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The Influence of Recombination Barrier Al_2O_3 Layer Thickness Formed by ALD on ETA-Cell Efficiency.

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ABSTRACT

The article discusses a possibility to improve efficiency of solid state solar cell with extremely thin absorbing layer by means of incorporation of photoelectric converter in the form of $TiO_2/In_2S_3/In_xPb_{1-x}S/CuSCN$ heterostructure of aluminum oxide recombination barrier layer between electron acceptor layer and chalcogenide layer. The recombination Al_2O_3 barrier layer has been generated by atomic layer deposition (ALD). A procedure has been developed for conform deposition of extremely thin Al_2O_3 layers onto developed surface of electron acceptor layer. The influence of thickness of generated recombination Al_2O_3 barrier layer on efficiency and other parameters of photoelectric converters of ETA-cell (extremely thin absorber) type have been studied. With this aim extremely thin aluminum oxide films of various thickness (various numbers of deposition cycles) have been deposited by ALD method onto TiO_2 layer surface and test samples of PEC (photoelectric converter) have been obtained. The obtained test samples have been used for measurements of current-voltage characteristics (CVC) and other main parameters of PEC. While analyzing the obtained results it has been demonstrated that existence of the recombination barrier layer at $TiO_2/In_2S_3/In_xPb_{1-x}S$ interface makes it possible to increase the efficiency of test PEC, however, optimum thickness of such layer exists, and upon further increase in the Al_2O_3 layer thickness the efficiency of generated PEC decreases due to resistance increasing in oxide layer.

Keywords: photovoltaics, solar cells, atomic layer deposition, aluminum oxide, SILAR (successive ionic layer adsorption and reaction), barrier layer, recombination

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INTRODUCTION

The recent 15 years have been marked with steady progress in mastering of innovative concepts of development of solar cells on the basis of nanostructured materials. Due to large surface area in nanostructured materials the light absorption and charge separation occur by several times more efficiently than in non-nanostructured materials. In particular, dye-sensitized solar cells (DSSC) are challenging and inexpensive alternative to conventional solar cells on the basis of semiconductor p-n junctions [1]. Efficiency of such converters in laboratory experiments amounted to 11 % [2,3]. However, a significant drawback of such solar cells is the existence of liquid between electrodes, which significantly decreases the range of operation temperatures of such devices, thus leading to restrictions of application area of this solar cell type, its operation lifetimes, and additional requirements for the substrates and photoelectrodes. A possible alternative to solve this problem is to replace organic liquid electrolyte with solid or gel one. However, up till now the most of them are characterized with similar issues of non-stable properties of the structure [4]. In order to avoid such instability issues a new concept of solid state solar cells was proposed: ETA-cell (extremely thin absorber) [4,5,6], where dye was replaced with solid light absorbing layer (absorber) made of inorganic semiconductor [7,8,9,10,11,12], and electrolyte was replaced with solid state vacancy acceptor, made of transparent wide-gap inorganic p-type semiconductors. Figure 1 illustrates the layout of solar cell with extremely thin absorbing layer (ETA-cell). The conversion efficiency was about 2-5 %, which confirms the validity of ETA concept [13,14].

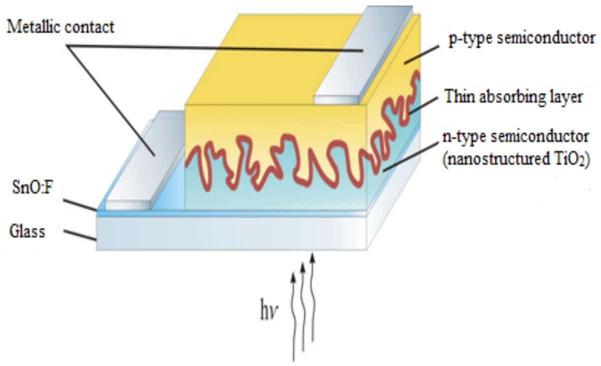

Fig.1. Layout of solar cell with extremely thin absorbing layer (ETA-cell).

One of the issues occurring upon application of such PEC structure is undesired recombination of charge carriers, generated in thin absorber layer, at absorber/photoelectrode interface.

