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MICROWAVE ANNEALING, A PROMISING STEP IN THE ROLL-TO-ROLL PROCESSING OF ORGANIC ELECTRONICS

Koen Gilissen, Jeroen Stryckers, Wouter Moons, Jean Manca, Wim Deferme

Institute for Materials Research (IMO-IMOMEC) – Engineering Materials and Applications, Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium

Abstract. *In recent years, organic printable electronics has gained more and more attention. The development and characterization of new printing techniques and functional inks is vital to accomplish solution processable, large area organic electronic devices e.g.: organic photovoltaics (OPV), organic light-emitting diodes (OLEDs). In this study a systematic comparison is made between hotplate annealing and microwave annealing of (screen) printed Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) layers. PEDOT:PSS films treated with both techniques were characterized and compared by their thin film morphology, their electronic properties and their annealing time. It is shown that no difference in the thin film morphology and final sheet resistance was observed for microwave annealed compared to the hotplate annealed samples. Above that the annealing time is decreased up to a factor 6. These results show that microwave annealing is a feasible fast annealing technique for PEDOT:PSS thin films and can therefor reduce the total processing time of organic and PEDOT:PSS based electronic applications.*

Key words: *microwave annealing, printed electronics, organic electronics, PEDOT:PSS, screen-printing.*

1. INTRODUCTION

The conjugated polymer PEDOT:PSS has been around for more than two decades [1]. Although its electronic properties are still under investigation [2] PEDOT:PSS is already used in a variety of organic based electro-optical applications, e.g.: Organic Photovoltaics (OPV)[3], Organic Light-Emitting Devices (OLEDs) [4], and other applications, e.g.: antistatic coatings[5], anode material for capacitors[6]. This wide applicability is due to its high optical transparency, low resistivity, its ability to be processed from solution and its environmental stability. A thin film PEDOT:PSS is an integral part of an OLED device stack [7] and has several purposes. It is deposited on top of a transparent electrode, most commonly an indium tin oxide (ITO) thin film. The PEDOT:PSS layer

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Corresponding author: Koen Gilissen
Institute for Materials Research (IMO-IMOMEC) – Engineering Materials and Applications, Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium
(e-mail: koen.gilissen@uhasselt.be)

prevents the diffusion of oxygen and indium originating from the ITO layer [8], [9] and modifies the surface wetting properties [10]. Due to its electronic properties it lower the energy barrier for the injection of holes and block electrons from reaching the hole-injecting contact preventing surface recombination [8], [11]. OLED device studies have shown that the incorporation of a PEDOT:PSS layer increases the external quantum efficiency and increase the lifetime [12]. As aqueous dispersion, PEDOT:PSS can be processed from solution by either spin-coating or other printing or coating techniques. To remove solvents and obtain a high conductivity a post thermal treatment is needed [13]. In a laboratory environment this post-deposition thermal treatment is performed via conventional thermal conduction methods e.g.: hotplate or oven. These conventional thermal conduction methods do not scale to industrial sized, high throughput production process. The annealing time is limited due to the onset of thermal degradation at temperatures above 200 °C [11][14]. In this paper we investigate the microwave annealing of PEDOT:PSS thin films [15] to overcome these limitations. Furthermore a comparison is made between hot plate annealing and microwave annealing of thin PEDOT:PSS films coated with the screen printing technique. Based on our results a significant reduction in annealing time is achieved using a microwave annealing system.

