



Droplet Lifetime under Spray Pyrolysis Deposition Conditions

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Abstract: In this paper, the evaporation of sprayed aqueous fine droplet containing zinc chloride ($ZnCl_2$) has been studied through the space limited by the droplet generator and the hot substrate surface. Behavior of moving droplet on various hot atmospheres condition has been investigated by using Runge-Kutta method. The differential equations system of droplet rate evaporation, diameter and temperature was solved. The effects of hot air temperature, initial droplet diameter and salt concentration were investigated. We found that, through its transportation on hot air, the droplet size decreases differently with the surrounding medium. A varied space temperature from hot substrate to the generator nozzle droplet leads to more increasing in the droplet surface temperature than that of isothermal one. The evolutions of droplet size reduction in spray medium can be approximated by parabolic variations. Decreasing in initial droplet size and increasing in salt solution concentration accelerate droplet evaporation. The prediction of the droplet properties near the heated plate is the goal of our work which is important to understand thin films deposition by spray pyrolysis process.

Keywords: ZnO thin films, Spray pyrolysis, $ZnCl_2$ aqueous solution, Droplet, Lifetime.

Introduction

During the past decade, the development and manufacturing of devices based on thin films have motivating research in various engineering fields^{1,2}, including electronic and optoelectronic applications, medical diagnostic equipment, gas sensors^{3,4}, steel industry⁵ and solar energy conversion⁶. Among the variety of thin films deposition processes, one can notice that the spray pyrolysis method became widely used because of its simplicity, low cost, requires no vacuum and giving the opportunity to combine a variety of chemical precursors with desired concentrations.

The deposition process begins with atomization of the dissolved precursor's solution on micro-droplets which then sprayed through a heated air zone. At this last, droplets evaporate partially and when reached the heated substrate, the pyrolysis reaction occurs to form the solid thin films⁷. Numerous studies of droplet evaporation through heated atmosphere are found in the literatures, such as, the formation of powders in spray pyrolysis⁸ and diesel engine fuel droplet evaporation in spray combustions⁹. Sprayed solution can be obtained by various physical processes like pressurized solution¹⁰ or ultrasonic fragmentation¹¹.

The purpose of this work deals with the development of numerical model for understanding the first sequence in process of ZnO spray pyrolysis deposition. This step starts by the atomization of precursor solution by ultrasonic generator in small droplets ($ZnCl_2$ dissolved in distilled water). Droplets leave the nozzle without velocity and moves through the hot atmosphere until reaching the substrate surface. During this phase

evaporation mechanism can be occur by heat and mass transfer at the interface droplet surface and the surrounding hot air. In order to predict the evolutions of droplet properties as function of time, air temperature, initial droplet diameter and salt solution concentration; a numerical model was presented.

Experimental Equipment

This experiment generally represented ultrasonic spray pyrolysis technique used to deposit thin films; a schematic diagram of the experimental device is shown in Figure1. Homogeneous micro-droplets (1) of a chemical solution (2) were created with ultrasonic generator waves at 40 kHz frequency (3). They leave the nozzle without velocity (4) and transported in hot ambient air caused by the heating of horizontal plate (5) by Joule effect (resistance) (6), because of this effect a chemical reaction occurs on glass substrate (7) to produce thin films.

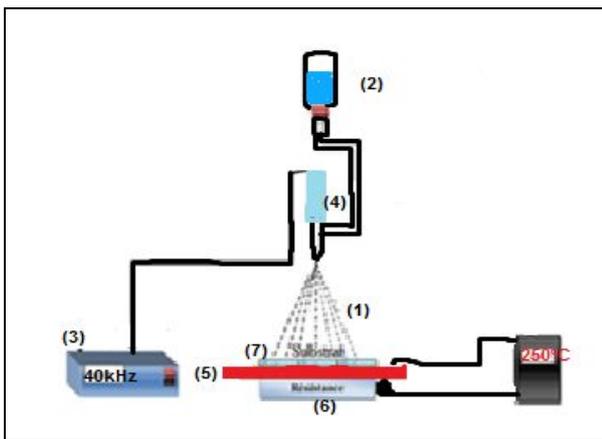


Figure1. Experimental schematic diagram of ultrasonic spray pyrolysis thin films deposition.