The concept of usage of extremely thin metal oxide layer as a barrier, which restricts both parasitic recombination and prevents metal migration from chalcogenide layer, is based on the concept of kinetic reservation, where more preferable charge transfer is sufficiently more rapid than competing processes. In particular, such cases involve electron injection into TiO_2, which is by far more rapid than competing recombination of charge carriers inside chalcogenide layer. In this situation implementation of barrier layer into photosensitive heterostructure can decelerate electron injection without decrease in the productivity of this process, still enabling decrease in recombination of charge carriers without negative impact on photocurrent collection.

One of the candidate materials for such barrier layer is aluminum oxide due to its wide band-gap. However, taking into consideration increase in series resistance of the applied heterostructure upon recombination barrier layer implementation, this layer thickness should be optimized in order to embody the concept of kinetic reservation.

The atomic layer deposition (ALD) was selected as a procedure for making of such recombination barrier layer [11,12,13].

The atomic layer deposition of Al_2O_3 films has certain advantages in comparison with other technologies of deposition of metal oxides [14]. Existing film technologies involve both chemical deposition from gaseous phase [15,16,17], and physical deposition from vapor phase. Application of chemical or physical deposition processes from gaseous phase due to fundamental reasons are inefficient upon thickness decrease to one hundred nanometers and lower. In the thickness range of 1-100 nm the atomic layer deposition of Al_2O_3, films has advantages in principal, providing possibility of precision control of their growth. The significant advantage of atomic layer deposition of Al_2O_3 films is low temperature of film deposition [16]. Due to this factor the process is environmentally safe.

Another peculiarity of atomic layer deposition of Al_2O_3 films is low growth rate: about 0.01 nm/cycle. Therefore, aiming at development of commercial technology of film deposition on the basis of atomic layer deposition it is required to build up multi-position assembly.

Taking into account the low required thickness of Al_2O_3 recombination barrier layer, limited by dielectric properties of oxide from one side and by high consistency requirements of the layer across the sample surface area from another side, ALD is the most acceptable method [18,19,20]. This work studied the influence of Al_2O_3 recombination barrier layer implemented into ETA-cell structure on the efficiency of obtained PEC, and the thickness of such layer was optimized.

EXPERIMENTAL

The substrates for PEC structures production were made of glass plates with applied conducting transparent electrode based on SnO_2:F by magnetron sputtering. Surface resistance of the transparent conducting layer (TCL) was about 8 Ω per square. Two-layer titanium oxide structures were produced on the substrate surface. Deposition was performed by means of pulling out the substrate from solution [21]. The first dense TiO_2 layer was deposited from 10 % $Ti(PrO)_4$ solution in propanol at the rate of sample extraction from solution of 2 mm/s at relative ambient moisture of 1 %. After immersion the samples were annealed in air at 500°C in 20 min. Structured porous layer was deposited at the rate of sample extraction from solution of 200 mm/s at relative moisture of 50 %. Then the samples were annealed in air at 500°C in 2 h in order to obtain transition of generated titanium oxide layers from amorphous state to anatase phase.

Deposition of extremely thin conformal oxide recombination barrier layer was performed by atomic layer deposition of Al_2O_3 films. The temperature in the reaction chamber was maintained at 180°C. Trimethylaluminum (TMA, Sigma-Aldrich) and deionized water were used as precursors, which were held at ambient temperature. Nitrogen was used as carrier and purging gas. In order to verify that precursors penetrate efficiently into mesoporous structure of titanium oxide layer and coat it conformally an additional stage was introduced into deposition cycle, which is comprised of holding of reacting chamber isolated from vacuum pump and access of precursor, similar to [22]. Therefore, at first TMA was introduced into the reacting chamber and then the chamber was maintained isolated for efficient absorbing; then, the chamber was purged with nitrogen and H_2O was added into the chamber with subsequent purging with nitrogen, similar to the previous purging.

The rate of this process was analyzed by an Ellips-1891 ellipsometer. This was made by deposition of Al_2O_3 layer onto preliminary cleaned silicon substrate Si(100) with natural oxide according to the aforementioned procedure with 100 deposition cycles. The measurements demonstrated that under such deposition mode the average oxide thickness is about 2 Å. In addition, this process was analyzed by Auger spectroscopy. With this aim the lateral chip of mesoporous TiO_2/Al_2O_3 was scanned. This study confirmed conformal deposition of Al_2O_3 layer onto developed structure of mesoporous titanium oxide. While optimizing deposition, the following process variables were selected:

- Temperature of operating chamber: 175°C;
- Vacuum in operating chamber: 1.5 mbar;
- Trimethylaluminum concentration in reactor gaseous phase: $1.3*10^{-3}$ cm^3;
- Water concentration: $1*10^{-5}$ cm^{-3};
- Duration of TMA feeding into reactor: 5 s;
- Duration of water feeding into reactor: 3 s;
- Duration of absorption: 40 s;

- Duration of purging: 70 s.

