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Optimisation of spray coating parameters for the preparation of polymer, nanocrystal and composite thin films.

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Abstract

The thin film technologies are implemented almost in all spheres of our life and plays especially significant role for application in touchscreens, solar cells, thermoelectric devices, and OLEDs. Such a films should satisfy the specific requirements of the field where they are used. Thus, for solar cells application thin films should be not only solid and homogeneous, but also smooth, when for the catalytic application the rough surface is beneficial. There are different ways for obtaining thin films, such as spin coating, dip coating, sputtering, spray coating etc. The ultra-sonic spray coating is one of the most promising methods for obtaining the thin films from the liquid solutions, due to its scalability and high reproducibility. The number of parameters that can be varied (substrate temperature, solution concentration, nozzle height, number of spraying cycles, nozzle speed and flow rate) allows to obtain the thin film with required properties. However, sometimes it's quite complicate to find all proper parameters and understand the role which plays each of them to the film formation. That's why in this research, we focused on the investigation of the impacts of ultrasonic spray coating parameters on the deposition quality and thin film formation of PEDOT:PSS, which is well known conductive polymer for photovoltaic and thermoelectric application. Characterization of the films was done using Atomic Force Microscopy (AFM) and optical microscopy. The established dependance between different parameters allows to obtain a smooth and solid thin film of PEDOT:PSS with thickness in range of 100-200 nm and Root Mean Square (RMS) roughness 20-25 nm. The founded optimal parameters and the relations between them have also been successfully applied for the obtaining of AgInS2 (AIS) and PEDOT:PSS mixed with AIS thin films with desired properties.

Acknowledgments

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Contents

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List of Abbreviations

PV Photovoltaics

TE Thermoelectric

ITO Indium Tin Oxide

QDs Quantum Dots

LEDs Light-emitting diodes

CdSe Cadmium selenide

PbS Lead Sulfide

AIS Silver Indium Sulfide

PEDOT:PSS Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

AFM Atomic Force Microscopy

SPM Scanning Probe Microscopy

STM Scanning Tunneling Microscopy

NCs Nano crystals

PVD Physical Vapor Deposition

DC Direct Current

RF Radio Frequency

DI Deionized

1 Introduction

1.1 Technological innovation of thin films

In the modern world, thin films plays an important role in manufacturing most of the devices for all spheres of life, from spectacles to mobile phones and to solar panels. Thin film technology is very promising for photovoltaic (PV) application, as it allows to produce light weight and flexible PV devices for integrated systems and portable electronics. The creation of touchscreens which are used in different electronic devices was greatly aided by thin film technology. Thin film technology makes it possible to manufacture of transparent conductive films, that are used as electrodes in touchscreens, photodetectors, solar cells and many other applications. Thin film technology has also allowed for the creation of flexible touchscreens that can be curled or folded without causing damage to the screen. This has opened up new design and functionality options for electronic gadgets such as wearable electronics and foldable cellphones. Thin film technologies are also used to improve the performance of thermoelectric (TE) materials and devices, which are used to directly generate electricity from a heat being very promising branch in renewable energy. The size and shape of the nanostructures in these thermoelectric materials can be precisely controlled using thin-film deposition processes. The material's thermal conductivity is decreased because of enhanced phonon scattering when the size of the nanostructures is comparable to the mean free path of phonons. The reduction in thermal conductivity increases the Seebeck coefficient which ultimately increases the efficiency of thermoelectric materials [10]. Advancements in photovoltaics, electronics, medical devices, and nanotechnology would not have been possible without thin film technology. These are just a handful of the numerous technological advancements that thin film technology has made possible. Future discoveries should be even more fascinating as researchers continue to investigate new materials and deposition processes.

1.2 Methods of obtaining thin films

Properties of the thin films, such as homogeneity, density and roughness can be related to the techniques used to create them. These can have significant impact to the performance of final device. Thus, it is crucial to obtain thin films with desired properties that satisfy the demands of the specific application. The most common deposition techniques are spin coating, spray coating, dip coating, drop casting and sputtering. Each of this technique has advantages and disadvantages, which together with the brief overlook of the techniques by themselves will be shown below.

1.2.1 Dip coating

Dip coating is an easy and economical method for depositing thin films by immersing a substrate in a liquid solution or suspension of the coating material. The thickness of the deposited layer can be controlled by varying substrate withdrawal speed, solution concentration, and viscosity [31]. Dip coating is commonly used for surface coating, in optics, and electronics with polymers, metals, ceramics, and composite materials. Dip coating has several advantages over other deposition methods, such as low cost, simplicity, and the ability to coat complex geometries. However, this technique has some limitations. For example, it is difficult to cover the substrate uniformly, especially for a non-wettable with the specific solvent surface. In addition, when ultra-thin (∼20 nm) or ultra-thick (∼1000 nm) layers need to be created, controlling the thickness becomes problematic [16]. Dip coating can be used to create large-scale films for a wide range of substrates, but the viscosity of the material solution and wettability of the surface limits its effectiveness. Despite these limitations, dip coating remains a popular and widely used technique for depositing thin films with controlled properties.

1.2.2 Drop casting

Drop casting is one of the simplest film-forming technique. Drop-casting is the formation of a thin solid film (with thickness from about 350 nm up to micrometers scale) by dropping a solution onto a substrate, with further evaporation of the solvent. By this method, the resulting film thickness is controlled by the concentration and deposited volume of the solution. The benefits of drop casting are that it does not require any special equipment or complex processing stages, the deposition can be done at any atmosphere. There are no substrate or solution limitations and it´s relatively fast.

On the other hand, this method has some limits. The main issue is reproducibility of the film thickness, as sometimes it is quite challenging to deposit the same amount of the material to the exactly the same area. Also, it can be difficult to obtain uniform film thickness or particle distribution across large areas. Furthermore, the solvent evaporation process can cause undesired particle aggregation or film breaking. Drop casting is widely used to create thin films or patterns of nano particles or other materials for a variety of applications such as chemical sensing, materials evaluation and solar cells [49]. It is a popular method among scientists for quick and easy sample preparation for further characterization [24].

1.2.3 Spin Coating

Spin coating is a method of thin film deposition from the liquid solutions by using centrifugal force. Spin coating is a versatile thin film deposition technique that can be used to deposit films with a range of thicknesses from, below than 10 nm up to 10 µm or even more [45].

In general, the spin coating procedure can be divided into four stages: deposition, spin-up, spin-off, and solvent evaporation [30]. At the first stage, the substrate is placed and fixed on the spin coater, and the solution is dropped on the substrate surface to cover it. On the next stage the spin coater device will be turned on and the substrate will begin to spin until it reaches a particular speed. The centrifugal force produced by the substrate's acceleration and angular speed causes the flow of solution outward the substrate surface. The third stage, also known as steady solution thinning, begins after the substrate is spinning at a constant rate, and viscous forces responsible for the solution thinning. In the final stage, evaporation takes place which determines the resulting thickness.

So, the main parameters of the spin coating deposition, that determines film thickness, roughness and homogeneity are spinning speed, acceleration, spin time, number of steps and/or repeats, solution concentration, surface tension, and viscosity of the solution. Their variation allows to obtain the film with desired thickness and properties.

A variety of thin films for photovoltaic, displays, and other applications are frequently made via spin coating. The advantages of this method are that it's easy, fast, cost effective. However, disadvantages of this method are difficulty in precisely controlling the film thickness, limited scalability, the tendency for the film's edges to be thicker than the middle part. Additionally, the spin coating might be challenging to use on substrates that are non-wettable with the specific solvent. [37]

1.2.4 Spray coating

The another commonly used technique for thin film deposition from the liquid solution is spray coating, where, in general, the solution is pushed through a nozzle, resulting in the formation of a fine aerosol [3]. After the aerosol formed, droplets of the solution fall on the substrate, forming a thin film. There are different types of spray coating, namely thermal spray coating, High Volume Low Pressure Spray coating, plasma spraying coating, ultrasonic spray coating and air spray coating. The spray coating method has several advantages:

1. Uniformity: The spray coating process can produce an uniform coating of the material on the substrate.

2. Efficiency and scalability: This method is relatively fast and can cover large areas.

3. Control: By altering spray parameters such as solution concentration, spray rate, and substrate temperature, the technique provides for precise control over the thickness and composition of the deposited layer.

4. High reproducibility: This method can produce consistent and repeatable results in terms of quality and properties of the deposited thin films.

However, as any other technique, spray coating has also some disadvantages:

1. It has number of parameters that needs to be optimized in order to obtain the desired film.

2. It requires maintenance and cleaning during each experiment, especially to prevent clogging in the spray nozzle.

Spray coaters have been used for a variety of purposes, from small area thin films for spectacles and screens, to large scale thin film solar panels. Overall, spray coating is a versatile and cost-effective process for depositing thin films with high control over thickness and homogeneity, making it a preferred choice for a wide range of applications [35].