2. EXPERIMENTAL

The PEDOT:PSS AGFA ORGACON EL-P3145 was screen printed using an 1 by 1 inch patterned screen on cleaned glass slides. The cleaning procedure for all substrates consisted out of an ultrasonic bath in soap solution for 30 minutes followed by an ultrasonic bath in MilliQ water for 10 minutes. After this the substrates were exposed to an ultrasonic bath for 10 minutes in acetone and as a last step boiling in isopropanol was performed for 10 minutes. After the cleaning procedure, prior to printing, all substrates were treated with UV ozone to improve the surface free energy of the substrates resulting in a better wetting behavior. In-situ current measurements were performed in a 4-wire sensing configuration using a Keithley 2400 source meter under a 10V DC bias. In order to insure good contact with the wet films, silver contacts where applied to the 4 corners of the 1 by 1 inch substrate prior to screen printing the PEDOT:PSS. The final film thickness was measured using a DEKTAK 3 ST Profilometer. The sheet resistance of the PEDOT:PSS film was measured using the van der Pauw technique [16]. Fig. 1 illustrates the configuration of the microwave annealing system. The electromagnetic waves (2.45GHz) are generated by the microwave source which is powered by a tunable microwave power generator. This tunable microwave power generator enables the system to vary the generated electromagnetic power from 50 to 1000 Watt. As the generated electromagnetic waves are coupled into the waveguide they pass the water cooled microwave circulator, i.e. reflection load, which protects the microwave source from being damaged by reflected electromagnetic waves. The electromagnetic waves propagating through the waveguide are stirred to a multimode electromagnetic field to prevent standing waves. By preventing standing (electromagnetic) waves in the waveguide and in the applicator area, which is located at the end of the waveguide, the probability of local hotspots is drastically reduced. The formation of local hotspots in the applicator area could potentially damage our samples and would cause a non-uniform heating of the samples present at the applicator. Part of the electromagnetic energy which are not transferred to the samples is absorbed by the dummy load or reflected back towards the start of the waveguide.

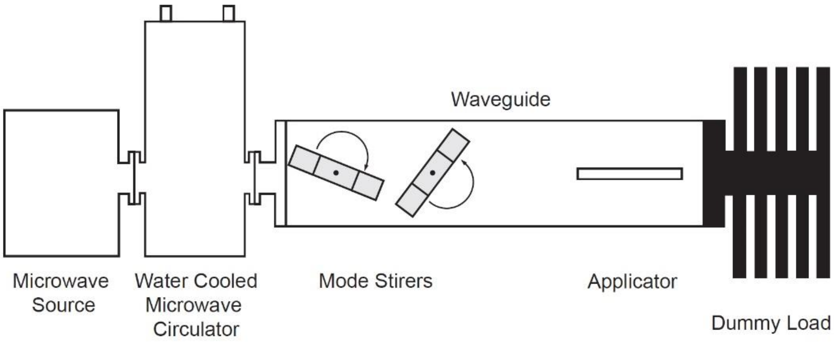

Fig. 1 Schematic overview of the microwave annealing system.

In order to meet the requirement of a multimode uniform electromagnetic field rotating mode stirrers where placed inside the waveguide. To insure the isolated effect of both mode stirrers, the physical orientation of each mode stirrers is shifted at least 90° with respect to each other. Furthermore the rotation speed of each mode stirrer is chosen as a prime number to insure that the rotation speeds are not a multiple of each other and the direction of their rotation is opposite. To obtain the correct behavior of the mode stirrers, the shape and material were experimentally determined. The selected group of materials was limited to dielectrics to prevent reflections from the mode stirrers. To further determine the mode stirrer material a systematic variation of the stirrer materials and careful measurement of the attenuation and phase shift caused by each material at 3 different orientations in the wave guide is performed. The test samples, with equal dimensions, where placed at the entrance of the waveguide, inline centered, inline against the waveguide wall and transversal centered. From these measurements it was found that the material Macor, a glass ceramic, caused an adequate differential phase shift of 26.8°. To further optimize the stirrer design different shapes, e.g.: cylindrical, square, and mutual configurations, e.g.: spacing between stirrer blocks, where systematically varied. From these result it was found that a square shaped stirrer designed as shown in Fig. 2.