Deposition of adsorber layer was carried out by successive ionic layer adsorption an reaction method (SILAR) from water solutions $InCl_3$, $Pb(AcO)_2$ and Na_2S, with the concentration of 0.01 mol/l. Deionized water with specific resistance of 18 MΩ*cm was used as solvent and rinsing solution. Directly before deposition the substrates were held in cationic solution of metal salt in 15 min in order to achieve chemically adsorbed layer of metal ions on oxide surface. After preliminary processing 35 cycles of In_2S_3 deposition were carried out, with subsequent placement of the samples into solutions of metal ions and sulfur for 30 s, with washing in deionized water between the stages. Then the cationic solution with indium ions was mixed with solution of lead acetate in amount of 0.1 of total solution volume, additional 15 deposition cycles according to the aforementioned procedure. Then, the generated structures were dried in argon stream and annealed in air ambient in 30 min at 120°C.

Stability of aluminum oxide layer in solutions for chalcogenide deposition by molecular layering was checked by measurement of etching rate of oxide layer applied onto silicon substrate (100 deposition cycles). Ellipsometry study demonstrated that in one hour of holding of sample in Na_2S solution the thickness of oxide layer decreased by less than 0.2 Å. Since during overall process of chalcogenide layer deposition on the Al_2O_3 layer deposited onto mesoporous TiO_2, layer was in Na_2S solution only in 25 min, this should not influence significantly on the oxide layer thickness.

In order to generate electric contact to upper $In_xPb_{1-x}S$ layer the sample surface was impregnated with hole adsorbing CuSCN layer.

The CuSCN planarizing layer deposition essence is in impregnation of dissolved copper thiocyanate in dipropyl sulfide. With this aim saturated 0.07M solution is prepared and agitated in 24 h. Then the resulted solution is settled in 12 h. After this stages the solution is applied onto the surface heated to 80°C. Upon coating the solution is fed via thin capillary so that a formed solution droplet is in continuous contact with moving substrate. The speed of substrate traveling with regard to stationary capillary is 0.5-1 cm/s.

The upper ohmic contacts were deposited by magnetron sputtering of nickel target. The thickness of contacts was about 500 nm.

During the experiments the test PEC samples were obtained after various number (from 0 to 5) of cycles of Al_2O_3 deposition.

RESULTS

In order to study current- voltage characteristics, fill factor and efficiency of obtained photoconverter structures with various thicknesses of recombination barrier layer the measuring bench was used with varying loading resistance in the range of 0–1 MΩ, and AKIP V7-78/1 voltmeter (measuring accuracy: 0.001 V), a Hewlett Packard 3478A ammeter (measuring accuracy: 1 µA) and a probe manipulator for provision of photoelectric converter contact terminals with circuit elements. During measurements the samples were lighted from glass substrate by means of solar radiation simulator, AM 1.5 - Newport Oriel model 67005, equipped with 150 W xenon lamp without ozone (6255) with radiation capacity error less than 0.5 %. The lamp radiation of 100 mW/cm^2 (1 sun) was calibrated using reference Si photodiode with infrared filter.

The acquired current-voltage characteristics were applied for determination of open-circuit voltage U_{oc}, short circuit current density J_{sc} and maximum value of specific output capacity P_m, as multiplication of current and voltage.

The acquired P_m determines efficiency of solar cell according to the known equation [5]:

$$Efficiency = \frac{P_m}{P_s}, \qquad (1)$$

where P_s is the specific capacity of incident solar radiation of about 100 mW/cm^2.

The fill factor (FF) of current-voltage characteristic is highly important for determination of solar cell properties and it is determined as follows [5]:

$$FF = \frac{P_m}{J_{кз} U_{хх}} \tag{2}$$

The values of U_{oc}, J_{sc} and FF make it possible to obtain complete parameters of solar cells.

Figure 2 illustrates the acquired voltage-current characteristics of photoelectric converters as a function of number of deposition cycles of Al_2O_3 as diffusion barrier layer.

