

Optimization of PNIPAm Thin Film Fabrication Using APDBD and Spin Coating Techniques

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Abstract:

Fabrication of Poly(N-isopropylacrylamide) (PNIPAm) thin films by plasma-initiated polymerization under atmospheric pressure dielectric barrier discharge (APDBD) conditions with controlled thickness is both desirable and challenging. Here, we combine APDBD technique with spin coating to achieve control over film thickness. By systematically exploring different parameters, including polymer concentration, spin speed, and spin time, under a controlled environmental condition with temperature of 40°C and humidity of 15%, we report an optimal condition with a 90% concentration of the polymer precursor solution, a spin speed of 8000 rpm, and a spin time of 7 seconds. Using Argon as the discharge gas, PNIPAm thin films with thickness range from 2.38 μm to 8.16 μm were fabricated on several glass wafers with plasma exposure time of 60 seconds and frequency of 17kHz. By TGA analysis, PNIPAm thin film of ~2 μm indicated weight loss of 63% between 350°C and 430°C. This means that, higher degree of polymerization can be achieved with thinner films as compared to films large thickness. This research provides valuable insights into the optimization of thin film polymerization techniques, advancing the development of functional coatings for various industrial and research applications.

Keywords — plasma polymerization, poly (N-isopropylacrylamide) film, spin coating.

I. INTRODUCTION

PNIPAm material consists of flexible, extending, and contracting polymer chains capable of perceiving changes in the surrounding temperature below and above 32°C showing a wide range of application prospects in various fields of biomedical, electronic, energy harvesting, textile, optical *etc*[1-4]. The preference of PNIPAm in most fields such as biomedical and textile is mainly dictated by the materials biocompatibility and having a reversible phase transition temperature (LCST) close to the human body temperature [5, 6]. However, like other polymers, addition of chemicals such as initiators or crosslinkers during the polymerization process may cause toxicity or presence of toxic residual chemicals [7, 8]. For example, Broyer *et al.* reported that the toxicity of Poly(ethylene glycol) diacrylate (PEGA) was

caused by the use of copper to initiate atom transfer radical polymerization (ATRP) process [9].

APDBD polymerization is an environmentally friendly process that involves the use of active gas species including radicals, excited atoms, *etc*, generated in between two parallel electrodes to initiate formation of highly crosslinked polymer chains [10]. The process has attracted the interests of several scientists since it does not involve the use of additional toxic chemicals, fast processing time, uniform modification over a large surface area, price control, *etc*[11]. Despite all these benefits, polymerization process of monomeric thin films by APDBD has less affect to film thickness during short exposure time. Getnet *et al.*, observed thinner films with increasing plasma intensity in comparison to lower intensities during film deposition process for 30 minutes [12]. Longer

plasma exposure time is energy consuming and also can cause degradation of the treated material [13]. Therefore, utilizing of a post APDBD process provides the possibility of fabrication of films with controlled thickness with short treatment time.

Spin coating is a solution based thin film deposition process that involves dispensing precursor solutions of suitable raw materials onto flat substrates [14]. The process operates on the principle of centrifugal, surface tensile and shear forces generated during the rotation of the substrate at various spin speeds [15]. The process is highly reproducible and associated with precise control over thin film thickness through variation of the precursor concentration, spin speed and spin time [16].

Previous study in our laboratory, PNIPAm thin films were fabricated under APDBD conditions of argon carrier gas, exposure time of 60 seconds and plasma frequency of 17kHz[17]. However, SEM data analysis indicated presence of non-uniform surface morphology which was attributed to the unpolymerized NIPAM on the surface resulting from uncontrolled film deposition by the drop coating method. In this present study, the film thickness is highly controlled by spin coating of the NIPAM monomer solution onto the substrate before APDBD polymerization process. Spin coating parameters of NIPAM concentration, spin speed, and spin time are highly optimized. The thickness of the PNIPAm thin films is measured using an optical microscope. SEM of surface morphology results of PNIPAm thin films prepared by spin coating method is also analyzed. The degree of polymerization is also tested by TGA.

