1. Materials and Methods
   1. Organic Solar Cell Fabrication
      1. Materials
      2. Cleaning
      3. Dr Blade Deposition
      4. Spin Coating Deposition
      5. Thermal Evaporation
      6. Encapsulation
      7. Annealing
   2. Nanoimprinting Soft Lithography
      1. Stamp Architectures and Replication
      2. Hand Press Nanoimprinting Lithography (Wet NIL)
      3. NIL Assisted Nanoimprinting
      4. Stamp Feature Depth
   3. Device Characterization
      1. Electrical Characterization
         1. IV Curves (17)
         2. EQE Curves
         3. LBIC
      2. Optical Characterization
         1. FTIR Spectra
         2. Integrating Sphere Spectra

2 Materials and Methods

ABSTRACT

This chapter describes the general procedures used in the fabrication and characterization of the various devices manufactured within this thesis. More specifically, it focuses on solar cell fabrication and characterization, including used materials, manufacturing techniques, and characterisation equipment. Special emphasis is placed on the modified solution-process techniques developed within our group, used to manufacture both extremely thick active layers and active layer gradient devices. The latter is especially advantageous for the manufacturing of a wide range of active layer thickness within one device, resulting in reduced material usage and accelerated device optimization. On the other hand, this chapter also describes the procedures used to manufacture NIL stamps and their role in solar cell and photodetector active layer nanostructuring, further discussed in chapter 4. Finally, the characterization section is focused on the explanation of generally available techniques, while novel measurement procedures developed within the scope of this thesis have been thoroughly described within their corresponding chapters.

2.1 Organic Solar Cell Fabrication

In this work we have focused on devices fabricated using the inverted architecture, where the transparent electrode is in contact with the electron transport layer (ETL), and the top metallic electrode contacts the hole transport layer (figure x). However, there have been some conventional architecture devices, for which the general fabrication procedure was the same, but with different ETL and HTL materials that accommodated to the necessary fabrication techniques.

Referenciar a cada cosa al seu material

Solar cell fabrication begins by cleaning glass substrates, which are sourced with a patterned ITO layer, according to the cleaning procedure of section x. On top of the clean ITO layer we deposit the ETL (HTL for conventional architecture) and the PAL via solution processing, which are made with a variety of materials depending on the specific device. In the case of nanostructured devices, NIL is performed on top of the active layer, either directly after deposition or after the solvent has had time to dry. On top of these layers, the HTL(ETL for conventional architecture) and the back electrode are deposited via thermal evaporation. Most devices have an extra step involving the encapsulation of the entire device to prevent environment related degradation, as well as a thermal annealing that modifies their crystalline properties.

After a device is completely finished it is thoroughly characterized by using a variety of techniques that help us determine their electrical and optical performance, as well as their basic topographical characteristics.

Fer figura del process de depositió totalgeneric

Continuous ITO.

* + 1. Materials

This section describes all the materials used for the manufacturing of devices.

* + - 1. Substrates

Used substrates mainly consist on a thin glass sheet of 1.1~mm that is covered with a 100~nm ITO layer with x% conductivity. Within this thesis various different substrate sizes have been used:

The biggest one used as a pre-scale up substrate is 7.5x2.5 cm, ever so slightly smaller than a glass slide. The ITO layer of this substrate is patterned (figure x), allowing us to manufacture 12 individual devices on each side of the slide, each one with an active area of 8 mm2, resulting in a total of 24 devices per substrate. We have taken advantage of this great number of devices to accelerate our research by changing parameters (thickness, nanoimprinting depth, material…) within the same substrate, with much lower material use and faster characterization times. (reference ossila)

A slight variation on this substrate is the continuous ITO substrate, where the ITO layer covers the entire slide homogeneously. (reference ossila)

Besides these big substrates we have also used smaller spin coater friendly, substrates in multiple experiments. The main difference between these and the previous ones is their smaller size and subsequent lower amount of pixels per substrate.

Glass with ITO of x conductivity and y nanometers bought in x and y

Pixelated substrates

Big and Small

Continuous ITO substrates

Hasselt Substrates

* + - 1. Electrode Materials

Pre-patterned and full ITO coated glass substrates (25x75 mm) with 20 Ω/□ and 100 nm thickness, provided from Ossila (ref:).