Theoretical Simulation

Physical Model

The filing of droplet in a hot ambient air conditions (Figure2) leads to partially evaporate its solvent which caused by heat and mass transfer between the droplet and the surrounding gas.

To study the lifetime of this droplet, the principle assumptions are as follows:

1. All droplets have an identical spherical shape.
2. Its transport is along the vertical axis of horizontal plate.
3. Droplet during its flight; has uniform intern temperature distribution.
4. Temperature of droplet surface is uniform and varies with time.

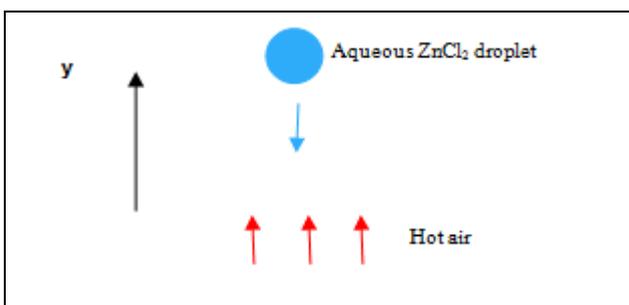


Figure 2. Schematic view of aqueous $ZnCl_2$ droplet in a hot air

Mathematical Model

During the flying of droplet in a hot air, the total heat power exchanged between them is the sum of two components: sensible and latent heat transfers. The energy balance makes it possible to calculate the variation in the temperature of the droplet, according to the following equation^{12, 13}:

$$L_v \dot{m}_l + (m_s C_{ps} + m_l C_{pl}) \frac{\partial T_d}{\partial t} = h S_i (T_g - T_d) \dots (a)$$

m_l Solvent mass (water)

m_s Salt precursor mass ($ZnCl_2$)

S_i Superficial area of the droplet ($[S]_i = 4\pi R_d^2$)

h Coefficient of convective heat is evaluated in terms of corresponding Grashof number Gr ¹⁴.

The mass of liquid in the droplet (presumably spherical) is given by: $m_l = \rho_l \frac{4}{3} \pi R_d^3$. The time-change of droplet radius is determined by:

$$\frac{dR_d}{dt} = \frac{1}{4\pi\rho_l R_d^2} \dot{m}_l \dots (b)$$

The difference of the water vapor concentration between the droplet surface and surrounding air produces a change of the liquid mass of the droplet. It is described by the following equation⁷:

$$\dot{m}_l = \frac{dm_l}{dt} = h_m S_i (C_d - C_g) \dots (c)$$

h_m Coefficient of mass transfer is evaluated in terms of corresponding Sherwood number Sh ¹⁴.

The fourth order Runge-Kutta method has been used to predict droplet temperature, size and rate evaporation evolutions as described by the system of differential equations (a), (b) and (c). To evade the total evaporation of droplet the computing process is forced by the limit $Sf \leq 1$: Solid fraction (Sf) is defined as the ratio between the salt precursor mass and solvent mass. This condition leads to the total evaporation of solvent and condensation of precursor molecules into crystallites to form a powder.

Results and discussion

With numerical simulation, the results of droplet temperature, diameter and solvent rate evaporation are presented under different terms, which including two states of air temperature; the first is isotherm at fixed temperature of 100°C and the second with a variable temperature along the distance (y) from substrate to nozzle. The parameters studied are: initial droplet diameter is varied from 20µm to 40µm and the initial salt concentration is ranged from 0.05mol/l to 0.15mol/l.

