Ink-Jet Patterning of Functional Materials

State of the Art and Prospect

Name: Xiaoran Li

Supervisor: Prof.dr.ir. Patrick R. Onck

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Contents

Abstract

Ink-jet patterning is considered as one of the key technologies in the field of defined polymer deposition, in particular in relation to plastic electronics.

This paper provides an in-depth overview of representative applications of ink-jet patterning in the fields of organic/polymer electronics and biochip manufacturing. Among the discussions, crucial physical and chemical problems involved in this technology are explained and special emphasis is placed upon the utilized functional materials and patterning conditions, such as polymer structure, molar mass, solvents, and concentration, etc.

The ink-jet printed multicolor polymer light-emitting diode (PLED) displays, organic photovoltaic diodes (Solar Cells), organic thin film transistors (OTFTs), and biomedical patterns (DNA microarray) are highlighted and described into more details.

At the end of this article, it addresses some of the key challenges that face the broad scientific and industrial community as it attempts to apply a mature and well-developed graphic arts printing technique to the deposition of functional materials.

Chapter 1:

Introduction to Ink-Jet Printing Patterning

In many fields of modern science and technology, patterning is of great importance for applications ranging from the production of integrated circuits, information display devices and storage units to the fabrication of micro electromechanical systems (MEMS), miniaturized sensors, bio-microarrays (DNA chips), micro fluidic devices, photonic bandgap crystals, and diffractive optical components [1]. During the past few years, the increasing need for patterned surfaces or structures in such areas above has fostered the rapid development of a number of Micro/Nanofabrication techniques. Thanks to the maturity of semiconductor industry which emerged decades ago, some high-level techniques, such as the sophisticated and advanced optical and e-beam lithography, have been greatly improved [2]. In any case, continuous advances in establishing appropriate patterning techniques continue to be the prerequisite for the success of these application developments.

The process of patterning involves a flow of information which typically begins with the design of a certain pattern in the form of a dataset and ends at a patterned arrays of features on the surface of a substrate. There should be several steps in between and each one could impose the possibility of losing information or pattern distortion [3].

Depending on their applications, the specific requirements for a successful patterning process can vary substantially. The critical feature size of the required pattern is the most obvious issue we should consider when selecting a proper patterning technique to proceed. There are a growing number of applications that require the delivery of small quantities of functional materials with specific electrical, optical, chemical, biological, or structural functionalities into well defined locations on a substrate. The increasing demand for higher densities of integration, less power consumption, better performance, and reduction in cost has been and still is the main driving force behind the continuous trend in downsizing the critical dimensions of both conventional inorganic semiconductor devices and novel organic ones [2].

The fabrication of integrated circuits, information storage devices, or display units usually involves many lithographic steps and demands the use of sophisticated technologies to meet the stringent requirements in terms of throughput, overlay accuracy, and resolution [4]. Nevertheless, among some other rapid growing techniques, the Ink-Jet Printing (IJP) technology we are going to discuss hereby, has been proved to be an attractive alternative for exploratory research or selected proper applications in which simplicity, versatility, and cost-efficiency are the main concerns [5].

As we know nowadays IJP technology is more than just a patterning technique, it has become a versatile tool in various industrial processes to deposit extremely small amounts of liquid material in a precisely controlled and defined manner. Examples include solder for the fabrication of print boards, lubricants for the lubrication of micromechanical parts, and UV-curable resins for the manufacturing of entire micro-optical parts, like waveguides, microlenses and arrays thereof [6].

Ink-jet printing is also considered as one of the key technologies in the field of defined polymer deposition, in particular in relation to plastic electronics [7]. The plastic electronics market is expected to grow very rapidly over the coming years, which is due to the ease of processing the corresponding conductive and electroluminescent functional polymers. Ink-jet printing is one of the promising choices because of its flexibility, low cost and ease of mass production. Ink-jet printed multicolor polymer light emitting diode (PLED) displays will soon enter the market for consumer electronics. Pilot lines are now being built for the manufacturing of thin-film transistors and RFID transponders, although many other applications of ink-jet printing, for example, in high-throughput experimentation, biochip manufacturing or rapid prototyping, are still being studied [5].

However, the application of ink-jet patterning in these fields is far from trivial. This is partially a result of the requirements in terms of resolution, which are much higher than in the conventional graphics industry. The rheological properties of functional polymers require the use of dilute solutions, giving rise to many additionally physical and chemical problems related to this particular fine patterning technology [6].

Outline of this report:

This paper will provide an in-depth overview of representative applications of ink-jet patterning in the fields of plastic electronics and biochip manufacturing, and then address some of the critical issues that face this particularly rapid growing patterning research and development community.

Among the discussions, crucial physical and chemical problems involved in this field will be explained and special emphasis will be placed upon the utilized functional materials and patterning conditions, such as polymer structure, molar mass, solvents, and concentration. Studies on viscoelastic fluid droplets and the formation of viscoelastic droplets under gravity will be discussed to find out the key parameters that determine the ink-jet printability of functional solutions.

The ink-jet printed multicolor polymer light-emitting diode (PLED) displays, organic photovoltaic diodes (Solar Cells), organic thin film transistors (OTFTs) for smart tagging devices, and biomedical patterns (DNA microarray) will be highlighted and described into more details.

At the end of this article, summary and prospects of ink-jet patterning of functional materials will be remarked.

