Rapid Convective Deposition at Nanoscale of Active Composite Materials for the Manufacture of Organic Field-Effect Transistors

Deposición convectiva rápida a escala nanométrica de materiales compuestos activos para la fabricación de transistores orgánicos de efecto de campo

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Abstract

Organic field-effect transistors based on composite materials has been manufactured using the rapid convective deposition technique. The manufacturing was carried out under environmental conditions (air, light and humidity). All manufactured transistors show a typical field-effect behavior with features of a p-type semiconductor, and exhibit field-effect mobilities around 10-2 cm2/V.s, fully comparable with transistors manufactured using thermal evaporation of the same active material. The deposition technique demonstrates that devices may be manufactured with high reproducibility and in all cases with a low threshold voltage of approximately 1V. Therefore, it is demonstrated here that rapid convective deposition can be used to manufacture organic field-effect transistors on large surface areas, showing high reproducibility among devices and high stability at environmental conditions.

Keywords: Organic field-effect transistors, Rapid convective deposition, Composite Materials.

Resumen

Transistores orgánicos de efecto de campo basados en un material compuesto han sido fabricados por medio de la técnica de deposición convectiva rápida. La fabricación fue llevada a cabo bajo condiciones ambientales (aire, luz y humedad). En todos los casos, los transistores fabricados muestran un claro comportamiento de efecto de campo con características de semiconductor tipo-p, y exhiben movilidades en el orden de 10^{-2} cm^2/V.s, totalmente comparables con transistores obtenidos por evaporación térmica del mismo material activo. La técnica de deposición demuestra que se pueden obtener dispositivos con alta reproducibilidad y que en todos los casos muestran una baja tensión umbral de alrededor 1 V. Por lo tanto, se demuestra que la deposición convectiva rápida puede ser usada para la fabricación de transistores orgánicos de efecto de campo sobre áreas amplias, con indicadores de reproducibilidad entre dispositivos y alta estabilidad en condiciones ambiente.

Palabras clave: transistores orgánicos de efecto de campo, deposición convectiva rápida, materiales compuestos

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1. Introduction

The development of organic electronics, particularly in the past two decades, has been of vital importance and has produced great impacts in the research community and in the electronic industry. Some of the devices with organic architecture, such as the organic light emitting diodes (OLED), currently shine with great success and at the moment are being manufactured in series. Thus, it is now easy to find in our daily life devices such as TVs or cell phones with OLED-based screens [1, 2].

At present, semiconductors have been adopted in a very broad range of applications such as screens, computers, phones, among others, becoming essential in our daily life, and almost without realizing it.

The core of all organic devices are the organic semiconductors (OS) and these may be used as active material of various devices, from single devices (transistors, diodes, sensors) developed in research labs, up to complex circuits. The discovery of organic semiconductors dates back to the 1940s [3]. With the purpose of comparing with silicon-based traditional electronics, organic electronics shows unique features, such as processing from solutions, mechanical flexibility and even a mixture of ionic and electrical conduction, which makes that organic electronics has captured the interest of many research laboratories around the world.

The OS are characterized by being conjugated molecules or even conjugated polymers. Their structure differs significantly from that of the traditional inorganic semiconductors, since the OS are characterized by weak Van der Waals bonds, while covalent bonds prevail in the inorganic semiconductors, and besides, the π electrons of the OS form the valence and conduction bands. It is very important to highlight that OS, as opposed to inorganic semiconductors, do not form a native oxide layer, thus promoting a clean interface between the materials, because the materials that can interact with the OS vary from metals to biological organisms [4].

The research efforts have focused in the manipulation of the chemical structures of different OS, their degree of ordering in nanometric layers, as well as in understanding and controlling the transport processes that occur in the interfaces [5]. However, with the purpose of being able to develop low-cost devices, it is necessary to process the OS with techniques based on their dissolution, to arrive to what is known as printed electronics.

The polymer semiconductors have good solubility in a wide range of organic solvents, however, the semiconductors with small molecules show problems in their solubility [2].

The operating principle of an organic field-effect transistor (OFET) is based on the application of an electric field that causes the formation of a conductive channel in the interface of the dielectric and the organic semiconductor. The typical and most commonly used configurations are the ones shown in Figure 1, which are known as top contacts and bottom contacts.

