Dense TiO_2 Thin Layers Prepared by Sol-Gel for Dye Sensitized Solar Cells: Electrochemical Properties

Marketa Zukalova, Jan Prochazka, Pavel Janda and Ladislav Kavan

J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i. Dolejskova 3, CZ-18223 Prague 8, Czech Republic

marketa.zukalova@jh-inst.cas.cz

TiO_2 films attract attention because of their interesting mechanical, chemical, electrical and optical properties, which find various applications particularly in photocatalysis and dye sensitized solar cells [1] (DSCs). The performance of DSCs is controlled by the transport of holes from the photooxidized dye on the photoanode towards the counterelectrode. Solar conversion efficiency of the device is limited by the back reaction (recombination) of injected electrons with the oxidized form of mediator taking place mainly at the FTO/TiO_2 interface [2]. To avoid recombination losses a compact blocking underlayer of TiO_2 is deposited on top of FTO. Besides the blocking effect, the compact layer can improve the adhesion of the FTO/TiO_2 interface as well, and creates more electron pathways from the porous layer to FTO and subsequently increases the electron transfer efficiency. Exceptionally dense TiO_2 films can be prepared via dip-coating from a sol containing poly(hexafluorobutyl methacrylate) as the structure directing agent [3]. The films cover perfectly even rough surfaces due to thixotropic properties of the precursor gel (Figure 1). They are mechanically and chemically stable, scratch-resistant and provide antireflection function to crystalline Si wafers for photovoltaic applications. The dense TiO_2 films contain amorphous titania with small amount of anatase and monoclinic TiO_2(B). These two phases withstand calcination at 900°C in films deposited on Si and no recrystallization to rutile occurs. The blocking properties of the films were tested by cyclic voltammetry using $Fe(CN)^{3-/4-}$ in aqueous electrolyte solution [4]. The occurrence of anodic current of ferrocyanide oxidation selectively indicates the naked FTO substrate, which is exposed to the electrolyte solution through pinholes, if any in the blocking layer. The as-grown films were found to exhibit an excellent rectifying interface with almost no pinholes. However, defects were formed by thermal treatment at 500°C in air due to anatase crystallization. The overall area of thermally induced pinholes is comparable to that in frequently used spray-pyrolyzed titania films. The above mentioned results favor as made sol-gel compact TiO_2 layers being an efficient blocking underlayer in classical liquid junction DSCs. Since the optimum buffer layer for practical solid-state and the most recent perovskite solar cells is predicted to be at the interplay of quasi-amorphous morphology (responsible for the good blocking function) and anatase crystallinity (responsible for the fast electron injection and transport in the conduction band), our sol-gel dense layers treated by optimized calcination procedure can meet requirements for buffer layers of these devices as well.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (contracts No. 13-07724S and P108/12/814).

References

[1] Zukalova, M.; Zukal, A.; Kavan, L.; Nazeeruddin, M. K.; Liska, P.; Gratzel, M. Nano Letters,5, 9 (2005), 1789-1792.

[2] Yuan, S. J.; Li, Y. G.; Zhang, Q. H.; Wang, H. Z. Electrochimica Acta, 79, (2012), 182-188.

[3] Prochazka, J.; Kavan, L.; Zukalova, M.; Janda, P.; Jirkovsky, J.; Zivcova, Z. V.; Poruba, A.; Bedu, M.; Döbbelin, M.; Tena-Zaera, R. Journal of Materials Research,28, 03 (2012), 385-393.

[4] Kavan, L.; Zukalova, M.; Vik, O.; Havlicek, D. Chemphyschem,15, 6 (2014), 1056-61.

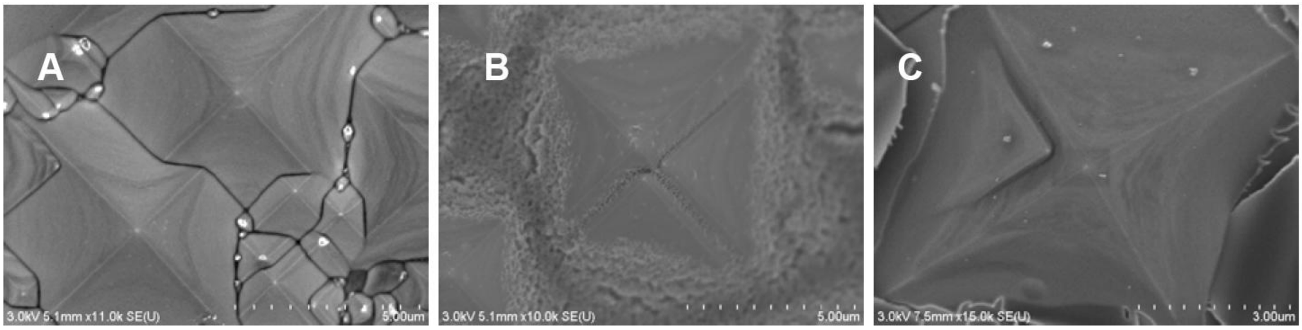

Figure 1. SEM pictures of crystalline (111) Si-substrate etched (textured) for photovoltaic applications:
A) Blank Si-substrate
B) Si-substrate dip coated from a Pluronic-P123 containing precursor sol.
C) Si-substrate dip coated from the poly(hexafluorobutyl methacrylate) containing precursor sol (Reprinted from Ref.3).