Opto-Electronics Review 29 (2021) 181-186

POLISH ACADEMY OF SCIENCES

Opto-Electronics Review

journal homepage: http://journals.pan.pl/opelre

Effect of heat treatment on the surface morphology and optical properties of the Al_2O_3 thin film for use in solar cells

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Article info

Article history:
Received 13 Sep. 2021
Received in revised form 19 Oct. 2021
Accepted 19 Oct. 2021
Available online 06 Dec. 2021

Keywords:
Antireflection coating, atomic layer deposition method, solar cells.

Abstract

The technology of manufacturing silicon solar cells is complex and consists of several stages. The final steps in succession are the deposition of antireflection layer and discharge contacts. Metallic contacts are usually deposited by the screen printing method and then, fired at high temperature. Therefore, this article presents the results of a research on the effect of heat treatment on the properties of the Al_2O_3 thin film previously deposited by the atomic layer deposition method. It works well as both passivating and antireflection coating. Moreover, heat treatment affects the value of the cell short-circuit current and, thus, its efficiency. The surface morphology, optical and electrical properties were investigated, describing the influence of heat treatment on the properties of the deposited layers and the manufactured solar cells.

1. Introduction

Renewable energy is an alternative to conventional energy sources whose resources are limited. One of the possibilities of using renewable energy sources (RES) is obtaining energy from solar radiation. At present, the sun is an inexhaustible source of energy and solar cells are devices that enable the change of solar radiation power into electricity. Photovoltaic cells are used to a large extent in places that are difficult to access for conventional energy, such as remote mountain resorts, boats, buoys, road lighting, so wherever a traditional connection to the power grid is not possible [1–3]. Production of energy from photovoltaic devices is one of the fastest growing industries. Its growth dynamics is compared with the growth dynamics of the microelectronics industry in the initial period of its development. The photovoltaic market is dominated by cells based on silicon and other inorganic semiconductors. Crystalline silicon solar cells account for over 83% of total production [1–6].

Technology of manufacturing silicon solar cells is complex and consists of several stages. This article focuses on the deposition of an antireflection coating which has a great influence on the solar cell performance [6–7]. Energy losses resulting from incomplete absorption of solar radiation and electricity generated in the cell affect the most important utility parameter of the solar cell which is energy efficiency. About 36% of the losses are due to the reflection of the light radiation from the outer surface of the cell (it is possible to obtain values below 0.5% using texture and antireflection coating). The antireflection coatings minimize the light reflectance, thus increasing the performance of the photovoltaic cell. Various materials used as antireflection coatings have been widely described in the literature, however, there are no reports on aluminium oxide, and it has favourable optical properties [6–8]. The reflection of light in the range of 400–1100 nm from the silicon wafer reaches 35÷50%. First, the texture is chemically performed on the plate in order to unfold the surface and multiply the reflection of light from a developed silicon surface. In this way, unfortunately, the negative reflection is not eliminated completely. Solar reflectance $R(\lambda)$ from silicon wafers can be reduced by

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https://doi.org/10.24425/opelre.2021.139602
1896-3757/ Association of Polish Electrical Engineers (SEP) and Polish Academy of Sciences (PAS). Published by PAS

using an antireflection coating. For a silicon plate with a refractive index of n equalling 3.87 at a wavelength of 632.80 nm, the appropriate antireflection coating will be a layer made of material with a refractive index n ranging from 1.6 to 2.4. As antireflection coating in solar cells, among others, TiO_2 and Si_3N_4 thin films deposited by chemical (CVD) or physical (PVD) vapour deposition techniques are used [4,9–10].

This article proposes the use of the atomic layer deposition (ALD) method. In this method, the injection of two precursors to the heated substrate is divided into two stages. In the first stage, the surface of the element is exposed to the precursor after which this compound is removed with an inert gas. During the exposure, a single-molecule layer of the reactant is adsorbed on the surface of the element. Then, in the second stage, the next compound is injected into the chamber, and it interacts with a single-molecule layer of the first reactant. Subsequently, one monolayer of a solid thin film of the desired material is formed. Then, the mentioned compounds and any possible gas phase reaction elements are pumped out of the chamber. These steps are repeated as many times as necessary to obtain a thin film of the planned thickness (Fig. 1).