1.2.5 Sputtering

Sputtering is often chosen over other physical vapor deposition (PVD) techniques for depositing thin films onto substrates because of its good quality film, highly controlled directionality and lower absorption compared to other PVD methods [4]. Sputtering is a technique for producing a film coating made of sputtered atoms from the solid materials. The method includes bombarding a target (material that we want to deposit) with energetic ions, which cause atoms or molecules to be ejected from the surface. These ejected atoms are also known as sputtered atoms which have high kinetic energy that helps them to travel through the distance from target to substrate [36]. There are several types of sputtering namely Direct Current (DC) sputtering, Radio Frequency (RF) sputtering and magnetron sputtering. In DC sputtering, the power source is direct current whereas in RF sputtering, the power source is alternating current and the power supply is a positive high voltage radio frequency. Sputtering provides numerous benefits over other deposition techniques, including a wide range of materials that can be deposited, good film quality, uniformity and excellent substrate adhesion. This method also enables precise film thickness, shape and composition control [41].

The primary challenge in performing the sputtering process is maintaining a sufficiently strong plasma to produce a large supply of ions over the target's surface with a shape appropriate for the desired substrate surface [43]. Sputtering also has some limitations, including high equipment and maintenance costs, limitation of target material, high vacuum requirement and damaging of substrate due to ion bombardment. The majority of energy that strikes the target converts to heat, which needs to be released. Sputtering is widely used to manufacture various products, such as integrated circuits, photovoltaic cells, magnetic sensors, and optical coatings. It is also essential in producing flat panel displays and hard disk drives. Despite its limitations, sputtering remains as a main process for a wide range of industries and applications.

1.3 Materials perspective for photovoltaic and thermoelectric

The growing concern about the impact of fossil fuel-based energy on global warming and climate change leads to significant increase of popularity of sustainable energy sources. One of the most promising renewable energy source is photovoltaic, which directly convert solar energy into electricity. There are several advantages of photovoltaic. Some of them are: low maintenance cost, zero fuel consumption, can be constructed to any size based on requirements, installing residential solar panels on rooftops or the ground. However, there are some disadvantages like low efficiency, weather dependent and high manufacturing cost [15]. One more promising source of renewable energy is thermoelectric which allows to directly convert heat into electricity. It can be applied to convert waste heat from solar panels, industrial operations, automobile engines, human body and other sources into electrical energy. Thermoelectric effect can be used for thermoelectric power generation, where heat energy is converted into electrical energy or for thermoelectric cooling, where an electric current is used to create a temperature difference, resulting in a cooling effect. This cooling effect is used in refrigeration and air conditioning. It has wide range of application in industries including aerospace, automotive, medical, wearable electronics and industrial temperature control [17]. Combining of photovoltaic and thermoelectric can be a next step for creating highly efficient solar panels [5].

To provide efficient energy conversion, materials for photovoltaic and thermoelectric should fulfill several requirements. In particular, materials for photovoltaic should have high absorption coefficient, high electron mobility, low recombination rates, long carrier lifetime and band gap that allows sufficient absorption in all solar spectral range [2]. In the same time, materials for thermoelectric application should have low thermal conductivity, high Seebeck coefficient, high electrical conductivity and must be stable under high temperatures and thermal cycling [39].

In photovoltaic and thermoelectric, nanocrystals (NCs) have shown great promise. It can be used as light absorbing material or charge transport layer in photovoltaic, whereas by controlling size, shape and composition of the nanocrystal, thermal conductivity can be reduced which increase the thermoelectric efficiency [20]. In general, NCs are crystalline particles with at least one dimension less than 100 nm. They have a high surface area to volume ratio due to their small size, which provides them unique optical, electrical, and catalytic properties that distinguish them from their bulk form. They have several applications including drug delivery where it is used as carrier for drug, protein and other bioactive molecule to the targeted cells and tissues. It is also used in biomedical imaging, environmental remediation, catalysis and optoelectronics [7].

Quantum dots (QDs) are the NCs which dimension is less than 10 nm. It has attracted interest as an advantageous material for enhancing the performance of solar cell due to its unique properties such as size-tunable band gap, multiple exciton generation and electron transport layer which can reduce recombination losses [22]. They are currently used in biological, medical research as in solar panels and television. QDs have shown great promise in photovoltaic application as it require low manufacturing energy, thin layer of absorber material and has potential to be used in flexible substrate [23]. In terms of thermoelectric application, quantum dots can increase thermoelectric conversion efficiency, for example decreasing thermal conductivity by scattering phonons on the QDs boundaries. Quantum confinement generates discrete energy levels, which can increase the density of states and improve the material's electrical properties [28]. Another type of materials, promising and widely used for photovoltaic and thermoelectric applications are polymers. They offers the potential for low cost, low toxicity, light weight and flexible devices [27].

1.3.1 PEDOT:PSS

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is a conductive p-type polymer, which is a mixture of two ionomers. Highly conductive, but hydrophobic positively charged PEDOT core is surrounded by a negatively charged shell of hydrophilic PSS, forming a micelle structure. In such a way, PEDOT:PSS can be easily dissolved in water, making it very suitable for application [42][48].

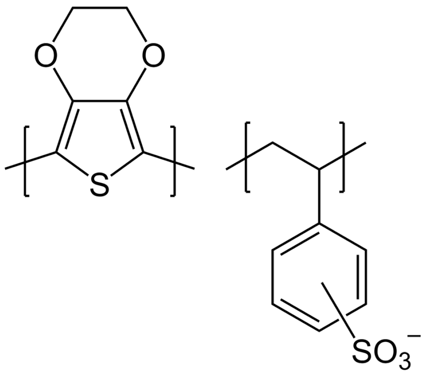


Figure 1.1: Chemical structure of PEDOT:PSS [44]

PEDOT:PSS got the popularity due to its flexibility, high electric conductivity, high Seebeck coeffecient, and good water solubility [26]. PEDOT:PSS is also very promising for future development of flexible and wearable electronics, photovoltaic and thermoelectric. The TE characteristics of PEDOT-based TE materials have been steadily improving over the last few years. Certain PEDOT:PSS-based materials have obtained high efficiency comparable to conventional inorganic TE materials like bismuth telluride at ambient temperature [14]. The most common use of PEDOT:PSS is in the form of thin film or layer, which can be obtained by various techniques, mentioned in section 1.2. In this project, we focused on the spray coating deposition of the aqueous solution of PEDOT:PSS onto a glass substrate to obtain a homogenous thin film with smooth surface.

1.3.2 AIS nanocrystal

Silver Indium Sulfide (AIS) NCs shows good potential for light absorption and emission. They can be produced using green colloidal synthesis and have optical properties that can be changed by adjusting the nanocrystal's size and composition [40]. AIS NCs have been investigated for possible applications in photovoltaics, particularly as an absorber material in thin film solar cells which can exhibit high conversion efficiency. AIS has several advantages including high absorption coefficient, direct band gap and low toxicity. It's quite important to obtain uniform and smooth thin film to ensure consistent performance across the device and to reduce light scattering from the surface. In this project, the thin film of AIS NCs was obtained on a glass substrate using spray coating deposition. It was shown, that parameters of spray coating and dependences in relations between them which we found for PEDOT:PSS can be expanded also to other materials. Thin film of mixed PEDOT:PSS and AIS NCs was also obtained by using the same parameters of spray coating that was found optimum for depositing thin film of PEDOT:PSS on the glass substrate. AIS NCs and PEDOT:PSS can be combined to create a thin film with improved conductivity and charge transport, which can enhance photovoltaic devices efficiency [33].

2 Instrument and Techniques

2.1 Ultrasonic spray coating

In general, the principle of ultrasonic spray coating is the next: the liquid flows through a nozzle that is vibrated at a high frequency by an ultrasonic generator. By this vibration, the liquid is separated into tiny droplets which then moves to the substrate. The benefits of ultrasonic spray coating are: possibility of coating different surfaces and shapes, high coating uniformity and high reproducibility. Ultrasonic spray coaters are widely used in many applications, including thin film deposition for photovoltaic, electrical devices, medical implant coating, and drug delivery systems. [6]

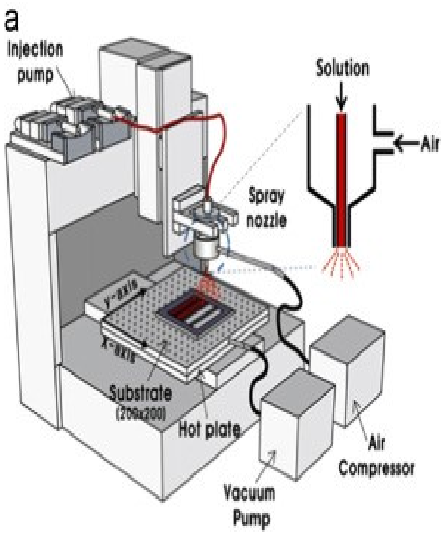


Figure 2.1: Schematic diagram of spray coater [32].

