

Development and characterisation of photoelectrochemical MIS structures with RuO₂/TiO₂ gate stacs for water oxidation

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This paper is dedicated to preparation and analysis of metal insulator semiconductor (MIS) photoanode with a metal organic chemical vapor deposited RuO₂ layer and TiO₂ protection layer for photoelectrochemical water splitting. It is shown that utilization of TiO₂ layers of 2, 4, and 6 nm thickness preserve the catalytic activity of underlying RuO₂. The origin of increased overpotential and decreased photovoltage of the photoanode upon the increase of TiO₂ layer thickness is discussed in the paper. Results revealed that utilization of TiO₂ layer in the MIS concept is suitable for photoelectrochemical water oxidation applications.

Key words: MIS, RuO₂, TiO₂, water splitting, water oxidation

1 Introduction

Photoelectrochemical (PEC) water splitting is an attractive way for the conversion of solar light into chemical energy of hydrogen [1]. Key part of PEC structures is the catalyst, which support high reaction rate of water oxidation. Recently, we have shown superior performance of RuO₂/SiO₂/n-Si compared to Ni/SiO₂/n-Si based metal-insulator-semiconductor (MIS) structure, which was achieved due to the high catalytic activity, good transparency, and good interface properties of RuO₂ [2]. To increase the stability of RuO₂, it is favorable to combine it with highly corrosive resistant TiO₂ to form RuO₂/TiO₂ bilayer catalytic gate. TiO₂/RuO₂ composition was recently shown to have a high catalytic activity and allows to increase the oxidation rate and pollutant degradation rate of TiO₂ photocatalyst [3, 4, 5]. The utilisation of TiO₂ in MIS PEC structures is under intense investigation [6, 7, 8] and needs further clarification of current transport through such layer and impact of TiO₂ on the water splitting performance. In this paper, we focus on the characterization and analysis of RuO₂ based silicon MIS structures covered by additional TiO₂ layer forming so called insulator-metal-insulator-semiconductor (IMIS) concept. The paper aims to describe the impact of TiO₂ layer with thicknesses of 2, 4, and 6 nm on the photoelectrochemical performance of IMIS structures.

2 Experimental

Silicon of n-type, resistivity 5 – 8 Ωcm, with orientation (1 0 0) and thickness of 625 μm were used to prepare MIS and IMIS structures. The counterpart MIS and IMIS structures were prepared on p-Si with resistivity 0.005 Ωcm and orientation (1 0 0). Such a structure does not exhibit any photovoltage and was used to determine the photovoltage generated from the n-Si MIS structure. A SiO₂ layer was formed on the Si substrate in the ALD equipment by exposure to ozone at 300 °C. Top RuO₂ layers with thickness of 5 nm were prepared by liquid injection metal organic chemical vapor deposition (MOCVD) in a horizontal low-pressure hot-wall reactor on both n-Si and p-Si substrates, forming RuO₂ based MIS structures. Amorphous TiO₂ thin films were prepared by atomic layer deposition (ALD) at 150 °C in Beneq TFS 200 equipment on MIS structure, forming IMIS structure. One reference MIS sample and three samples with TiO₂ thicknesses of 2, 4 and 6 nm were prepared for photoelectrochemical characterization. Photoelectrochemical characterisation under light and at dark was carried out in a three-electrode set-up with a saturated Ag/AgCl reference electrode and a platinum counter electrode by using a PalmSens potentiostat. As an electrolyte, 1M H₂SO₄ with pH = was used. The thermodynamic potential of water oxidation (E_{O_2/H_2O}^0) is calculated to be +1.23 V vs normal hydrogen electrode (NHE). Photovoltage (V_{op}), overpotential (V_{phot}) and Tafel slope were

