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The influence of technological parameters on photovoltaic properties of TiO_2

***Abstract**. The aim of the study was to obtain structures of TiO_2 thin films with photovoltaic properties. The layers were produced by magnetron sputtering. The influence of basic process parameters (power, frequency and duration of sputtering) on the of photovoltaic properties was investigated. The results obtained showed that the power of magnetron sputtering and annealing temperature of samples is crucial for the proper formation of the crystalline structure and photovoltaic activity of titanium oxide films.*

***Streszczenie.** Celem pracy było otrzymanie cienkowarstwowych struktur TiO_2 o właściwościach fotowoltaicznych. Warstwy wytwarzane były metodą rozpylania magnetronowego. Wyniki badań wykazały, że moc rozpylania oraz temperatura wygrzewania próbek ma decydujący wpływ na powstanie odpowiedniej struktury krystalicznej i aktywność fotowoltaiczną warstw tlenku tytanu. (**Wpływ parametrów procesu technologicznego na właściwości fotowoltaiczne warstw TiO_2**).*

Keywords: titanianum dioxide, photovoltaics, magnetron sputtering.
Słowa kluczowe: dwutlenek tytanu, fotowoltaika, rozpylanie magnetronowe.

Introduction

Production of electricity from renewable energy sources causes increasing interest in the world. This is due to many factors. One of the most important is the elimination of harmful effects on the environment, e.g. excessive noise and pollution. Renewable energy does not increase greenhouse gas concentrations in the atmosphere and the same does not introduce alarming climate change.

An important advantage of renewable energy sources is the fact, that in contrast to the conventional sources, they are available around the world, although not everywhere in the same extent. Nowadays predominant source of energy is still oil (it makes 40 percent of total energy consumption), next coal (27%), methane (23%) and nuclear energy (7%). Alternative sources of energy currently represent only about 3% of total energy consumption, but the future is to be a significant increase in their share [1].

Among the non-conventional sources of energy, particularly important is solar energy. Technologies based on it are developing very dynamically and in addition to wind power now they play a major role in world energy production. The amount of solar energy, which is possible to obtain more than 1000 times the global demand, but the main obstacle to its practical use are problems with its storage. Forecasts predict that by the end of the century the ratio of other renewable and non renewable energy sources compared to solar energy will be negligible [1,2].

The Sun is of fundamental importance for life and it was always the most important source of energy. Solar energy can be directly converted into electricity through the photovoltaic cells, which can be made of different materials. Among them most commonly used is silicon, but the cells made from it are expensive and complicated. The high price is still one of the biggest drawbacks of photovoltaic systems. Therefore, for many years many researches try to overcome this barrier.

One of the solutions is selection of suitable material for application in photovoltaic cells. Such material should be characterized by low price, the high chemical stability, high photovoltaiv activity and non-toxicity as well.

Among the materials that meet most of these requirements is titanium dioxide (TiO_2), therefore it has recently attracted enormous attention of many researchers. Although its range of light absorption is small, but this can be improved by adding of certain elements [3,4], other compounds [5,6,7], or by application suitable method for its preparation, like chemical vapor deposition, sol-gel method or novel method developed in recent years – liquid phase deposition (LPD) [8-12].

In this work titanium dioxide thin films were deposited on indium-tin-oxide substrate by magnetron sputtering method. This method allows the manufacturing of large-area of thin films, but to obtain layers with good photovoltaic properties the selection of sputtering process parameters is extremely important. Threfore investigation of their influence on photoactivity of TiO_2 films was the object of this study.

Experimental

TiO_2 films were manufactured by the magnetron sputtering method. The magnetron was equipped with a titanium target (99.9% purity) of a diameter 100 mm. The substrate-to-target distance was fixed (18 cm). The films of titanium dioxide were deposited onto glass substrates coated with ITO (indium-tin-oxide) layer in oxygen atmosphere, at the pressure 9.4 10^{-3} Tr.

For the deposition process ITO substrates were cut in 10 x 45 mm samples. Next, they were carefully cleaned with isopropanol in an ultrasonic bath. After that treatment, samples were dried in air, at the room temperature and fixed on the matrix in the magnetron chamber.