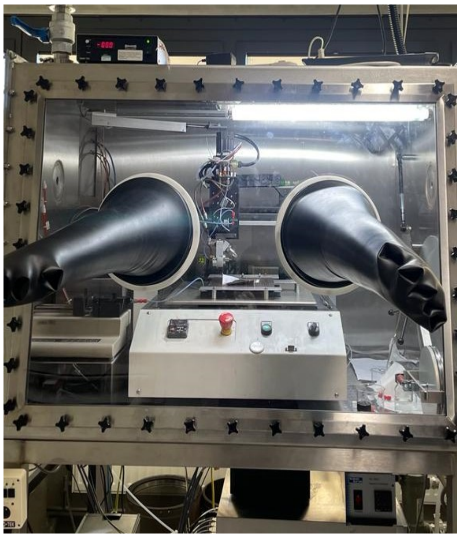


Figure 2.2: The photo of spray coater used for this project.

In this project, Ultrasonic spray coating Sono-Tek 06-5108 was used. The general schematic view of spray coating systems and photo of one used in this work shown in Fig. 2.1 and Fig. 2.2 respectively. In our case, the spray-coating system located in the glove-box (Fig. 2.2) with nitrogen atmosphere and allows precise control of nozzle height, nozzle speed, flow rate, substrate temperature and number of spraying cycles to obtain the film with desired properties.

2.2 Optical microscopy

An optical microscope, also called a light microscope, magnifies images of small objects by using visible light and lenses. It's a versatile equipment for a wide range of applications, including biology, physics, materials research, forensics, quality control, and education. The typical view and build of the optical microscope are shown in Fig. 2.3. In general, the working principle is: the light focuses onto the sample and after that passes through the objective lens, which can magnify the image up to 100 times and go into the eyepiece, where the magnified image of the sample can be observed by eye or camera [11].

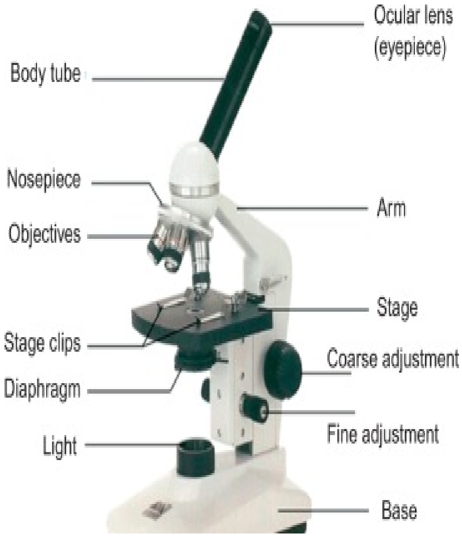


Figure 2.3: General scheme of the optical microscope [38].

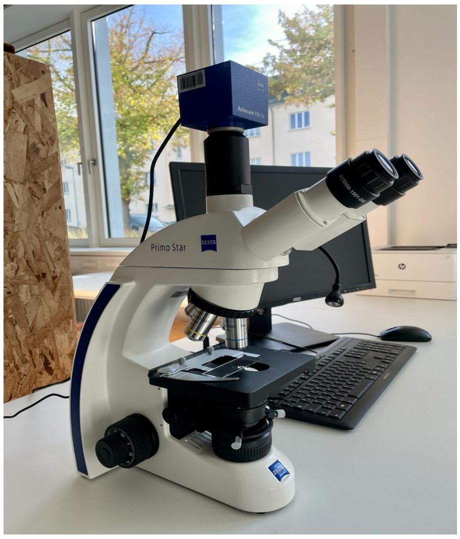


Figure 2.4: Optical microscope used for this project.

In this project, optical microscope ZEN 2.5, from Primo star company was used (Fig 2.4). In our setup, four objective lenses for providing different magnification (4x, 10x, 40x, 100x) are available. Parameters like coarse adjustment knob and fine focus must be use carefully for obtaining sharp image.

2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is technique that allows to study surfaces at the nanoscale level. The general principle is, the sample's surface is scanned with a very sharp (in range of tens nanometers) tip mounted on a cantilever and measures the three-dimensional topography, surface roughness and mechanical properties like young's modulus [13]. The working principle of the AFM device is based on the interaction between a tip and a sample surface at the atomic scale. When the tip comes into contact or close enough to the sample, the atoms or molecules on the surface interact with it, causing the cantilever to deflect slightly. This deflection is detected by a laser beam, which reflects from the end of the cantilever and goes to the detector (Fig: 2.5) [21][46].

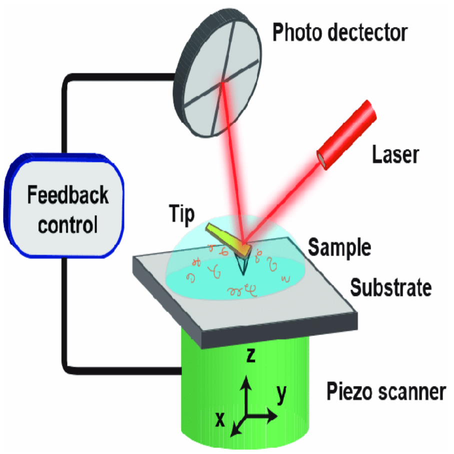


Figure 2.5: Schematic diagram of AFM [21].

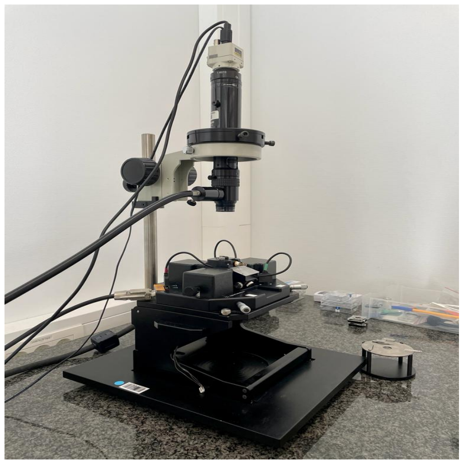


Figure 2.6: Photo of AFM device used for this project.

AFM 5500 device from Agilent company for producing high resolution AFM images (Fig. 2.6) was used in this project. There are several parameters that need to be carefully kept like: gains, scanning range, scanning speed, distance, amplitude and resolution to ensure the good image quality without presence of artifacts. AFM has the potential to be used in a variety of fields, including life science, materials science, electrochemistry, polymer science, biophysics, nanotechnology, semiconductor physics and biotechnology [25].

2.4 Software for Data analysis

In this work, for processing the AFM images and analyzing data, Gwyddion software was used. The AFM data treatment were done in the following steps: plane leveling, facets leveling, aligning rows, correcting horizontal scars, color representation, extraction of profiles, roughness measurement and applying mask. Thickness of the obtained film were determined by extracting the profiles from the edge of the film and measuring the height [47].

2.5 Choose of the substrate

In this project, glass substrate has been used. The main reason for using glass substrate is it's low thermal and electrical conductivity, which is needed for future thermoelectrical studies of PEDOT:PSS, AIS NCs and mixed PEDOT:PSS and AIS NCs thin films. Cost effectiveness is also one of the factors for popularity of glass substrate among scientists. Cleaning of the glass substrate before depositing thin film is very important as it can be contaminated with dust or any other substances during handling or storage. For this reason, the cleaning procedure of rinsing the glass substrate with deionized (DI) water, ultrasonication in ethanol for 15 minutes, repeated in DI water rinsing and drying with nitrogen gas was performed.

3 Result and discussion

3.1 Optimization of spray coating parameters for obtaining thin films of PEDOT:PSS on glass substrate

In this project, optimization of spray coating parameters to obtain the thin films of PEDOT:PSS with desired properties was done.

