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Transparent platinum counter electrode for dye-sensitized solar cells

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ABSTRACT

Purpose: The objective of this article was to compare the surface morphology and structure of thin films deposited by screen printing and sputtering (PVD) methods.

Design/methodology/approach: The morphology of the surface of the platinum thin films was performed using a scanning electron microscope Zeiss Supra 35. The detailed surface topography studies were made using an atomic force microscope XE-100 Park systems company. Roughness parameters were calculated using the software XEI. The whole study was complemented by X-ray crystallography.

Findings: Results and their analysis show that the physical vapour deposition method allows the deposition of thin films with a better quality than the screen printing method.

Practical implications: The platinum thin films are good potential material for electronics, optoelectronics and photovoltaics.

Originality/value: The paper presents results of investigations on platinum thin films prepared with screen printing and sputtering (PVD) methods on a FTO glass substrate.

Keywords: Dye-sensitized solar cells; Counter electrode; Platinum thin film

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MATERIALS

1. Introduction

Nonrenewable energy is energy from fossil fuels (coal, crude oil, natural gas) and uranium. This natural resources take thousands of years to form naturally and cannot be replaced as fast as they are being consumed. Additionally, burning fossil fuels generates greenhouse gases and relying on them energy generation is unsustainable. Hence the need to use renewable, sustainable ways of generating energy [1].

Renewable resources are replenished naturally and over relatively short periods of time. Utilization of renewable energies is a major importance because of the increase in fossil energy costs in combination with carbon dioxide reduction preventing global warming. The major renewable energy resources are solar, wind, water, biomass, and geothermal [2].

Sunlight is Earth's predominant source of energy. Converting the sun's radiation directly into electricity is done by solar cells. These cells usually are made of semiconductor like silicon. When sunlight is absorbed by these materials, the solar energy knocks electrons loose from their atoms, allowing the electrons to flow through the material to produce electricity [3-6].

Alternative to silicon solar cells can be found in dye-sensitized solar cells. This type of cell imitates the natural conversion of sunlight into energy by plants. Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their simple fabrication process, low production costs, relatively high conversion efficiency, and being environmental friendly [5-8].

The working principle of dye-sensitized solar cells is not based on a p-n junction like in the conventional solar cells but on the photogeneration of an electron by a dye, as in photosysnthesis. Figure 1. shows the operation principle of a DSSC. The anode of a DSSC consists of a glass plate which is coated with a transparent conductive oxide (TCO) film. Indium tin oxide (ITO) or fluorine doped tin oxide are most widely used. Nanocrystalline TiO_2 is deposited on the conducting electrode to provide the necessary large surface area to adsorb dye molecules. The dye (photosensitizers) is mostly a ruthenium complex or various organic metal free compounds. The cathode of a DSSC is a glass plate with a thin platinum film which serves as a catalyst. Electrolytes containing I^-/I^{3-} redox ions is used as an electron mediator between the TiO_2 photoelectrode and the counter electrode [7-9].

The incident photon is absorbed by ruthenium complex photosensitizers adsorbed on the TiO_2 surface. The dye injects an electron into the conduction band of TiO_2. The electron passes through the nanoporous TiO_2 layer, flows through the external circuit and performs work. Then at the counter electrode the electron is transferred into a hole conducting medium (electrolyte). The reduction at the counter electrode is catalyzed by a thin film of platinum [6-9]. The Pt in the counter electrode helps in the regeneration of dyes by catalysing the I^- regeneration from the I_3^- species in the redox couple. The morphology of platinum and its surface roughness play a crucial role in determining the overall efficiency of a dye-sensitized solar cells [10-12]. Rapid progress in modern industries, including photovoltaics depended mostly on the capabilities of materials forming and surface engineering [13,14].

The paper presents results of investigations on platinum thin films prepared with screen printing and sputtering (PVD) methods on a FTO glass substrate.

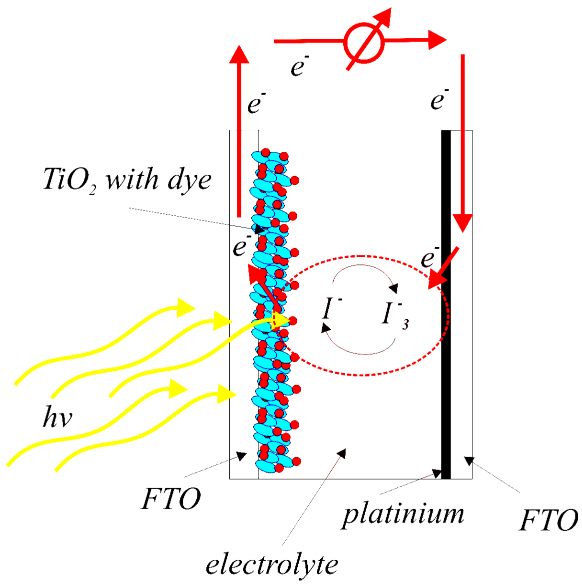

Fig. 1. Operating principle of dye-sensitized solar cell

2. Materials and methodology

The objective of this article was to compare the surface morphology and structure of thin films deposited by screen printing and sputtering (PVD) methods.