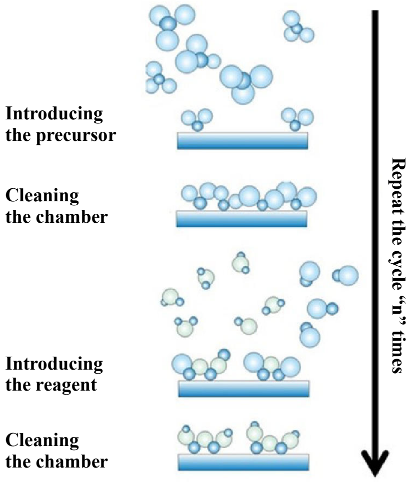

Fig. 1. Diagram of the ALD cycle.

A unique advantage of the ALD method is the ability to evenly cover complex surfaces geometrically, including porous or textured materials and 3D objects. In addition, it is proposed to use aluminium oxide, the layer of which can play a passivating role and minimize reflection on the structure of a silicon photovoltaic cell [6–10]. The use of a thin dielectric film on the surface of the photovoltaic cell improves its electrical properties. Especially, it increases the value of the short-circuit current and, consequently, improves the solar cell efficiency. Layers of this type (passivating) are normally produced using the thermal oxidation process in classic semiconductor heat treatment furnaces. The layers produced in this way, however, are uneven and non-uniform, and a precise control of the layer thickness is difficult. An interesting solution is also to prepare a diffused layer using liquid dopant solutions [11]. Therefore, this article proposes the ALD method [12–15]. During the production of a silicon solar cell, after the antireflection coating is deposited, metallic contacts are deposited by screen printing and burned out. Such heat treatment may affect the surface topography and optical properties of the previously deposited thin film and, consequently, the performance of finished photovoltaic cells. The study results are presented in this article. There are already known attempts to use the A_2O_3 layer as a silicon passivating layer [16–18], but it was not used simultaneously as a passivating and antireflection layer. In addition, the previously used layers, such as TiO_2 or Si_3N_4, were thermally stable at high temperatures, therefore, the problem of heat treatment of metallic contacts was not discussed earlier. In the case of new materials such as Al_2O_3 or ZnO, which have several crystallographic varieties, this heat treatment has a significant impact which is the subject of this article.

2. Material descriptions and research methodology

The Al_2O_3 layers have been deposited by the ALD using an R-200 basic reactor from Picosun corporation. As a precursor of Al_2O_3, trimethylaluminum (TMA) has been used which reacted with H_2O allowing the layers deposition. It is a highly self-inflammatory and reactive compound. The ALD process was thermally assisted. The Al_2O_3 layers were deposited in a reaction chamber (growth chamber) into which reagents were separately introduced. The process temperature was of 300 °C (Table 1). Reagent dosing time was equal to 0.1 s. An inert gas in the form of nitrogen was used to transport the reactants and pump out unreacted residues. The inert gas flow was equal to 200 SCCM. The purging time was 3 s for TMA and 5 s for water. Both the temperature and the number of cycles were constant. Only an additional heat treatment was introduced (see Table 1).

Table 1.
Variations of the deposited samples.

No.	Deposition temperature [°C]	Number of cycles	Heat treatment [°C]
1.			–
2.			500
3.	300	1000	700
4.			900
5.			500÷900

Thin films were deposited on the electrochemically polished silicon and on the p-type monocrystalline silicon wafers of a thickness of about 330 μm, an area of 50×50 mm, and a resistivity of 1 Ωcm. In order to produce a p-n junction, wafers were doped with phosphorous in the open tube furnace using a conventional liquid phosphorous oxide trichloride ($POCl_3$) as a dopant source. The research was carried out on silicon photovoltaic cells with one bus bar.

The surface morphology of the prepared samples was evaluated by the atomic force microscope (XE-100 Park Systems). The study was conducted in a non-contact mode, in the areas of 2 × 2 μm. The cantilever vibration frequency was of 1 Hz, and the recorded test results were developed in the Park Systems XEI 4.3.0 program. 2D and 3D images were recorded, and basic roughness parameters such as root mean square (RMS) and arithmetical mean height (R_a) were calculated. Furthermore, the scanning electron microscope (SEM) images were taken on a Tescan Mira III high-resolution scanning microscope equipped with an X-ray microanalysis system. The accelerating voltage was of 4 kV and the maximum magnification was 100 000×.