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extracted from the measured cyclic voltammetry curves to describe the performance of the structures. The V_{op} is defined as a voltage, which must be supplied to the structure to obtain a photocurrent of 10 mA/cm^2 . The current 10 mA/cm^2 is chosen as a device relevant value for practical oxygen and hydrogen generator systems. The V_{phot} generated in the n-Si structure is estimated by comparison of light cyclic voltammetry of n-Si based structure and dark cyclic voltammetry of p⁺-Si type structure. This analysis assumes that the current in the p⁺-Si structure is formed by majority holes and the current in n-Si based structure is formed by photogenerated holes. In our case, the photovoltage is calculated as a sum of voltages extracted for n-Si and p-Si based MIS and IMIS structures at 1 mA/cm^2 by equation $V_{phot} = V_p + V_{phot-n}$, where V_p is the difference between the voltage of p⁺-Si structure measured at 1 mA/cm^2 and 1.23 V and V_{phot-n} is difference between 1.23 V and voltage of n-Si structure measured at 1 mA/cm^2 . The Tafel slope is calculated around current of 10 mA/cm^2 . The lower Tafel slope indicate a higher catalytic efficiency.

3 Results and discussion

3.1 Photoelectrochemical characterisation

Photoelectrochemical characterisation of $\text{RuO}_2/\text{SiO}_2/\text{Si}$ MIS and $\text{TiO}_2/\text{RuO}_2/\text{SiO}_2/\text{Si}$ IMIS structures was conducted to analyse the impact of the TiO_2 layer on the oxygen evolution reaction (OER) of RuO_2 catalyst. Figure 1 shows cyclic voltammetry of MIS and IMIS structures prepared on n-Si substrate drawn with potential *vs* NHE representation. The cyclic voltammetry was conducted in the $1 \text{ M H}_2\text{SO}_4$, (aq) electrolyte with pH 0 under the light of solar simulator. Measurements were carried out under light AM1.5, 1000 W/m^2 in electrolyte $1 \text{ M H}_2\text{SO}_4$ (pH 0). All photosensitive structures prepared on n-Si exhibit a photoresponse with saturation of $> 25 \text{ mA/cm}^2$ at voltages $> 1.6 \text{ V vs NHE}$. This suggests that the TiO_2 coverage does not cancel the catalytic activity of RuO_2 layer. To further confirm RuO_2 as a source of increased current, structures with 6 nm thick TiO_2 are compared with $\text{TiO}_2/\text{RuO}_2$ based structures with TiO_2 of 0 to 6 nm thickness. Structures were prepared on p⁺-Si substrate to suppress the impact of different diffusion voltage and thus photovoltage, which can arise in case of moderate doped silicon structures with different metal oxide layer stacks. The cyclic voltammetry of such structures was carried out in $1 \text{ M H}_2\text{SO}_4$, (aq) electrolyte with pH 0 at dark, Fig. 2. The results revealed that only a structure with $\text{TiO}_2/\text{RuO}_2$. Figure 2(b) shows increased current with increased voltage, while the structure without RuO_2 , Fig. 2(a) has negligible low current. The increase of the current with voltage for $\text{TiO}_2/\text{RuO}_2$ is attributed to the catalytic activity of RuO_2 .

Analysis of light cycling voltammetry of MIS and IMIS structures prepared at n-Si (Fig. 1) showed a shift of the

current onset upon an increase of the TiO_2 layer thickness. To evaluate this shift, V_{phot-n} and V_{op} were extracted at current values of 1 mA/cm^2 and 10 mA/cm^2 , respectively. The cyclic voltammetry of MIS and IMIS structures prepared on p⁺-Si substrate was measured at dark to extract V_p . This parameter is required for the calculation of photovoltage, Fig. 2(b). The V_p of 0.31 V measured at 1 mA/cm^2 current was obtained for all studied p-Si MIS and IMIS structures. The values of photovoltage V_{phot} were then calculated as a $V_p + V_{phot-n}$. Tafel slope was calculated for n-Si MIS and IMIS structures to compare catalytic activity of structures with different $\text{RuO}_2/\text{TiO}_2$ layer stack. All extracted parameters are summarized in Tab. 1.