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Chapter 2:

Fundamentals and Principles of Ink-jet Printing Technology

§ 2.1 Continuous Mode Ink-Jet Technology

The phenomena of uniform drop formation from a stream of liquid issuing from an orifice were noted as early as 1833 by Savart [1] and described mathematically by Lord Rayleigh [2, 3] and Weber [4]. In the type of system that is based on their observations, fluid under pressure issues from an orifice, typically 50-80 µm in diameter, and breaks up into uniform drops by the amplification of capillary waves induced onto the jet, usually by an electromechanical device that causes pressure oscillations to propagate through the fluid. The drops break off from the jet in the presence of an electrostatic field, referred to as the charging field, and thus acquire an electrostatic charge. The charged drops are directed to their desired location, either the catcher or one of several locations on the substrate, by another electrostatic field, the deflection field. This type of system is generally referred to as 'continuous' because drops are continuously produced and their trajectories are varied by the amount of charge applied. Theoretical and experimental analysis of continuous type devices, particularly the process of disturbance growth on the jet that leads to drop formation, has been fairly extensive [5, 6]. Continuous mode ink-jet printing systems produce droplets that are approximately twice the orifice diameter of the droplet generator. Droplet generation rates for commercially available continuous mode ink-jet systems are usually in the 80-100 kHz range, but systems with operating frequencies up to 1MHz are in use. Droplet sizes can be as small as 20 µm in a continuous system, but 150 µm is typical.
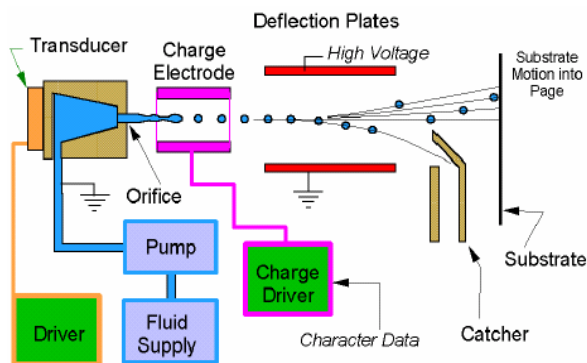

Fig. 2-1: *Schematic of a continuous type ink-jet printing system.*

Fig. 2-1 shows a schematic of this type of ink-jet printing system, and Fig. 2-2 shows a photomicrograph of a 50 µm diameter jet of water issuing from a droplet generator device and breaking up due to Rayleigh instability (continuous mode) into 100 µm diameter droplets at 20,000 per second.
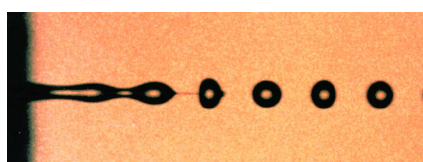

Fig. 2-2: *A 50 µm jet of water breaking up due to Rayleigh instability into*

100 µm droplets at 20 kHz.

§ 2.2 Demand Mode Ink-Jet Technology

In the 1950's, the production of drops by electromechanically induced pressure waves was observed by Hansell [7]. In this type of system, a volumetric change in the fluid is induced by the application of a voltage pulse to a piezoelectric material that is coupled, directly or indirectly, to the fluid. This volumetric change causes pressure and velocity transients to occur in the fluid and these are directed so as to produce a drop that issues from an orifice [8, 9, 10]. Since the voltage is applied only when a drop is desired, these types of systems are referred to as drop-on-demand, or 'demand mode'.

A recent demand mode droplet generation technology uses focused acoustic energy to cause a droplet to be emitted from a free surface. This type of technology has been employed in industrial processes for adhesive coating, and in NASA's liquid metal droplet free form fabrication efforts [11].

In many commercially available ink-jet printing systems today, a thin film resistor is substituted for the piezoelectric drive transducer. When a high current is passed through this resistor, the ink in contact with it is vaporized, forming a vapor bubble over the resistor. This vapor bubble serves the same functional purpose as the piezoelectric transducer [12]. This type of printer is usually referred to as a thermal ink-jet printer.

Fig. 2-3: *Schematic of a drop-on-demand ink-jet printing system*

Fig. 2-3 shows a schematic of a drop-on-demand type ink-jet system, and Fig. 2-4 shows a drop-on-demand type ink-jet device generating 50 µm diameter drops of ethylene glycol from a device with a 50 µm orifice at 2,000 per second. Demand mode ink-jet printing systems produce droplets that are approximately equal to the orifice diameter of the droplet generator [13]. As Fig. 2-3 indicates, demand mode systems are conceptually far less complex than continuous mode systems. On the other hand, demand mode droplet generation requires the transducer to deliver three or more orders of magnitude greater energy to produce a droplet, compared with continuous mode, and there are many complex array demand mode print head designs [14].

Fig. 2-4: Drop-on-demand type ink-jet device generating 50 μm diameter drops at 2 kHz.

§ 2.3 Printing Patterns and Strategies

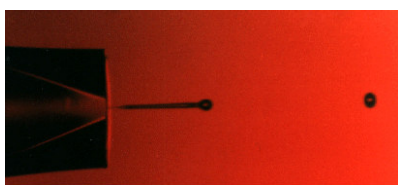A variety of patterns can be printed using drop-on-demand (DOD) ink jet process. The most commonly used patterns for printing thin films are lines, arrays and array of arrays. There are two modes used in DOD ink jet printing [15]. They are print-on-position (POP) and print-on-fly (POF). In POP, stages move and stop at each target location, then precise number of drops is dispensed before the stages move to the next target location. In POF, drops of material are dispensed as the stages underneath move. Here, the stage speed and spacing between the drop locations determine the rate of dispensing. While the POP is more accurate in terms of drop placement it is much slower than POF, which can enable significantly higher throughput with very little penalty in drop placement accuracy.

In either print mode, drops can be placed in non-interlaced or interlaced schemes. In a non-interlaced printing scheme, drops are placed sequentially and usually with some degree of overlap between two adjacent drops creating one smooth line. This is repeated across the whole printing area by printing successive lines with some degree of overlap to create one solid area of a thin film. In an interlaced printing scheme, alternate drops are dispensed within a line and alternate rows of lines are printed in the first pass of printing. In the second pass, printing begins with an offset filling the area between the printed drops and printed lines, creating one continuous thin film. The difference comes in the amount of time allowed for the material to spread and dry before the next drop or line is printed. Depending on the solvent and material being printed one scheme may produce better results than the other. A matrix of experiments was generated using print modes and print schemes for a given set of materials.