Ag: Thermally evaporated (pellets from Kurt J. Lesker)

Au: Thermally evaporated (pellets from Kurt J. Lesker)

* + - 1. Electron and hole transport layer Materials

In inverted solar cells:

A ZnO nanoparticle dispersion (N-10 Avantama) in isopropanol (IPA) was used as the electron transport layer. It was deposited by dr Blade

ZnO sol gel solution, manufactured by ourselves by using recepie described in x.

The hole transport layer was thermally evaporated Molybdenum trioxide (MoO3) in powder from Alfa Aesar.

In conventional solar cells:

PEDOT alfa aesar blade coated

LiF alfa aesar thermally evaporated

* + - 1. Solvents

Every solvent used for solution processing of the blends was purchased from Sigma-Aldrich. The solvents were used as is, without any further treatment. Used solvents were chlorobenzene (CB), o-dichlorobenzene (DCB), toluene and o-xylene. Solvents used for cleaning purposes such as acetone, 2-propanol and ethanol were purchased from Labbox.

* + - 1. Active Layer Materials

The active layer usually consists of a blend between an electron acceptor material and an electron donor material. All active layer materials used within this thesis are commercially available. The concentration and ratio at which these materials were used varied significantly between experiments so they will be specified within each chapter. The only common step was to dissolve them and stir them overnight at 80ºC.

* + 1. Cleaning

Every substrate was thoroughly cleaned before deposition to ensure proper electrical contact and wettability. The substrates were cleaned by sequentially immersing them for 5 min in ultrasonication baths of different cleaning solutions rinsing them with water in between baths to minimize bath contamination. They were, in this order: acetone, 2% vol. Helmanex solution in H2O, isopropanol and finally 10% w/v NaOH in an aqueous solution. Finally, substrates were dried with compressed air. As an additional step we sometimes ozone treated substrates for 20 min at x W to further improve wettability. This whole cleaning procedure was optimized during this work and several upgrades were designed and manufactured to enhance the cleaning procedure performance.

* + 1. Dr Blade Deposition

Even though the best OPV performing devices are generally manufactured using spin coating, this thesis is mainly focused on the use of Dr Blade deposition, since it is a much more scalable technique that is usually regarded as a previous step for large scale manufacturing.

Dr Blade deposition, or Blade-Coating, is a solution deposition method widely used within research in the field of organic electronics in general, and specially in organic photovoltaics. In figure X we can see a simplified sketch that depicts the typical process in a schematic way. A droplet with a specific volume of solution is placed within the gap between the blade and the substrate, ideally wetting both the blade and the substrate forming meniscus on both blade sides. Afterwards, the blade is moved forward at a constant speed by a motor, and shear forces modify the liquid meniscus shape behind the blade. The blade motion evenly distributes the liquid along the substrate, with the thickness being directly proportional to meniscus volume, which itself is proportional to blade speed. The drying process is mainly governed by the temperature of the substrate, placed on a regulable heated platform, and air currents around the substrate, which promote evaporation.

The final film thickness depends on several parameters as can be seen in the empirical equation EQUATION where g is the gap distance between the blade and the substrate in nm, c is the concentration of the solid material in the ink in g cm-3 and, ρ is the density of the material in the final film in g cm-3. However, from a practical point of view, cast volume (V) and blade speed (v) usually have a the most significant effect on final film thickness.

Since blade speed is one of the main parameters used to control layer thickness, in our group Dr. Bernhard Dörling modified a commercial blade coater unit (ZUA 2000, Zehntner) by connecting its motor controller to an Arduino, so that the blade coating motor can operate at different speeds and accelerations. In this way we are able to deposit gradient layers with varying thicknesses by changing the speed of the blade during deposition, as can be seen in figure x. All active layer films with a thickness gradient were cast by decelerating the blade from 99 mm/s to 1 mm/s during the deposition across the entire substrate length (75 mm) to provide the widest possible thickness range.

This variable speed approach enables the characterization of material thickness dependent performance in one sample. Such a strategy can be applied to all the solution-processed layers, but in this thesis, it has been only applied to PAL optimization. Most Using this approach, the thickness gradient in the PAL can vary from 200 to 50 nm, see Figure 2.5Final film thickness depends on the specific processing parameters and the choice of donor/acceptor materials. In order to check the reproducibility of accelerated dr Blade deposition, in our group Dr Enrique Pascual prepared three batches of P3HT:O-IDTBR devices with the same processing conditions but on different days. For the range of explored PAL thickness the results are reproducible and lie within 5% of standard deviation .