Figure 3 shows, the air temperature measurements along the central axis from the heated plate within 5 cm in which the spray droplet are carried out. Measurements were obtained by using five thermocouples (K type) connected to a programmable recorder multichannel of type PHILIPS PM 8237 A. As can be seen, the air temperature (Kelvin) was decreased with distance from the hot substrate (250°C) to the nozzle; this variation can be approximated by polynomial equation as following:

$$T_a(y) = 523 - 458.6 * y - 45.96 * 10^4 * y^2 + 1.54 * 10^7 * y^3 - 1.62 * 10^8 * y^4 \dots (d)$$

Figures 4 and 5 present respectively diameter, temperature and rate evaporation of droplet during flying time between the nozzle and the substrate. The initial droplet diameter is 40µm and salt concentration is 0.05mol/l, however the air temperature is variable along y axis (equation (d)). At the beginning about very short time (10ms), droplet temperature increases slightly. After that period, due to the absorbed heat through the contact air-droplet surface, the droplet temperature increases (Figure 4 dash dot line) and solvent (water) evaporates. As a result of these reasons the rate evaporation reducing towards zero and droplet size decreases

until a value equal to 6.6 (μm), which means that the droplet is no longer be aqueous but it is transformed into humid powder.

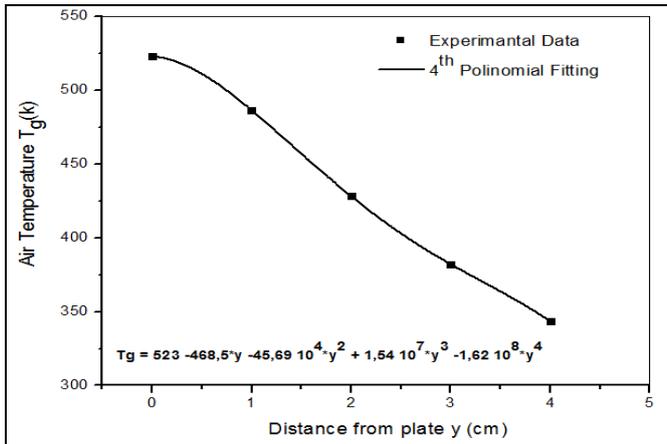


Figure3. Approximation of air temperature measurements versus distance (y) from plate

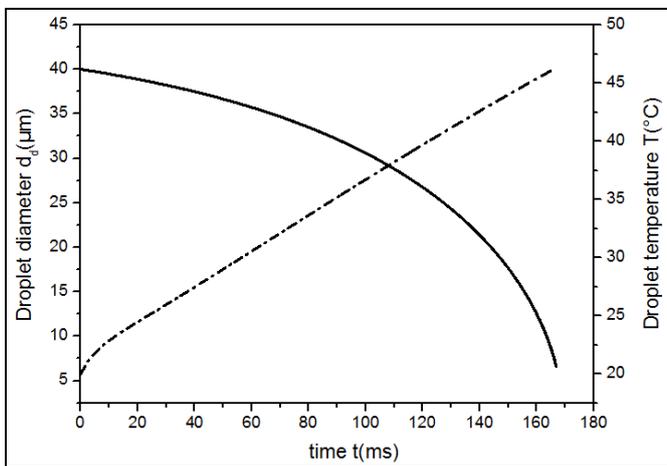


Figure4. Temporal evolution of droplet diameter and temperature

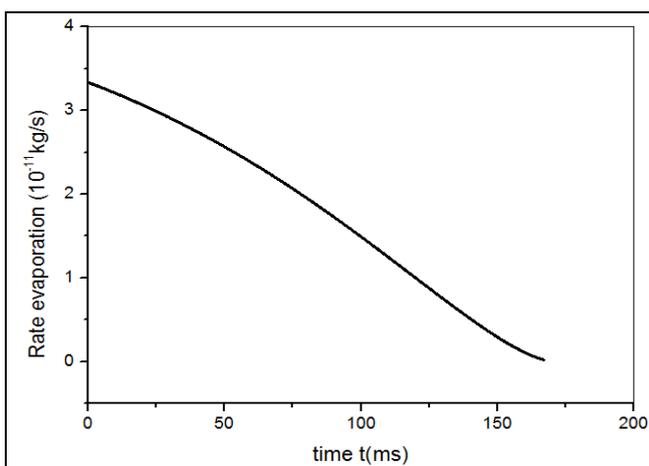


Figure5. Variation of droplet rate evaporation as a function of time

Droplet Lifetime-Air Temperature Dependent

Figures 6 and 7 present the droplet surface temperature and diameter curves under typical experimental conditions, which including initial droplet diameter is $40\mu\text{m}$, salt concentration is 0.05mol/l .