The refractive index of the Al_2O_3 thin films was appointed with an alpha spectroscopic ellipsometer (SE) from Woollam (Lincoln, OR, USA). In this technique, the linearly polarized light reflects off a surface element, turns elliptically polarized, and moves through a constantly rotating polarizer (called analyser). The portion of the light transmitted will depend on the polarizer orientation with respect to the "ellipse" of the electric field from the sample. The detector converts the light into an electrical signal to determine the reflected polarity. The azimuth and ellipticity measurements were carried out on bare silicon in the first stage and on silicon with a deposited Al_2O_3 layer in the next stage. The refractive index and thickness value were determined with the computer program based on the model used which contains few elements (silicon/native oxide/aluminium oxide/environment), where the parameters of separate thin films were fitted stage by stage (in the first stage just for the silicon and in the second stage for the silicon with a deposited layer). The Al_2O_3 layer was fitted with a Cauchy model.

Changes of the short circuit current in the whole photovoltaic cell were registered using Corescan by the light beam induced current (LBIC) technique. The LBIC measurement technique scans the whole surface of a photovoltaic cell by a light beam and measures the short circuit current changes for each position (Fig. 2). The classic LBIC technique uses a very small beam (down to 0.1 mm) for measurement. As a result, a high measurement resolution is obtained. The Corescan device allows the LBIC to be measured with a larger beam (approx. 10 mm). This results in a lower resolution but benefits in terms of speed and measuring area. In this variant, a longer wavelength halogen lamp is used for lighting which penetrates deep into the sample. This type of the LBIC variant is used for quick diagnostics of entire photovoltaic cells and enables visualization of the difference in bulk lifetime.

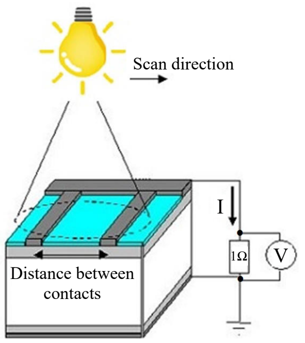

Fig. 2. Light beam induced the current mode of Corescan devices.

Current-voltage characteristics of monocrystalline photovoltaic cells were registered using a solar simulator SS150AAA model. The measurements were carried out under standard conditions (P_{in} = 1000 W/m^2, AM1.5G spectrum, T = 25°C). The basic electrical parameters of the photovoltaic cells were calculated by using the software I-V curve tracer.

3. Results

The heat treatment of thin layers at 500 °C did not obviously affect the surface morphology of the deposited layer [Figs. 3(a)–(d)]. After the heat treatment of thin layers at 500 °C, the RMS and R_a values are of 0.44 and 0.34 nm, respectively (Table 2). The surface of the thin film is characterized by small clusters of atoms. Images from the atomic force microscope show differences in the surface topography depending on the value of the heat treatment temperature higher than 500 °C. After the heat treatment of the thin film, carried out at a temperature of 700°C, the characteristic clusters of atoms increase their width to 20 nm [Figs. 3(e)–(f)]. The heat treatment performed at a temperature of 900 °C significantly influences topography of the deposited thin films [Figs. 3(g)–(h)]. The structure of small clusters changes into large, irregularly spaced, elliptical shapes exceeding 5 nm in height and 40 nm in width. The RMS and R_a values also increase to the values of 2.11 and 1.71 nm, respectively. Heat treatment in the range of 500÷900 °C and for a short time (less than 4 min) clearly changes the topography of the thin films surface [Figs. 3(i)–(j)].

Atoms clusters combine with each other, as it is in the case of the treatment at 900°C, into large irregularly spaced elliptical shapes and even into elements of a ribbon-like structure. The RMS and R_a values are of 1.95 and 1.55 nm, respectively.

