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Advances and perspectives of spin coating techniques

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Abstract. Spin coating is a kind of economically friendly technology accompanied by outstanding application performance, which has been widely adopted in the functional thin film fabrication field. Widespread attention has been attracted owing to their superior controllability. In this paper, the fundamental principles, film quality evaluation methods, and the current development of the spin coating technique are discussed. Through the ideal model and empirical formula, the key factors controlling the film thickness are obtained and are ready to produce marvelous functional films. Currently, the manufacturing demand for solar cells in the energy market is calling for high-quality thin films. Therefore, spin-coating has become a promising candidate. The characteristics of the spin-coating methods reviewed in this paper are adopted to maximize the properties of the obtained films and provide theoretical support for the preparation of high-efficiency solar cells. Finally, this novel growth point of using the spin coating method in the photovoltaic film is forecasted.

Keywords: spin coating, theoretical model, film quality evaluation, spin coating application

1. Introduction

Thin film technology and materials, which arose in the 1960s, have become the basic elements for the construction of high-tech industries in a rapidly developing way. The so-called thin film is a 2D material with a thickness limited to the micron scale [1]. There have been lots of thin film fabrication techniques, within which dipping coating is one of the simplest ones that succeeds in a low-cost way but may be constricted by its inferior quality [2]. Meanwhile, the sol-gel method could achieve large-scale manufacture with low cost but was incapable of thick film production, which limits its industrial application. Furthermore, inkjet printing can reach a thickness of a submicron scale but is unsuitable for large-scale production. Nevertheless, a large area of the high-quality film could be readily made through the magnetron sputtering method, though the potential damage from the secondary sputtering must be carefully monitored. At last, for a multicomponent fabrication purpose, pulsed laser deposition is an ideal choice, although film quality is also the key factor to be concerned about [3].

In contrast to these film-making methods, spin coating is uniform and controllable in thickness, simple in preparation, tolerant of the substrate, and can be used for both organic and inorganic coatings. In the spin coating method, three key steps are involved in the fabrication processes. As displayed in Figure.1.(a), firstly, the spin coating solution is dropped on the surface of the substrate, then spread by high-speed rotation to form a uniform film, and the residual solvent is removed by drying to obtain a stable film. Using such a simple procedure, a well-designed thin film can be produced.

Accompanied by the rapid progress in fabrication crafts, theoretical understanding has also been boosted in the last few centuries. In 1958, Emslie was the first to simulate the mechanics of the

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unfolding of a thin film during an ideal spin coating process. Then, Washo considered the influence of different droplet methods and obtained the corresponding model and empirical formula. A few years later, Chen gave the estimation method of the thickness of the liquid film in different polar and non-polar solution systems. Besides, Birnie et al. solved the thermocapillary instability phenomenon, which led to the awareness of the importance of thermal management during spin coating. To ensure the uniformity of the entire liquid film, Schwartz et al. simulated the diffusion process of the liquid film in the process of spin coating and proposed a "wall tower" boundary model [4]. Through the study of these models, key factors that affect the film formation results can be found, which is essential to controlling the film quality. However, the spin coating also has some disadvantages, especially concerning the size and shape of the substrate. There are several difficulties associated with the placement of large scaffolds uniformly, such as their easiness being affected by parameters such as velocity, rotation time, acceleration, and so on, which will ultimately lead to a number of quality issues [5, 6]. In order to give full play to the advantages of spin coating, the theoretical principles and the corresponding quality evaluation strategies are summarized in the following work.

