

Low cost instrumentation for spin-coating deposition of thin films in an undergraduate laboratory



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Abstract

We describe the implementation of an inexpensive spin-coating system to deposit thin films of materials dissolved in a volatile solvent. The system can be easily built with interdisciplinary knowledge of mechanics, fluid mechanics and electronics at undergraduate level. The system allows the deposition of thin films of up to 5cm^2 in area and is constructed from a commercial DVD player drive motor and an electronic circuit designed to control the spinning speed and spinning time up to 10,000rpm and 60seg, respectively. In our design, both variables can be adjusted manually through an array of micro push button switches and a varistor. To illustrate the use of our spin-coating system, were prepared films of MDMO-PPV conjugated polymer from solutions in chlorobenzene and tetrahydrofuran and their optical absorption and photoluminescence properties are analyzed and discussed.

Keywords: Instrumentation, thin films, conjugated polymers, spin coating.

Resumen

Se describe la implementación de un sistema de bajo costo spin-coating para depositar películas delgadas de materiales disueltos en un solvente volátil. El sistema puede ser fácilmente construido con el conocimiento interdisciplinario de la mecánica, mecánica de fluidos y la electrónica a nivel de pregrado. El sistema permite la deposición de capas delgadas de hasta 5cm^2 de área y es construido de un motor comercial de DVD y un circuito electrónico diseñado para controlar la velocidad de giro y tiempo de giro de hasta 10.000rpm y 60seg, respectivamente. En nuestro diseño, ambas variables se pueden ajustar manualmente a través de un arreglo de micro interruptores y un varistor. Para ilustrar el uso de nuestro sistema de spin-coating, fueron preparadas películas de MDMO-PPV conjugando polímeros a partir de soluciones en clorobenceno y tetrahidrofurano y sus propiedades de absorción óptica y propiedades fotoluminiscencia son analizadas y discutidas.

Palabras clave: Instrumentación, películas delgadas, polímeros conjugados, recubrimiento por rotación.

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I. INTRODUCTION

One of the objectives of Physics and Chemistry oriented courses at undergraduate level is the study and understanding of the properties of various substances. An added goal is to develop abilities to manipulate these substances for useful applications or even to encourage the development of new materials with unique properties. Conjugated polymers are materials prone to easy manipulation. By controlled chemical doping they can display a wide range of electrical conduction properties that can be varied from insulating or semiconducting behavior or reach metallic characteristics close to that of copper. In recent decades, these polymers have been studied with the purpose of manufacturing electronic devices such as light-emitting diodes, solar cells, transistors, etc. Manufacturing techniques of these devices are relatively simple but sometimes require expensive equipment. It is increasingly

common to find undergraduate laboratory courses that address the study of these materials. To tackle the problem of high instrumental costs, in this work we propose the development of apparatus of easy implementation in an undergraduate laboratory for the preparation of conjugated polymer films using recycled electronic components.

Deposition of thin films by spin-coating is a very simple and widely used technique [1, 2, 3] to prepare films of uniform thickness of non-volatile materials initially found in liquid solution dissolved in a volatile solvent. The technique is particularly appropriate to obtain thin films of conjugated polymers [4] from their solutions in organic solvents or in liquids that contain them in suspension [5, 6]. Typical example of such kind of polymers is poly-phenylene vinylene (PPV) and its derivatives, and typical organic solvents are chlorobenzene $\text{C}_6\text{H}_5\text{Cl}$ and tetrahydrofuran $(\text{CH}_2)_4\text{O}$.

Conjugated polymers are characterized by sp^2 hybridization of carbon atoms that form the backbone of the polymer. For each carbon atom, a delocalized π electron is almost free to move along the polymeric chain. Technologically, these polymeric materials are important because by chemical doping, their electrical properties can be tuned from semiconductor to metallic behavior. The use of conjugated polymers in devices such as light emitting diodes, photovoltaic cells, photodetectors, transistors, etc. is already a commercial reality. Although devices built with these polymers still have low levels of efficiency compared with those based on inorganic semiconductors such as Si, Ge, GaAs, CdTe, etc., they have the advantage of lower production costs and unmatched elastic properties [7]. For the construction of single-layer or multilayer small area devices based on conjugated polymers the spin-coating deposition is a simple technique that can be easily implemented at low cost. Spin coating film deposition is a four step process, as illustrated in Fig. 1:

- i) Solution pouring: the material dissolved in a volatile solvent is poured by dripping on the center of a rotating substrate initially at rest;
- ii) ‘Spin-up’: While the substrate spins, the liquid flows radially driven by the centrifugal force;
- iii) ‘Spin-off’: liquid that reaches the substrate edge is expelled in drops; as the film thins down, the rate of elimination of excess fluid decreases because the thinner the film, the higher its resistance to flow, and because viscosity increases as solvent evaporates;
- iv) Evaporation: Though evaporation occurs at all times from the beginning of the spin-coating process, when spin-off is slow and for less volatile solvents, the evaporation becomes the main mechanism of solvent removal and thinning of the film.

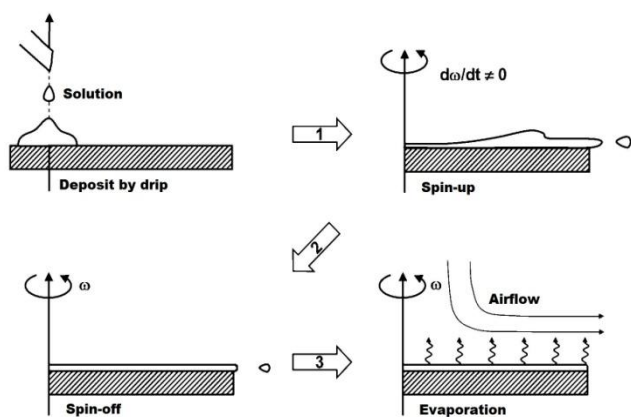


FIGURE 1. Stages of thin film deposition by the spin-coating method.

Deposition by spin coating produces films with thickness that become uniform during spin-off if the viscosity is homogeneous everywhere on the substrate and is independent of the sliding force. The uniformity of the film thickness results from the balance of two opposite main forces: the centrifugal and the viscous forces. During spin-

up, the centrifugal force overcomes the gravitational force and the rapid thinning of the film exceeds all non centrifugal inertial forces. When the film becomes very thin and viscous, the thickness continues to decrease but now controlled by evaporation. Rotation of the substrate with constant speed causes uniform evaporation of the solvent and, consequently, thickness of the film also becomes uniform.

In this work we describe a system for thin film deposition by spin coating that can be constructed from electronic spare parts readily available as surplus material in any academic institution today. Students in an undergraduate laboratory course involved in its design and construction could benefit from the application of physical concepts in mechanics, fluid mechanics and electronics. In addition, this system may contribute to reduction of costs in the development and production of organic optoelectronic devices that use this deposition technique, either for educational or research purposes. Currently, the cost of a commercial spin-coating system fluctuates between 3,000 to 5,000 USD, while our system was built at a cost that does not exceed 150 USD.

II. EXPERIMENTAL

A. Design of the spin-coating deposition system

In a first design we utilized the 11,000rpm AC motor of a commercial Black & Decker grinder, controlling the spinning speed by varying the voltage supply from 0 to 110V using a variable transformer, and interphasing a relay switch to a personal computer to control the time of spinning. This design, however, was quickly discarded due to inaccurate control of the speed. In substitution, we chose a commercial DVD player drive motor that is easy to obtain and has the advantage that works with direct current, so that control of the spinning speed can be done in a precise way with an appropriate electronic circuit. The torque of a DVD motor is enough and adequate for the light weight substrates employed and, in addition, their spinning speed is within the range needed for our purposes (500 to 8,000rpm). In our case we used an 11,000rpm DVD drive motor (MDN-4RB3LY AS). The dependence of spinning speed against voltage of this motor was characterized for a constant current of 800mA. Voltage variation is accomplished with a potentiometer in such a way that 10% of its full range corresponds to 1,000rpm and 100% to 10,000rpm.