(a)   (b)
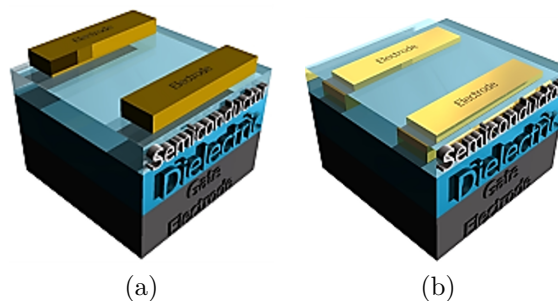
Figure 1. Typical configurations used in practice for OFET: (a) top contacts, (b) bottom contacts

In both cases, the organic semiconductor that is deposited on a dielectric layer is in contact with two metallic electrodes, named source and drain; and the gate electrode is typically placed in the bottom part. Then, the current that flows between the source and the drain (I_{SD}) may be modulated by the voltage applied to the gate electrode (V_G) between the source and the gate, this voltage produces an electric field responsible for the formation of a layer of accumulated charges in the semiconductor/dielectric interface. In addition, depending on the polarity of the voltage applied to the gate (V_G), it is possible to control the nature of the charge carriers that accumulate in the interface, thereby holes for p-type semiconductors and electrons for n-type semiconductors [6].

The OS may be deposited on the surfaces in vapor phase or in solution, the processes depend on the vapor pressure and on the solubility of the semiconductor material. The different deposition methods typically result in different morphologies of the resulting films, as well as they increase the variability in the performance of the manufactured devices. However, during past years, new functionalized OS have emerged in which functional groups have been added that have improved the solubility of the rigid conjugated cores. This has enabled to drastically improve the solubility without losing the inherent electrical properties, neither sacrificing its molecular packing [2, 5].

In this way, a very important factor to consider is manufacturing layers at the nanoscale that enables the deposition of OS, functionalized or not, on substrates that further enable the construction of architectures of transistors. One of the most promising OS that has been found is the dibenzo tetrathiafulvalene (DB-TTF), which for this reason is selected for this study [7–10]. From the point of view of manufacturing processes, the organic thin films have been manufactured with processes at low temperatures, among which stands out the centrifugal coating that is widely used in

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various research labs. The centrifugal coating enables to have control of the thickness of the manufactured films, most of which are homogeneous and without ruptures; however, such processing method cannot be scaled.

The reason why centrifugal coating cannot be used on large processing surfaces, is the need to use great amounts of solution, which makes centrifugal coating not feasible for application in manufacturing field-effect organic transistors on large areas. For this reason, the development of new manufacturing techniques that reduce the waste of OS solution, which is typically expensive, and likewise enable the deposition of thin layers of organic materials on substrates, is a research topic of continuing interest. Among the unconventional methods, convective self-assembly is widely used for the deposition of coatings on large areas in a small time-scale.

One way to use convective self-assembly, also known as rapid convective deposition, is to use a bar coater such as the one shown in Figure 2, to disperse the OS solution on the desired substrate and cause the self-assembly of the selected molecules on the substrate surface [11, 12].
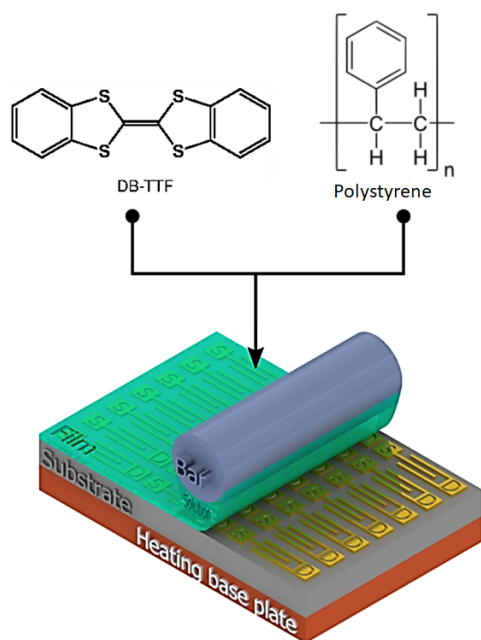
Figure 2. Typical graphical scheme of the rapid convective deposition of insulating polymers, semiconductors and/or their mixtures

Despite the promising features of small-molecule semiconductors, manufacturing homogeneous films is complicated, however, in order to overcome such difficulty, the most promising path to this day is creating composite materials, in typical mixtures of a polymeric material as matrix and the organic semiconductor as active material. The application of composite materials has significantly facilitated the processability of organic semiconductors and, besides, has improved the crystallinity of the films obtained, as well as the stability of the films when facing environmental conditions [2], [13].