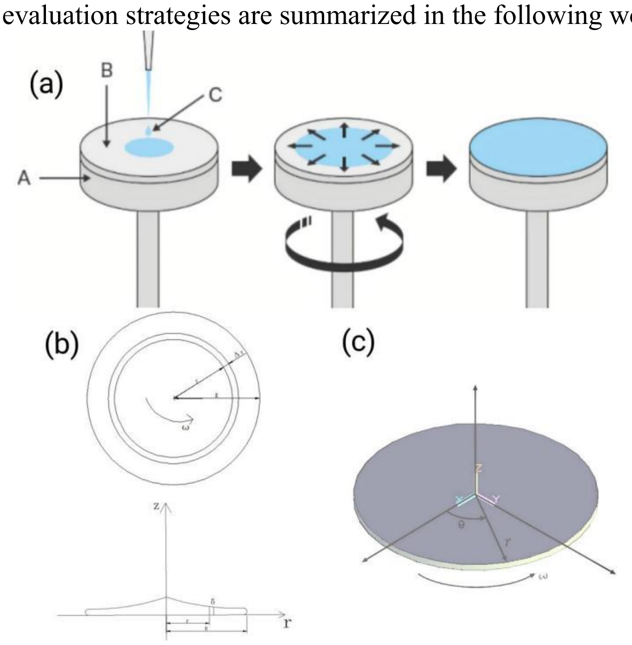

Figure 1. (a)Step diagram of spin coating method [7]. (b)Overall structure model of spin coating process (c)Film thickness model of spin coating method.

2. Fundamental principles of the spin coating method

2.1. Ideal model for force equivalence in the spin coating method

As displayed in Figure 1. (b), at the beginning of the spin coating, there is a distinct stack in the middle of the flow profile, which is the flow source in the substrate. After that, the flow quickly spreads out into a flatter curve. (The steady state curve $\delta \approx r^{-\frac{2}{3}}$, δ is the thickness of the film, and *r* is the position of the radius.) When the spin coating process stops and the film on the substrate dries or condenses, the surface tension causes the thickness profile to be flat, uniform, and conformal.

From the phenomenological equation:

$$\rho \frac{\partial v}{\partial t} = \nabla \boldsymbol{\tau} - \nabla \boldsymbol{P} + \boldsymbol{\rho_g} \tag{1}$$

In equation (1), $\frac{\partial v}{\partial t}$ means the derivative of the fluid velocity vector concerning the time, $\boldsymbol{\tau}$ stands for the stress tensor, $\nabla \boldsymbol{P}$ means the pressure gradient vector, $\boldsymbol{\rho_g}$ means the gravity vector and ρ is the fluid density.

Suppose the material obeys Newton's law of viscosity. In this way, the fluid shear stress is proportional to the shear rate. That is, the viscosity is independent of the shear rate:

$$\tau = \mu \frac{\partial v}{\partial z} \tag{2}$$

In equation (2), μ is the viscosity and $\frac{\partial v}{\partial z}$ means the velocity gradient, and shear rate in the z-direction.

Combining equations (1) and (2) gives an empirical formula for Navier-Stokes, expressed in vector form as

$$\rho \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{t}} = -\nabla \boldsymbol{P} + \nabla^2 \boldsymbol{v} + \boldsymbol{\rho_g} \tag{3}$$

The equation can be simplified and solved only in the case of steady-state, constant pressure, constant temperature, uniform, and symmetrical flow of fluid on the rotating platter, and the net flow is only in the radial direction, with no volatilization loss, and no gravity or surface force.
In general, the thickness of a spin-coated film is proportional to the inverse of the square root of spin speed, as in the below equation, where ω is angular velocity/spin speed and h_f is the final film thickness.

$$h_f \propto \frac{1}{\sqrt{\omega}} \tag{4}$$

This means that a film spun at four times the speed will be half as thick [8].

2.2. Thin film thickness evaluation

According to Emsile's Newton fluid spin coating principle, in the establishment of the cylindrical coordinate system (r, θ, z), as displayed in Figure 1.(c), the substrate rotates at constant acceleration, assuming an infinite radius of the substrate and radial symmetry of the flow; gravity is negligible compared with centrifugal force; the fluid layer only has shear resistance in the radial direction. Coriolis force, solvent volatilization, constant concentration, and constant viscosity are ignored; the wind shear forces on the free surface are also ignored. Based on these assumptions, the equation of motion (the N-S equation) reduces to

$$\gamma \frac{\partial^2 u}{\partial z^2} = \omega^2 r \tag{5}$$

It can be understood that the tension and centrifugal force are equal in magnitude and opposite in direction, where γ is the kinematic viscosity of the fluid, and u is the flow velocity of the fluid in the R direction. The equation of motion is combined with the boundary equation and continuity equation to obtain the droplet flow equation:

$$h = \frac{h_0}{\left(1+\frac{4\omega^2 h_0^2 t}{3\gamma}\right)^{\frac{1}{2}}} \tag{6}$$

$$r = r_0 \left(1 + \frac{4\omega^2 h_0^2 t}{3\gamma}\right)^{\frac{3}{4}} \tag{7}$$