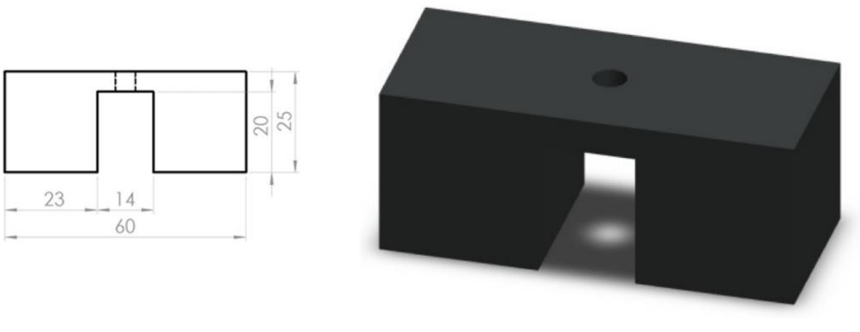

Fig. 2 (left) 2D CAD drawing of the stirrer design, units: mm
(right) 3D render of the stirrer design.

When the stirrer is inline (0°) it introduces a phase shift of 168°, when the stirrer is rotated by 45° it introduces a differential phase shift of 195° and when it is transversal positioned in the waveguide (90°) it introduces a phase shift of 271°. By introducing 2 stirrers in the waveguide, a uniform multimode electromagnetic field is obtained, ideal to test microwave annealing as alternative for hotplate annealing.

3. Results and Discussion

The annealing time of a PEDOT:PSS film is meanly depended on the amount of PEDOT:PSS wet solution, the specific heat of the solution and the annealing temperature. To gain insight into the annealing time of these PEDOT:PSS films in-situ current measurements were performed. These measurements were performed by applying a 10 V bias on the screen printed PEDOT:PSS thin films while annealing the samples on a conventional hotplate. As shown in Fig. 3 a clear distinction is observed when annealing the samples at different temperatures on a hotplate. While the solvents and additives evaporate, the current increases rapidly and then stabilizes. The maximum value of the current is independent of annealing temperature but the time to reach this value is temperature specific and the time to reach the maximum current decreases with increasing temperature. The time to reach the maximum current will serve as a reference to compare the annealing time of hotplate and microwave annealed samples.

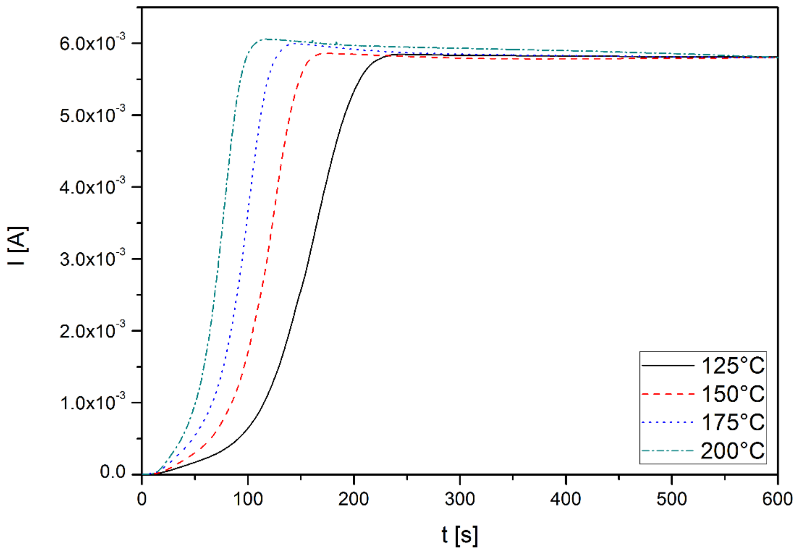

Fig. 3 In situ current measurement while annealing of screen printed PEDOT:PSS film on a hotplate at various temperatures.