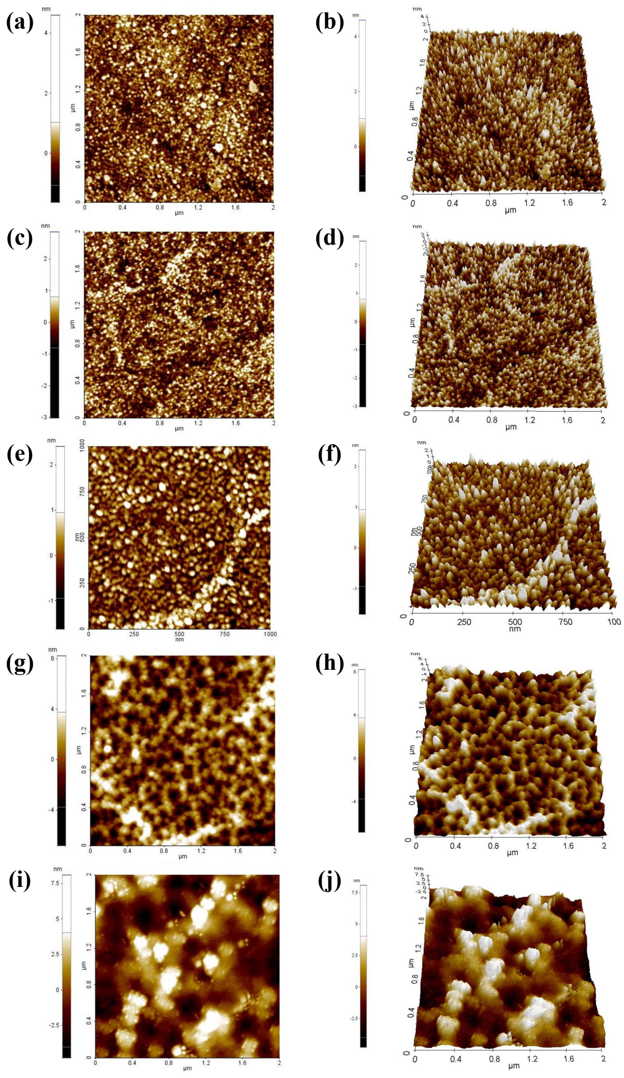

Fig. 3. AFM image of the surface topography and its 3D representation of the Al_2O_3 thin film without heat treatment (a, b), and after heat treatment at a temperature of 500 °C (c, d), 700 °C (e, f), 900 °C (g, h), and 500÷900 °C (i, j).

Table 2.
Summary of roughness values for the layers deposited by the ALD method.

No.	Temperature [°C]	Heat treatment [°C]	Surface development [μm^2]	RMS [nm]	R_a [nm]
1.		–	4.010	0.53	0.41
2.		500	4.005	0.44	0.34
3.	300	700	4.005	0.48	0.37
4.		900	4.006	2.11	1.71
5.		500÷900	4.013	1.95	1.55

The results obtained on the scanning electron microscope (SEM) correlate with the results obtained on the atomic force microscope. The SEM images of the surface topography show a significant effect of the heat treatment. Especially, the heat treatment performed at 500÷900 °C (Fig. 4).

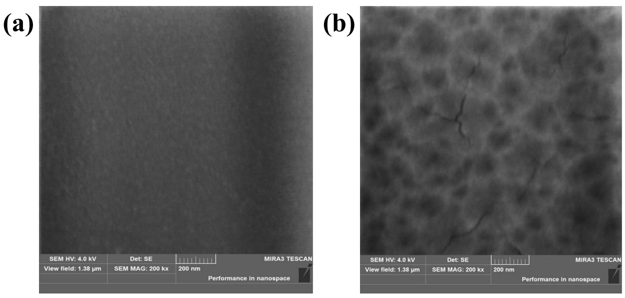

Fig. 4. SEM image of the surface morphology of the Al_2O_3 thin film without heat treatment (a), and with heat treatment at 900 °C (b).

Influence of the heat treatment temperature on the layers refractive index was investigated. The refractive index of the layer without heat treatment decreases with an increasing wavelength (300 to 900 nm) and takes values ranging from 1.680 to 1.618 (Fig. 5). For the light wavelength of 650 nm, it reaches an average value of 1.622. The heat treatment carried out at 500 °C adversely affects the dispersion reducing the refractive index by 0.03. There was no clear effect of the heat treatment carried out at 700 °C on the refractive index dispersion. Heat treatment at 900 °C of thin films deposited by ALD on a silicon substrate shifts the refractive index to higher values between 1.71 and 1.687. For the most efficient silicon solar cells, the light wavelength (650 nm) is of 1.689. Similarly, the refractive index dispersion is influenced by a heat treatment in the range of 500÷900 °C. Its value for a light wavelength of 650 nm is of 1.66. Both the SEM surface and the refractive index studies suggest structural changes. Optical constants change only when there are structural changes. This will have to be investigated in detail in the future studies.