(r_0, h_0) represents the initial coordinates of a point on the surface of the film, and (r,h) represents the evolution of this point over time.

The fluid layer with uneven initial film thickness distribution becomes thinner and the film thickness distribution tends to be uniform under the action of centrifugal force [9].

2.3 Key stages of spin coating and their influencing factors

There are three key steps involved in a spin-coating thin film fabrication, and each of these steps contributes to the quality of the final film. These steps include dropping, spinning, and drying.

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In the dropping stage, if the concentration of the precursor is low, different concentrations of coating liquid should be precisely tuned, as the relaxation time during spin coating is different, and the different relaxation time will affect the initial radius and determine the critical radius value [10].

When it comes to the spinning stage, spinning speed and a small rotation acceleration should be accurately controlled in order to prevent the solvent in the spin coating solution from being wasted by evaporation. A relatively slight difference of ±50 RPM can produce a change in the resulting thickness of about 10%. In general, a low-speed rotation of around 500 RPM (Revolutions Per Minute) is best. The destructive fluid is ejected from the substrate surface, and the centrifugal force generated by the acceleration and angular velocity applied to the substrate causes the fluid to flow out of the substrate surface. At this point, fluid has spread across the surface and the edges of the substrate are ignorable as the film becomes thinner. Thus, the thickness of the film also depends on the surface tension and viscosity.

Ultimately, drying becomes another key stage determinant of the final film thickness. As the time of evaporation increases, the concentration and viscosity of the solution will also increase, resulting in a thicker film. Therefore, the solution must evaporate immediately when a designed thin film is achieved [11].

3. Techniques for thin films quality evaluation

X-ray Diffraction (XRD) is an excellent technique for studying thin films with crystalline structures [12]. which is widely used to identify unknown crystalline materials, especially fine-grained minerals that are difficult to determine by optical methods. A pure single crystalline phase can be proved if no secondary peaks are found in the XRD pattern, and a finer peak with higher strength represents excellent crystallinity [13].

As shown in Fig. 2(a), the as-deposited SnS_2 spin-coated thin film is evaluated via an XRD pattern. The value of the average crystallite size was obtained from the Hall–Williamson plot, Figure 2. (b), as 6.49 nm. The slope of the plot provides the amount of residual strain present in the deposited thin film. And the amount of residual strain could be deconvoluted from the slope of the plot. Here's another example: X-ray diffraction studies were conducted to investigate the crystal structure of the TiO_2 stack and the perovskite layer on top, as provided in Figure 2. (c) and (d). The resultant XRD patterns reveal the formation of clear characteristic peaks corresponding to the reflections of the TiO_2 anatase phase and the perovskite crystals [14].