In conjunction with this motor, an integrated circuit L293DD-SO (12+4+4) of SGS-Thomson Microelectronics was used. This device is a monolithic integrated high voltage, high current four channel driver designed to accept standard DTL or TTL logic levels and drive inductive loads (such as relay solenoids, DC and stepping motors) and switching power transistors. For programming the speed and time of spinning we used a programmable integrated circuit PIC16LF876A (abbreviated PIC) of Microchip Technology, coupled with a DATA BUS LCD to view the

selected parameters. The PIC was programmed to interpret the entered parameters using a so called “training card”, which is actually a card that interfaces with a PC where a logical program can be created in special languages such as MicroCode Studio, MpLap and TexasC. In a more sophisticated design, the PIC could be programmed to apply changes in velocity at constant angular acceleration during specified time intervals. The diagram of the circuit (operating at 6V and 800mA) for the control the DVD motor is shown in Fig. 2.

The circuit and the motor were mounted inside a box of 20x16x8cm with the axis of the motor passing through one of the walls. On the outside, a convenient arrangement of two microswitch push buttons and potentiometer knob was chosen for programming speed and time of spinning. A third microswitch functions as the start button. To set different values for these parameters, the corresponding push button is actuated while simultaneously turning the knob of the potentiometer and monitoring the numeric value with the LCD display. Substrates are placed on top of a flat disk fixed to the motor axis. The plane of the disk should be perfectly perpendicular to the spinning axis to avoid rocking of the substrate during spinning.

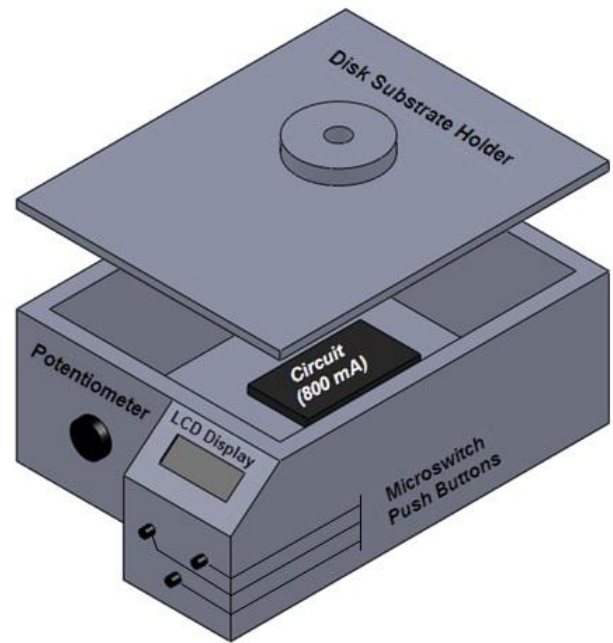


FIGURE 3. Appearance of the spin coating system.

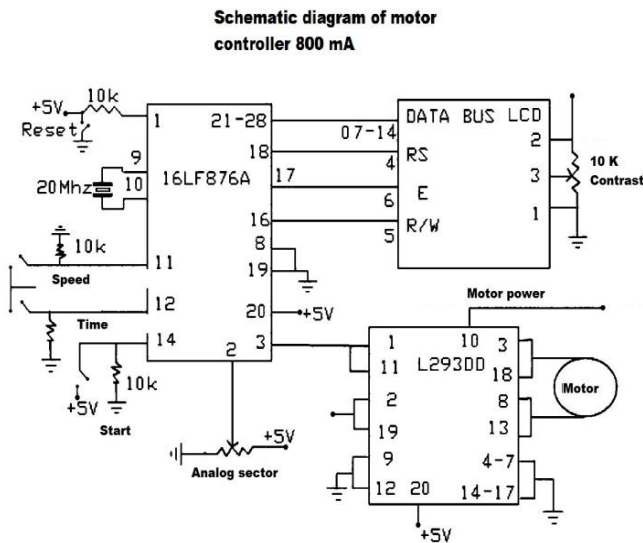


FIGURE 2. Diagram of the electric circuit designed for the control of the DVD drive motor employed in the design of the spin-coating system developed in this work.

The substrate can be attached to the supporting disk using a small piece of double face adhesive tape. To avoid sprinkling of the solution and isolate film deposition from undesired air currents, a covered Petri dish was adapted to enclose the spinning substrates. The final appearance of our system is shown in Fig. 3.