§ 2.4 Characteristics & Applications of Ink-Jet Systems

One of the characteristics of ink-jet printing technology that makes it attractive as a precision fluid micro-dispensing technology is the repeatability of process. The images of droplets shown in Fig. 2-2 and Fig. 2-4 were made by illuminating the droplets with an LED that was pulsed at the droplet generation frequency. The exposure time of the camera was about 1 second, so that the images represent thousands of events superimposed on each other. The repeatability of the process results in an extremely clear image of the droplets, making it appear to be a high speed photograph. To further illustrate this point, Fig. 2-5 shows two 60 μm diameter jets of water breaking up into 120 μm diameter droplets streams at 20,000 per second, and being caused to merge into a single droplet stream. Again, this image was created using a 'strobed' LED and an exposure time around 1 second. Not only is the droplet formation process so repeatable that the image of the droplets is sharp, but when the droplets are caused to merge, the formation of the highly contorted merged droplets is seen to be just as repeatable.

Continuous mode ink-jet systems are currently in widespread use in the industrial market, principally for product labeling of food and medicines. They have high throughput capabilities, especially array continuous mode systems, and are best suited for high duty cycle applications. Few continuous mode ink-jet systems are multicolor, but two color systems are in use. Continuous mode ink-jet systems require the unused drops to be re-circulated or wasted.

Fig. 2-5: Two streams of 120 μm water droplets merging into a single droplet stream at 20 kHz.

Drop-on-demand ink-jet systems have been used primarily in the office printer market and have come to dominate the low-end printer market (HP's DeskJets, Cannon's Bubble Jets, and Epson's Stylus). Demand mode ink-jet systems have no fluid recirculation requirement, and this makes their use as a general fluid micro-dispensing technology more straightforward than continuous mode technology. Thermal demand mode ink-jet technology systems can achieve extremely high fluid dispensing performance at a very low cost. However, this ratio of performance/cost has been achieved by highly tailoring the ink: thermal ink-jet systems are restricted to fluids that can be vaporized (without igniting the fluid) by the heater element and their performance/life can be degraded drastically if other fluids are used. In practice, thermal ink-jet systems are limited to use with aqueous fluids.

As a non-contact printing process, the accuracy of ink-jet dispensing is not affected by how the fluid wets a substrate as is the case when positive displacement or pin transfer systems 'touching off' the fluid onto the substrate during the dispensing event. In addition, fluid source cannot be contaminated by substrate, or contamination on the substrate, in a non-contact dispensing process. Finally, the ability to free-fly the droplets of fluid over a millimeter of more allows fluids to be dispensed into wells or other substrate features (e.g., features that are created to control wetting and spreading).

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Note: Fig. 2-1~ Fig. 2-5 were reproduced from UniJet Co., Ltd.: *Introduction of Ink Jet Printing (Presentation at Fudan Univ.)*, September 5, 2004.

Chapter 3:

Crucial Physical and Chemical Aspects Involved in Ink-Jet Printing

§ 3.1 Fluid Properties Effects on Ink-Jet Device Performance

§ 3.1.1 General Requirements

The general fluid property requirements for a fluid to be used in a piezoelectric demand-mode ink-jet device are as follows [1]:

- **Newtonian**
  - Viscoelastic behavior undesirable

- **Viscosity**
  - 0.5-40 cP[*]

- **Surface Tension**
  - 20-70 dynes[†]/cm

- **Particle Laden Fluids**
  - particle size < 5µm
  - ideal nanoparticles
  - stable dispersion required

Some fluids with properties outside these ranges may be dispensed using ink-jet devices, but with increased difficulty or decreased performance. Combinations of the extreme values may also have poorer performance. If the fluid is heated or cooled, the above properties are required at the orifice.

The values above are appropriate for fluids with a specific gravity near 1. For high density fluids, such as molten metals, the values above should be converted to kinematic values using the density of water.

Newtonian behavior is not strictly required, but the fluid properties at the orifice flow conditions must be in the above range. Thus as shear thinning fluid could have a low shear rate viscosity much higher than the 40cP. Viscoelastic behavior causes significant performance problems.

Particle suspensions, such as inks, are acceptable as long as the particle or agglomerate size and density do not cause the suspension to depart from the fluid properties range given above. Particles that are >5% of the orifice diameter will cause at least some instability in drop generation behavior, but still may be acceptable in low concentrations.

§ 3.1.2 Newtonian & non-Newtonian Fluid

A Newtonian fluid (named for Isaac Newton) is a fluid that flows like water—its stress / rate of strain curve is linear and passes through the origin. The constant of proportionality is

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[*] The SI physical unit of dynamic viscosity is the pascal-second (Pa·s), which is identical to 1 $kg·m^{-1}·s^{-1}$. In the CGS physical unit it is the poise (P): 1 P = 1 $g·cm^{-1}·s^{-1}$; it is more commonly expressed, particularly in ASTM standards, as centipoise (cP). The relation between Poise and Pascal-second is: 10 P = 1 $kg·m^{-1}·s^{-1}$ = 1 Pa·s; 1 cP = 0.001 Pa·s = 1 mPa·s.

[†] In CGS physical unit: 1 dyne = 10^{-5} N; 1 dyne/cm = 1mN/m.

known as the viscosity. Examples: Water, Milk, Sugar solution, Mineral oil. A simple equation to describe Newtonian fluid behavior is:

$$\tau = \mu \frac{du}{dx}$$

where τ is the shear stress exerted by the fluid ('drag') [Pa]; μ is the fluid viscosity - a constant of proportionality [Pa•s]; *du/dx* is the velocity gradient perpendicular to the direction of shear [s^{-1}].

In common terms, this means the fluid continues to flow, regardless of the forces acting on it. For example, water is Newtonian, because it continues to exemplify fluid properties no matter how fast it is stirred or mixed. Contrast this with a non-Newtonian fluid, in which stirring can leave a 'hole' behind (that gradually fills up over time - this behavior is seen in materials such as pudding, oobleck, or, to a less rigorous extent, sand), or cause the fluid to become thinner, the drop in viscosity causing it to flow more (this is seen in non-drip paints, which brush on easily but become more viscous when on walls).

For a Newtonian fluid, the viscosity, by definition, depends only on temperature and pressure (and also the chemical composition of the fluid if the fluid is not a pure substance), not on the forces acting upon it.