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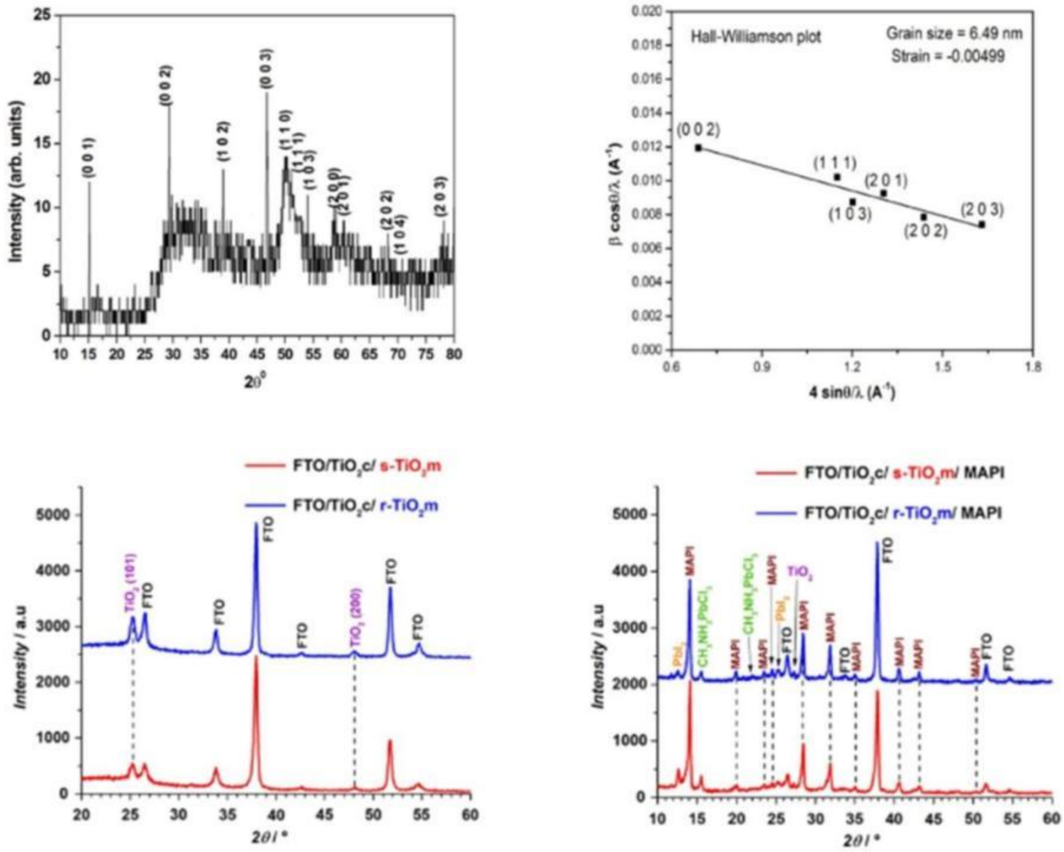

Figure 2. (a)XRD pattern of SnS_2 thin film (b)Hall-Williamspon plot of SnS_2 thin film [15]. **(c)**XRD data for spin-coated and sprayed TiO_2m films, **(d)**XRD data for spin-coated and sprayed mixed halide perovskite (MAPI) films [14].

Scanning Electron Microscopy (SEM) is a powerful tool used to characterize the morphology and composition of thin films. The fracture morphology displayed by SEM presents the nature of material fracture from a deep and high depth of field perspective, which is of great help in spin coating film analysis, especially for fracture causes and the determination of process rationality [16]. As shown in Figure 3.(a), the STF (SiO_2-photonic crystal/TiO_2 composite film) films prepared under different spin-coating conditions were monitored by SEM, and it can be found that the morphology of the films obtained by spin-coating with different layers is significantly different, such as when the number of layers is 5, there is almost no existence of the spheres, which is caused by too little content. When the number of layers is small, the photonic crystal structure under the layer is visible [17].

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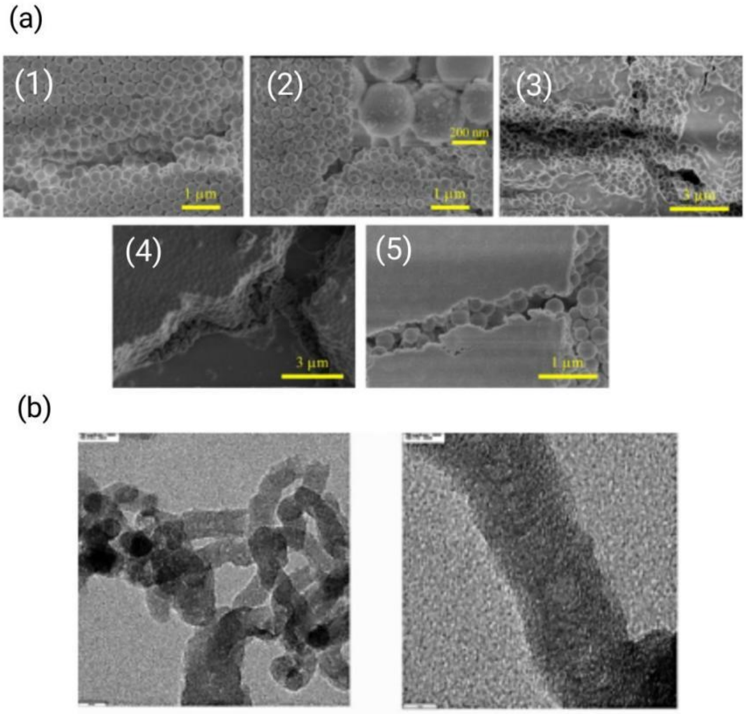