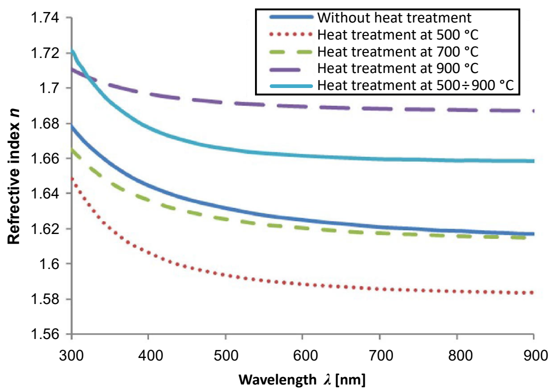

Fig. 5. Refractive index as a function of the wavelength of deposited layers.

Influence of the heat treatment temperature on the light reflection curve shape from the thin film surface was investigated. The reflection of light from the layer deposited with the ALD method without heat treatment decreases in the wavelength range of 420÷900 nm, changing from 35 to 2% (Fig. 6). The heat treatment performed at a temperature of 500 and 700 °C does not obviously influence the shape of the light reflection curve from the thin film surface. Reflection of light at a wavelength of 650 nm is on average 15%. The heat treatment carried out at 900 °C causes a shift in light reflection for a wavelength of 650 nm from 15 to 20%. The heat treatment in the range of 500÷900 °C causes the curve to decrease in the wavelength range of 400÷900 nm, changing from 39 to 2%.

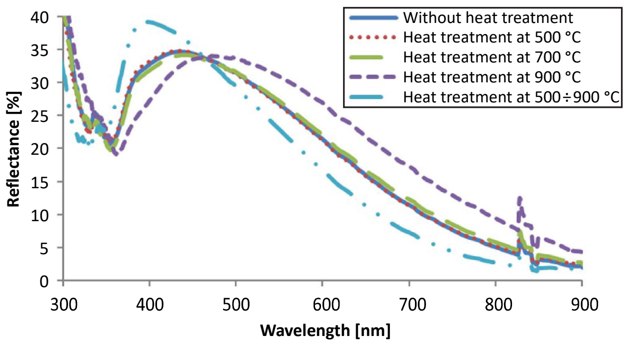

Fig. 6. Light reflection as a function of the wavelength of deposited thin films.

The short-circuit current of a photovoltaic cell without a passivating layer measured by the LBIC method is approximately of 20 mA as described in the previous results [10]. Depositing a passivating layer increases its value even threefold (Fig. 7). The heat treatment performed during the preparation of the metallic contacts influences this value. Temperature increasing to 700 °C does not significantly affect the current value and is in the range of 45÷49 mA. Temperature rising to 900 °C worsens the value obtained to 42 mA. The best results are obtained for a quick heating in the temperature range of 500÷900 °C. The short-circuit current is of 59 mA.

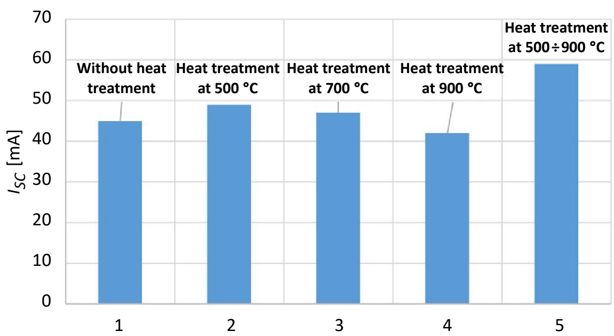

Fig. 7. Comparison of the short-circuit current I_{sc} of the manufactured solar cells obtained by the LBIC method.

Figure 8 shows changes in the shape of the current-voltage characteristics of the manufactured photovoltaic cells. The highest values of voltage and current are characterized by a solar cell annealed at a temperature of 500÷900 °C (Table 3). The sample annealed in 900 °C has the lowest values. This may be due to crack defects recorded in the SEM image.