One of the caveats of typical Dr Blade deposition is that the range of thicknesses is somewhat limited on the higher end, rendering the deposition of several µm thick films a challenge. In this work we have developed a rather simple approach of subsequent layer deposition to achieve the very thick films that can be seen in Chapter . The method relies on the fact that when we perform a Dr Blade deposition on top of an already existing film, if the solution is concentrated enough and the substrate is hot enough the lower film is barely affected while a new film is being deposited on top. In this way we can stack film after film to achieve increased thicknesses of up to 8 times the maximum thickness of a single deposition.

The main drawback of this technique is that each subsequent film has small imperfections that stack up, so after many depositions the film homogeneity can be severely compromised. Another small inconvenience is that any gradient generated by uneven deposition can be exaggerated after subsequent film depositions. The latter can be easily mitigated by rotating the substrate 180 degrees on each deposition. This technique not only prevents strong gradients from forming, but evens out the small gradients that formed during deposition.

A part from these small drawbacks this technique provides robust devices that have good electrical properties and do not exhibit layer separation, thanks to the fact that, being deposited from the same solvent, the newly deposited layer lightly dissolves the already deposited layers forming a seamless bond and good electrical connection.

* + 1. Spin Coating Deposition

Spin coating deposition is a thin film coating technique that produces thin homogeneous films with a high degree of control and reproducibility. This technique relies on the fact that the deposition of a viscous fluid on a horizontal rotating surface produces a uniform liquid layer. If the viscos fluid is composed of a solvent and a solute, when the solvent evaporates the solute is left behind forming an equally uniform solid film.

Common practice dictates that when depositing the liquid, the substrate should either be static or be rotating at a low angular velocity. After the liquid has covered the entire substrate, this is rapidly accelerated to a high angular velocity (spin speed). The adhesive forces at the liquid/substrate interface and the centrifugal forces acting on the rotating liquid result in strong sheering of the liquid which causes a radial flow in which most of the deposited solution is rapidly ejected from the substrate . The combination of this process with the evaporation of the solvent results in a thinner, more concentrated (and more often than not more viscous) liquid film over time. This process continues until we have a practically solid solute film with very little solvent left.

Over the last several decades a great deal of experimental work has been performed trying to deduce empirical correlations between experimental parameters and film thickness. The results from these studies indicate that angular velocity, solution viscosity and solution concentration significantly affect the film thickness, and that the amount of solution initially deposited on the substrate, the rate at which it is deposited, the history of rotational acceleration prior to the final acceleration, and the total spin time have limited or no effects.

The generalized correlation between spin coating parameters and film thickness is a widely observed experimental result and it is therefore generally accepted that their relationship can be described by the following, empirically derived, formula:

Where h is the film thickness, η0 is the viscosity of the deposited solution, ω is the angular velocity, α and β are empirically found exponents and k2 is an empirically calculated constant that is strongly related to the specific polymer/solvent blend.

For a polymer solution the concentration is positively related to the viscosity, meaning that the viscosity increases for higher concentrations (typically not linearly). That means that to make thicker films one can simply increase the concentration of the solution to increase the initial viscosity, which will lead to thicker films at similar speeds. On the other hand, one can also control the thickness more easily by changing the spin coating speed.

* + 1. Thermal Evaporation

The last two layers of our devices were deposited by thermal evaporation.

The process of thermal evaporation is quite self-explanatory, it consists on the evaporation of a coating material by heating it up in a high vacuum. In the case of metals and oxides such as the ones used in this work, for that to happen there needs to be a really high vacuum of around 10-4 Pa. That is because their vapour pressures even at such high temperatures are extremely low due in part because of their strong atomic and molecular bonds.

In order to achieve such levels of high vacuum a combination of a mechanical and a turbomolecular pump are used. This combination is capable of maintaining stable levels of vacuum along the deposition process, and pump out any adsorbed gas that is released during the evaporation. Maintaining a stable vacuum is more important than it might seem at first, because a slight rise in pressure levels can completely impede the evaporation process.

Thermal evaporation was used to subsequently deposit the MoO3 HTL and the Ag BE through a series of custom designed shadow masks to produce a series of electrode distributions. Such distributions are further explained in . The thermal evaporator used was a ECOVap from MBraun attached to a nitrogen glovebox, and the layer thickness was measured using a quartz balance crystal.

* + 1. Encapsulation

In order to prevent oxygen and moisture degradation, most devices were encapsulated by using a UV curable epoxy resin and a glass coverslip that acted as a physical barrier for ambient oxygen and humidity. In this way the life of our devices was extended significantly enabling us to perform longer testing without much degradation. This method, however, could not diminish light degradation.