Figure 3. (a) SEM images of STF with different spin coating times of TiO_2 sol:(1)5 times (2)10 times (3)15 times (4)20 times (5)25 times[17] (b) TEM images of carbon tube.

Transmission Electron Microscopy (TEM) is similar to light microscopy but at a much higher magnification than light microscopy. Any sample in TEM needs to be thin to work, and the transmission forms a diffraction pattern in the posterior focal plane, amplifying the image in the receiving plane. Currently, TEM can provide information such as film mass, thickness, interfacial structure, orientation, strain, chemical properties, and defects to understand film growth and interpret device function [18]. Especially for some opaque and complex internal structures, TEM is the best way to solve the problem. For example, TEM can be used to directly image and analyze the structure of carbon nanotubes prepared by spin coating. As shown in Figure.3.(b), these structures are mainly hollow tube structures, where the shell of the synthesized carbon nanotube consists of short film multi-walled carbon cones connected along the length of the fiber [19].

Atomic Force Microscopy (AFM) can be used to determine the chemical structure, morphology, and growth of a thin film. Films of different compositions can be characterized by different numbers of tips (attached to cantilevers) and modes employed [20]. For instance, the AFM is used to measure the geometry of film lamination caused by indentation and calculate the interfacial ductile fracture. Coatings are often applied to improve the driving force of the lamination, such as the coating on polystyrene films and polymethyl methacrylate, and then to further study the interfacial fracture mechanism. In practice, it is also necessary to pay attention to whether there is a crack between the central contact zone and the surrounding direction as well as the average crack length [21]. For hybrid films containing new substances, the roughness may increase due to a coalition of smaller crystals. In this case, the morphology of the film could be studied with AFM, and the resulting image analysis allowed assessment of the roughness [22].

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4. Application of the spin coating

4.1. Optical

The optical disc dye layer is the recording layer of the disc. By concentrating the laser beam, the recorder can permanently carve different lengths of pits in the recording layer from the inside out in a spiral trajectory, and these pits and the original flat surface are the data.[4] Taking the Blu-ray disc as an example, as followed in Figure 4. (a). As mentioned above, the spin coating method is more suitable for viscous fluids, so the high spin coating speed can limit the surface tension effect near the coating edge when the Blu-ray disc is coated.[4, 23].

The anti-reflective antireflection film, as illustrated in Figure 4. (b), a double-sided poly (methyl