II. MATERIALS AND METHODS

A. Materials and Devices

N-isopropylacrylamide(NIPAM, purity 98%, Shanghai Wujing Chemical Co., Ltd.), Argon (purity 99.990%, Shanghai Canghai Industrial Gas Co., Ltd.), Deionized water, Electronic Balance ME204E (METTLER TOLEDO Instruments Shanghai Co., Ltd.), Optical microscope MSD105 (Maishidi Technology Co., Ltd.), Single-channel pipette M1000 (Group Scientific Instrument Co., Ltd.), Spin coating machine KW-4A (Beijing

Xidekesi Electronics Co., Ltd.), Low temperature plasma power supply CTP-2000K (Nanjing Suman Electronics Co., Ltd.)



Fig.1 Type KW-4A spin coating machine

B. Solution preparation and spin coating

NIPAM granules were mixed with deionized water and measured using a high-precision weighing balance to attain desired concentration of NIPAM in the solution. In this study, NIPAM of range from 60% to 95% in the solution was prepared to investigate the influence of concentration on the resulting thin films. The mixture underwent vigorous stirring using an ultrasonic frequency vibrator until complete dissolution of the NIPAM granules in the water was achieved. This thorough mixing process facilitated the formation of a homogenous solution, critical for maintaining consistency in subsequent procedures.

This was followed by regulating the operating temperature and that of NIPAM at 40°C. Also, humidity level was kept low at 15%. These conditions ensured less moisture in the surrounding and also keeping NIPAM hydrophobic to prevent structural changes that could affect film thickness during spin coating process under atmospheric conditions [18]. A micropipette was then calibrated and employed to dispense precisely 5mL onto several square glass wafers of dimensions 18*18mm² each placed on the stage of spin coater during deposition as in **Fig. 2**. This ensured maximum utilization of NIPAM solution with minimal flung off [14]. NIPAM solution was spread onto the glass wafer while observing film thickness at several spin times and speeds. The spin coating machine (**Fig. 1**) was characterized by four key parameters:

initial (low) speed, final (high) speed, initial time, and final time. The range of spin time was from 4 to 10 seconds while the speed ranged from 500 to 8000 rpm.

However, the initial time and initial speed were kept constant throughout the spinning process. The initial spin time was maintained at 4s and this is explained in Fig. 4 and initial speed was maintained at 500 rpm as this was enough to spread and cover the NIPAM solution onto the glass wafer. Therefore, spin time in Fig. 5 includes a total of both initial and final spin times.

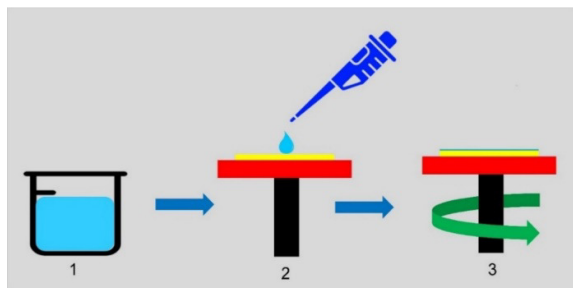


Fig.2 Schematic diagram of the spin coating process

III. RESULTS AND DISCUSSIONS

C. Spin coating time

The initial spin time was first investigated in the range from 1 to 9 seconds. Thickness corresponding to PNIPAm films spin coated for 1, 2, and 3 seconds could not be accurately measured as a result of several defects and insufficient centrifugal forces to cause the solution to completely cover the glass wafers. This can be observed in images of Figure.3 in the supporting information.



Fig.3 Images of 1-3s spin coating (from left to right)

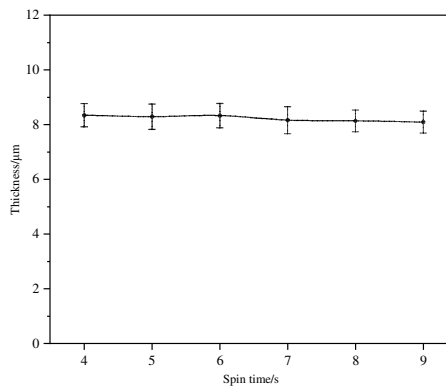


Fig.4 The relationship between initial spin time and thickness with 90% NIPAM concentration in the solution and initial spin speed of 500 rpm.

From Fig.4, it can be observed that there are no significant variations in the thickness of the films, with a maximum of 8.34 µm at 4s and a minimum of 8.09 µm at 9s.