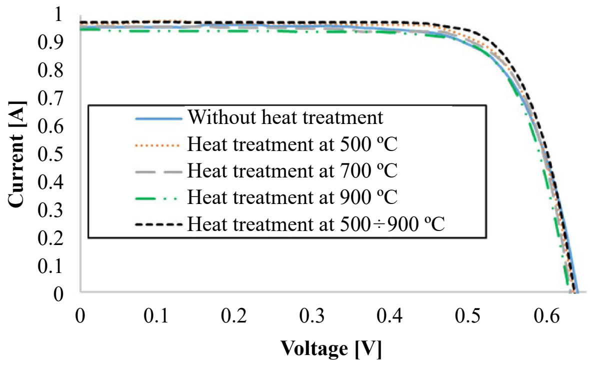

Fig. 8. Current-voltage characteristics of the prepared photovoltaic cells.

The electrical parameters such as short-circuit current density (J_{sc}), short-circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and an efficiency (η) were calculated and listed in Table 3 correlating with the LBIC test. The short-circuit current has the same trend of change.

Table 3
Electrical parameters of all prepared photovoltaic cells.

Sample	Area [cm^2]	J_{sc} [mA/cm^2]	I_{sc} [mA]	V_{oc} [V]	FF	η [%]
Without heat treatment	25	38.3 ±0.2	957.572 ±0.002	0.6387 ±0.0003	0.734 ±0.002	17.89 ±0.01
500 °C	25	38.7 ±0.3	968.305 ±0.004	0.6328 ±0.0002	0.752 ±0.002	18.14 ±0.02
700 °C	25	38.3 ±0.2	958.075 ±0.001	0.6297 ±0.0003	0.758 ±0.004	18.01 ±0.02
900 °C	25	38.2 ±0.4	954.219 ±0.002	0.6270 ±0.0001	0.751 ±0.005	17.88 ±0.04
500÷900 C	25	39.0 ±0.1	974.037 ±0.006	0.6346 ±0.0002	0.770 ±0.001	18.74 ±0.01

4. Conclusions

The use of the layer in optoelectronic and photovoltaic elements and devices is intended to improve the physical properties of the substrate. The surface formation of silicon material is, therefore, one of the significant challenges in the research on photovoltaic materials to obtain even higher performance or to better adapt their properties depending on the performed function. Presence of a thin dielectric layer on the silicon surface improves the properties of the solar cell. The main optical advantages of aluminium oxide are a favourable refractive index value and a very good transparency in a wide spectral range. In addition to good optical properties, Al_2O_3 shows many other desirable properties, e.g., high resistance to mechanical damage, chemical resistance, long-term stability. Additionally, it can act as a passivating layer, increasing the value of the short-circuit current and improving the solar cell efficiency.

Manufacturing silicon photovoltaic cells with the use of screen printing to apply contacts requires baking the pastes at high temperature. The effect of the additional heat treatment on the structure and properties of the deposited antireflection coating should, therefore, be considered. In the case of Al_2O_3 layers deposited by the atomic layer deposition technique, changes in the refractive index dispersion depending on the heat treatment temperature value were found. Heat treatment at 900 °C increases the refractive index. Change in the optical constant may suggest a change in the material structure, but the previous studies have not confirmed it. Moreover, it has been proven that heat treatment affects the electrical properties of the finished solar cell. Despite the lower refractive index, the cells heated at 500 and 700 °C were characterized by similar parameters of the short-circuit current and efficiency to the unheated cell. This may be due to a greater surface development. The highest electrical parameters were obtained for a cell heated at a temperature of 500÷900 °C. In turn, the heat treatment at 900 °C worsened the properties of the cell despite the highest refractive index of the deposited layer. This is most likely related to the defects visible in the SEM image. The research results have practical implications. Deposition of metallic contacts by screen printing and annealing them is one of the basic steps in the production of silicon solar cells. Knowing about the influence of heat treatment on the refractive index of anti-reflective layers, it is possible, for example, to plan a shorter process with a thinner layer, saving time and reducing costs.

Authors' statement

Research concept and design, M. S.; collection and/or assembly of data, M. S. and M. M. S.; data analysis and interpretation, M. S. and M. M. S.; writing the article, M. S.; critical revision of the article, M. S. and M. M. S.; final approval of article, M. S.

Acknowledgements

This publication was supported under the scholarship fund of the Silesian University of Technology in the field of scientific research and development works in 2021.

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