2. Materials and methods

The silicon substrates were acquired from Fraunhofer IPMS and have an n-type doping, and besides a silicon dioxide layer with a thickness of 230 nm. The gold electrodes have a height of 30 nm, and were deposited on a layer of indium thin oxide (ITO) with a thickness of 10 nm; the ITO layer acts as a bonding layer. The dibenzo tetrathiafulvalene (DB-TTF) thermally evaporated films were prepared at a low evaporation velocity of about 0.5 $\mathring{A}$/s on Si/SiO$_2$ substrates with ITO/Au contacts, the thickness of the films was determined as 110 nm by means of an AFM analysis. The thin films of the active composite material were produced by adapting a commercial coater to the requirements of the experiment. DB-TTF and polystyrene for GPC Mw 10000 (PS10k) were acquired from Sigma-Aldrich and used without any subsequent purification.

In this study, polystyrene for GPC Mw 10000 (PS10k) is used together with the DB-TTF organic semiconductor. Two-percent solutions in chlorobenzene anhydrous of both the insulating polymer and the semiconductor were prepared. Likewise, using a 1:3 proportion, semiconductor solution *versus* insulating polymer solution were prepared in separate vials such that, in all cases, the mixtures do not exceed a volume of 500 μl. Heavily doped n-type silicon, and with a thickness of 200 nm of native silicon oxide (dielectric) were used as substrate and gate electrode, respectively. The substrates employed for coatings were acquired from Si-mat, in which the electrodes were designed using photolithography; such electrodes consist of a layer of 4 nm of Cr (bonding layer) and 40 nm of Au, both metals deposited by thermal evaporation. Prior to the coating process, the substrates are cleaned with acetone and isopropanol, both HPLC grade solvents. At last, the substrates are dried under a nitrogen stream.

Prior to the experiments, the coating equipment was preheated to 105 ºC. The substrates with prefabricated electrodes were previously cleaned. The substrates have to be arranged carefully in the coating machine; a small amount of solution, around 30 µl, is used to make the coating. The solution is deposited, and the meniscus dragged at a constant speed of 10 mm/s; during the process of rapid convective deposition, the substrate is always maintained static and at 105 ºC. Immediately after the coating process, the coated substrates are carefully removed from the equipment and placed in Petri boxes, and then subjected to a stage of vacuum curing (Pabs = 7 kPa) and at 60 ºC for a period of at least 2 h, with the purpose of

removing any remain of solvent. After the curing, the transistor characteristics are measured at environmental temperature and in darkness.

The optical microscopy photographs were obtained using an Olympus BX51 microscope equipped with polarizer and analyzer. The study of the cross section of the films was performed using a FIB-SEM Neon40 Crossbeam™ workstation from Carl Zeiss. The topography of the surface of the films deposited was studied thanks to the use of an SPM 5500LS from Agilent Technologies; the processing of the topography data was carried out using the software Gwyddion. The measurements of x-rays diffraction were taken with a diffractometer from Rigaku, equipped with a rotating anode.

The electrical measurements were carried out with a Keithley 2612AB with an interface programmed in MATLAB®, typically in a Süss test station with pointed probes and in darkness.

3. Results and discussion

Figure 3 shows an image of a DB-TTF:PS10k film obtained by optical microscopy in a mixture ratio 1:3 deposited in an architecture of bottom contacts; it may be observed a film well-formed and free of ruptures on all the area photographed. It is important to note that even though it is an architecture of bottom contacts, the deposited film is homogeneous.