Ideally the epoxy resin does not interact with the device in any way. However, we have seen that, in general, there is a hindering in device performance because the active layer blend is somewhat soluble in the epoxy resin. Even though it is mostly protected by a silver layer (the back electrode) the active layer will leech into the epoxy in the BE edges, which we suspect is causing a small hindering of our device performance.

* + 1. Thermal Annealing

One of the most important properties of Organic Electronic Devices is the morphology of the organic layers. Since polymers are long chain molecules they can exhibit a wide variety of phases as well as a varying degree of crystallinity. If we combine that with the fact that most of our active layers not only consist of polymers but also have small molecules this leads to a wide variety of states and phases that our active layer can have.

One of the most common approaches to achieve a more favourable blend morphology is to subject the final device to a thermal annealing process. There have been a limited number of studies in this work regarding the effect of the annealing process on the active layer morphology further described in Chapters , but in general most devices underwent a constant temperature annealing on a homogeneous temperature hotplate (SD162, Stuart) inside of the glovebox and after encapsulation.

* 1. Nanoimprinting Soft Lithography

Nanoimprinting lithography is based on the more general process known as lithography, which can be generally described as a process that consists on transferring the superficial features of a mould onto any desired substrate. The process relies on the fact that the substrate can deform to accept the superficial mould features and retain them when the mould is detached from the substrate. This can be achieved in several ways such as heating the substrate up to the melting point, or heating it up to the glass transition and applying pressure or even using a solvent to dissolve the surface of the substrate and waiting for the solvent to evaporate before releasing the mould, among others. Over the last decades, this process has been refined up to the point where nanometric features can be easily obtained with high fidelity and reproducibility. The main advantages of this process are related to its simplicity. On one hand, one single mould can reproduce the same feature a significant amount of times before degrading, which drastically drives the relative cost of the mould down. We can see an analogue situation in plastic injection moulding, where the cost of a mould is on the order of 10.000 € - 100.000 € for small plastic items but the final cost per item can be as low as 1 € including the mould cost. Besides, the mechanical nature of this technique, minimizes the usage of costly and complex optical setups and ultra-high vacuum dependant technologies such as electron beam lithography, further reducing the overall cost. This simplicity and reusability of the process make it really scalable, hence really interesting for industrial applications, because it can be used to cover a wide area with nanostructures seamlessly. Nanoimprinting lithography has been refined up to the point where it can be implemented in roll to roll processes, where a continuous roll of substrate can be nanostructured from start to finish, continuously by rolling the mould on top of the substrate, without any interruption in the process.

Another significant advantage of this process, is that the size limitation is defined by the mould material and not by light diffraction. So, we can easily achieve sub-micron features and even several nanometre features comparable to those of current technologies such as photolithography, but on a much larger scale.

Furthermore, nanoimprinting lithography is a very versatile technique that can be used with a wide range of materials, since they do not need to be sensitive to radiation, or atomically flat or have a specific composition. As long as they have one way to accommodate the surface features and a way of retaining them, we can use a whole variety of characteristics to achieve these two goals. This is a great advantage, because it means that this technique can be implemented along almost any step of a given fabrication process without a significant disruption. Especially due to the fact that it does not add extra specific resists or sacrificial layers, or any need to transfer features through complex etching and resist removal procedures. This ease of implementation does not only make it more appealing for cost related reasons but it ends up being less aggressive on the overall fabrication process, making the final device much less susceptible to fabrication defects.

Because of all these advantages NIL has been gaining popularity over the last decades and has been used not only in the semiconductor industry but on flexible organic electronics, biocompatible materials and other experimental materials, with a variety of applications from solar cells and metamaterials to nanofluidics and nanoelectronics.

* + 1. Thermal nanoimprinting lithography

Being the original NIL technique, Thermal Nanoimprinting Lithography is, within all nanoimprinting lithography variants one of the simplest and easiest to implement. The process consists on heating a thermoplastic substrate above its glass transition temperature to reduce significantly its storage modulus, making plastic deformation the main deformation mechanism. This means that all the mechanical energy imparted on the material will result in a permanent, non-elastic, deformation. In this state we place the nanostructure mould on top of the substrate and depending on its viscosity we will need to apply a certain amount of pressure to force the surface features into the substrate. For certain low viscosity materials, the weight of the mould itself is enough to transfer the features whether for others we need a huge amount of force to transfer them. With the nanostructured mould in close contact with the substrate we lower the temperature so that the substrate becomes rigid again. After that, the mould is carefully removed with a soft continuous motion to prevent damaging the newly created nanostructures. A rapid or discontinuous demoulding lead to inconsistencies and defects on the nanostructures. The negative features of the mould can be immediately seen along the substrate surface after demoulding usually as an iridescent pattern.