3.2 Discussion

The parameters extracted from photoelectrochemical analysis (Tab. 1) can provide insight on the role of TiO_2 in IMIS performance. The values of $V_{phot} = 0.49 \text{ V}$ and $V_{op} = -0.01 \text{ V}$ obtained for reference MIS structure are in accordance with our previously published results [2] and indicate the state-of-the art performance of RuO_2 based MIS structure as well as good reproducibility of our technology. The IMIS structures revealed decreased V_{phot} from 0.49 to 0.32 V and increased V_{op} from -0.01 to 0.18 V upon the increase of TiO_2 thickness from 0 to 6 nm . The source of V_{phot} and V_{op} change is not straightforward and needs to be discussed in detail. The first mechanism, which needs to be assumed as an origin of such effect, is the increase of the resistivity losses at TiO_2 with the increase of thickness. This mechanism should result in the increased voltage losses with increased current, hence, decreased current slope and thus Tafel slope of cyclic voltammetric curves. For samples with higher TiO_2 thickness, the effect of decreased Tafel slope should be more obvious. In addition, the same trend should be presented also for structures prepared at p-Si silicon substrate. Table 1 shows that only a slow increase of the Tafel slope from 262 to 345 mV/decade and thus decrease of the catalytic efficiency is observed with the increase of the TiO_2 thickness for n-Si based structures and no systematic trend is observed in Tafel slope for p-Si structures. This allows us to neglect the TiO_2 resistivity as a dominant source of observed change in cyclic voltammetry for IMIS structures. Thin TiO_2 layers exhibit a strong leakage [9], which suppresses evolution of resistivity losses in the layer.

The second assumed source of the different IMIS photoelectrochemical behaviour is the change of catalytic effectivity for different $\text{RuO}_2/\text{TiO}_2$ stacks. This change should be presented for both n-Si and p-Si type structures. As was mentioned above, results revealed a low increase of the Tafel slope and thus catalytic efficiency for n-Si MIS structures, and no systematic trend of the Tafel slope change for p-Si structures. Therefore, we cannot clearly connect the observed systematic change in photoelectrochemical performance of IMIS structures with different catalytic performance of $\text{RuO}_2/\text{TiO}_2$ stacks.

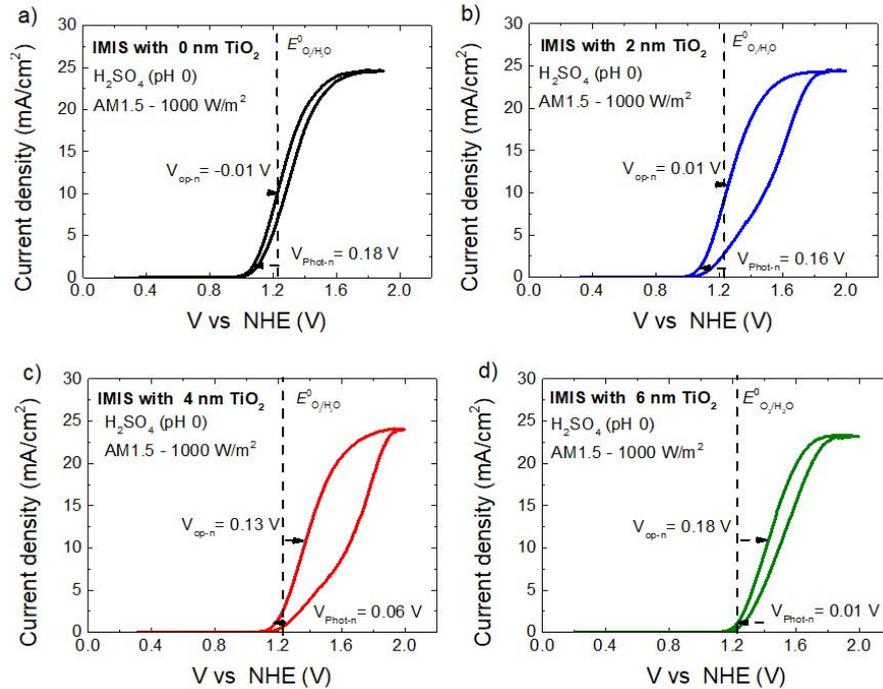


Fig. 1. Photoelectrochemical characterization: (a) – reference RuO₂/SiO₂/n-Si MIS structure, and TiO₂/RuO₂/SiO₂/n-Si IMIS structures (b) – 2 nm, (c) – 4 and (d) – 6 nm thick TiO₂ layer