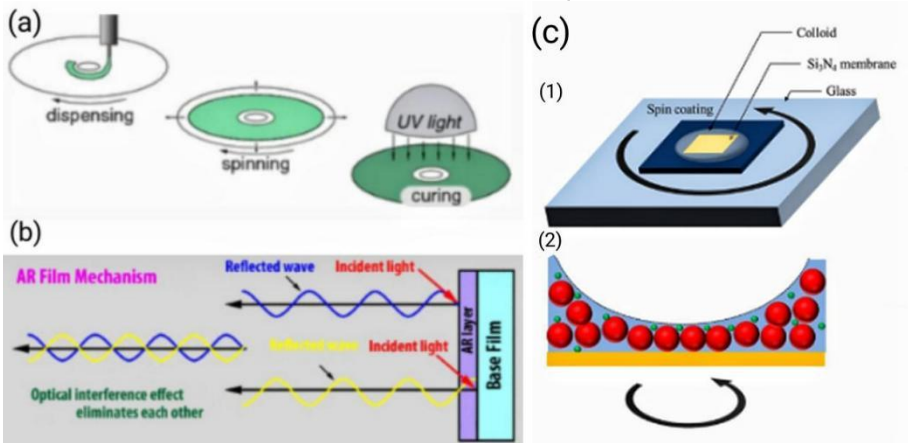

Figure 4. (a) Optical disc dye layer manufacturing [24], (b) Anti-reflective antireflection film [25],(c) (1)Schematic illustration of the spin coating method for the fabrication of binary colloidal crystals and (2) cross-sectional view of the fabricated binary colloidal crystal on the Si_3N_4 membrane substrate [26].

methacrylate) film on slides, was prepared by a spin coating method, which could act as an antireflection coating film. Moreover, an all-directional angular antireflection could be achieved by using micron-sized SiO_2 particles on a spin-on-glass substrate. These antireflection films can be used in quantum dot thin film devices, flexible solar thin film cells, and so on.

The photonic crystal is a dielectric microstructure whose refractive index changes periodically in space. The characteristics of photonic crystals can be used to accurately design a variety of functional devices. In 2002, the spin coating method was first chosen to fabricate an organic polymer optical waveguide. The obtained optical waveguide film thickness is less than 1 μm, and various types of passive and active waveguides can be obtained.

4.2. Microelectronics

In the preparation process of an integrated circuit board, the spin coating method is usually used to prepare the etching, welding, and other processes of the anti-reverse film step and physical protective film. And the fabrication parameters, including the feeding point, feeding amount, and speed, should be delicately controlled, as the various devices distributed on the integrated circuit board would make the surface of the circuit board not flat, as illustrated in Figure 5.(b) [4].

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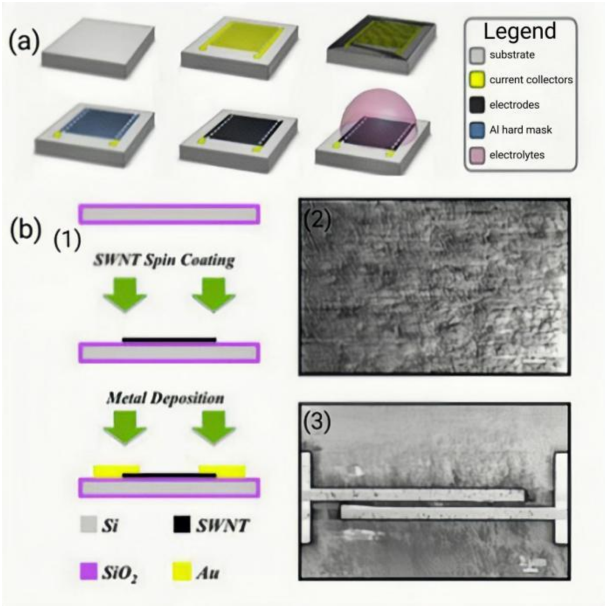

Figure 5.(a) Fabrication process of micro-supercapacitors using GO (graphene oxide) and rGO solutions as materials for spin coating. Reproduced with permission [27].(b) Shown in (1) is a schematic of the TFT fabrication process. Top viewed SEM micrographs of the spin-coated SWNTs and the fabricated TFT device are shown in (2) and (3), respectively [28].

The transistor is the key driving element of all modern electrical appliances, and the spin coating method could help to produce continuous and uniform nanoscale field-effect thin film transistors (TFTs), which have excellent electron migration rate, switching current ratio, potential voltage, and other properties, and can remain stable in different humidity environments, as shown in Figure 5.(b).

4.3. Photoelectric Energy Conversion

Organic light-emitting diode (OLED) thin films are a type of display that uses charge carriers in electricity. Chao et al. estimated the optimal 3D structure (thickness, process interval, etc.) of OLED thin films by using the 3D finite-difference time-domain method and achieved this optimized structure by using a spin coating method and focused ion beam printing (FIB) technology [4].