This specific NIL methodology, also known as “Hot Embossing”, is particularly useful for structuring plastic materials with glass transitions above room temperature such as many resists, biopolymers or organic polymer and polymer blends such as those used in this work.

* + 1. Solvent Assisted Nanoimprinting Lithography

Solvent assisted nanoimprinting lithography is another variant of NIL that relies on the use of solvents to ensure feature transfer between the mould and the substrate. This process takes advantage of the chemical interactions between a solvent and a substrate to, temporally, reduce its elasticity and change it towards a more plastic phase. It is crucial that the solvent does this in a reversible manner, since we need to make sure the nanostructures remain after demoulding. The process consists on exposing the substrate to a solvent, either by directly dropping solvent onto the substrate, or exposing the substrate to vapours of the solvent, or even applying some amount of solvent into the mould itself. This solvent will weaken the bonds that keep the substrate components together and the latter will transition to a more malleable phase. When on that phase we can lower the nanostructured mould onto the malleable substrate and depending on the substrate’s viscosity the features will be automatically transferred or they will be transferred after applying some amount of pressure. After the substrate has conformed to the mould nanostructures we need to evaporate the solvent so that the substrate regains its original stiffness. For that we can use heat or just rely on ambient temperature and evaporation until most of the solvent goes away. Once the substrate is rigid again, we can slowly and carefully remove the mould to reveal the nanostructured substrate surface once again.

This process works extremely well in combination with solution deposition techniques such as spin coating and dr blade coating since they operate on a viscous liquid regime. This means that immediately after we deposit the layer we can perform this solvent assisted NIL step, without any intermediate step, since the material is still soaked on solvent after deposition.

* + 1. Stamp Fabrication and Architecture

Even though a wide range of materials are used to manufacture NIL moulds, in this work we will focus on moulds based on the curable polymer resist Polydimethylsiloxane (PDMS).

To manufacture our nanostructured moulds, we first need what we call a “Master Stamp” or a “Master” for simplicity. This “Master” usually consists on a high precision nanostructured silicon wafer that is fabricated using electron beam lithography, interference lithography and deep UV lithography. Although it might seem that this master is extremely complicated to manufacture and costly, we need to keep in mind that one master will provide hundreds, if not thousands of moulds if treated with care. Especially with the optimization processes that will be later explained, developed within my group by A. Mihi and his brilliant students.

The first step for master replication is to silanize the silicon nanostructures, meaning that we cover the entire substrate with a molecularly thin layer of perfluorooctyl-trichlorosilane that acts as a release agent so that the replica does not stick to the master. Since we are using silicone-based resins, if we did not add this layer, bonds would start to form between the resin and the silicon wafer during the curing process. That would lead to either nanostructure destruction or directly to the replica being stuck on the master, rendering the master completely useless. In order to deposit the layer, we first subject the master to a vapour of perfluorooctyl-trichlorosilane, and then we rinse it with acetone and heat it up to 150ºC to remove excess silane. This last step is to ensure we do not have too much silane which would smooth the nanostructures on the silicon master, diminishing the reliability of the replication process.

Once our master is silanized we deposit a thin layer of photocurable polymer resist to replicate the negative features of the original master. In our case we use the Ormostamp resist (Microresist technology), a photocurable polymer resist with high young modulus (650MPa) suitable to replicate fine structures with high aspect ratio and excellent mechanical stability. We then place a glass slide on top of the resist layer and gently press to remove all air bubbles. Once the resist fully covers the area of interest it is UV cured for 5 minutes until it hardens. Finally, we heat it up to 160ºC to detach it from the silicon master due to differential thermal expansion of the materials. Once the Ormostamp is released we obtain really stiff mould with the negative pattern of our silicon master that will be itself used as a master to be replicated with other more robust and useful resists such as PDMS. In case we want the same features on our final substrate, we would need to manufacture another Ormostamp master from this one to invert the features.

In this work we have mainly used what we call “Hybrid Moulds”, which have been developed within our group to overcome some of the disadvantages of the different available stiffnesses of PDMS. They are an intermediate solution between soft flexible moulds and hard rigid moulds that combines the two to compensate some of the drawbacks that they tend to exhibit when used separately.