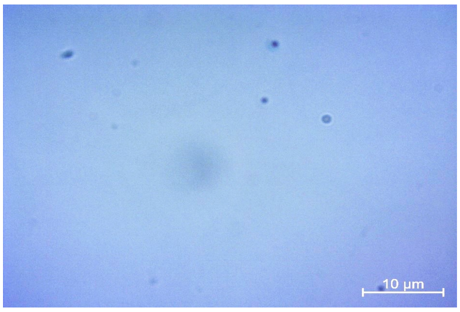
3.1.1 Variety of parameters

The parameters of the spray coating deposition that can be varied are related to the specific device. For the setup used in this work, following parameters can be changed:

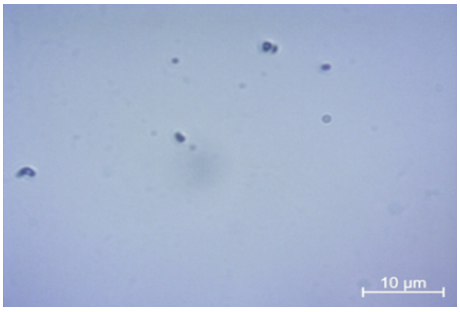
1. Temperature of substrate
2. Height of nozzle
3. Nozzle speed
4. Concentration of solution
5. Spraying cycles
6. Solution flow rate
7. Generator frequency

3.1.2 Reproducing a thin film deposition from a literature review

As a starting point, we attempted to reproduce a result of PEDOT:PSS spray coating deposition reported in literature [29]. For this, parameters was settled as follow: maximum (10.7 cm) nozzle height, flow rate 10ml/hr, substrate temperature 35°C and 1 spraying cycle. The ratio of 15% PEDOT:PSS and 85% DI water was used to ensure the same concentration of the solution as reported [29]. In the article, the height of the nozzle was 12 cm, which is out of the limit for the spray coater device used in our study. As there was no information about the nozzle speed in the article, the study in the range of 5 mm/s to 30 mm/s nozzle speed was done.



(a)



(b)

Figure 3.1: Optical microscope image of PEDOT:PSS film deposited at 35°C substrate temperature, maximum (10.7 cm) nozzle height, 85% dilution, 10 ml/hr flow rate, 1 spraying cycle at (a) 5 mm/s and (b) 25 mm/s nozzle speed.

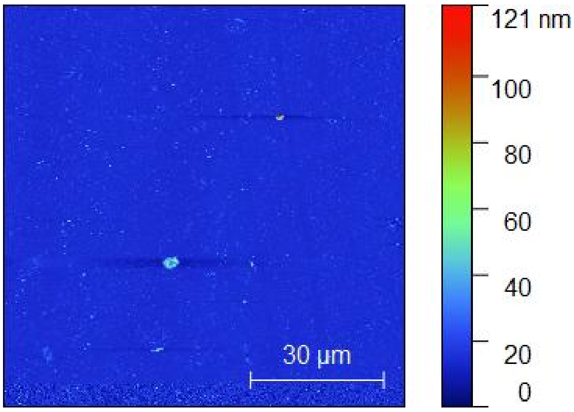


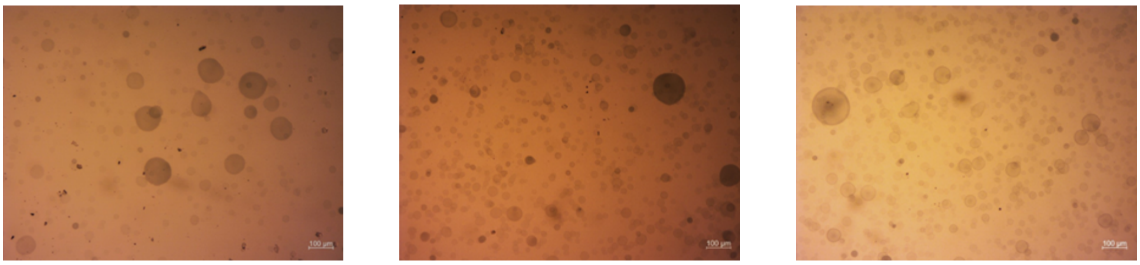
Figure 3.2: AFM image of PEDOT:PSS film deposited at 35°C substrate temperature, maximum (10.7 cm) nozzle height, 85% dilution, 10ml/hr solution flow rate, 1 spraying cycle and 5 mm/s nozzle speed.

The resulting thin film obtained by reproducing experiment from the paper [29] had quite good roughness (2.43 nm) and uniformity. However, the thickness of such a film even at the low nozzle speed of 5 mm/s was in the range of 30 nm. The purpose of this project is to be able to produce a film with the appropriate thickness, which should be in the range of 100 nm for many applications and research [18]. To achieve this and to better understand the spray coating process, influence of its parameters to film formation and relations between parameters, the next step by step investigation was done, what will be shown below.

3.1.3 Dependence from substrate temperature

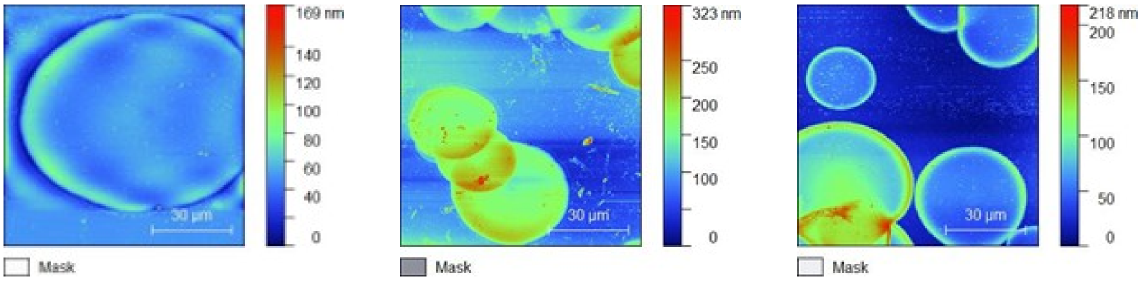
In the literature it can be found, that general approach to choosing substrate temperature for spray coating deposition is the substrate temperature should be below the boiling point of solvent of the solution which is being deposited [12]. The main reason for this is: at high temperature, the droplet-substrate contact is reduced by the rapid formation of vapor. Consequently, droplets appear to shatter and bounce off the surface and forms coffee ring. But in some papers it can be found that they using the substrate temperature which is much higher than the boiling point of the solvent they used [19]. In our study, we are using the water-based solution with boiling point around 100°C. So, to cover both cases, the temperature range from 30°C to 130°C was chosen. Other parameters were settled as follow: 1 spraying cycle, 0.1 ml/min solution flow rate (by default), middle (7.2 cm) height of nozzle, 60 mm/s nozzle speed.

Despite the fact, that according to literature data the diluted PEDOT:PSS solution is more preferable to obtain good quality film by spray coating [29], we decided to go with concentrated solution of PEDOT:PSS to better understand the influence of the substrate temperature to the film formation.



(a) (b) (c)

Figure 3.3: Optical microscope images of PEDOT:PSS films deposited at 60 mm/s nozzle speed, concentrated solution, 0.1 ml/min solution flow rate, 1 spraying cycle and substrate temperature: (a) 50°C, (b) 70°C and (c) 130°C.

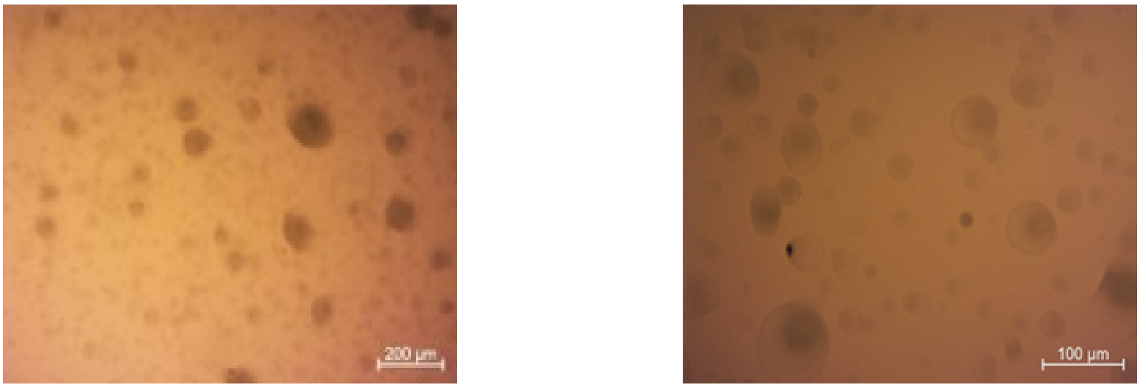


(a) (b) (c)

Figure 3.4: AFM images of PEDOT:PSS films deposited at 60 mm/s nozzle speed, concentrated solution, 0.1 ml/min solution flow rate, 1 spraying cycle at substrate temperature: (a) 50°C, (b) 70°C and (c) 130°C.