Then, the final or spin time in the high-speed region was investigated while keeping spin speed in this region constant at 4000 rpm. The initial or spin time for low speed region was maintained at 4s and speed of 500 rpm. The spin time was varied from 0 to 6 seconds in the high-speed region which means that the spin time in Fig.5 is a sum of both initial and final spin times.

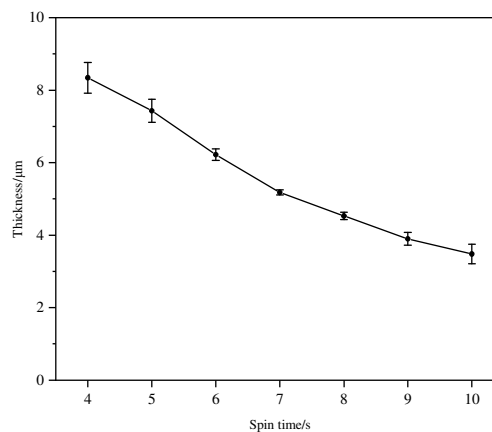


Fig.5 The relationship between spin time and thickness with 90% NIPAM concentration in the solution and spin speed of 4000 rpm.

As shown in Fig. 5, increasing the spin coating time directly influences the film thickness. Extended spin times allow for more thorough spreading and flow of the solution, compensating for the slower flow rates associated with the solution's viscosity. Additionally, irregularities in

the film decrease until a certain point, specifically at the combined initial and high-speed spin times of (4+3) seconds. Beyond this point, irregularities begin to slightly increase due to a further decrease in film thickness.

D. NIPAM concentration

Due to the high-water content and rapid evaporation of the solvent, achieving high-quality films through the spin coating process is challenging with low concentrations. In this experiment, solutions with concentrations of 60%, 70%, 80%, 90%, and 95% were used for spin coating. The total spin coating duration was 7 seconds, with the high-speed phase set at 4000 rpm. The thickness of each film was measured at five different positions on the samples. The relationship between concentration and film thickness is depicted in **Fig. 6**.

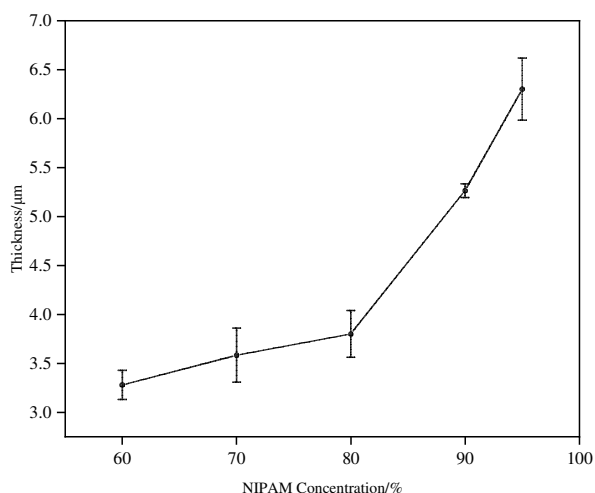


Fig.6PNIPAM film thickness at various concentrations spin coated at for 7 seconds and high-speed of 4000 rpm.

In this experiment, the 90% concentration solution produced thin films with fewer defects and more uniform morphology compared to lower concentrations, as clearly demonstrated in **Fig.6**. This may be attributed to its higher viscosity, which facilitates a more controlled and even spread of the solution across the substrate during the spin coating process. The higher viscosity helps counteract the rapid solvent evaporation typical of high-water content solutions, allowing more time for the solute to form a cohesive film. Additionally, suitable solute content at this concentration ensures

complete substrate coverage, significantly reducing defects such as pinholes.

E. Spin coating speed

The effect of spin coating speed on the thickness of PNIPAM films was also investigated. We focused on the impact of varying spin speeds from 500 to 8000 rpm while maintaining a constant concentration of 90% and a spin time of 7 seconds. The results of these variations are comprehensively plotted in **Fig.7**. This figure illustrates how changes in spin speed influence the film thickness, showcasing a trend where higher spin speeds generally result in thinner films. This behaviour is attributed to the increased centrifugal force at higher speeds, which effectively spreads the NIPAM solution more thinly across the substrate.