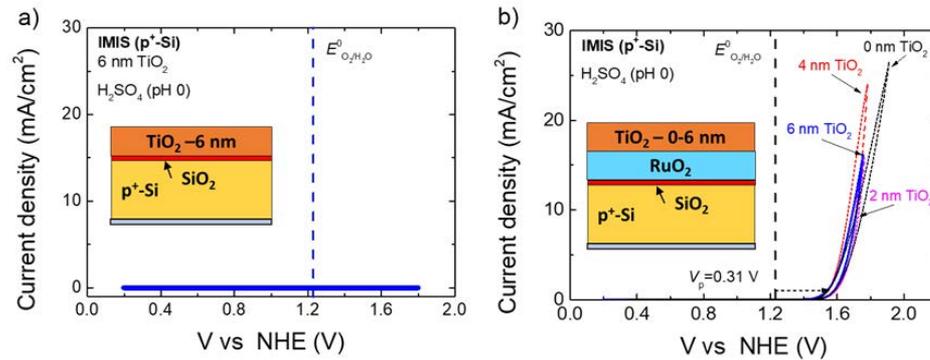


Fig. 2. Photoelectrochemical characterization of: (a) – TiO₂/SiO₂/n-Si and (b) – TiO₂/RuO₂/SiO₂/n-Si structures carried out under light AM1.5, 1000 W/m² in electrolyte 1M H₂SO₄ (pH = 0). Insets show the layer sequence of the structures.

Table 1. Summary of extracted and calculated parameters, voltages in V

TiO ₂ (nm)	0	2	4	6
V _{phot-n}	0.180	0.16	0.06	0.01
V _p	0.31	0.31	0.31	0.31
V _{phot}	0.49	0.47	0.37	0.32
V _{op}	-0.01	0.01	0.13	0.18
*TS n-Si	262	323	320	345
*TS p-Si	264	200	174	202

*Tafel slope IMIS (mV/decade)

The third possible mechanism of observed changes in photoelectrochemical performance is the different diffusion voltage and thus internal electrical field in the struc-

tures with different RuO₂/TiO₂ gate stacks. The IMIS structure can be considered as a two-part system. The first part is silicon/metal oxide structure responsible for the absorption of light, collecting photogenerated carriers and generation of photovoltage. This part represents a MIS Schottky structure with diffusion voltage, which is defined by the difference in work function of metal oxide and silicon substrate. The diffusion voltage determines the generated photovoltage. The work function of 5.1 eV was previously determined for the RuO₂ based gate [2] in MIS structure. The TiO₂ has in general low work function in the range of 3.5 – 4.6 eV [10]. The lower work function of RuO₂/TiO₂ stack compared to RuO₂ layer can be thus considered for IMIS structures. The second part is RuO₂/TiO₂ catalyst, which is responsible for oxygen evolution reaction. Therefore, for IMIS structures, the RuO₂/TiO₂ fulfills two functions it acts as