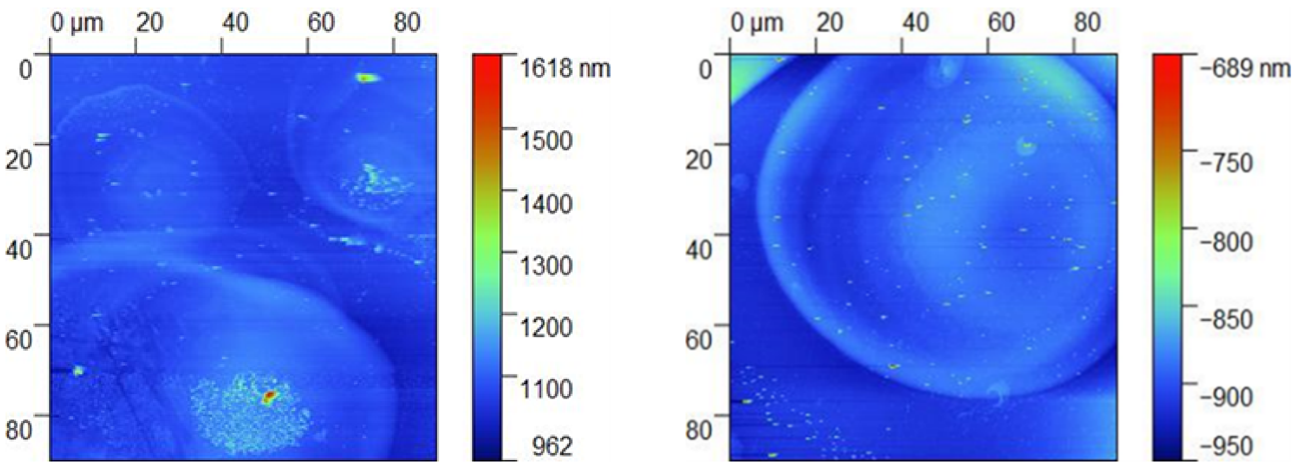
From the optical image, (Fig 3.3(a)) it can be seen that at chosen deposition parameters the PEDOT:PSS doesn't form a film, but just separate droplets on the glass substrate. Analysis of the latter can give the clear view of the peculiarities of the film formation by the substrate temperature changing. For example, the size distribution of the droplets decreases with increase in temperature (Fig 3.3(c)), but simultaneously the effect of coffee rings become more pronounced, that can be seen in AFM image (Fig 3.4(c)). The coffee ring effect is typically observed during the drying process of a liquid droplet in which the solute particles in the droplet are deposited around the droplet's edge, forming a ring-shaped pattern. This phenomenon is created by the evaporation of the solvent, which causes the solute particles to accumulate near the droplet's edge due to the convective flow of the solvent toward the droplet's center [34] [9].

In the case of spray coating of PEDOT:PSS at high temperatures, the coffee ring effect occurs due to the faster evaporation rate of the solvent. Moreover, at higher temperatures, the PEDOT:PSS solution's viscosity decreases, allowing the solute particles to move more easily toward the droplet's edge. The coffee ring effect has a negative impact on the properties of the produced PEDOT:PSS film because it can increase the surface roughness, create local inhomogeneities and decrease the electrical conductivity of thin film. As a result, it is essential to minimize this effect by optimizing the spray coating parameters.



(a) (b)

Figure 3.5: Optical microscope images of PEDOT:PSS films deposited at 60 mm/s nozzle speed, concentrated solution, 0.1 ml/min solution flow rate, 1 spraying cycle at substrate temperature: (a)65°C and (b)75°C.



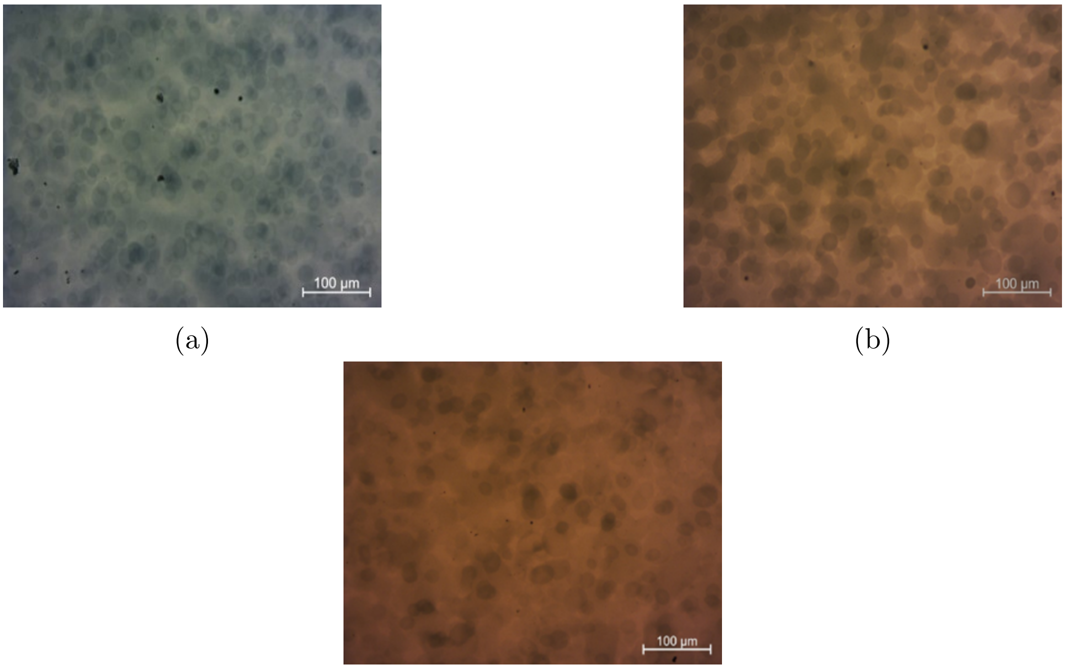
(a) (b)

Figure 3.6: AFM images of PEDOT:PSS films deposited at 60 mm/s nozzle speed, concentrated solution, 0.1 ml/min solution flow rate, 1 spraying cycle at substrate temperature: (a)65°C and (b)75°C.

Narrowing the temperature range to get the small size distribution, fast drying of the deposited film but as small as possible coffee rings effect, it was found that the optimal balance between these effects observed for the samples deposited with substrate temperature of 65°C. Also, the decreasing of the nozzle height allows us to get more denser droplets distribution on the substrate, but still without forming a close film (Fig. 3.5).

3.1.4 Dependence from nozzle speed

After establishing the optimal substrate temperature, even at the minimum (3.8 cm) nozzle height, as it was mentioned above, we did not obtained the close film of PEDOT:PSS. As the nozzle speed determines the surface coverage, and the film's thickness, it was chosen as the next parameter to study. During the investigation of influence of the substrate temperature, the nozzle speed was 60 mm/s. It was obvious, that significant decrease of it is needed, so the range from 1 mm/s to 28 mm/s was chosen with other parameters as follow: the substrate temperature 65°C, minimum (3.8 cm) nozzle height, 1 spraying cycle, flow rate of the solution 0.1 ml/min and the concentrated PEDOT:PSS solution.



(a) (b) (c)

Figure 3.7: Optical microscopy images of PEDOT:PSS films deposited at 65°C substrate temperature, minimum (3.8 cm) nozzle height, 1 spraying cycle, 0.1 ml/min solution flow rate and nozzle speed: (a) 2 mm/s, (b) 14 mm/s and (c) 24 mm/s.