If the fluid is incompressible and viscosity is constant across the fluid, the equation governing the shear stress, in the Cartesian coordinate system, is:

$$\tau_{ij} = \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

with co-moving stress tensor P (also written as σ):

$$\mathbb{P}_{ij} = -p\delta_{ij} + \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

where, by the convention of tensor notation, τ_{ij} is the shear stress on the ith face of a fluid element in the jth direction, u_i is the velocity in the ith direction, x_j is the jth direction coordinate.If a fluid does not obey this relation, it is termed a non-Newtonian fluid, of which there are several types.

A non-Newtonian fluid is a fluid in which the viscosity changes with the applied strain rate. As a result, non-Newtonian fluids may not have a well-defined viscosity. Depending on how viscosity changes with time the flow behavior is characterized as:

a) Thixotropic: time thinning, i.e. viscosity decreases with time;
b) Rheopectic: time thickening, i.e. viscosity increases with time.

Thixotropic fluids are quite common in chemical as well as in food industry. Rheopectic fluids are very rare.

The viscosity of a Non-Newtonian time independent fluid is dependent not only on temperature but also on shear rate.

Depending on how viscosity changes with shear rate the flow behavior is characterized as:

1) Shear thinning - the viscosity decreases with increased shear rate;
2) Shear thickening - the viscosity increases with increased shear rate;
3) Plastic - exhibits a so-called yield value, i.e. a certain shear stress must be applied before flow occurs.

Sear thinning fluids are also called pseudoplastic and shear thickening fluids are also called dilatant (as Fig. 3-1 shows below).
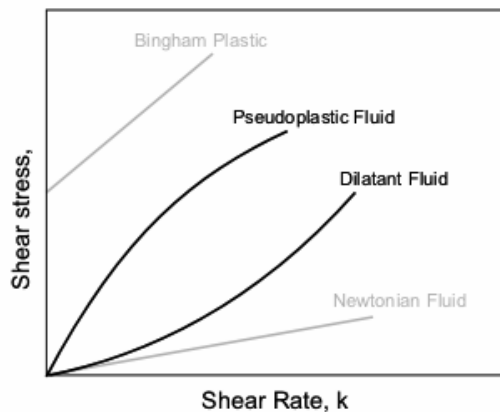

Fig. 3-1: Non-Newtonian fluid [2].

Although the concept of viscosity is commonly used to characterize a material, it can be inadequate to describe the mechanical behavior of a substance, particularly non-Newtonian fluids. They are best studied through several other rheological properties which relate the relations between the stress and strain tensors under many different flow conditions, such as oscillatory shear, or extensional flow which are measured using different devices or rheometers. The rheological properties are better studied using tensor-valued constitutive equations, which are common in the field of continuum mechanics.

§ 3.1.3 Viscosity Effects

a) Newton's Theory on Viscosity

Isaac Newton postulated that, for straight, parallel and uniform flow, the shear stress, τ, between layers is proportional to the velocity gradient, $\partial u/\partial y$, in the direction perpendicular to the layers, in other words, the relative motion of the layers.

$$\tau = \eta \frac{\partial u}{\partial y}$$

Here, the constant η is known as the coefficient of viscosity, the viscosity, or the dynamic viscosity. Many fluids, such as water and most gases, satisfy Newton's criterion and are known as Newtonian fluids. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity.
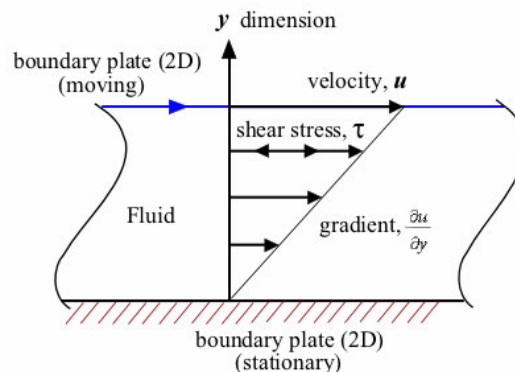

Fig. 3-2: Laminar shear of fluid between two plates. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid's viscosity. This type of flow is known as a Couette flow [11].

b) Viscosity Effects on IJP

Increasing fluid viscosity acts to dampen the acoustic waves used to create a drop. Increasing viscosity also causes an increase in drive voltage required to create a drop of fixed velocity and a decrease effect of the orifice diameter, thus decreasing the drop size at fixed drop velocity.

Although surface tension and density are weak functions of temperature, viscosity is a strong function of temperature. Thus the effect of viscosity variation can be shown most clearly by the operation of a fluid in a range of temperature.
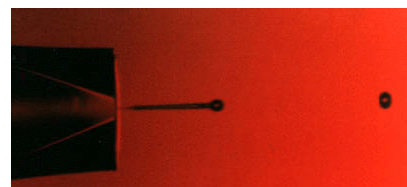

Fig. 3-3: Satellite-free drop formation [8].

Fig. 3-4: Satellite drop formation [8].

Also, viscosity acts to dampen the instabilities that lead to satellite formation. Fig. 3-3 shows satellite-free drop formation with ethylene glycol (18cP, 47 dynes/cm). Fig. 3-4 shows drop formation for isopropanol (2cP, 22 dynes/cm), with a satellite forming after each drop is ejected.

§ 3.1.4 Density Effects

Variation of density does not directly affect the performance of a fluid in a demand mode ink-jet device, but usually indicates a variation of acoustic speed or bulk modulus of the fluid, both of which affect the optimum waveform timing

(see **§3.2**) and amplitude requirements. In practice, density, acoustic speed, and bulk modulus effects are minor, and even liquid metals have waveform requirements similar to water and low density solvents.

§ 3.1.5 Surface Tension Effects

a)   The Cause of Surface Tension

Surface tension is caused by the attraction between the molecules of the liquid by various intermolecular forces. In the bulk of the liquid each molecule is pulled equally in all directions by neighboring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside the liquid but they are not attracted as intensely by the molecules in the neighboring medium (be it vacuum, air or another liquid). Therefore all of the molecules at the surface are subject to an inward force of molecular attraction which can be balanced only by the resistance of the liquid to compression. Thus the liquid squeezes itself together until it has the locally lowest surface area possible.
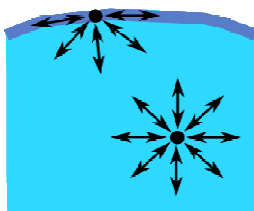

Fig. 3-5: Diagram of the forces on a molecule of liquid [3].