B. Test of the system and sample preparation

After performing several tests of the device, initial conditions that can be recommended for a good film deposition are the following:

- It must be assured that the plane of the disk that supports the substrates is perfectly leveled with the horizontal;
- The solution to be deposited should wet the substrate. If this does not happen, the solution will be thrown away from the substrate by centrifugal force without leaving any trace of material on the substrate. The flatness and/or roughness of the substrate are also a parameter that could affect the deposit;
- The solution that contains the material to be deposited should be uniform and homogeneous, free of lumps and air bubbles. The substrate must be clean and free of dust particles;
- There is an optimal relationship between spinning speed and concentration of the solution so that viscosity does not become an impediment to the flow of the solution on the substrate during spinning. It is not possible to establish a simple rule to determine these optimal conditions because there is a complex interplay between the material to be deposited, the substrate, the volatility of the solvent, spinning acceleration and speed, and even with turbulence of the surrounding air and conditions of atmospheric humidity.

With the device built, films of the conjugated polymer MDMO-PPV [poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] were prepared with material obtained from Sigma-Aldrich (CAS Number 177716-59-5, average molecular weight 23,000), using chlorobenzene (CB) and tetrahydrofuran (THF) as solvents. Substrates were fused quartz plates with 12.5 x 12.5mm² area and 1mm of thickness. Solutions were prepared by dissolving 8mg of polymer powder in 1ml of each solvent and homogenized for 10min in ultrasonic bath. Few drops of the

solution are deposited on the substrate using a syringe conditioned with a filter (Millex Millipore, pore 0.45 μ m, diameter 13mm) to eliminate remaining lumps of undissolved polymer powder. Several tests were conducted at different spinning times and speeds; best results were obtained for 30 seconds and 3,000rpm. Samples prepared with these conditions were characterized by optical absorption using a spectrophotometer (Perkin-Elmer, Lambda 35) and by photoluminescence using a spectrofluorometer (Horiba-Jobin-Yvon, Nanolog with detection extended to UV-VIS).

Illustration of some unsuccessful attempts of deposition is shown in Fig. 4. In (a), the resulting film ended up with air bubbles and pin-holes. This result can be avoided if bubbles are carefully removed before the solution is dispensed on the substrate. In (b), full coverage of the substrate was not completed because the amount of dispensed solution was insufficient, and in (c), the resulting film shows a spiral pattern of uneven thickness. This last effect was caused by the combination of the following factors: (i) too high viscosity (concentration) of the solution and/or rate of evaporation; (ii) solution drops were dispensed out of the spinning center, and (iii) spinning speed and acceleration were too large.

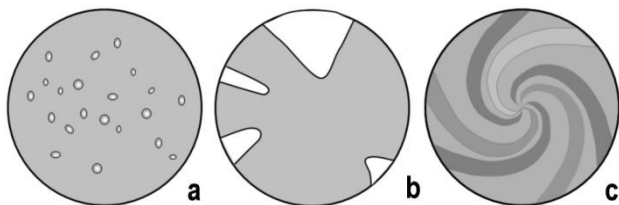


FIGURE 4. Undesirable results found in film preparation trials by spin-coating the polymer MDMO-PPV using the instrumentation developed in this work: (a) film with air bubbles and pin-holes; (b) film with incomplete substrate coverage; (c) film of uneven thickness in a spiral pattern.

III. RESULTS AND DISCUSSION

As example of application of our device, in Fig. 5 we present the optical absorption (OA) and photoluminescence (PL) spectra of films of the conjugated polymer MDMO-PPV on quartz substrates prepared from solutions in chlorobenzene (CB) and tetrahydrofuran (THF) under conditions described previously. Proof that our spin coating system is competitive with commercial ones is the quality of the prepared MDMO-PPV polymer films. The OA and PL spectra of our films are in good agreement with those published by other authors [10, 11].