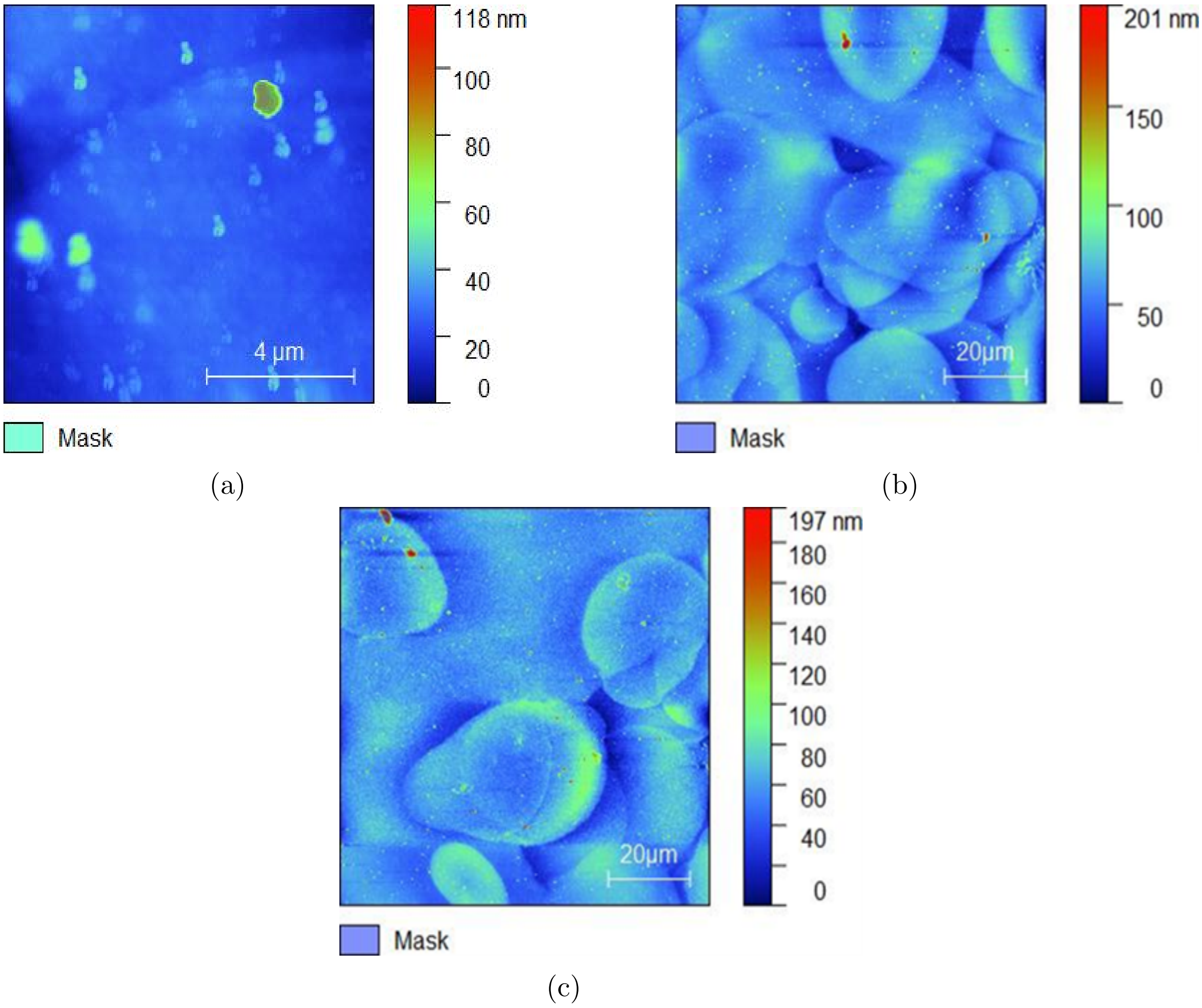
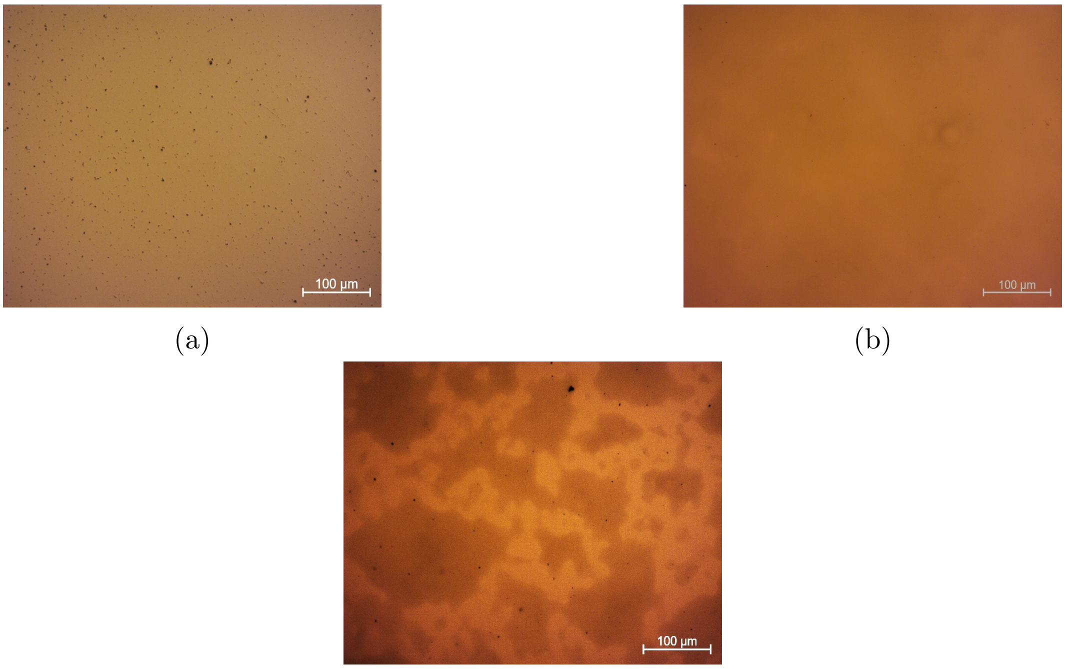


Figure 3.8: AFM images of PEDOT:PSS films deposited at 65°C substrate temperature, minimum (3.8) nozzle height, 1 spraying cycle, 0.1 ml/min solution flow rate and nozzle speed: (a) 2 mm/s, (b) 14 mm/s and (c) 24 mm/s.

As it can be seen from the optical images (Fig. 3.7), almost in all the cases the solid film was obtained. The roughness of obtained films was highly dependent from the nozzle speed. According to this, the optimum nozzle speed is between 2 mm/s and 14 mm/s which will also depend to the other parameters, as it will be shown below.

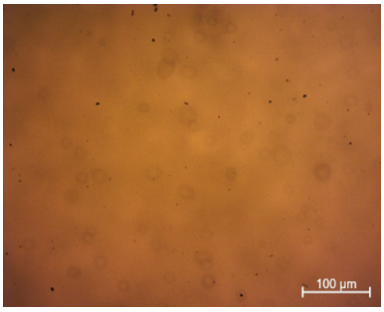
3.1.5 Relation between PEDOT:PSS solution concentration, nozzle speed and substrate temperature

The concentration of the solution not only influences numerous essential properties of the solution by itself, such as viscosity and surface tension, but also play a role in droplet size during the spray coating deposition affecting film thickness, morphology and surface coverage. To study the influence of the PEDOT:PSS concentration to the properties of the thin films obtained by spray coating, two sets of samples were prepared. First set A was prepared using substrate temperature 35°C, minimum (3.8 cm) nozzle height and nozzle speed 5 mm/s or 14 mm/s. The three different solutions were deposited with PEDOT:PSS : DI water ratios 50:50, 25:75 and 15:85 respectively. The set B was prepared in the similar way, but with the substrate temperature 65°C.

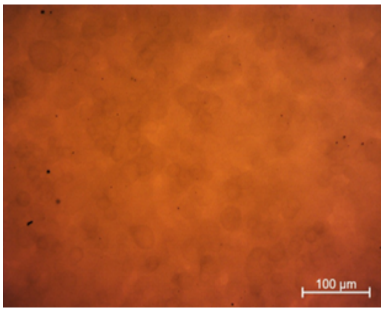


(a) (b) (c)

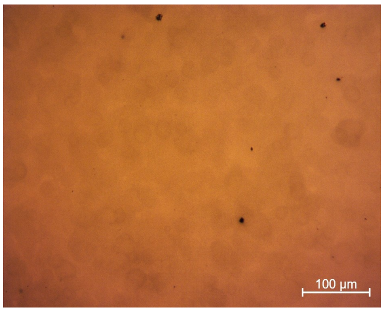
Figure 3.9: Optical microscopy images of Set A of PEDOT:PSS films deposited at 35°C substrate temperature, minimum (3.8 cm) nozzle height, 1 spraying cycle, 0.1 ml/min solution flow rate at 3 different dilution and nozzle speed: (a) 50% dilution with 5 mm/s nozzle speed, (b) 75% dilution with 14 mm/s nozzle speed and (c) 85% dilution with 14 mm/s nozzle speed.



(a)



(b)



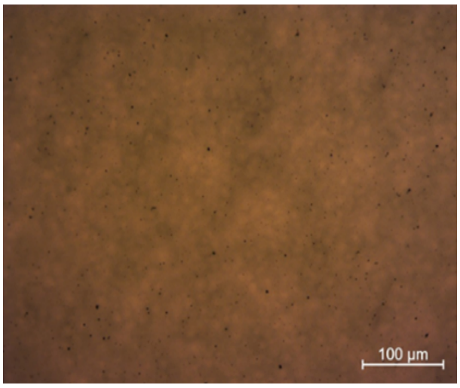
(c)

Figure 3.10: Optical microscopy images of Set B of PEDOT:PSS films deposited at 65°C substrate temperature, minimum (3.8 cm) nozzle height, 1 spraying cycle, 0.1 ml/min solution flow rate at 3 different dilution and nozzle speed: (a) 50% dilution with 5 mm/s nozzle speed, (b) 75% dilution with 14 mm/s nozzle speed and (c) 85% dilution with 14 mm/s nozzle speed.