Nanocolloidal platinum paste (3D-nano, Cracow, Poland) was used as a catalytic counter electrode. Platinum paste was applied on FTO glass with screen-printing method. Screen-printing is one of the versatile, simple, fast, cost-effective coating deposition methods, which doesn`t require expensive vacuum technology and can be applied to flat, round, oval and square elements. Screen-printing method has been successfully used in dye-sensitized solar cells fabrication to deposition of thin films greater than 0.5 μm thickness. In this article Screen-printing machine MS300FRO (Fig. 2) was used. Technical data of screen printing machine MS300FRO are shown in Table 1. The stainless steel cloth screen (90 mesh/cm) was used for the platinum film preparation. The stainless steel cloth consists of stainless steel wires of the diameter of 0.09 mm. The screen mesh has an opening of 25 mm × 25 mm. A rubber squeegee was used in the screening printing process. Squeegee printing angle was 60°. The gap between the substrate and the screen was set as 0 mm.

After printing, the wet film was dried in 125°C for 10 minutes and two more layers were applied. After that, three layers of platinum paste were sintered in an oven. The oven was heated from room temperature to 500°C with heating rate of 15°C/min and maintained at 500°C for 30 minutes.

After sintering, the paste is reduced to a minimum amount of platinum for optimum use of the material, while it remains perfectly transparent and the catalytically active.

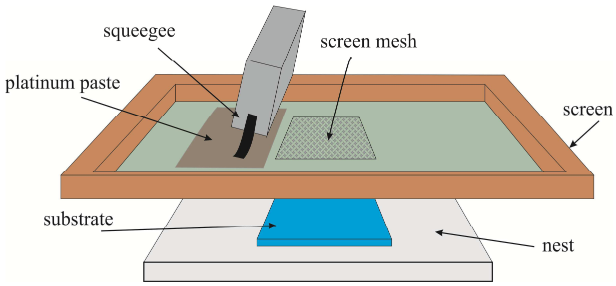

Fig. 2. Schema of screen printing method

Fig. 3. Sputter coater Bal-Tec company

In the second method platinum thin film deposition process was made in a device based on the sputtering method (PVD) in an Ar atmosphere (Fig. 3). The sputtering time was 90s, current - 50mA and a voltage -50V.

In this sputtering method argon gas is introduced through a gas dosing valve to a specimen chamber. Flushing the chamber with argon makes it easier to remove undesired gases, particularly water vapour. After flushing process, the atmosphere in the chamber should consist of as much pure argon as possible. A working pressure need to be between 5 and 10 Pa. Then the sputtering process can be started.

Table 1.
Technical data of MS300FRO screen-printing

Properties	Value
The maximum size of screen, mm	400 x 570
The maximum print area, mm	oval 280 x 250
The maximum angle/tilt, °	7
The maximum height of the	300
Print speed, pc/h	1300
Power supply, V	110/220 (50/60 Hz)
Net weight, kg	136

To start the sputtering process, a high voltage is applied to the target (cathode). This produces a high voltage field between the target and the specimen table (anode). The free electrons in this field are forced into a spiral path by a magnet system where they collide with the argon atoms in the field. Each collision knocks an electron out of the outer shell of the argon atom, positively charging the otherwise neutral argon. This is a cascading process that causes a glow discharge (plasma) to ignite. The positively charged argon ions are now accelerated to the cathode (target) where they impinge, knocking out metal atoms as they hit. Collisions also occur between the metal atoms thus released and the other gas molecules in the vacuum chamber. This causes the metal atoms to scatter widely, forming a diffuse cloud. The metal atoms from this cloud impinge on the specimen from all directions and condense evenly on it.

The morphology of the surface of the platinum thin films was performed using a scanning electron microscope Zeiss Supra 35. The accelerating voltage was from 5-15kV. In order to obtain images of the surface topography the detection of secondary electrons by the detector In Lens was used. The detailed surface topography studies were made using an atomic force microscope XE-100 Park systems company. Roughness parameters were calculated using the software XEI. The whole study was complemented by X-ray crystallography.