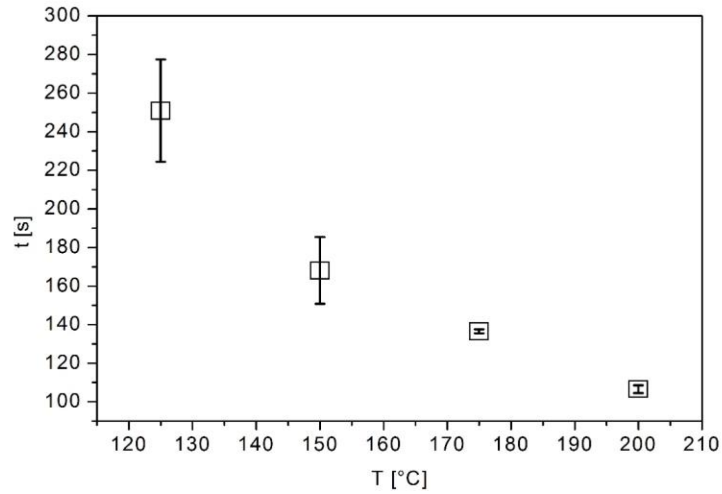

Fig. 4 Average times to reach a stable current of PEDOT:PSS films on a hotplate.

Fig. 4 shows the average times to reach the stable current on a conventional hotplate, as the temperature increases the time to stable current decreases and gets less disperse. When repeating this experiment in our microwave annealing system, as depicted in Fig. 5Error! Reference source not found., a similar trend is observed when varying the emitted power of the microwave. It is also clear that the stable current is reached much faster than in the hotplate experiment. These results suggest that the microwave could potentially be a much faster technique than the hotplate for annealing these PEDOT:PSS films without change of the morphological and electrical properties.

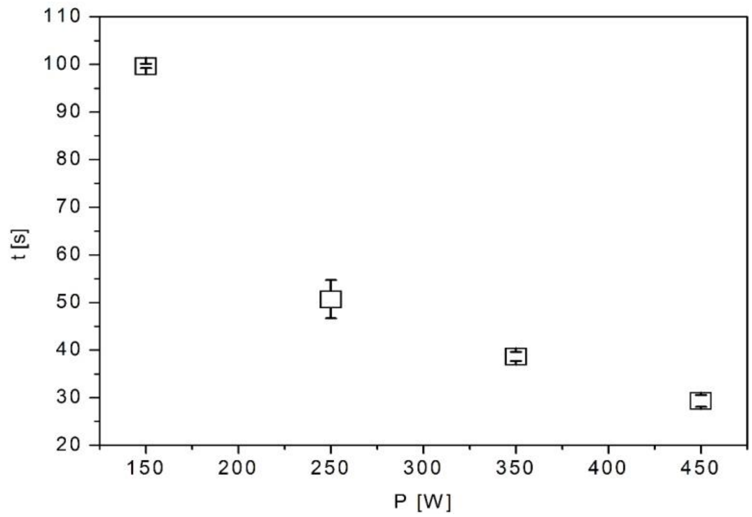

Fig. 5 Average times to reach a stable current of PEDOT:PSS films on our microwave annealing system.

To be able to confirm these presumptions the morphology of the annealed PEDOT:PSS films is compared on a Scanning Electron Microscope (SEM), as shown Fig. 6. From these SEM images it is clear there is no distinct structural or morphological difference between the hotplate annealed samples at 130°C and 200°C, column a and b. More importantly there is also no evidence of a change in morphology between the hotplate annealed samples and the microwave annealed samples, column a/b and column c resp.