In this work we have study two cases of the surrounding air temperature; *i) isothermal air (100°C)* and *ii) variable air temperature*. It's obvious (Figure 6) that, when the droplet is transported in isothermal air medium (solid line), after a rapid increasing ($\sim 10\text{ms}$) in its temperature it remain stable at 32°C . This can be explained by the equilibrium between absorbed heat and the evaporation heat; this phenomenon corresponds to the saturation temperature of droplet.

In reality the spray medium don't have a fixed temperature, this why the measurements of air temperature were taken. The flying of droplet in hot air with variable temperature (*ii*) in the range ($65, 250^\circ\text{C}$), is presented by the dash dot line. It's clear that, the droplet temperature increases in air quasi linearly with time until the substrate impact or its complete evaporation. This can be due to the variation of air temperature, hence, the equilibrium (steady state) in heat exchange air-droplet and evaporation can't be realized. These evolutions of droplet temperature predict accurately the variation of droplet size versus time evaporation which is plotted in Figure 7. As can be seen in this figure, for isothermal medium a decrease in droplet diameter is controlled by aquasi linearly approximation whereas, the reduction of droplet diameter which is transported in a medium case (*ii*) can be approximated by a parabolic variation.

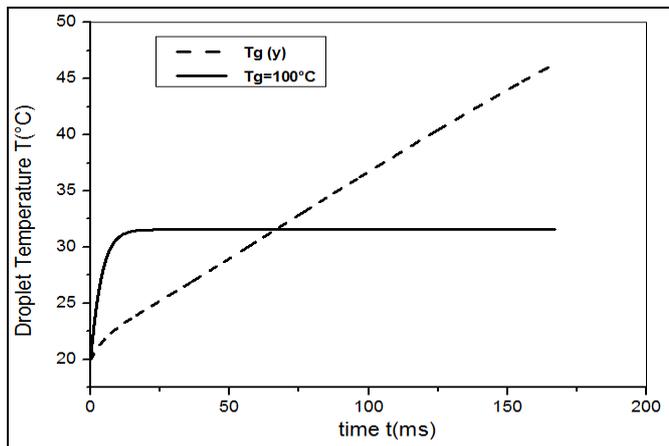


Figure6. Droplet temperature-time dependent: Effect of air temperature condition.

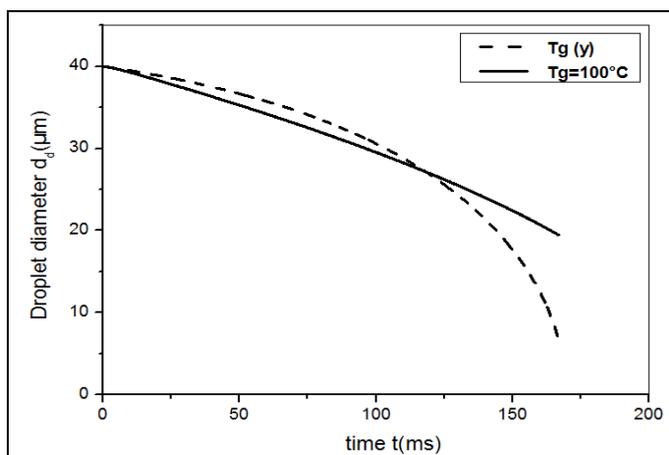


Figure7. Droplet diameter-time dependent: Effect of air temperature condition.

Droplet Lifetime-Initial Droplet Diameter Dependent

Droplets of the same component but of different initial droplet size or volume have different evaporation lifetimes and different final diameters. Diameter change curves of different initial diameters are presented in Figure8. This figure shows that, at the same conditions (air temperature, concentration) the smaller droplet (20 μm) evaporates rapidly in 68ms, whereas the lifetime of larger droplet (40 μm) is about 167ms. This is related to the initial quantity of the solvent. Consequently, the initial diameter affects the surface temperature and has greatly impacts on evaporation.