3. Results and discussion

Observing the morphology of the surface of the prepared samples crystalline structure of fluorine doped tin oxide (FTO) was recorded at the magnification of 50 000. The grain size was generally between 100-500nm (Fig. 4). Grains are generally characterized by irregular shapes, but can also be observed grains with shape of a pyramid. Platinum tends to increase as the so-called "islands". Examples of where the layer growth in the form of islands indicated by the arrows (Fig. 4).

The increase in the layer of platinum better recorded at a magnification of 120 000 (Fig. 5). Figs 6-7 shows the surface morphology of a thin film of platinum deposited by screen printing method. Also it documented structure of the FTO with embedded islands of platinum. However, the more densely packed. Also in Fig. 8 it has been indicated (using squares) elements with larger concentration of platinum. To confirm that the observed thin films are platinum were performed qualitative chemical composition study using Energy Dispersive Spectrometer - EDS In Figs 8-9 spectra with the reflections typical for platinum (about 2.127keV) were registered.

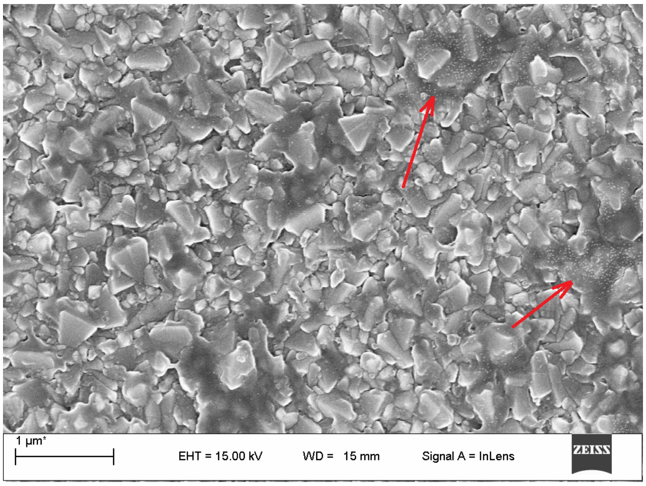

Fig. 4. SEM image of platinum thin film deposited by sputtering method on a FTO glass substrate, at a magnification of 50 000

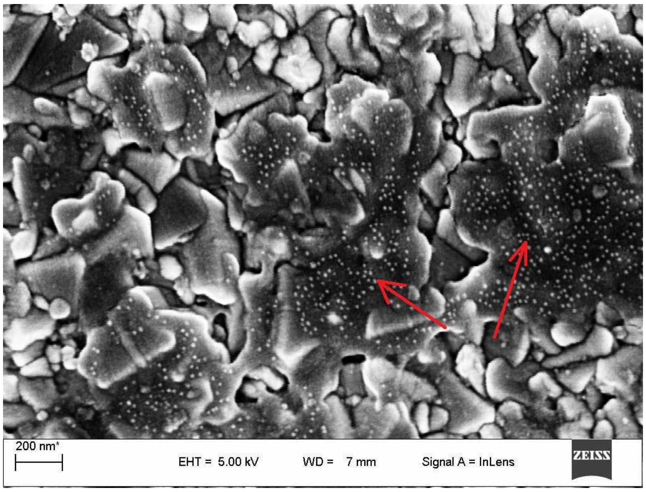

Fig. 5. SEM image of platinum thin film deposited by sputtering method on a FTO glass substrate, at a magnification of 120 000

Detailed studies of surface topography were performed using atomic force microscope. Images were obtained using a non-contact mode by observing 5x5 µm area. Roughness parameters were calculated using the software XEI and summary in Table 2. Inequalities on the surface of a thin film PVD Pt do not exceed 108 nm heights. It has been found that visible in the images (Fig. 10) repetitive aggregations of atoms have similar geometrical features.

The thin film of platinum deposited by screen printing has a more nonuniform growth. A surface irregularity exceeds 300 nm in height. A width of aggregations of atoms exceeds even 2µm (Fig. 11). The whole structural studies were complemented by the X-ray examination (Figs 12-13). Platinum thin films were characterized by a constant angle of incidence identifying characteristic peaks of the platinum and tin oxide.