We will denote as CB the samples prepared with chlorobenzene and THF those prepared with tetrahydrofuran. It can be noticed that both spectra OA and PL for sample CB (thick full lines) are found slightly displaced towards lower energies (redshifted) compared with the spectra for sample THF (dashed lines). Peak maxima for OA spectra are located at 2.13 and 2.15eV for CB and THF respectively, while those for PL are at 2.45

and 2.50eV referred in the same respective order. The red shift in CB samples respect to THF samples is explained by a difference in effective length of conjugation of the polymer chains in the films due to differences in the interaction with solvent molecules. In Fig. 5 the molecular structures of the MDMO-PPV polymer and of the solvents CB and THF are also illustrated. Due to the different molecular symmetries of CB and THF molecules, their interaction with MDMO-PPV chains is dissimilar. The

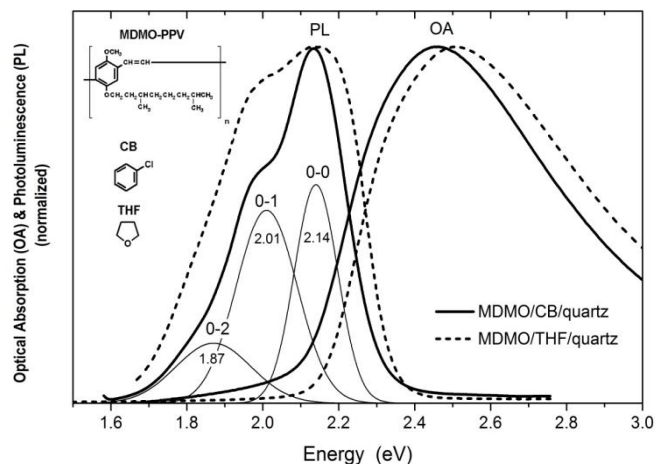


FIGURE 5. Optical absorption (OA) and photoluminescence (PL) normalized spectra of MDMO-PPV polymer thin films on fused quartz substrates prepared with the instrumentation developed in this work. Spectra of samples prepared from the solution in chlorobenzene (CB) are drawn with full thick line; those prepared with tetrahydrofuran (THF) are drawn with dashed line. Line shape analysis of PL signal with three Gaussians (thin full lines) for the CB sample. Molecular structures of the polymer MDMO-PPV and of the solvents CB and THF are also shown.

polymer chains originally in solution are folded and curled in a different way when the solvent is CB or THF. This morphological state of the chains is, to a large extent, inherited in to the film when the solvent is evaporated. The greater the folding and curling of polymer chains, the lesser their conjugation length is. Studies carried out in the polymer MEH-PPV (structurally similar to MDMO-PPV), indicate that as the conjugation length increases, optical absorption is increasingly red shifted [12]. This also explains PL red shift, since it has been found likewise that the energy of excitation is transferred to chains of larger conjugation length before luminescent emission is produced [12]. Light dispersion experiments also show that effective size of MEH-PPV polymer chains in solution is double when dissolved in CB than in THF [12]. We may conclude from the results displayed in Fig. 5 that what is observed in MEH-PPV can be extended to the case of MDMO-PPV polymer, that is, conjugation length of MDMO-PPV in CB is larger than in THF.

Another notorious characteristic in spectra of Fig. 5 is that while absorption curves are very similar in shape, those of PL differ in the size of the shoulder around 2eV. Gaussian line shape analysis of PL spectra reveals three components in positions around 2.14, 2.01 and 1.87eV