Another way to think about it is that a molecule in contact with a neighbor is in a lower state of energy than if it weren't in contact with a neighbor. The interior molecules all have as many neighbors as they can possibly have. But the boundary molecules have fewer neighbors than interior molecules and are therefore in a higher state of energy. For the liquid to minimize its energy state, it must minimize its number of boundary molecules and therefore minimize its surface area [4].

As a result of this minimizing of surface area, the surface will want to assume the smoothest flattest shape it can (rigorous proof that 'smooth' shapes minimize surface area relies on use of the Euler-Lagrange Equation). Since any curvature in the surface shape results in higher area, a higher energy will also result. Consequently, the surface will push back on the disturbing object in much the same way a ball pushed uphill will push back to minimize its gravitational energy.

b)   Physics Definition of Surface Tension

Surface tension is represented by the symbol σ, γ or T and is defined as the force along a line of unit length where the force is parallel to the surface but perpendicular to the line. One way to picture this is to imagine a flat soap film bounded on one side by a taut thread of length, L. The thread will be pulled toward the interior of the film by a force equal to γL. Surface tension is therefore measured in Newtons per meter ($N \cdot m^{-1}$), although the CGS unit of dynes per cm (dynes/cm) is normally used [5].
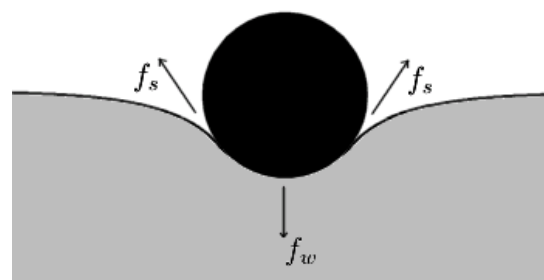

Fig. 3-6: Diagram shows, in cross section, a needle floating on the surface of water. Its weight, f_w, depresses the surface, and is balanced by the surface tension forces on either side, f_s, which are each parallel to the water's surface at the points where it contacts the needle. Notice that the horizontal components of the two f_s arrows point in opposite directions, so they cancel each other, but the vertical components point in the same direction and therefore add up [6].

A better definition of surface tension, in order to treat its thermodynamics, is work done per unit area. Since mechanical systems try to find a state of minimum potential energy, a free droplet of liquid naturally assumes a spherical shape. This is because a sphere has the minimum surface area for a given volume. Therefore surface tension can be also measured in joules per square meter ($J \cdot m^{-2}$), or, in the CGS system, ergs per cm^2.

c)   Formation of Drops

Formation of drops occurs when a mass of liquid is stretched. Fig. 3-7 shows water adhering to the faucet gaining mass until it is stretched to a point where the surface tension can no longer bind it to the faucet. It then separates and surface tension forms the drop into a sphere. If a stream of water were running from the faucet, the stream would break up into drops during its fall. This is because of gravity stretching the stream, and surface tension then pinching it into spheres [5].

Fig. 3-7: Water drop formation [7].

d)   Surface Tension Effects on IJP

Surface tension has a small effect on the drive voltage requirements for a device. As surface tension increases, the drive voltage required to achieve a constant drop velocity will increase. Very low surface tension can result in an increased likelihood of air ingestion, particularly at high drop velocities. Meanwhile, very high surface tension materials require special consideration in the selection of orifice materials and coatings.

§ 3.2 Actuation Amplitude & Drive Waveform Effects on Ink-jet Device Performance

§ 3.2.1 Flow Patterns on the Nozzle Plate of a Piezo-driven Printhead

Actuation of a single nozzle with a sufficiently high voltage can induce a flow in the ink layer on the nozzle plate. Several flow patterns (as Fig. 3-8 shows below), depending on the actuation amplitude (voltages) and frequency (kHz), were observed on the nozzle plate [12].
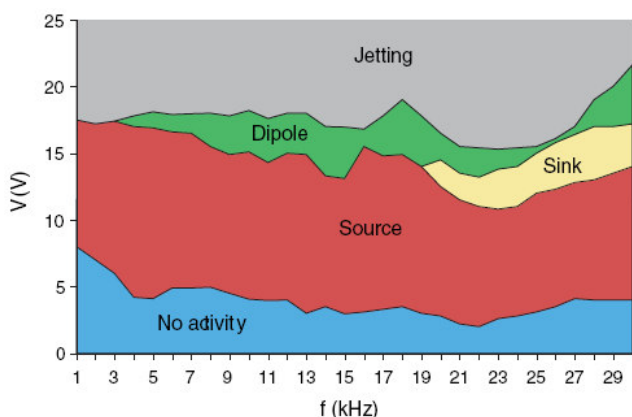

Fig. 3-8: Phase diagram of the nozzle, showing the different nozzle states as a function of the actuation amplitude and firing frequency [12].

In the case of jetting actuation, the jet of droplets transfers momentum to the surrounding air, which results in a suction of air towards the jet. Friction between the ink layer and the air flow induced by the jet of droplets causes a radial flow of ink towards the nozzle. The flow resembles an ideal 2D sink flow, but a small deviation occurs due to the non-uniform ink layer thickness. In the case of non-jetting actuation, the motion of the meniscus in the nozzle is strong enough to cause an equally strong ink flow on the nozzle plate. The most striking is the dipole-like flow, with the direction of the dipole always aligned along the ink layer thickness gradient. Small deviations from an ideal 2D dipole occur due to a non-uniform ink layer thickness. Two possible driving mechanisms for the flow induced by the meniscus motion are:

a)   Acoustic streaming due to capillary waves;

b)   Marangoni (surface tension gradient-driven) flow caused by local changes in surface tension.

The majority of the experiments show a flow in the ink layer towards the actuated nozzle. Particles caught in this ink layer are likely to reach the jetting nozzle and may cause nozzle failure. For increasing the jetting stability of the printhead, an ink layer near the nozzles should be prevented. The absence of the ink layer would prevent transport of particles towards the nozzle. This can be achieved by using a nozzle plate with poor wetting properties, or by creating specific structures on the nozzle plate to prevent the formation of an ink layer.

