformability and quality of $TiO_2$ films deposited on FTO were quantified by electrochemical tests with suitable redox probes, such as $[Fe(CN)_6]^{3-/4-}$, which selectively distinguish the charge-transfer reactions occurring on $TiO_2$ surface and on the supporting FTO. The blocking properties of ALD-$TiO_2$ films are expressed as the effective pinhole area (EPA) determined from the peak current density of ferrocyanide oxidation[3]. Value of EPA indicates the percentage of FTO electrode area uncovered by $TiO_2$. Chemical stability in alkaline (phosphate buffer (pH 8)) and acidic solution (0.1M $HClO_4$) was studied. Dissolution rates of ALD-$TiO_2$ films were evaluated from concentration of the titanium in solution analyzed by inductively coupled plasma spectrometry (ICP). Photoelectrochemical properties and band gap of $TiO_2$ films were determined from incident photon to current conversion efficiency (IPCE) measurements.

## RESULTS AND DISCUSSION

Two types of $TiO_2$/FTO electrodes were prepared by ALD with different deposition temperatures, 150 °C (LT-ALD-$TiO_2$) and 250 °C (HT-ALD-$TiO_2$). While both types of as-grown ALD-$TiO_2$ were quasi-amorphous, subsequent annealing at 500 °C /1 hour led to the formation of anatase crystalline structure in the case of LT-ALD-$TiO_2$, but for HT-ALD-$TiO_2$ neither anatase nor rutile were detected. AFM doesn't show significant difference in nanomorphology between different types of ALD-$TiO_2$/FTO samples. Blocking properties of 8 nm thick $TiO_2$ films are similar (EPA ≈ 8%) for both as-grown ALD-$TiO_2$ films, while for post-annealed films pinholes area increased to 20% and 45% for HT-ALD-$TiO_2$ and LT-ALD-$TiO_2$, respectively. All tested ALD-$TiO_2$ films were stable in phosphate buffer solution (pH 8). Exposure to acidic solution for 72 h caused dissolution of ~ 60% and 40% of $TiO_2$ film thickness in case of as-grown HT-ALD-$TiO_2$ and LT-ALD-$TiO_2$, respectively. Band gap energies determined from the electrochemical Tauc plot[3] were found 3.0 and 3.1 eV for post-annealed HT-ALD-$TiO_2$ and LT-ALD-$TiO_2$, respectively.

## CONCLUSION

As grown LT and HT ALD film are amorphous, post-annealing is necessary to obtained crystalline phase. ALD-TiO2 films were chemically stable in phosphate buffer (pH 8), but dissolved in acidic solution.

## REFERENCES

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