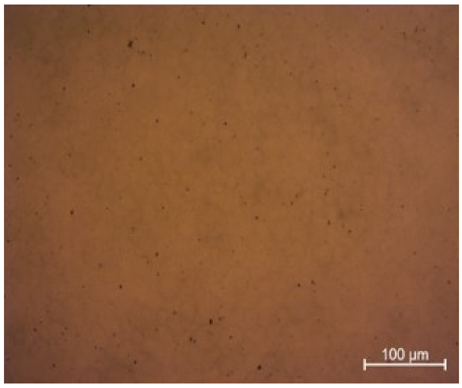
The images from Set A (Fig. 3.9) shows quite good homogenous film at 35°C substrate temperature, but due to lower temperature the drying of droplet is slow and could not give the immediate dried film, what can be critical if several deposition cycles are needed. From (Fig. 3.10), it can be seen that deposition of 50% diluted PEDOT:PSS at 65°c substrate temperature and nozzle speed 5 mm/s gives good homogenous film.

3.1.6 Relation between number of spraying cycles and nozzle height

The spraying cycles can make influence not only to the resulting thickness, but also to the film morphology [8]. As it was shown in previous paragraphs, another parameter that have significant influence not only to the film thickness (as, for example, nozzle speed) but also to the morphology of the surface is nozzle height. That's why it is important to understand the relation between these two parameters to have possibility to obtain the films with approximately the same thickness, but different surface morphology, what can be beneficial for different fields of application. To study this, two sets of samples were prepared. Set A was made using diluted 85% solutions of PEDOT:PSS, the minimum (3.8 cm) nozzle height, the substrate temperature 65°C, the flow rate 10 ml/hr, the nozzle speed 5 mm/s with 3 or 5 spraying cycles. In Set B all the parameters are similar to Set A, but the nozzle height is settled to maximum (10.7 cm).

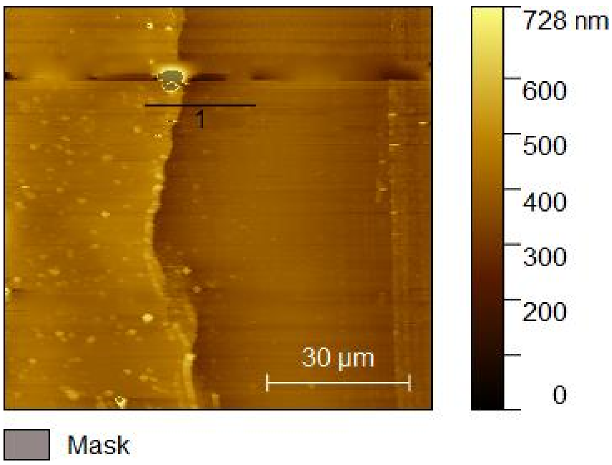


(a)

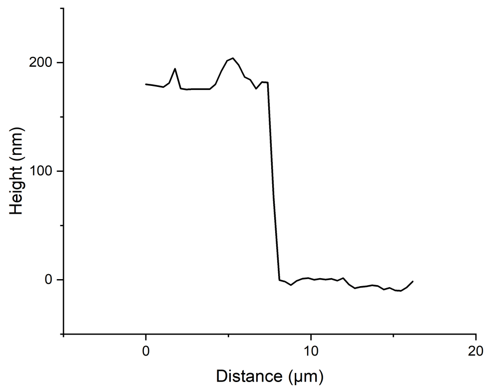


(b)

Figure 3.11: Optical microscope images of PEDOT:PSS films deposited at 65°C substrate temperature, 5 mm/s nozzle speed, 3 spraying cycles, 85% PEDOT:PSS dilution, (a) minimum (3.8 cm) and (b) maximum (10.7 cm) nozzle height

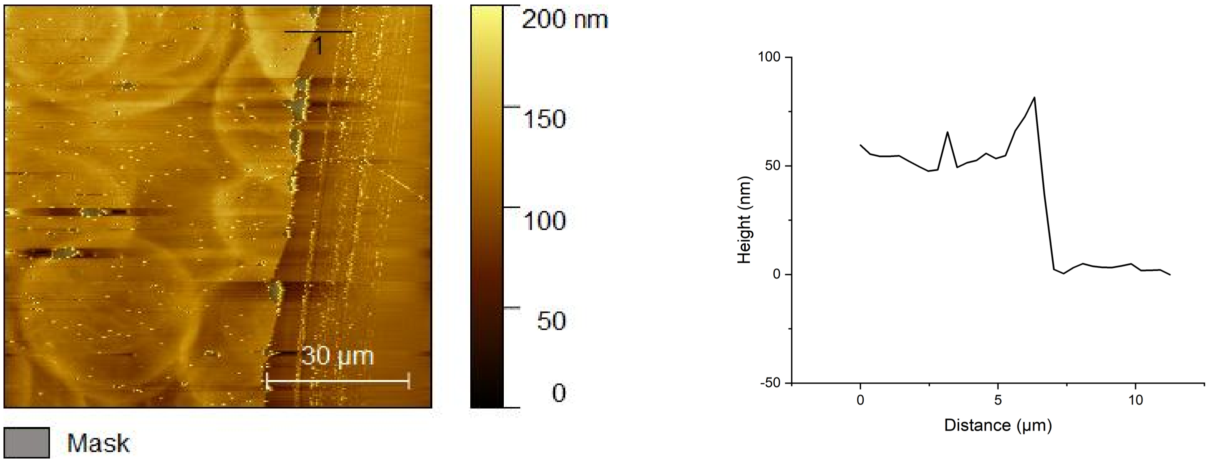


(a)



(b)

Figure 3.12: (a) AFM image taken on the edge of PEDOT:PSS film deposited at 65°C substrate temperature, 5 mm/s nozzle speed, 3 spraying cycles, 85% PEDOT:PSS dilution and minimum (3.8 cm) nozzle height and (b) extracted profile.



(a) (b)

Figure 3.13: (a) AFM image taken on the edge of PEDOT:PSS film deposited at 65°C substrate temperature, 5 mm/s nozzle speed, 3 spraying cycles, 85% PEDOT:PSS dilution and maximum (10.7 cm) nozzle height and (b) extracted profile.

The estimated thickness for minimum (3.8 cm) nozzle height (Fig 3.12) is around 181 nm and roughness of 15.43 nm whereas the estimated thickness for maximum (10.7 cm) nozzle height (Fig 3.13) is around 79 nm and roughness of 10.54 nm. In general, increasing the number of spraying cycles may give a thicker film with better surface coverage and smoother surface morphology. But in our case with the 5 spraying cycles and minimum (3.8 cm) height, the thickness of PEDOT:PSS film was higher than 4 µm, which is under our AFM device limitations and much higher than we want to obtain.

Comparing the samples obtained with the maximum (10.7 cm) nozzle height with the minimum (3.8 cm) nozzle height, (Fig. 3.11, 3.12 and 3.13) gives the thickness in desired range. It is worth to note, that deposition of highly diluted solutions at high nozzle position can lead to the too thin film thickness, or even to the film will not be formed. In such a way, to obtain smooth (RMS around 15.43 nm) PEDOT:PSS thin (in range of 180 nm) film, the optimum parameters are 65°C substrate temperature, the minimum height of nozzle (3.8 cm), 85% dilution of solution (85% DI water, and 15% PEDOT: PSS), 5mm/s nozzle speed, 3 spraying cycles and 10ml/hr flowrate. To obtain smooth films with other thicknesses the next correlation between changing parameters should be followed: for obtaining homogenous thin film of thickness below 100 nm, the height of the nozzle should be maximum (10.7 cm) with 1 spraying cycle and 5 mm/s nozzle speed. If thicker film is required then the height of the nozzle should be decreased and the number of the spraying cycle should be increased keeping the nozzle speed 5 mm/s. At some point, the minimum (3.8 cm) height of the nozzle with 5 or more spraying cycle will give very thick film with high roughness. To prevent this, height of the nozzle should be increased with every increase in number of spraying cycle.

3.1.7 Spray coating of AIS nanocrystal

After obtaining the thin film of PEDOT:PSS on the glass substrate with desired properties using spray coating we decided to expand our study. To check if the parameters and correlations between them found earlier will work for other materials, the AIS NCs solution obtained by colloidal synthesis was chosen. For the spray coating deposition the concentrated AIS NCs solution was diluted, in the ratio of 90% DI water and 10% AIS NCs solution and following parameters were used: 65°C temperature, 5 mm/s nozzle speed, 10ml/hr flowrate, 1 spraying cycle and minimum (3.8 cm) nozzle height.