§ 3.2.2 Study of Wave Propagation Phenomena in Drop-on-Demand Ink-jet

The experimental observations show that the operation of drop-on-demand ink-jet nozzle assemblies (Fig. 3-9) comprised of piezoelectric transducer (PZT) tubes with a silicon plate nozzle attached to one end and an ink supply connected to the other end depends strongly on the length of the cavity [10].
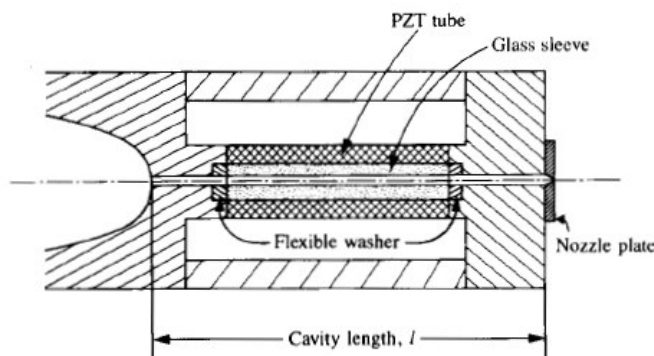

Fig. 3-9: Schematic of ink jet nozzle assembly [10].

Four measurable quantities appear to be linearly dependent on this length and on the speed of sound wave in the ink:

1)   Optimum (rectangular) pulse width is equal to l/c;

2)   Delay time before the meniscus starts to protrude is equal to $3l/2c$;

3)   Period of meniscus oscillation is equal to $4l/c$;

4)   Period of low-frequency resonant and antiresonant synchronous operation is equal to $4l/c$;

where c is the speed of acoustic waves in the fluid (1658 m/s for ethylene glycol at room temperature).

There are some deviations from these linear dependencies, as shown in Fig. 3-10, but the preponderance of data support this linear behavior with length.

Fig. 3-10: Period of oscillation, delay before appearance of drop, and optimum pulse width as a function of cavity length. Straight lines (dashed) having slopes of 4/c, 3/2c, and 1/c are also shown [10].

The linear behavior follows from a simple one-dimensional acoustics analysis with reflection coefficients based on the presence of a closed end at the nozzle and an open end at the supply. Expansions and contractions of the tube resulting from an applied voltage pulse generate rarefaction and compression waves, which, after appropriate end reflections,

reinforce or interfere with each other to enhance or impede the velocity of the ejected drops. An upper limit on the frequency of this resonance type phenomenon is set by the time required for the separation of a drop. Several reflected waves can contribute to the process. In the higher frequency range, resonances and antiresonances in the operation occur in accordance with the fundamental and higher harmonics.

§ 3.2.3 Pulse Width Effects

A piezoelectric demand mode ink-jet device can be driven by a simple 'On-Off' pulse that moves the piezoelectric transducer and then returns it to the rest state. Given finite rise and fall times, the waveform becomes trapezoidal, as shown in Fig. 3-11.
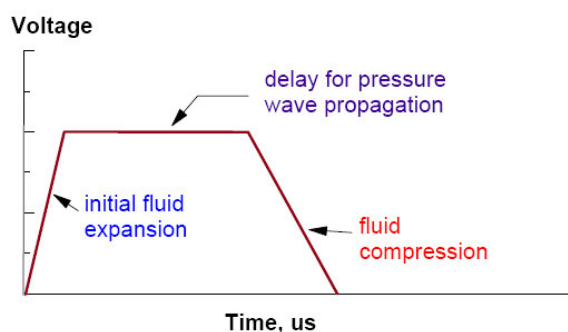

**Fig. 3-11:** Drive waveform for drop-on-demand IJP [8].

All demand mode ink-jet devices have fluid acoustic resonances due to compressibility effects. This implies the existence of an optimum pulse width, which is a well known phenomenon associated with drop-on-demand devices [9, 10]. Optimum is defined as achieving the highest drop velocity and mass for a given amplitude pulse. The optimum pulse width is more distinct if the piezoelectric transducer is driven so that a negative pressure is created in the fluid initially, and the return to the rest state creates a pressure rise, as is indicated in Fig. 3-11.

§ 3.2.4 Complex Waveform Effects

The simple waveform shown in Fig. 3-11 can be extended to become a bipolar pulse, as shown in Fig. 3-12. The function of the initial portion of the waveform remains the same. The second part of the waveform can be used to cancel some of the residual acoustic oscillations that remain in the device after drop ejection. For the case when the piezoelectric transducer is centered of the acoustic cavity, the optimum bipolar waveform has the positive and negative going amplitudes are equal, and the second dwell time is twice the initial dwell time.
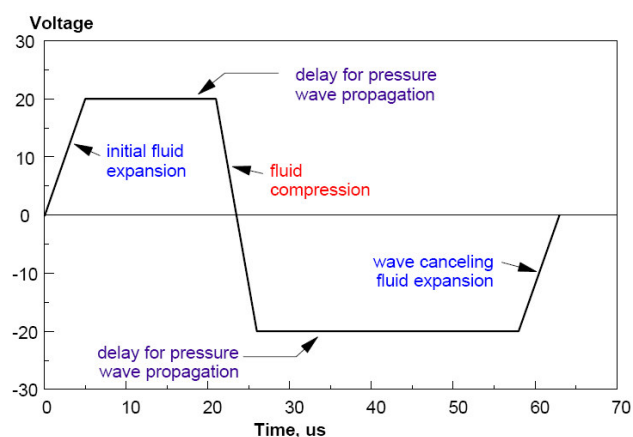

**Fig. 3-12:** Complex drive waveform for drop-on-demand IJP [8].

§ 3.3 Physical Issues for Ink-jet printing of Polymers

§ 3.3.1 Current Status of Ink-jet printing of Polymers

The most crucial part of ink-jet printing of polymers is probably the polymer ink and its physical properties, in particular the viscosity and surface tension. The viscosity should be suitably low, typically below 20cP. When too much kinetic energy is viscously dissipated then no droplet is ejected. Eventual polymer solutions should therefore be sufficiently dilute. The shear rates involved in ink-jet printing are usually of the order $10^5 s^{-1}$, hence shear-thinning may occur. For a given pressure wave at the orifice (nozzle), the lower the viscosity the greater the velocity and amount of fluid propelled forwards, which usually leads to the formation of long tails behind the head of the drop. The surface tension is responsible for the spheroidal shape of the liquid drop emerging from the nozzle. In practice, surface tension ranges from 28 dynes/cm (e.g. xylene), to 350 dynes/cm for a molten solder [13]. Finally, the wetting behavior of fluid and nozzle material is of importance also, as wetting of the nozzle outlet face results in spray formation. Droplet formation during ink-jet printing as a function of fluid properties was also modeled numerically [14].