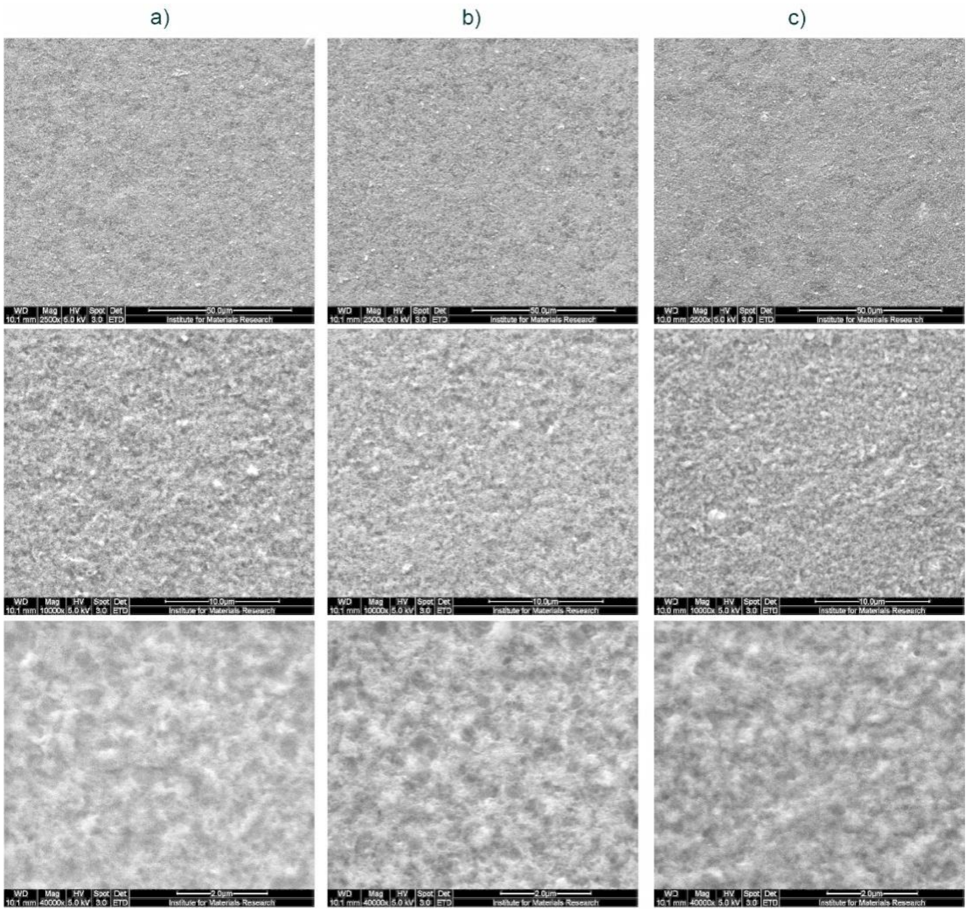

Fig. 6 SEM images of annealed PEDOT:PSS films. Column a: hotplate annealed at 130 °C for 600s. Column b: hotplate annealed at 200 °C for 600s. Column c: Microwave annealed at 200W for 70s.

The thin film morphology and chemical structure are the main film properties that influence the electronic properties the PEDOT:PSS films. The well-known onset of thermal degradation for conventional thermal convection and radiation is 200 °C [14] has not been correlated to microwave power. The electromagnetic energy transfer from microwave source to the thin wet film is generally accepted to consist out of two main mechanisms, i.e. ionic conduction and dipolar polarization. The absorbed microwave energy is converted in kinetic energy by movement of molecules [17]. The electronic properties of both hotplate and microwave annealed films were evaluated by measuring the in-plane sheet resistance using the Van der Pauw method [16]. Fig. 7 shows the in-plane sheet resistance of the hotplate annealed PEDOT:PSS films. These films were annealed in air for 600s and cooled down to room temperature before measuring the sheet resistance. The results show the increasing sheet resistance with increasing annealing temperature. This effect can be attributed to the hydroscopic nature of PEDOT:PSS films, as these films are annealed in atmospheric conditions they take up oxygen and water vapor from their surroundings [11] [14] .