A hybrid mould consists on an extremely thin layer of highly stiff (hard) PDMS, several micrometres thick, and a thick low stiffness (soft) PDMS substrate that serves as the backbone for the entire structure. We use the hard PDMS to replicate the features because we can take advantage of its high stiffness to reproduce the features from the master with a really high resolution. It also provides excellent mechanical stability when transferring the nanostructure into the substrate and its small features do not collapse when applying pressure. And, since it is an extremely thin layer it behaves in a much less brittle manner, being able to more easily conform to slight substrate undulations and imperfections. On the other hand, the soft PDMS backbone provides the necessary flexibility and macroscopic conformability. Having a low stiffness, it easily deforms to accommodate the substrate shape and to provide a conformal contact over a wide area. Furthermore, both being, basically, the same polymer, the adhesion between the soft and the hard layer is excellent, which makes for a really robust and reusable mould.

With this material combination we have been able to faithfully reproduce features with patterns down to 200 nm with holes of 100 nm.

In order to fabricate such a mould, we first prepare the hard PDMS mixture, which consists on vinylmethylsiloxane and hydroxyl siloxane, the polymer precursors, Platinum divinyltetramethyldisiloxane, the catalyst to cure the resin, 1,3,5,7 – tetramethylcyclotetrasilane a reaction modulator, and some toluene to . We take the resulting solution and we cover our silanized Ormostamp master with it making sure no bubbles get trapped. Finally, we cure it at 60ºC for one hour and, once the hard PDMS layer is completely cured we start preparing the solution for the soft PDMS backbone.

To do so we take the PDMS Precursor, Sylgard 184, and we mix it in a ratio 10:1 with the curing agent that comes in the same package. We mix it thoroughly for 5 min and then we leave it degassing for 1h to remove most of the bubbles. The exact degassing time depends both on the shape of the container as well as on the amount of precursor. We pour this degassed mixture with care to not introduce any bubbles over the hard PDMS thin layer until it is completely covered below, at least, a 4mm layer of soft PDMS. We place the PDMS again for degassing to fully eliminate any bubble and then we cure the polymer by heating it to 100°C for another hour. Once the mould is cured we slowly and carefully demould it from the Ormostamp master, being careful not to bend it too much. That is because, even though the majority of the mould is soft PDMS that is highly flexible, the topmost layer is still hard PDMS which can crack under severe bending. After demoulding we have a fully functional mould that can be used many times to nanostructure a variety of substrates.

* + - 1. Stamp Feature Depth

The described fabrication method allows us to obtain moulds that present features with a variety of lattice parameters, mainly defined by those on the silicon master. However, the depth of such features is usually fixed to around 300 nm. In one part of this study, we needed to lower the depth of such features for several reasons that are better explained on Chapter . To achieve these shallower features, my colleague Dr. Molet, developed and optimized a reproducible process that uses Reactive Ion Etching to obtain moulds with variable feature depth.

Reactive Ion Etching (RIE) is an etching technique that is very attractive because it is dry and is able to combine both chemical and physical etching. The working mechanism consists on ionizing a low-pressure gas surrounding a substrate, by applying a high-power radio frequency electromagnetic field to the substrate holding platelet. When gas molecules are ionized they become very reactive and they are attracted towards the substrate, etching material from the surfaces they contact. This technique presents a variety of advantages, such as high etching anisotropy, because the reactive spices are accelerated towards the substrate by an electrical field. That is in contrast to wet etchings where the etching is much more conformal, since reactive spices are controlled by diffusion. Nevertheless, one of the main advantages of this technique is that offers a fairly selective etching if the plasma composition is correctly chosen, so we can use resists to prevent some areas from being etched. The plasma composition is usually tailored to maximize the ration between substrate and resist mask etching. In this way we have a much wider window to control the feature depth.

In our particular case we covered a silicon substrate with a photocurable resin (SU8) and nanostructured with the desired features. After curing we etched the silicon substrate with our nanostructure, for different amounts of time, which resulted on several new silicon master moulds. These masters had the same nanostructure patters, but a variety of feature depths, depending on the amount of time they had been etched. We could then use these shallower features to fabricate new shallow nanostructure moulds to nanostructure our polymer layer blends as we can see in Chapter .

* 1. Device Characterization

In order to assess the performance and fundamental characteristics of our devices, a variety of characterization techniques were used. The main scope of these techniques is being able to understand and guide our scientific developments forwards. They are arbitrarily separated between electrical characterization, where we majoritarily evaluate the device performance and electrical characteristics, and optical characterization, where we evaluate mostly device morphology and its light interaction characteristics.