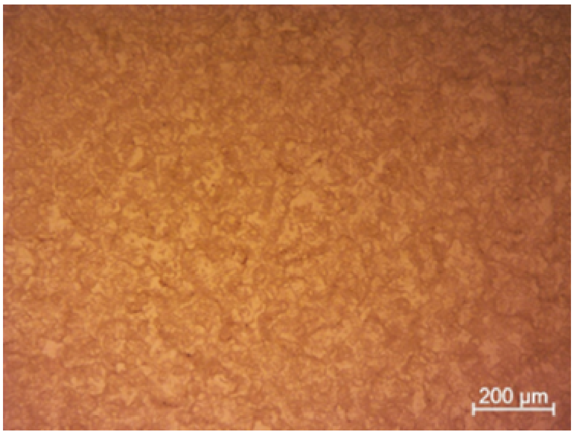
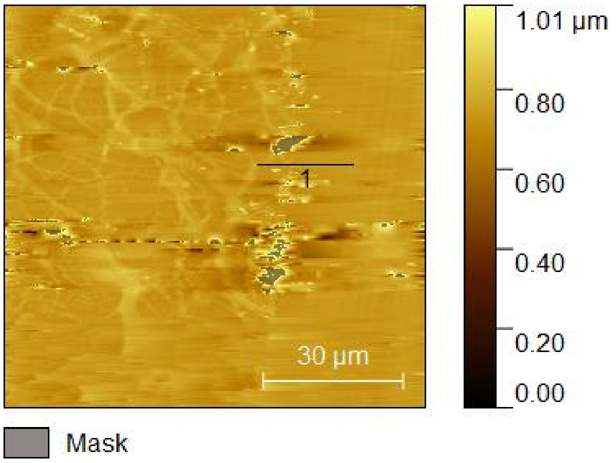
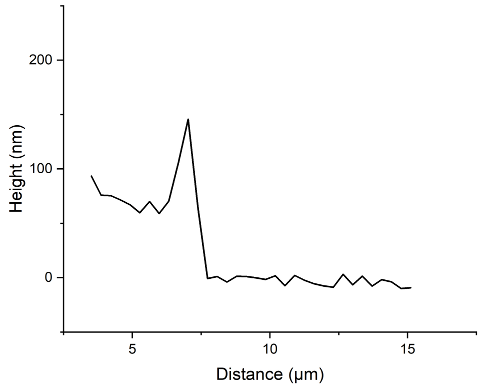


Figure 3.14: Optical microscope image of AIS NCs film deposited at 65°C substrate temperature, 1 spraying cycle, 90% AIS NCs solution dilution, 5 mm/s nozzle speed and minimum (3.8 cm) nozzle height.



(a)



(b)

Figure 3.15: (a) AFM image from the edge of AIS film deposited at 65°C substrate temperature, 1 spraying cycle, 90% AIS NCs solution dilution, 5 mm/s nozzle speed and minimum (3.8 cm) nozzle height and (b) extracted profile.

The thickness (Fig. 3.15) of AIS film is around 145 nm with roughness RMS of 24.49 nm. As it can be seen from Fig. 3.14 and Fig 3.15, the obtained films of AIS NCs shows quite good surface morphology and the thickness in the desired range. There is still a way to improve surface roughness, but we got the clear confirmation, that obtained knowledge about spray coating procedure can be expand from PEDOT:PSS to other materials.

3.1.8 Spray coating of AIS nanocrystal mixed with PEDOT: PSS

The mixture of PEDOT:PSS and AIS NCs can be very promising for photovoltaic and thermoelectric application, as addition of conductive polymer to NCs can improve charge transport efficiency and minimize recombination losses. Spray coating of AIS NCs combined with PEDOT:PSS can potentially be a technique that shows promise for fabricating cost-efficient solar and thermoelectric devices [1]. Here the solution of 50% diluted PEDOT:PSS and 90% diluted AIS NCs in the ratio of 50:50 was deposited onto a glass substrate with the spray coating parameters used for the deposition of pure AIS NCs which listed above.

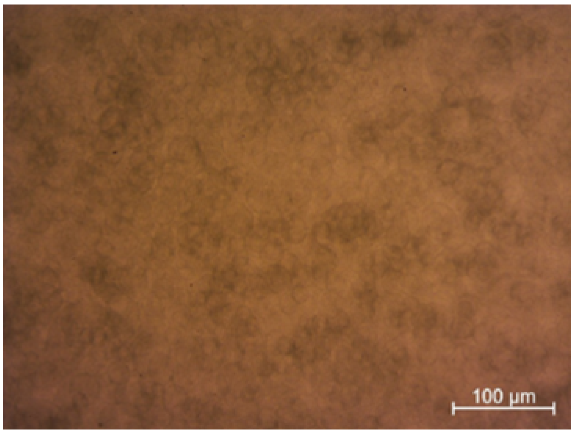
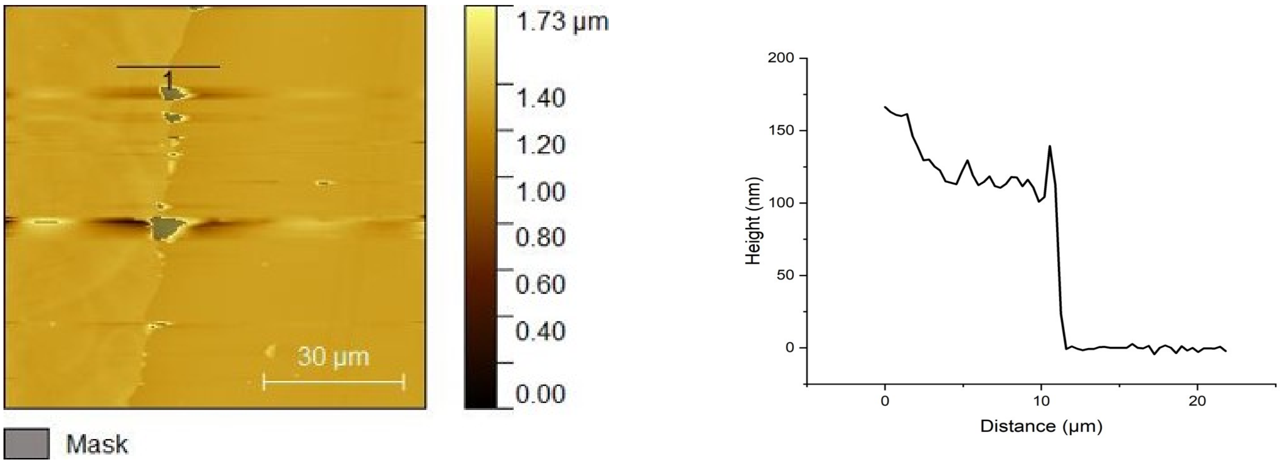


Figure 3.16: Optical microscope image of mixed PEDOT:PSS and AIS NCs in 50:50 ratio. Film deposited at 65°C substrate temperature, 5 mm/s nozzle speed, 1 spraying cycle, minimum (3.8 cm) nozzle height and 10ml/hr flow rate.



(a) (b)

Figure 3.17: (a) AFM image from edge of mixed PEDOT:PSS and AIS NCs in 50:50 ratio. Film deposited at 65°C substrate temperature, 5 mm/s nozzle speed, 1 spraying cycle, minimum (3.8 cm) nozzle height and 10ml/hr flow rate and (b) extracted profile.

The thickness of such a film is around 138 nm and roughness RMS of 14.17 nm. As it can be seen from Fig. 3.16 and Fig. 3.17, obtained results are in the agreement with the results for pure AIS NCs and for PEDOT:PSS.

4 Conclusion

Influence of the spray coating parameters such as substrate temperature, solution concentration, nozzle speed, nozzle height, flow rate, and the number of spraying cycles to the deposited film properties was investigated. The correlation between the spray coating parameters was established. It is shown that to obtain homogenous thin film of thickness below 100 nm, nozzle height should be maximum (10.7 cm) with 1 spraying cycle whereas for obtaining thin film of thickness above 100 nm, nozzle height should be minimum (3.8 cm) with 1 or more number of spraying cycles. The height of the nozzle and number of spraying cycles should be balanced to get homogenous film with desired thickness. For PEDOT:PSS, dilution of more that 50% PEDOT:PSS solution is better for good homogenous film. This allows to obtain thin film of PEDOT:PSS with desired properties, as well as successfully expand the knowledge to other materials, such as AIS NCs and mixed AIS NCs and PEDOT:PSS composite.

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