Figure 3. Photograph obtained by optical microscopy of a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio; the angle between the polarizer and the analyzer is 0°

Since crystallinity is one of the main characteristics of the small and semiconductor DB-TTF molecule, Figure 4 shows the image obtained by polarized optical microscopy in which it is shown, and it may be clearly inferred the formed crystalline structures (spherulites); these are embedded in the film deposited by rapid convective deposition, and crystalline networks form together with paths, also crystalline, for transportation of holes between the electrodes.

When composite materials are used, parameters such as the polymer nature, the relationship between

the polymer and the active material, in combination with the mechanical parameters of the deposition process, turn the systems complex. In the field of organic semiconductors, all the phases of the OS are obtained even though they do not reach thermodynamic equilibrium, thus the phases obtained must modify the extrinsic parameters. These crystalline phases observed will be named according to the kinetic polymorphs. Even though the DB-TTF shows complex polymorphism it is obtained a crystallin kinetic phase, and as shown in Figure 4 it is observed the gamma kinetic phase that has plate-like shape, which are easily observable along the electrodes of the device analyzed. Since the deposition technique promotes a rapid crystallization, it tends to form the most favorable kinetic crystalline phase [14–16].

Figures 5 and 6 show the frames obtained by FIB-SEM, technique widely used for the study of cross sections of devices and which, similarly, enables the study of the interfaces between materials, thanks to a focused beam of Ga+ ions that is used for obtaining the image and even used for nanostructuring. With the purpose of calibrating and obtaining a clean cut, 100 nm of Pt are evaporated on the sample, as observed in Figure 5, together with the hole made.


Figure 4. Photograph obtained by optical microscopy of a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio; the angle between the polarizer and the analyzer is 90°
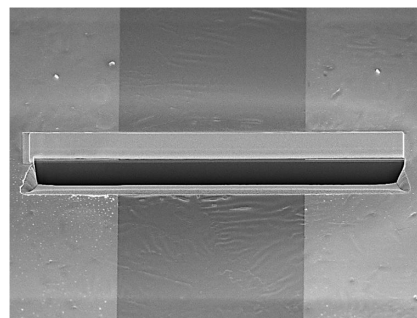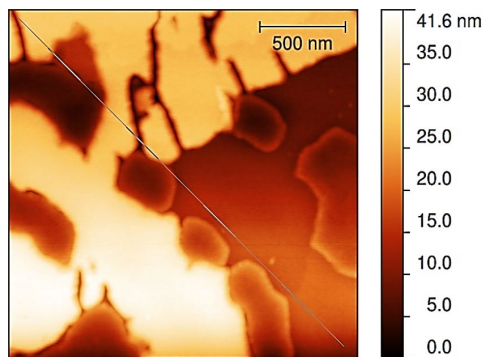

Figure 5. Image obtained by FIB-SEM of a typical device manufactured from a film of the DB-TTF and PS10k composite material in a 1:3 ratio. Mag = 6.89 kX, EHT = 5.00 kV, FIB Probe = 30 kV:10 pA, FIB Imaging = SEM, vacuum = 1.72e-6 mbar

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On the other hand, Figure 6 shows the cross section of the sample, after the internal rotation of the FIB-SEM; in addition, note the Pt, SiO_x, Si, and that thanks to this technique it is possible to measure a thickness of 52.33 nm of the film deposited on the substrate with bottom contacts.
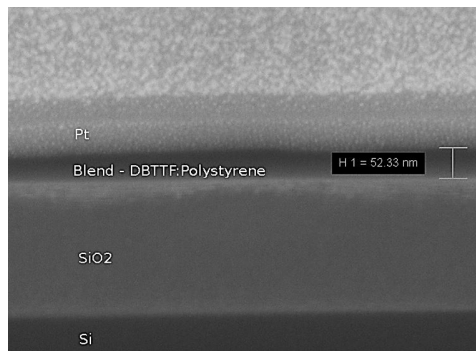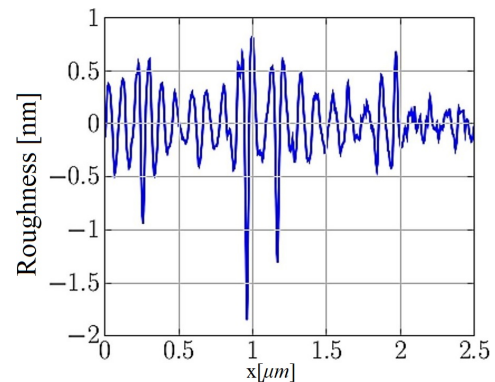