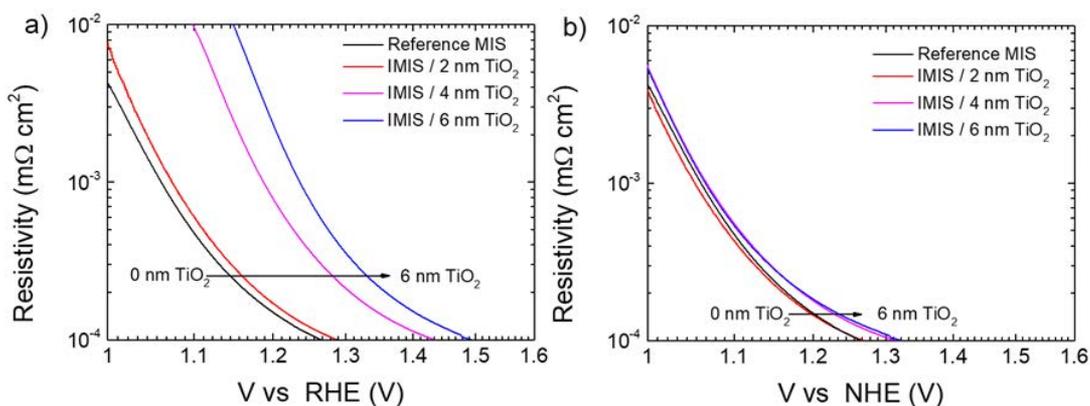


Fig. 3. Resistivity as a function of voltage *vs* NHE for: (a) – IMIS prepared on n-Si and (b) – IMIS prepared on n-Si with shifted voltage along the *x*-axis by V_{phot}

a gate contact for MIS Schottky structure and provides OER for water splitting. By considering these two parts, the generated photovoltage in the MIS structure provides an additional voltage, which shift the current onset of the $\text{RuO}_2/\text{TiO}_2$ catalyst. This additional voltage shift is equal to photovoltage generated in the MIS. The decrease of the diffusion voltage and photovoltage in IMIS structure with $\text{RuO}_2/\text{TiO}_2$ stack leads to decrease of this voltage shift and does not have any impact on the catalyst efficiency or Tafel slope. As a result, the Tafel slope should not be affected, however, the V_{phot} and the V_{op} parameters will be strongly affected. This is the case for presented IMIS structures. This explanation is supported by the fact, that only $V_{\text{phot-n}}$ part of the V_{phot} is changed with the increase of TiO_2 thickness. All IMIS structures prepared on p-Si revealed a similar cyclic voltammetry behaviour, which has no trend with the change of TiO_2 thickness. Due to the p-Si substrate, no diffusion voltage and photovoltage is generated in such structures, and thus the change of the work function of $\text{RuO}_2/\text{TiO}_2$ stack has negligible impact on the current transport and cycling voltammetry of p-Si IMIS structures.

The resistivity as a function of voltage *vs* NHE was calculated for n-Si structures to further confirm the above proposed mechanism. Figure 3(a) shows the calculated resistivity of MIS and IMIS structures with different TiO_2 layer thicknesses. Figure 3(b) shows the same resistivity curves shifted along the voltage axes by the V_{phot} . A similar voltage trend of shifted resistivity curves indicates that the main difference between the structures is the different photovoltage of the MIS Schottky part of MIS PEC structure.

4 Conclusion

Presented work focused on the photoelectrochemical performance analysis of MIS and IMIS structures and the impact of the TiO_2 layer on the oxygen evolution reaction. The MIS structures with RuO_2 catalytic layer revealed a state-of-the-art performance with $V_{\text{op}} = -0.01$ V and $V_{\text{phot}} = 0.49$ V. The important finding from the

study is that the preparation of the TiO_2 layer with thicknesses of 2 – 6 nm on the top of the RuO_2 layer did not cancel the catalytic performance of IMIS structures. The decrease of V_{phot} and increase of V_{op} was observed upon the increased thickness of TiO_2 in the $\text{RuO}_2/\text{TiO}_2$ stacks. The analysis allowed us to neglect the resistivity losses and change of the catalytic performance of RuO_2 to be the dominant sources for the observed changes in photoelectrochemical behaviour. Instead of this, the change of diffusion voltage for different $\text{RuO}_2/\text{TiO}_2$ stacks was suggested as a possible origin of the observed shift in V_{phot} and V_{op} . The presented study revealed a possible utilisation of TiO_2 layer in connection with RuO_2 catalyst coupled with silicon-based MIS PEC structures for photoelectrochemical water splitting.

Acknowledgments

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