(shown only for sample CB in Fig. 5 with thin lines), which are approximately equidistant in energy by 0.13 eV. This is evidence of vibronic (vibrational + electronic) structure in the luminescent emission, that is to say, the electronic transitions that originate the emission occur between electronic states which are found in different vibrational states as seen in Fig. 6. The separation of 0.13eV in energy between the gaussian components corresponds very well with the energy of C–C stretching vibration which is around 1000cm^{-1} . As schematically illustrated in Fig. 6, the component of 2.14eV is assigned to the emission between 0–0 vibrational states (zero-phonon line) and those of 2.01 and 1.87eV are ‘phonon replicas’ that correspond to emission bands involving 0–1 and 0–2 vibronic transitions, respectively. The designation of 0, 1 and 2 vibrational states corresponds to values of the quantum number for a harmonic oscillator, as illustrated in Fig. 6. The difference observed in the shape of the PL bands in Fig. 5 is due to the presence of an additional emission occurring in sample THF in the 1.9–2.0eV range which overlap with the phonon replicas described above. Studies carried out in the polymer MEH-PPV report the appearance of an extra emission around 1.9eV due to an increased interaction between polymer chains (inter-chain interaction) when aggregates are formed as the concentration of the polymer in solution is increased [12, 13]. Extrapolating these results to the case of MDMO-PPV, we may interpret that the emission of aggregates for this polymer is also located in the spectral region around the 0–1 and 0–2 phonon replicas and that its contribution is more important in the THF sample as manifested by the larger shoulder in the PL signal of this sample in Fig. 5. This interpretation is consistent with the previous discussion in which we concluded that polymer chain folding and curling is greater in solution with THF, a morphology that promotes not only stronger inter-chain interactions but also may increase chain self-interactions (intra-chain interactions).

As it can be seen from the above discussions, the form in which the polymer chains remain intertwined and interacting in the final film depends on the type of solvent employed, as is well documented in the literature [13, 14, 15]. The final state of polymer chains in the film not only depends on the state they had in solution, but also on how fast the solvent evaporates during the process of deposition, as well as on how fast the substrate spins. It is known for example, that the rate of evaporation of THF without solute depends on spinning speed and is near 10 times faster than for CB [16].

As we observe in our samples, inter-chain interactions of MDMO-PPV are greater when prepared from THF solution than from CB solution. For the same spinning speed of the substrate, the slowest evaporation rate of CB gives rise to a better chain ordering during spinning because the polymer stays longer in liquid solution. The faster evaporation of THF quickly increases viscosity of the solution which might end up in a non uniform film thickness as observed in the tests of our spin-coating system.

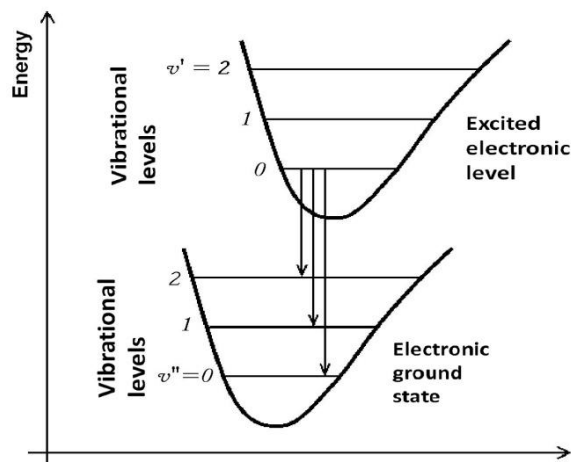


FIGURE 6. Schematic diagram showing the electronic transitions responsible for the observed vibrational structure in the spectrum of fluorescence of the samples prepared with instrumentation developed in this work.

Our spin coating system has been used for general applications in undergraduate electronics laboratories (UPIITA-IPN) to deposit epoxy resin films over small printed circuit phenolic plates for electrical insulation. As part of advanced undergraduate courses in semiconductor devices (ESFM-IPN and UPIITA-IPN), our spin coating system has also been used to illustrate the architecture and fabrication of flexible light emitting diodes and photovoltaic cells based on conjugated polymers such as MDMO-PPV using ITO-covered PET substrates.

Usually, commercial spin coating systems are sold in basic configurations. To take full advantage of the device capabilities, however, accessories must be added at an extra cost. Our device can be easily upgraded at a much reduced expense to include features of the most sophisticated commercial models. Senior undergraduate students in UPIITA-IPN are presently participating in the redesign and construction of an automated spin coating system based on the original design presented in this work. Their participation has been very enthusiastic.

IV. CONCLUSIONS

Instrumentation for deposition of thin films by the spin-coating method is simple and can be built at low cost using a DVD drive motor controlled by an appropriate design of integrated circuits easily obtained in the electronic market. We describe a design of a spin-coating system with a cost nearly 20 times cheaper than that of a commercial system. Films of the conjugated polymer MDMO-PPV prepared with our device show absorption and photoluminescence properties that are in agreement with results reported in the literature.

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