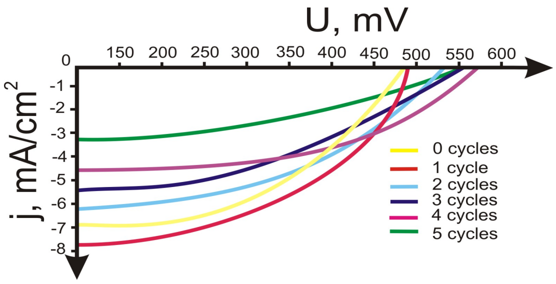

Fig.2. Voltage-current characteristics of generated test structures of photoelectric converters with various numbers of atomic layer deposition cycles of recombination barrier Al_2O_3 layer.

DISCUSSIONS

It can be seen in Fig. 2 that for the sample with one cycle of Al_2O_3 deposition the short circuit current (J_{sc}) increases in comparison with reference sample without barrier layer, which can be attributed to increase in efficiency of charge collection, since the electrons diffusing through the TiO_2 layer have higher chances to reach electrode than to recombine. Increase in J_{sc} and U_{oc} with one deposition cycle of barrier layer by ALD results PEC energy conversion efficiency increasing from average efficiency of 1.38 % (without barrier layer) to 1.47 % (with 1 deposition cycle). Nevertheless, for the devices with thicker barrier layers J_{sc} drops notably (by 52 % after 5 deposition cycles), thus enabling decrease in PEC efficiency despite total gain in U_{oc}. The current drop can be associated with slight decrease in the quality of films deposited on Al_2O_3 on TiO_2 layer. Measurements of transmittance spectrum in visible IR range (Fig. 3) reveals ~ 20 % decrease (as per the Beer–Lambert law) in chalcogenide layer, deposited onto TiO_2 with Al_2O_3 coating in five cycles, however, this is insufficient to explain the U_{oc} drop by 52 %.

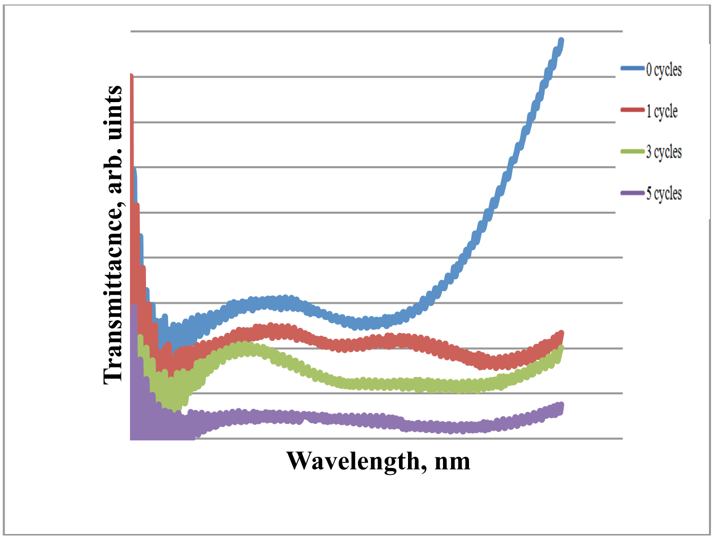

Fig.3. Transmittance spectra of photoelectric converters as a function of number of deposition cycles of barrier Al_2O_3 layer.

High conduction zone of Al_2O_3 can inhibit the injection of electrons, excited in photoactive chalcogenide layer, into TiO_2 layer, if the barrier layer is too thick, as a consequence of which both current decrease and recombination of excited electron-vacancy pairs in chalcogenide layer competes with the injection. This injection deceleration influences on significant reduction of U_{oc} in 3-5 cycles of Al_2O_3 deposition by ALD, which corresponds to the thickness of barrier layer of about 0.4 ~ 0.7 nm, respectively. In photoelectric cells with liquid electrolyte (DSSCs) barrier layers of similar thickness also prevent electron injection [22,23].