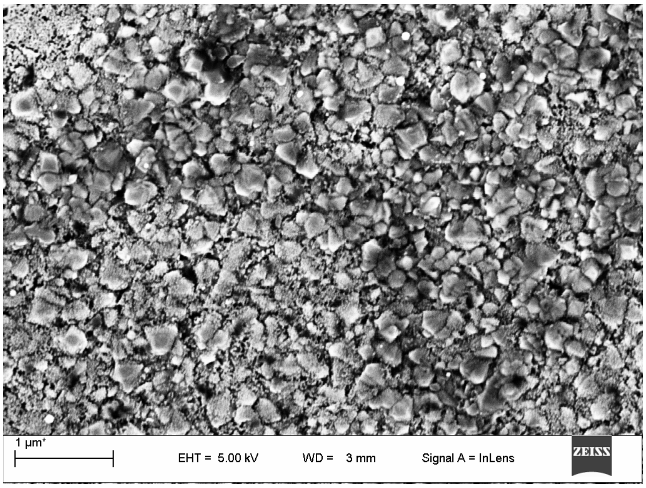

Fig. 6. SEM image of screen printed platinum thin film deposited on a FTO glass substrate, at a magnification of 50 000

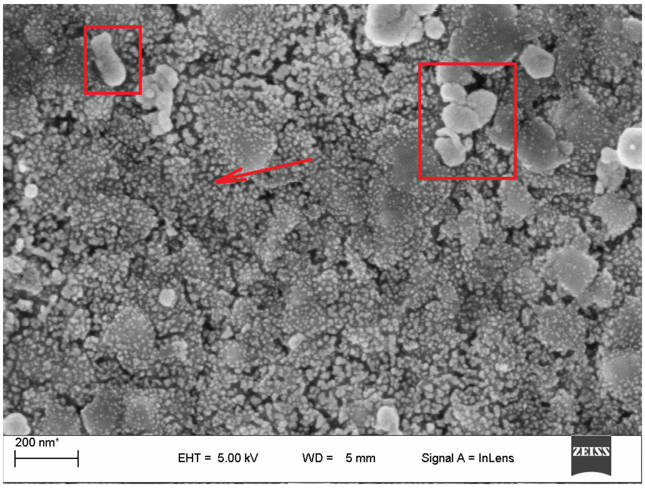

Fig. 7. SEM image of screen printed platinum thin film deposited on a FTO glass substrate, at a magnification of 160 000

Table 2.
Summary of roughness parameters for deposited Pt thin films

Specimen	Max. irregularity [nm]	R_q [nm]	R_a [nm]	Geometric area [µm^2]	Surface Area [µm^2]
Pt sputtering thin film	108	28	22	25	27.5
Pt screen printing thin film	358	98	82	25	33.9

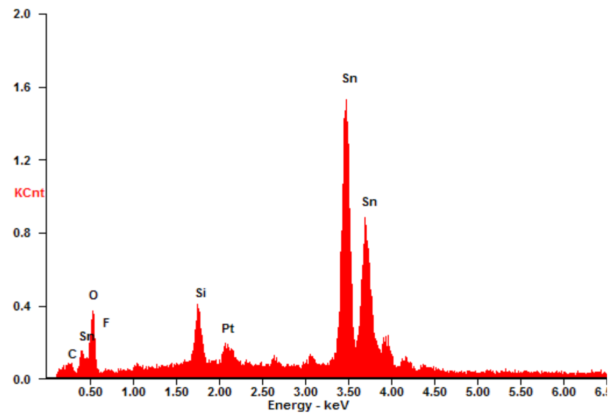

Fig. 8. EDS spectrum of platinum thin film deposited by sputtering method on a FTO glass substrate

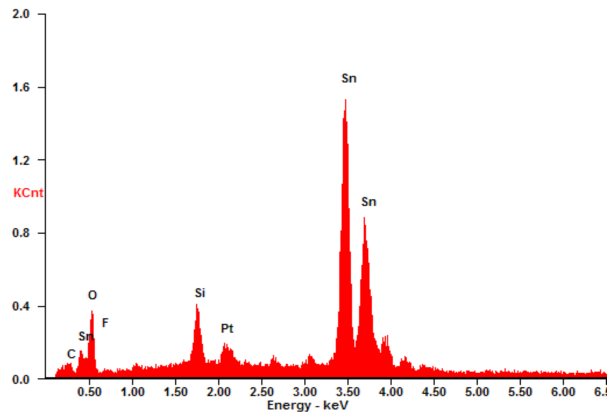

Fig. 9. EDS spectrum of screen printed platinum thin film deposited on a FTO glass substrate