* + 1. Electrical Characterization

The main techniques used to electrically characterize our devices are JV-Curves, which measure current density of our device at different voltages; External Quantum Efficiency (EQE) curves, which measure the efficiency of our devices at converting incoming photons into electrons; and Light Beam Induced photoCurrent (LBIC) maps, where we can evaluate the local performance of a solar cell at several positions creating an effective efficiency map.

* + - 1. JV Curves

JV curves are amongst the simplest ways to characterize a diode or, by extension, a solar cell. One way to obtain them is to force a voltage between the two leads of our device and measure the passing current. We repeat this process for as many voltage points as we desire and we obtain a graph that represents the current response of that device at all those voltages. For a typical solar cell or photodetector, the curve looks like Figure and, in the central region can be accurately described by the following equation:

Where J is the current density at any voltage point, J0 is the diode constant that varies with the device, q is the charge of the electron, V is the current Voltage between the two diode leads, n is the ideality factor, a measure of how closely does this device behave compared to the ideal diode, k is the Boltzmann constant T is the junction temperature and Jph is the photogenerated current.

For any JV curve there are 6 parameters which provide us with much useful information to assess the performance of our device. These are the Open Circuit Voltage Voc ; the Short Circtuit Current Jsc ; the Fill Factor FF; the Efficiency; the Series Resistance Rs ; and the Shunt Resistance Rsh. Although most of these parameters are related up to a certain degree, they each provide an important piece to fully understand our device performance.

In our lab, the IV curves were measured using a homemade semi-professional demultiplexing setup in combination with a LabView application that were fully developed within the umbrella of this work and are further described in chapter . This demultiplexing setup is connected to a Keithley 2400 Sourcemeter that performs the high precision current and voltage measurements. In order to illuminate our devices, we use a solar simulator (XES-100S, SAN-EI Electric) under AM 1.5G (Air Mass 1.5 Global) and 1000 W · m-2 illumination. Being AAA class, this solar simulator guarantees a homogenous illumination area of 10 cm x 10 cm, which has proven to be extremely useful to characterize our sale up devices, which measure up to 7.5 cm long. The solar simulator was calibrated before each measurement to ensure the reliability of the measurements with a certified silicon solar cell (Oriel, Newport).

* + - 1. EQE Curves

Another, slightly more complex, but maybe more insightful tool to characterize optoelectronic devices is the External Quantum Efficiency curve, or EQE curve. This curve is obtained by illuminating the optoelectronic device with a very narrow range of wavelengths, ideally one single wavelength, and measuring its current output. We then repeat this process changing the illumination wavelength until we cover the entire spectrum of interest. By comparing the number of photons going in and the number of electrons going out we obtain the EQE value, either unitary or in a percentage, at each wavelength. This value gives us an idea of how efficient is that optoelectronic device at converting light into free moving electrons at any given illumination wavelength.

All the EQE measurements were performed on a homemade semi-automated experimental setup with its associated LabView controlling Software, which were fully developed within the umbrella of this work, further described on chapter . This experimental setup was coupled to a Supercontinuum laser light source and a computer-controlled monochromator (LLTF contrast, Fianium) that was further filtered to provide a continuous spectral range. With this setup we are able to illuminate the sample with light ranging from 400 nm to 1100 nm, range which can be further extended into the infrared by changing the monochromator. The current measurements were performed with a Keithley Sourcemeter 2450.

* + - 1. LBIC

Light Beam Induced photoCurrent (LBIC) maps are a really useful tool to assess the local performance of a optoelectronic device since they do not only provide an average response of the overall device but can distinguish which areas are contributing more or less to this average. To obtain such maps the optoelectronic device is illuminated with a really concentrated beam of light, around 50 µm in our case, and, while moving the beam in a scanning pattern over the whole sample, the current is measured at each point. In this way we obtain a photocurrent map of our entire device that shows the areas where we have higher and lower light power conversion efficiencies. This is usually performed either under monochromatic light or white light. However, in this work, we modified the setup and connected it to the Supercontinuum/Monochromator source, so that we could illuminate the sample with any desired wavelength. The results of this modification can be seen on chapter .