Magnetron sputtering process was carried out for various input power, time of deposition, and the frequency. Power was varied in the range 1 - 3 kW, frequency of 100 Hz to 4.3 kHz, and the time of spraying the samples ranged from 2.5 to 25 min. The adjustment of plasma impulses frequency was difficult, because there was no possibility in the system to check their exact value before the starting point of main stage of sputtering.

Suitable setting of technological parameters was very important. If too much power was applied (even for the short time) destruction of the films was observed. They were detached from the matrix and showed surface damages by the temperature. Therefore after many attempts deposition of layers was modified in this way that after each of 5 minutes of sputtering the process was stopped for a few minutes. This procedure prevented excessive heating of the samples.

Magnetron sputtered TiO_2 films made at the room temperature may not exhibit crystalline phases. In applied magnetron system substrate temperature was constant and its value was slightly higher than the ambient temperature. Therefore most of samples were annealed for half an hour at temperature in the range 350-700°C in order to verify the impact of this process on the photovoltaic properties.

Samples from the same series were annealed at constant temperature.

The crystal structure of TiO_2 films was investigated by conventional X-ray diffraction (XRD) method. It allows primarily to determine the degree of order structure of the material. It also provides information about the content of each crystalline phase. Structural studies were carried out both for annealed and not annealed samples.

To determine the photovoltaic properties of obtained titanium oxide layers current-voltage characteristics *I(U)* were measured. These curves were tested without light (so called dark current was meaured) and under illumination of light.

Dependences of current intensity on the wavelength of light *I(λ)* were also determined. Measurements were performed using the system equipped with a monochromator, power supply and electrometer. The measurement data was recorded using appropriate software.

Preparation of thin TiO_2 films was carried out in many series. For each of them several samples were manufactured. The paper contains the results of research carried out for selected seven runs.

Results and discussion

During the manucaturing of TiO_2 thin films several parameters of magnetron sputtering process were varied. The values of these factors influenced not only the quality of the obtained layers - their proper adhesion to the substrate, cohesion, roughness but also their photovoltaic properties.

Titanium oxide can occur in three crystalline phases, but only two of them - rutile and anatase are important for the photovoltaic properties of the compound. The structure of sputtered TiO_2 films were tested by XRD method that has shown that after deposition at temperature near to ambient one, mostly amorphous samples were obtained. Their XRD patterns did not contain any diffractions peaks of either anatase or rutile phase. After annealing process in XRD patterns appeared difraction peaks corresponding to crystal phases mainly anatase structure.

Comparison of spectra obtained for samples annealed at different temperatures showed that after increasing the annealing temperature the content of anatase crystalline phase was increased.

In the Figure 1 exemplary XRD pattern for annealed TiO_2 film is presented.

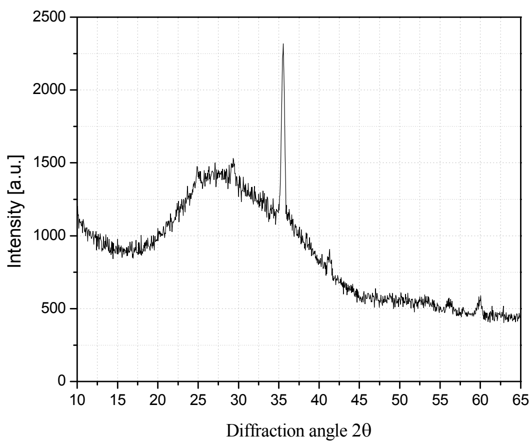

Fig.1. XRD pattern of TiO_2 thin film, deposited at sputtering power: 3 kW (sample 4B), annealed at 550°C for 30 min.

Most of samples which were not annealed did not show crystall phases of titanium oxide. Some of the visible in the Figure 1 X-rays peaks correspond to the anatase phase of TiO_2, the others can be attributed to the ITO-coated glass.

The influence of applied power can be seen in Figure 2, where the dependencies of the current intensity on photovoltaic wavelength for titanium dioxide films obtained at different sputtering power are shown. Other technological conditions, frequency and duration of the sputtering process, were the same. From this figure can be seen that the sample 6B manufactured at 3 KW of sputtering power shows much higher photocurrent value in a whole wavelength range than sample 3B, prepared at 1 kW of sputtering power.