Photovoltaic devices are particularly important in artificial photosynthesis applications. The functional thin film of the photovoltaic device can be prepared by the spinning coating method. More common applications of solar energy on the composition of the film are TiO_2, ZnO, perovskite, etc. Taking the dye-sensitized solar cell film as an example, different thicknesses of the film were obtained by different times of spin coating. The higher the number of spin-coated, the larger the pore size of the sample. The film thickness and film formation also increased with the increase of spin coating times. The experimental results show that the higher the concentration, the higher TiO_2 the visible light absorption, which allows the surface to absorb more dye layers. The TiO_2forward current increased with the number of spin coatings, as shown in Figure 6. (1). Using the spin coating method to prepare high-efficiency solar cells can save nearly seven times the amount of spin coating liquid. However, the rotary coating method still needs to be improved for battery amplification in today's increasing demand for energy [29].

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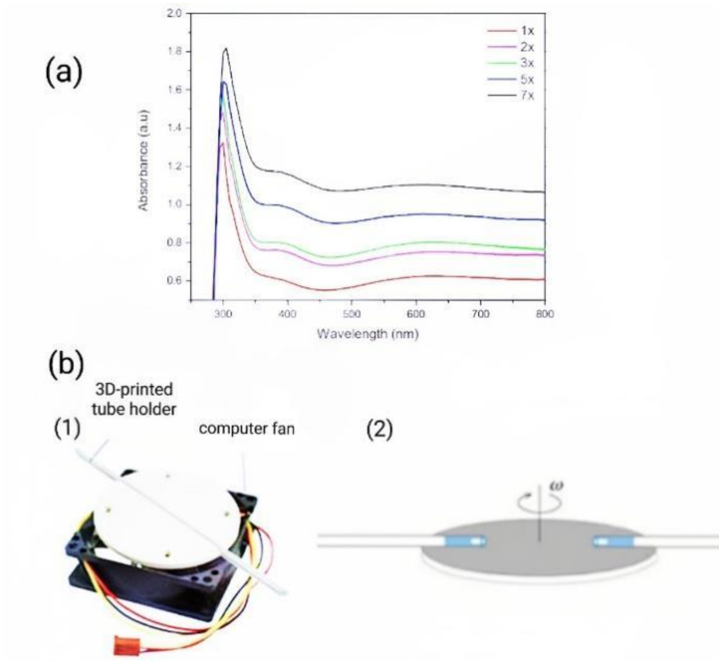

Figure 5. (a)UV-V is absorption spectra for TiO_2 thin films with different numbers of spin-coating[30],(b)(1) and (2) are physical structures and models of capillary tubes using the spin coating method, respectively [31].

4.4. Applications in diverse fields

In addition to the areas mentioned above, spin-coating would usually be carried out to fabricate protective films. For instance, the spin-coated film could achieve antifouling to prevent the chemical corrosion effect via preparing a super hydrophilic or hydrophobic film on a specific surface (such as metal, glass, polymer materials, and other substrates). Besides, a plasma-effect gold nanoparticle film was spin-coated on the glass surface to attain a waveguide protective surface for the acoustic sensor. Further, if the spin coating technique was applied to capillaries' inner chamber coating, curable polymers could be used to precisely control the film geometry and wettability, as shown in Figure 6(2). [31]. The last and most common technique is spin coating, which has already become a conventional method for obtaining protective films on the surfaces of precious metal and optical devices [4, 32].

5. Conclusion

Spin coating is a kind of functional thin film fabrication technology with high controllability, a simple preparation process, and large area fabrication capability. In this paper, the principle and present development situation of the spin coating method are summarized in detail, which could contribute to improving the quality of thin films and expanding their application fields. As an energy-saving and low-pollution film making method, it is easy for spin coating to occupy a place in the modern energy market, especially since it has already been involved in the manufacture of photovoltaic solar cells. Since the spin coating method integrated in this paper has both advantages and disadvantages, its feature can be utilized to maximize the quality of the functional film resulting, to increase energy conversion efficiency and to provide theoretical support for the preparation of efficient solar cells given the advantages and disadvantages of the spin coating method.

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