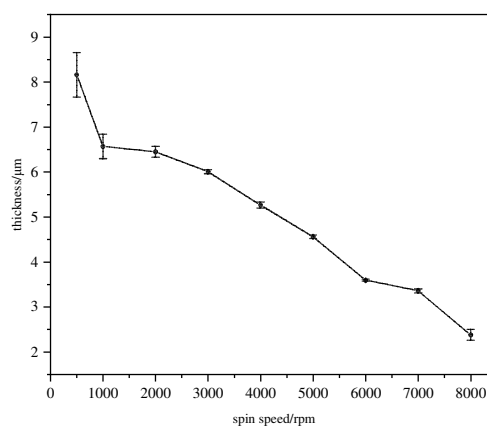


Fig.7Effect of spin coating speed on thickness of PNIPAM films of 90% concentration monomer solution spin coated for 7s.

F. Film uniformity

In **Fig. 8**, the SEM image of the PNIPAM coating displays a remarkably uniform surface texture throughout the entire area examined. The coating appears smooth with no visible defects such as cracks, voids, or pinholes, indicative of excellent control during the coating process. The thickness of the film, as observed from cross-sectional views within the image, is consistent, showing no significant variations or deformations from one region to another. Additionally, the edges of the film are well-defined and sharp, suggesting effective spreading and adhesion on the substrate during the spin coating process.

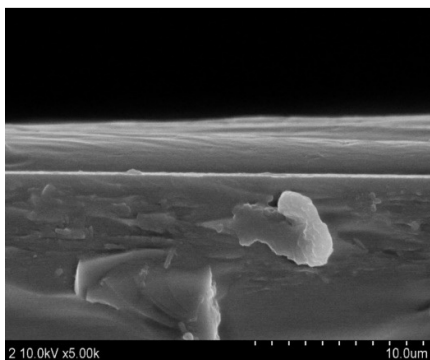


Fig.8 SEM cross-section of PNIPAm thin film of thickness $\sim 2 \mu\text{m}$.

G. Detection of polymerization degree

The thinnest PNIPAm film was prepared, and 5.4 mg was scraped off for thermogravimetric analysis. As depicted in **Fig.9**, the weight loss curve with increasing temperature can be divided into three stages. The first stage from the beginning to about 100°C , corresponds to the evaporation of NIPAM monomer and water, resulting in an approximate 8% total weight loss. In the second stage, from 100°C to about 350°C , the curve shows a nearly linear weight loss, corresponding about 24%. It is speculated that during this stage, the lower molecular weight PNIPAm evaporates and degrades linearly with the increase in temperature. The third stage, from 350°C to 430°C , is marked by a sharp weight loss of about 63%. This significant reduction is presumed to result from the complete decomposition of the PNIPAm material within this temperature range. The degree of polymerization increases about 20% comparing to the previous research in [17].

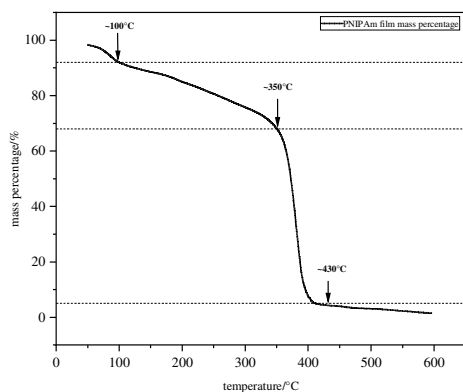


Fig.9 TGA curve line of PNIPAm film

IV. CONCLUSIONS

In summary, PNIPAm thin films with controlled thickness ranging from $2.38 \mu\text{m}$ to $8.16 \mu\text{m}$ were fabricated under APDBD conditions. Due to the surface treatment of the plasma, the thickness reduction will increase the overall degree of polymerization, optimum spin coating conditions were determined as 90% NIPAM concentration in the solution, spin coating time of 7 seconds and spinning speed of 8000 rpm for the thinnest film. The results of SEM and TGA showed that uniform PNIPAm films with higher degree of polymerization could be prepared when the spin coating speed was 8000 rpm. It provides a simple and effective guidance for the mass production of pure PNIPAm thin film materials with high degree of polymerization.

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