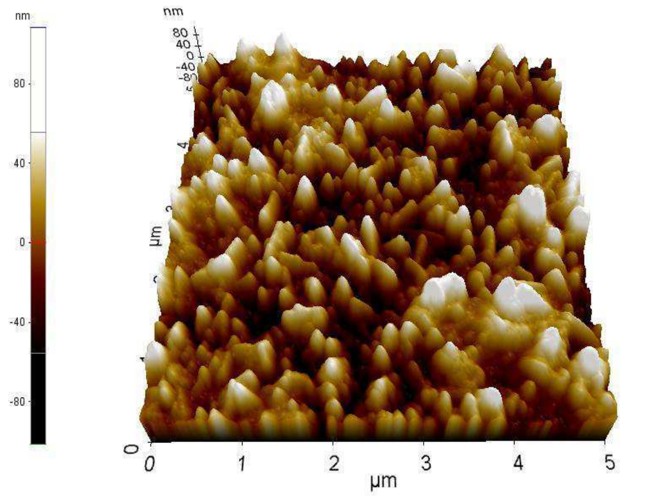

Fig. 10. AFM 3D image of the surface topography of platinum thin film deposited by sputtering method on a FTO glass substrate

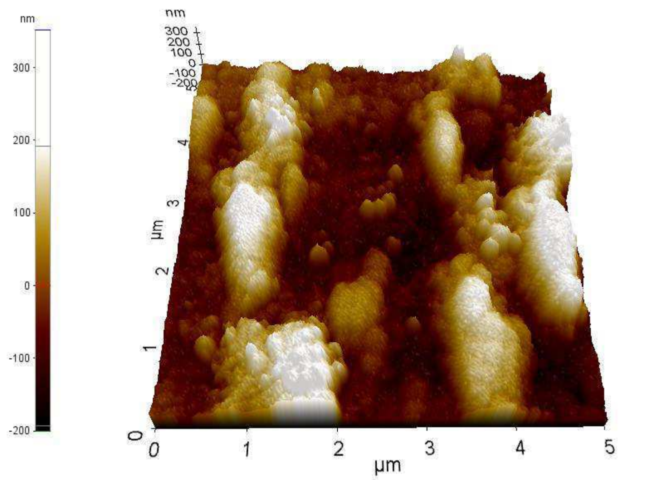

Fig. 11. AFM 3D image of the surface topography of screen printed platinum thin film deposited on a FTO glass substrate

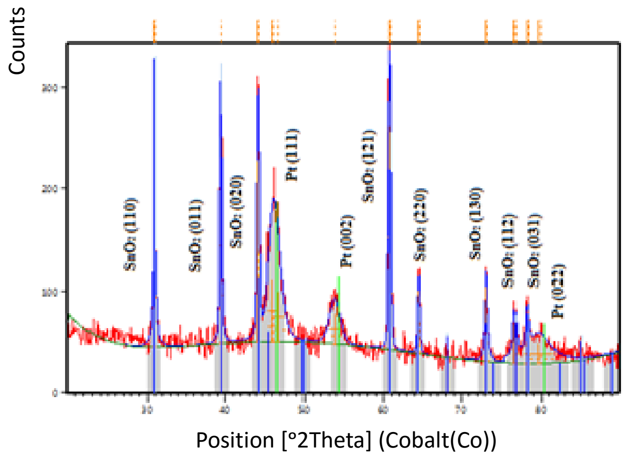

Fig. 12. The diffraction pattern of platinum thin film deposited by sputtering method on a FTO glass substrate

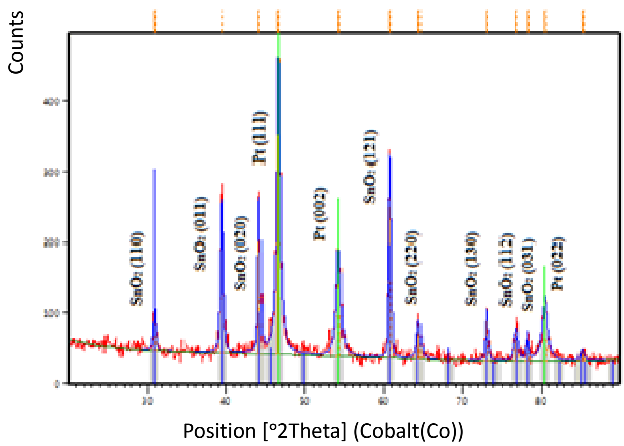

Fig. 13. The diffraction pattern of screen printed platinum thin film deposited on a FTO glass substrate

4. Conclusions

The purpose of this article was to compare the surface morphology and structure of thin films deposited by screen printing and sputtering methods. Results and their analysis show that the sputtering method allows to the deposition of thin films with a better quality and less densely packed than the screen printing method. Inequalities of thin films deposited using screen printing even exceed 300 nm, while the thin films deposited by sputtering method does not exceed 110 nm. The platinum thin films are good potential material for electronics, optoelectronics and photovoltaics.

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Additional information

Selected issues related to this paper are planned to be presented at the 22^{nd} Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10^{th} anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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