LBIC measurements were performed using a semi-professional experimental setup, assembled within our group, mainly using parts bought from Thorlabs. As stated before the illumination source was the Supercontinuum laser light source and a computer-controlled monochromator (LLTF contrast, Fianium), the sample was moved using Thorlabs motors and the current was measured using a Keithley Sourcemeter 2400. The entire setup was entirely controlled using LabView software that was developed within our group.

* + - 1. Time Dependant Measurements

The time dependant measurements that can be seen in chapter X were performed by placing a mechanical chopper in the EQE setup, that temporally occluded the path of the laser. In this way we could easily control both the rate and the wavelength of the illumination without having to construct any other setup. The current measurements were performed with an Oscilloscope.

* + 1. Optical Characterization

In order to characterize the morphology and optical performance of our devices we decided to use a variety of optical characterization methods. These gave us a lot of insight about the quality of our nanostructures, as well as the various absorption spectra that our different active layer materials provided.

* + - 1. Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) is a fast and quite reliable way to obtain the absorption spectra of a sample. This spectroscopic technique differs significantly from the more conventional “dispersive spectroscopy” where the sample is illuminated by one wavelength at a time, and we measure how much light is absorbed at each wavelength over a defined range. On the other hand, in FTIR spectroscopy we shine the sample with light containing multiple wavelengths and we measure how much light is absorbed. Next, we change the wavelength combination of the incoming beam and repeat the measurement. This process is rapidly repeated many times over a short time span and, when finished, a computer takes all the data, which at this stage we call an interferogram, and by applying a Fourier Transform it calculates the absorption of the sample at each wavelength. The various wavelength combinations used in this technique are achieved with a broadband light source, which covers the entire spectrum to be measured, and a Michelson interferometer.

To perform absorption spectra we measured both transmission and reflection spectra of our samples using a Bruker Vertex 70 FTIR spectrophotometer attached to an optical microscope (Bruker Hyperion). The microscope allowed us to accurately position the sample within the measuring spot. The spectra were recorded using a 4x objective with numerical aperture (NA) of 0.1, for both emission and collection, having a spot size of 400 µm2. The reflectance measurements were normalized against silver and gold mirrors, for visible and infrared ranges respectively, and a cleaned glass slide for the transmission measurements.

* + - 1. Integrating Sphere Spectra
      2. Raman Spectra
    1. Topological characterization methods

To study the surface and thickness of our devices we decided to use two of the most commonly used techniques in material sciences, Scanning electron microscopy and Profilometry. These techniques give us insight on the surface topography, the layer thicknesses and the coating conformality of our devices among other information.

* + - 1. Scanning electron microscopy (SEM)

Scanning electron microscopy is a really powerful technique that provides close to nanometric resolution of a sample surface topology. This technique is based on accelerating electrons, collimating them into a beam, and then shooting them into a sample. These accelerated electrons will interact in different ways with the sample depending on the angle between the beam and the sample and its composition. By using different kinds of detectors, we can extract information about these interactions, and construct several images that provide topology and compositional information about the sample.

In this work, SEM has been extensively used to analyse the topology of nanostructures and to assess the conformality of the different layers on our devices. We have used a Quanta FEI 200 FEG-ESEM 53 electronmicroscope. For metal coated, or fairly conductive substrates, we have used the high vacuum mode (10-3 Pa) and voltages ranging from 10 to 15KV. In the case of poorly conductive substrates, such as PDMS, low vacuum conditions with a 60Pa water vapor atmosphere and voltages form 5 to 10KV were used to minimize the aberrations caused by surface charge build-up.

* + - 1. Profilometry

Profilometry is another useful technique that gives us information about the surface topology with high resolution. The main working principle is not that different from a record player, where a needle is gently moved in close contact through a surface and the movement of the needle is amplified with a cantilever. This movement is transduced into an electrical signal and then measured by a computer. This measurement can be directly related to the relative height of the sample along the needle’s path.

In this work we have mainly used profilometry to determine the thickness of our devices’ various layers. To do so we deposited the layers with a gap, or sharply scribed a gap within the layer, where afterwards we will perform the measurement, to obtain the total layer thickness. The equipment used was a KLA Tencor D-500 profilometer. To perform the measurements, the needle, with a diamond in the tip, is placed in contact with the substrate with a specified contact force (in our case 0.03mg), and it slowly scans the sample (in our case 0.1mm/sec) along a specified line. It can measure the scanned features with almost nanometric vertical resolution and submicrometric lateral resolution.

This technique has been extensively used to know how deposition conditions were related to final layer thickness, and to make correlation studies between active layer thickness and the final performance of the optoelectronic devices.