In principle, polymers can be printed from the melt when the complete ink-jet system can be heated. This technology is used in graphical industry for printing waxes [15, 16]. Another possibility for ink-jet printing of polymers is represented by the utilization of colloidal suspension of polymer lattices, which has the advantage of presenting a high-molecular-weight polymer in a low-viscosity form. In recent years the use of colloidal matter in the form of pigments in ink-jet ink formulations has become more and more widespread, thanks to their superior light-fastness as compared with molecular dyes. However, when particle size becomes of the order of 1 µm, printability problems may occur [17].

§ 3.3.2 Physical Aspects

Up to now, few articles have been published that provide detailed information on how ink-jet printability correlates with the rheological properties of a polymer-containing ink, and therefore with the polymer structure, molecular weight, and concentration. Nevertheless, the work of Meyer et al. is

drawing our attention on this subject [18]. The influence of added polymer on drop formation and filament break-up was studied at different concentrations, using various molecular weight polyacrylamides. Concentrations ranged from 0 to 200 ppm and molecular weights from 500 000 to 6×10^6. Four different regimes were observed with increasing concentration or molecular weight. Normally, a long tail is formed that simultaneously disintegrates along its axis to form satellite droplets. At higher concentrations or molecular weights only a few satellites appear at the tails' ends. A single droplet without a tail represents the third regime. Finally, the droplet does not detach and returns into the nozzle. A scaling argument, taking into account only viscoelastic effects, showed that disintegration of the filament into small droplets does not occur if the typical Newtonian break-up time is smaller than the longest relaxation time of the polymer solution. However, as strain hardening was neglected the validity of this result is questionable. Not long ago a study using polystyrene solutions was also showing a decrease of printability with molecular weight [18].

Valuable information can also be found in studies on viscoelastic jet stability and the dynamics of drop formation. The relationships between (viscoelastic) jet stability and continuous Ink-jet printing, and between drop formation and Drop-on-Demand Ink-jet printing, are obvious. In this section some of the main results will be presented.

An ordinary Newtonian jet is unstable to disturbances whose wavelength exceeds the diameter of the jet. This effect is known as the Rayleigh-Tomotika instability. The wave grows exponentially until the jet breaks to form droplets. The first experimental results on viscoelastic jet stability were published in the late 60s. The break-up length, i.e., the distance between the nozzle where the jet emerges and the point where the jet breaks up into droplets was studied using dilute solutions of polyisobutene in tetralin [19]. A break-up length decrease with increasing elasticity or increasing molecular weight was found. Goldin et al. studied dilute aqueous solutions of highly branched carboxy-polymethylene (Carbopol), poly (ethylene oxide), and poly (acryl amide) / (Separan) [20]. It was found that the viscous but inelastic Carbopol solution behaved similarly to water. However, the viscoelastic solutions of Separan and poly (ethylene oxide) behaved totally differently. The growth of the wave was arrested, and strings of droplets connected by thinning filaments were formed. The filaments were remarkably persistent and the break-up length increased greatly. Fig. 3-13 shows the effect of increasing molecular weight on fluid jet break-up and the formation of a bead-on-a-string structure. Later studies confirmed these findings [21, 22].
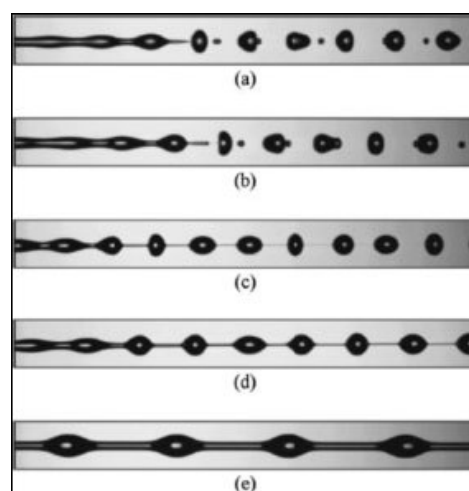

Fig. 3-13: The influence of polymer molecular weight and concentration on the break-up of a fluid jet: a) glycerol/water. b) 0.3% 100 000 poly (ethylene oxide). c) 0.1% 300 000 poly (ethylene oxide). d) 0.05% 1 000 000 poly (ethylene oxide), e) 0.043 % 5 000 000 poly (ethylene oxide). The bead-on-a-string structure is formed when the molecular weight is equal or higher than 3 00 000 [24b].

Mun and co-workers investigated viscoelastic jet stability of poly (ethylene oxide) in glycerol/water, using molecular weight ranging from 8000 to 10^6 and differing concentrations [23]. Solvent composition was chosen such that all fluids had the same (shear) viscosity and surface tension. Above M_w 300 000 the break-up length increased and the bead-on-a-string structure was formed. Elongational viscosity measurements showed that above M_w 100 000 these fluids were strongly strain hardening, i. e., the elongational viscosity increased with elongation rate. Using the same fluids as Mun, Christanti and Walker showed that the elongation rate (ε) could be estimated from the thinning of the filaments connecting the beads, via $\varepsilon \approx -2/r \ (dr/dt)$, where r denotes the filament diameter [24]. The measured elongation rates agree with the critical elongation rates discussed above where strain hardening was found, indicating that the elongational viscosity is the key rheological parameter governing jet break-up. In addition, it was shown that these filaments thin exponentially with time [24b]. The measured relaxation time (τ) agrees qualitatively with the longest relaxation time according to the Zimm model, and scales with molecular weight as $\tau \propto M_w^{3v}$, as predicted by Zimm, where v denotes the molecular expansion coefficient [25].