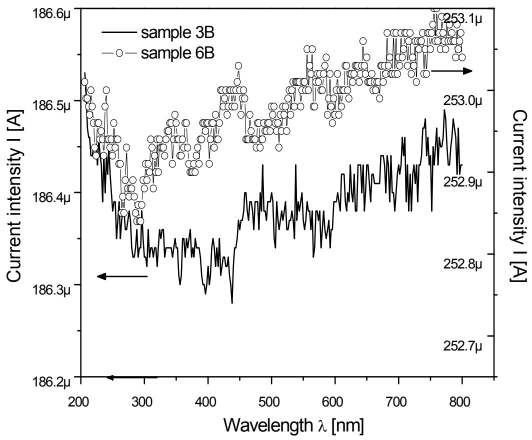

Fig.2. Photocurrent spectrum of TiO_2 thin films deposited with different sputtering power: 1 kW (sample 3B), 3 kW (sample 6B)

Figure 3 shows the relationship between photocurrent and the wavelength for titanium oxide thin layers obtained at the same sputtering power (3 kW) and frequency (3.3 kHz), but at various time deposition. Both presented in the Figure 3 samples were annealed at 450°C for 30 min.

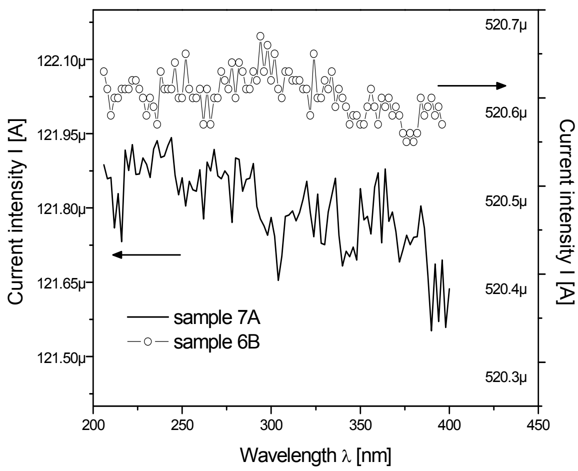

Fig.3. Photocurrent spectrum of TiO_2 thin films prepared at different time deposition: 5 min (sample 7A), 10 min (sample 6B)

These dependences indicate that the sample formed for 10 min. (6B) demonstrates more than three times higher current value, compared to that one which was formed for 5 min (7A).

The plots presented in the Figures 2-3 were obtained for source of light covered the spectral range of UV, visible light and near infrared (wavelength ranged from 380 to 770 nm).

In the Figures 4-6 current-voltage characteristics for TiO_2 layers manufactured at the same parameters of deposition process (sputtering power 3 kW, time of deposition 5 min, frequency 4.3 kHz), but for different annealing temperature are shown. The *U(I)* plots were recorded for selected wavelength.

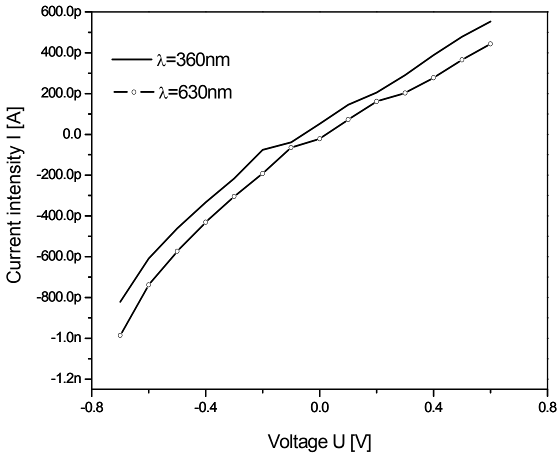

Fig. 4. Current - voltage characteristics for TiO_2 thin film measured at different wavelentgh (sample 7C, without annealing)

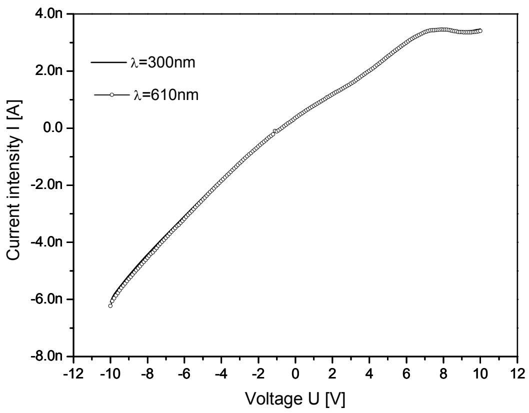

Fig. 5. Current - voltage characteristics for TiO_2 thin film measured at different wavelentgh (sample 7A, annealing temperature 450^{o}C)

Photovoltaic properties of titanium oxide films obtained were determined by measuring the current-voltage characteristics for different wavelengths of light.