Decrease in recombination rate at the TiO_2 boundary should lead to increase in electron lifetime (τ_n) in TiO_2. In order to check the influence of Al_2O_3 layer on the electron lifetime we measured transient photovoltage of $TiO_2/Al_2O_3/In_2S_3/In_xPb_{1-x}S$ (Fig. 4). The observed decrease in the electron lifetime with applied offset voltage is well known for DSSCs and can be attributed to positive dependence of recombination rate constant on electron concentration in TiO_2 and increase in electron concentration with increase in applied voltage [24,25]. The values of electron lifetime of reference sample with 0 deposition cycles of aluminum oxide are similar to those published previously for solid state DSSCs, where spiro-OMeTAD is used as vacancy acceptor layer [26].

As illustrated in Fig. 4, we found that with increase in Al_2O_3 layer thickness the electron lifetime increases, which is in agreement with the statement that Al_2O_3 layer acts as a barrier for electron recombination.

Thus, these results evidence the ability of Al_2O_3 barrier layers to increase significantly the electron lifetime and to assume that recombination in photoactive chalcogenide layer plays an important role in limitation of the electron lifetime. In general, the efficiency of Al_2O_3 layers as a recombination barrier makes it possible to establish approach to achievement of advantage of increased U_{oc} without losses in J_{sc}. Decrease in recombination rate (as a consequence of increase in the electron lifetime and track length) would make it possible to use thicker photoactive semiconductor layer in thin-layer solid state PEC and establish possibilities for significant increase in efficiency as a consequence of increase in light absorption rate. In addition, solution of the problem of recombination in adsorber layer in photoelectric converters with extremely thin absorbing layer is highly attractive, since this type of PEC possesses higher temperature stability in comparison with photoelectrochemical cells based on dyes and provides possibility to produce the material of vacancy acceptor layer by infiltration of melts, which could efficiently solve another problem of transition to thicker photoactive layers, namely: hindered conformal and planarizing filling of pores with solid state materials - vacancy acceptors [27,28].

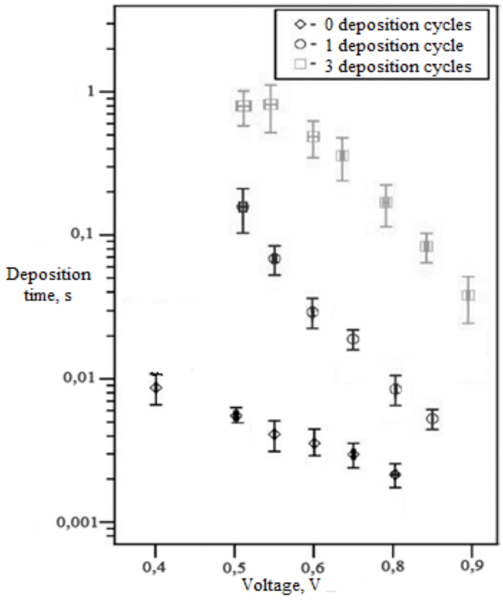

Fig.4. Electron lifetime in $TiO_2/Al_2O_3/In_2S_3/In_xPb_{1-x}S$ structure as a function of number of Al_2O_3 depositions by ALD.

CONCLUSIONS

Photoelectric converters with extremely thin absorbing layer have been manufactured with incorporated recombination Al_2O_3 barrier layer deposited by ALD. The role of Al_2O_3 layer has been mainly to act as a barrier of electron recombination, thus increasing significantly electron lifetime at the interface with TiO_2. The PEC structure in the configuration of $TiO_2/Al_2O_3/In_2S_3/In_xPb_{1-x}S$ has demonstrated the following trends in the device capacity with increase in the barrier layer thickness, namely: at first U_{oc} increases with appropriate increase in efficiency. Upon increase in the barrier layer thickness the dielectric properties of aluminum oxide hinder the stage of charge transfer, required for photocurrent collection, resulting in decreased efficiency of test photoelectric converters. Decrease in J_{sc} with increase in barrier thickness can be attributed to the fact that injection of electrons into TiO_2 is sensitive to occurrence of recombination barriers. Since the maximum efficiency is achieved at optimum thickness, it is required to provide its stringent control and reproducibility, which is implemented to the highest extent by atomic layer deposition. Therefore, challenging application of efficient recombination layer in fabrication of PEC depends on advantages in designing of high-efficient ALD equipment. Subsequently it is planned to study the influence of recombination barrier layer of various composition and thickness generated by ALD, located at $In_xPb_{1-x}S$/CuSCN interface, as well as combination of such layers. These studies will make it possible to apply such barrier layers in other types of solar cells, for instance, on the basis of perovskite layers.

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