Figure 6. Image obtained by FIB-SEM of the cross section of a typical device manufactured from a film of the DB-TTF and PS10k composite material in a 1:3 ratio. Mag = 6.89 kX, EHT = 5.00 kV, FIB Probe = 30 kV:10 pA, FIB Imaging = SEM, vacuum = 1.72e-6 mbar.

Figure 7 was obtained by AFM, in which it is shown structures that are non-periodic and non-structured in a particular region of the deposited film. In addition, it is observed a variability in is topography with a maximum of 41.6 nm.


Figure 7. Image obtained by AFM of a typical device manufactured from a film of the DB-TTF and PS10k composite material in a 1:3 ratio

Figure 8 shows the roughness as a function of the position, obtained along the diagonal profile shown in Figure 7. Thus, the deposited film shows a relatively low roughness with a maximum of 2.0 nm at the approximate position of positive 1 μm in the x-axis. The smooth surface indicates that it is possible to have a clean interface with the potential of being used in the future for other applications, such as organic field-effect transistors with electrolytic gate electrodes and even in the development of sensors [17].

Figure 8. Roughness (nm) as a function of the position in the x-axis [μm] extracted from the diagonal profile shown in Figure 7, for a typical device manufactured from a film of the DB-TTF and PS10k composite material in a 1:3 ratio.

Due to the crystallin nature of the DB-TTF active material, the study by x-rays diffraction is essential, since knowledge of the crystallin structure is key to be able to determine and understand the electrical characteristics of a material. Figure 9 shows the diffractogram of the film, obtained both by rapid convective deposition and by thermal evaporation of the pure DB-TTF material, with the purpose of verifying the formation of crystallin networks, and ruling out that an amorphous film is obtained.
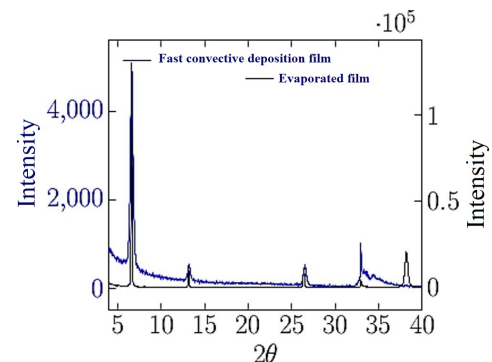

Figure 9. X-rays diffractogram for a thermally evaporated film of DB-TTF, and for a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio

Then Figure 9 shows the coincidences at the peaks, which are observed at 6.72°, 13.48°, 20.22°, 27.08° and 41.22°. Thus, the formation of the gamma crystallin phase can be appointed as reported by Brillante *et al.* [18], however the crystallin structure of the gamma phase has not been resolved yet. Notably, the unit cell of the gamma phase contains two DB-TTF molecules, although the increment of volume per molecule in this phase *versus* the alpha-polymorph indicates that the gamma-polymorph is a less stable phase [14].

Figures 10 and 11 show the output and transfer characteristics for a typical device based on the DB-TTF:PS10k (1:3) active composite material. The figure

of merit in the output characteristic shown in Figure 10 exhibits characteristics that are reproducible between devices and which show a quasi-ideal behavior in its linear and saturation response.
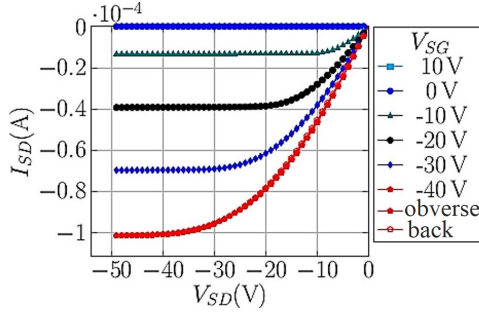
Figure 10. Output characteristic of the OFET of a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio. Device L = 75 um, W = 75000 um
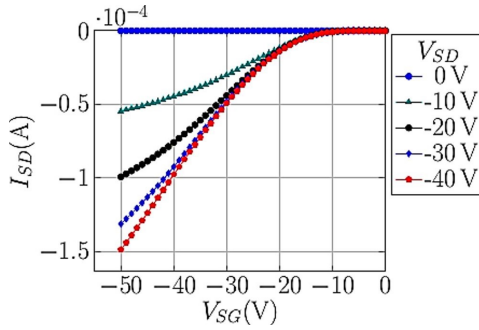
Figure 11. Transfer characteristic of a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio. Device L = 75 um, W = 75000 um