Significant differences in the course of these relationships occurred for samples annealed at different temperatures. For the sample annealed at 450°C (Fig. 5) values of photocurrent were much lower compared with the sample annealed at 550°C (Fig. 6). In Fig. 4-6 *U(I)* plots measured at the wavelength 360 nm and about 610 nm are presented, but such significant difference between values of photocurrent obtained for annealed and non annealed samples was seen in the whole measured spectral range.

Measurements of photovoltaic properties of TiO_2 films were conducted for different types of light sources, and thus in a wide spectral range. This is important because depending on the structure of the titanium oxide film its optical response can be different. It is related not only to the content of TiO_2 phases (mainly anatase and rutile), but also to their grain size (effect of light scattering at the grain boudaries). During light illumination with different wavelentgh sample response may be also associated with trap levels in TiO_2 phases. The band gaps of crystall anatase phase and rutile were determined to be 3.54 and 3.26 eV, respectively [13]. Because anatase has wide band gap, thus only light below 400 nm is absorbed and can cause formation of the electron-hole pairs. However photoactivity of TiO_2 can depend also on many other factors, such as conatminations, electron-hole recombination processes in the bulk, intrinsic defects, crystal morphology, spectral distribution of the illuminating light. Therefore it is possible that obtained sample of titanium dioxide can show better photocurrent response, also in visible light region.

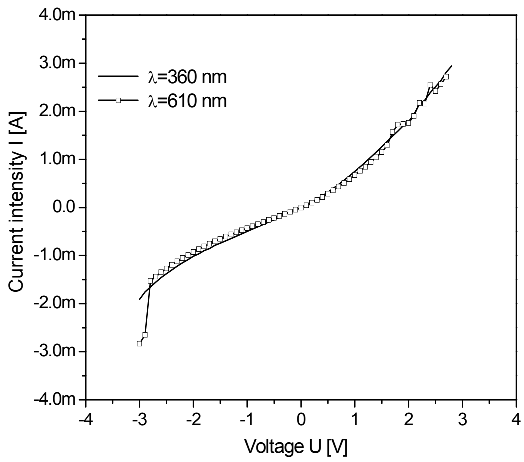

Fig. 6. Current - voltage characteristics for TiO_2 thin film measured at different wavelentgh (sample 7B, annealing temperature 550^{o}C)

Conclusion

The aim of the study was to investigate the influence of technological parameters on photovoltaic properties of TiO_2 thin films obtained by the magnetron sputtering. During technological process several parameters were changed. were varied.

The structure of manufactured films was investigated by the X-ray diffraction method. The X-ray diffraction spectra showed that the crystalline phase of titanium oxide appeared only in annealed samples, therefore after deposition most of the films were annealed. The higher annealing temperature was applied, the more anatase phase contained sample.

In the tested TiO_2 films there was no rutile crystalline phase. Probably annealing temperature was too low and such arrangement of the structure did not occur.

It was found that photovoltaic properties of TiO_2 thin films were strongly affected by the various deposition parameters. The main parameter determining the formation of appropriate phases of TiO_2 and its photovoltaic properties was the sputtering power, that affected the energy of sputtered particles.

The layers obtained at lower sputtering power showed negligible photoelectric activity, regardless of the applied wavelength of the light.

Other conditions of TiO_2 layer formation, such as frequency and time of deposition, also played an important role, but their influence on the photovoltaic properties of titanium oxide films has not yet been studied sufficiently.

As a result of this study samples which differed significantly in photovoltaic activity were obtained. The best parameters showed titanium oxide films deposited at maximum applied sputtering power (3 kW), frequency of 4.3 kHz and the sputtering time 5 min. These samples were annealed at temperature 550 °C, which was sufficient to produce an ordered crystalline structure of the compound, with a particularly high content of anatase phase.

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