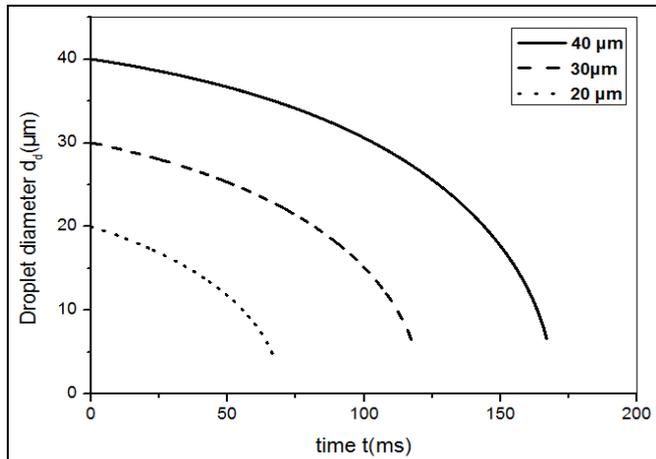


Figure8. Droplet diameter change curves under different initial droplet diameter.

Droplet Lifetime- Salt Concentration Dependent

To study the effect of the salt concentration, three salt concentrations were taken: 0.05mol/l, 0.10mol/l and 0.15mol/l. Figure9 gives the variation of droplet diameter as function of time. It shows that, a steeper and identical diameter curves appear but with a small different evaporation time and different final size, which means the same surface temperature for the three cases. The droplet with less concentration has a larger time (166.67 ms) to evaporate and smaller final diameter (6.60 μm); this is due to more solvent quantity in the droplet, whereas, the droplet with highest concentration has a smaller time (161.64 ms) to evaporate and larger final size (11.35 μm).

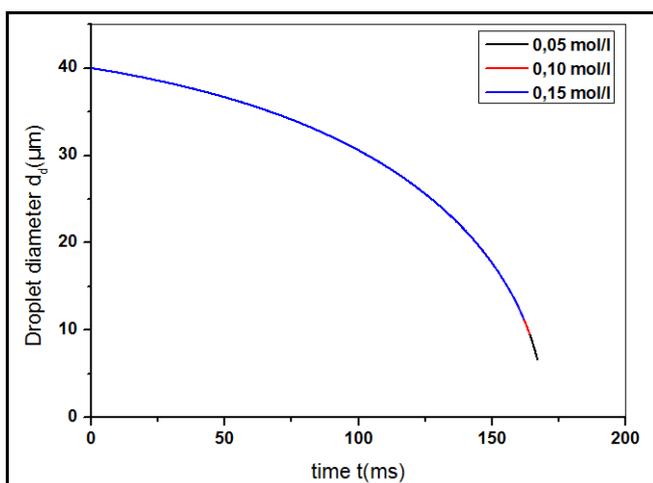


Figure9. Droplet diameter change curves under different initial salt concentration.

Conclusion

Under various spray pyrolysis deposition conditions, aqueous ZnCl_2 solution droplet lifetime in a hot air was studied. The effects of hot air temperature condition, initial droplet diameter and salt concentration on

droplet evaporation were investigated. According to the results, air temperature has a great impact on the droplet temperature evolution. Size droplet reduction can be described by parabolic approximation. Decreasing initial droplet size or increasing in solution concentration accelerates droplet evaporation. This study allows determining droplets properties just before reaching hot substrate which is important to understand thin films deposition by spray pyrolysis process.

Nomenclature

Alphabet letters		
C_d, C_g	Concentrations of the drop and ambient gas	
C_p	Specific heat	J/kg.K
$D_d(R_d)$	Droplet diameter (radius)	μm
Gr	Grashof number	
L_v	Latent heat evaporation of water	J/kg
m	Mass	kg
Nu	Nusselt number	
Re	Reynolds number	
Sh	Sherwood number	
S	Droplet interfacial area	m^2
T	Temperature	$^{\circ}\text{C}$ (K)
t	Time	s
y	Coordinate perpendicular to the substrate	m
v	Droplet velocity	m/s
Greek Symbols		
ρ	Density	kg/m^3
Indices		
d	droplet	
g	Gas (air)	
l	Liquid (water)	
s	Solid (salt precursor)	

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