Then, the device analyzed electrically shows typical characteristics of field effect, observed in the output characteristics of Figure 10, in which it is clear that the voltage applied at the gate modulates the current measured between the source and drain electrodes; similarly, it is observed how the source-drain current tends to saturate as it gets closer to the voltage applied to the gate electrode. It is also important to mention the minimum hysteresis formed during the current-voltage mapping in the positive direction (obverse sweeping) and in the opposite direction (reverse sweeping). A distinctive characteristic of the existence of traps if the hysteresis of the device, where there is a significant difference between the obverse and reverse sweepings, this may occur when charges are trapped and then released, respectively, which may happen altogether due very polar dielectrics [5].

Table 1 summarizes values of mobility and threshold voltage extracted at the saturation regime for various lengths of the channel; despite the significant difference in the length of the channel, the mobility remains between the same values, suggesting the manufacturing

homogeneity between different devices selected. The threshold voltage indicates that transistors need very low voltage to turn on, and the transfer characteristic shown in Figure 11 suggests that there are at least four orders of magnitude between the off and on states in the manufactured organic field effect transistors.

Since the OFETs are considered and viewed as elements in technological applications, the low-cost manufacturing and the stability at environmental conditions are crucial factors to be considered [19]. In this way, and with the purpose of testing the stability along time under controlled conditions, a transistor was subjected to various measurements inside an incubator (T = 25 °C). Thereby, Figure 12 shows the logarithmic transfer characteristic measured at discrete times; such plot suggests that the stability has been significantly improved, since thermally evaporated DB-TTF films are extremely sensitive to environmental conditions [12], [20], [7].

Table 1. Summary of mobility and threshold voltage data as a function of the length of the transistor channel

Length of channel $[\mu m]$	Movility $[\mathrm{cm^2/V.s}]$	Threshold voltage [V]
25	9,75e–3	-1,81
50	1,42e–2	0,38
75	1,02e–2	1,18
10	1,27e–2	-1,11

All devices are manufactured from a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio.
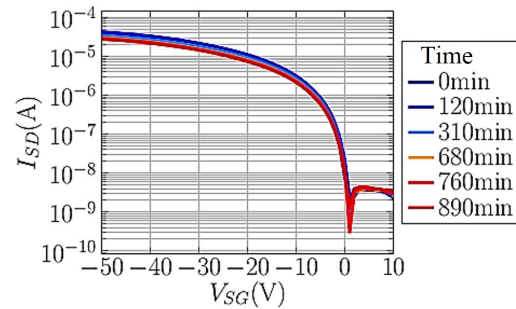
Figure 12. Logarithmic transfer characteristic for a device manufactured from a typical film of the DB-TTF and PS10k composite material in a 1:3 ratio

4. Conclusions

Organic field effect transistors have been successfully manufactured from a composite material based on a TTF as active material, using a methodology based in the rapid convective deposition from a dissolution of the composite material. Polystyrene was chosen

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as bonding matrix to achieve environmental stability. All the devices were manufactured and measured at environmental conditions of light and humidity, thus exhibiting a drastic improvement in their stability compared with the manufactured by thermal evaporation. The mobilities of the devices manufactured oscillate in 10^{-2} cm^2/V.s con un $\pm$ 10^{-3} cm^2/V.s.s, and such mobility is perfectly comparable with the devices manufactured by thermal evaporation from pure DB-TTF. Therefore, it is demonstrated that the manufacturing technique applied to a composite material provides a promising path for manufacturing devices of low cost and high stability.

Acknowledgements

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