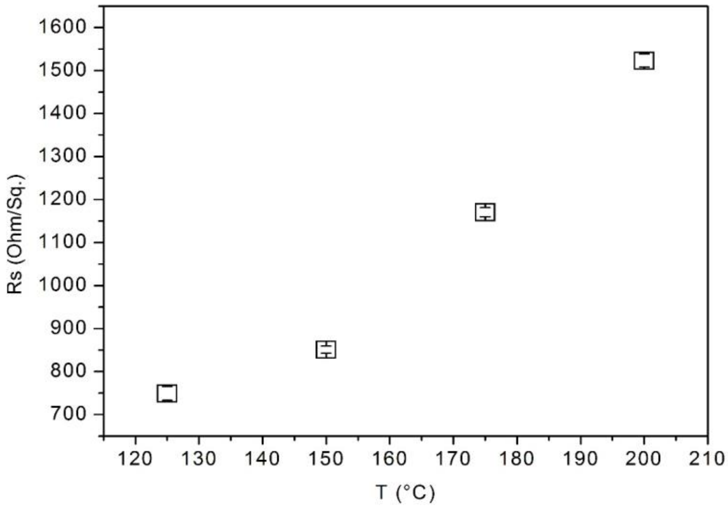

Fig. 7 The in-plane sheet resistance as function of hotplate annealing temperature.

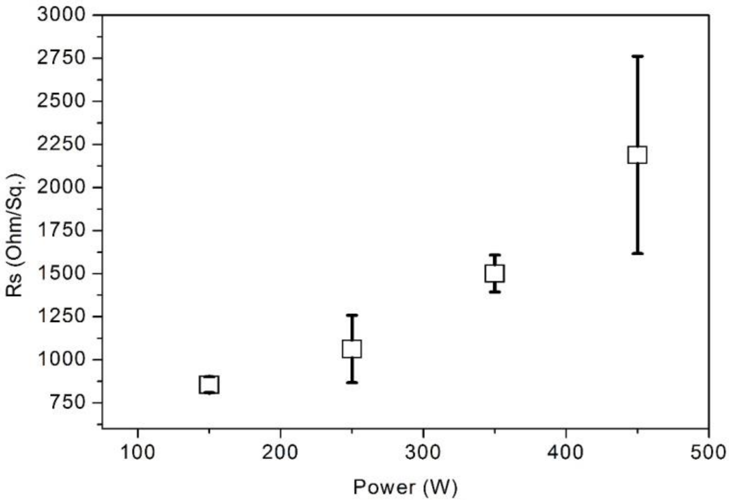

Fig. 8 The in-plane sheet resistance as function of the microwave power.

Fig. 8 shows the in-plane sheet resistance of the microwave annealed films at various microwave powers. These measurements were performed after the films cooled down to room temperature and the annealing time was based on the time to reach a stable current. A similar trend is observed as with the hotplate annealed films, with increasing microwave power the in-plane sheet resistance increases. It is shown that the annealed PEDOT:PSS films in our microwave system at 150 W for 100 s reached a similar sheet resistance as the hotplate annealed samples at 125 °C for 251 s. The microwave annealing step is 2.5 times faster than the conventional hotplate annealing step without interfering with the electronic properties of the conjugated polymer PEDOT:PSS.

4. CONCLUSION

We studied the effects of microwave annealing as post-deposition treatment on PEDOT:PSS thin films in comparison to conventional hotplate annealing treatment. We investigated effects of these treatments on the morphological and electronic properties of PEDOT:PSS thin films to determine the applicability of the microwave technique. In – situ current measurements suggest that the microwave annealing technique is 2.5 times faster than the hotplate technique. Morphological investigations show no difference in morphology between hotplate annealed and microwave annealed samples. From the investigation of the electronic properties of these annealed PEDOT:PSS films, we have observed that the sheet resistance increases rapidly when the power of the microwave is increased above 150W. Using powers lower or equal to 150W will yield comparable results in terms of sheet resistance for both techniques. Furthermore the measured annealing time decreases by a factor of 2.5 times, showing that microwave annealing is a feasible post-deposition thermal treatment for PEDOT:PSS thin films.

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