Studies on the dynamics of viscoelastic drop formation under gravity showed a behavior that in many respects resembles that of a viscoelastic jet. Experiments using fluids that were identical to those used by Mun revealed that in the case of a Newtonian drop a neck is formed that gradually thins prior to detachment, according to a power law [26]. For viscoelastic fluids the neck eventually turns into a filament, sustained for a period of time that increases strongly with molecular weight. Pictures of the difference between Newtonian and viscoelastic drops are shown in Fig. 3-14. Amarouchene et al. also found that the addition of small amounts of high molecular weight poly (ethylene oxide) gave rise to long-lived cylindrical filaments [27]. Filament

thickness decreased exponentially with time. The fluids used were shown to be strain hardening. When using the rigid rod polymer xanthan (M_w of 3×10^6) the authors observed that thread formation and strain hardening were absent. Neck thickness followed the same power law as for Newtonian fluids.
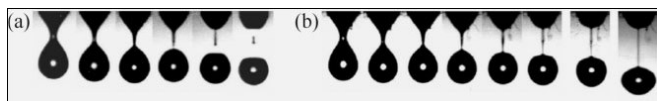

Fig. 3-14: a) Formation of a Newtonian drop consisting of glycerol/water. Pictures were taken as a function of the time before detachment, in milliseconds. b) Effect of 0.1 wt -% 1 000 000 poly (ethylene oxide). The drop was connected to the nozzle via a thinning filament. The time to break-up increases strongly. Droplet size is of the order of a few millimeters [26].

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Chapter 4:

Recent Advances in Applications of Ink-jet Printing

§ 4.1 Fabrications of Organic/Plastic Electronic Devices

Ink-jet printing technologies provide opportunities both for significant cost reduction in existing organic devices and for new device configurations [1]. Ink-jet methods based on printing with two types of ink-jet heads: namely, the piezoelectric and acoustic types are most commonly used for fabrication of organic electronics. Thermal-type ink-jet printheads also exist. The structure of the thermal-type head is much simpler than that of the piezoelectric device. Thermal-type heads use a small electrical heater to heat the ink in a cavity above its boiling point. A bubble is created that pushes ink out from the nozzle. This type of ink-jet head is not used in the case of organic electronics because heat damage of the functional organic material is possible. With the use of ink-jet printing techniques, the deposition of all parts of the transistor device, contact electrodes, semiconducting layers, and insulating materials is possible. Table 1 shows the results achieved after patterning of different inorganic and organic materials by ink-jet printing techniques [2].

Table 1: Summary of Methods for Patterning of Organic Electronics Based on Ink-Jet Printing Techniques [2]

InkJet Head	Printed Material	Substrate	Semiconductor	Resolution [μm]	TFT	
					Mobility (cm^2/Vs)	On-off ratio
Piezoelectric Drop on demand	Cu-rich deposits	Glass	-	550.0	-	-
	Au and Ag nanoparticles	Glass	-	100.0	-	-
	Pentacene	Si/SiO$_2$	Pentacene	50.0	0.02	10^5
	CdSe	Glass	CdSe	10	1.00	10^4
	Polyimide	Plastic	-	-	-	
	PEDOT [a]	Polyimide	F8T2 [b]	5.0 - 100.0	0.02	10^5
Acoustic	Polythiophene	Si/SiO$_2$	F8T2 [b], PHT [c]	35.0 μm	0.10	10^6

§ 4.1.1 Pixel Ink-Jet Printing of Organic Displays

Polymer light-emitting diodes (PLEDs) and organic light-emitting diodes (OLEDs) have a potential for extensive applications such as multicolor emissive displays, road signs, indicator lights, and logos [3]. One of the major advantages of PLEDs and OLEDs is their color tuning capability with various emission colors easily obtained through the change of chemical structure of the organic compounds. Another advantage is the solution processability of the conjugated organics [4]. Traditionally, the polymer solutions are deposited by spin-coating: a technology incapable of patterning materials, since it non-selectively distributes the materials all over the substrate. However, to realize the abovementioned applications, such as multicolor displays, it is necessary to achieve a lateral control during deposition of the different polymers such that multicolor emission can be achieved. This drawback of spin-coating can be overcome by using the ink-jet printing (IJP) technology. IJP technology is a common technology used for desktop publishing. It is a contactless method of printing and has found wide applications in the packaging and printing industries. Ink-jet printers work on the principle of ejecting a fine jet of ink through nozzles 10-200 mm in diameter. The jetted stream is broken up into a series of droplets that are deposited as a dot matrix image. The advantages of the ink-jet printing technology over the conventionally used spin-coating technology are shown in Table 2 [5].

Table 2: Comparison of spin-casting and ink-jet printing technologies [5]

Characteristics	Spin-casting	Ink-jet printing
Patterning capability	No patterning capability	Capable of patterning with micrometer resolution
Large device area capability	Sensitive to dust particles and substrate defects, and not suitable for large area processing.	Not sensitive to substrate defects, and it is a better technology for the fabrication of large area device.
Efficiency of using material	More than 99% of the polymer solution is wasted.	Less than 2% of the material is wasted.
Multicolor display fabrication capability	No multicolor patterning capability.	Ideal for multicolor patterning.

In 1998, Bharathan and Yang produced the first PLED device using ink-jet printing [5], a light-emitting logo, which was fabricated in a sandwich structure with substrate size of 30 mm×30 mm (as shown right in Fig. 4-1). Poly[2-methoxy-5-2'-ethylhexyloxy-1,4-phenylene vinylene] (MEH-PPV) was used as the active material (or it is the buffer layer), and ITO was the anode and calcium was the cathode. The PEDOT solution was printed onto ITO by using a commercial available Ink-jet printer. The MEH-PPV films were prepared via spin-casting at 2500 rpm from a 1% MEH-PPV solution, and the thickness of MEH-PPV films was determined to be around 1200 Å as obtained using an alpha-step profilometer. Afterwards they made four different types of devices [6]: polymer light-emitting logos, dual-color PLEDs, multicolor OLEDs, and pixel PLEDs. These four devices and the ink-jet printed materials are listed in Table 3.
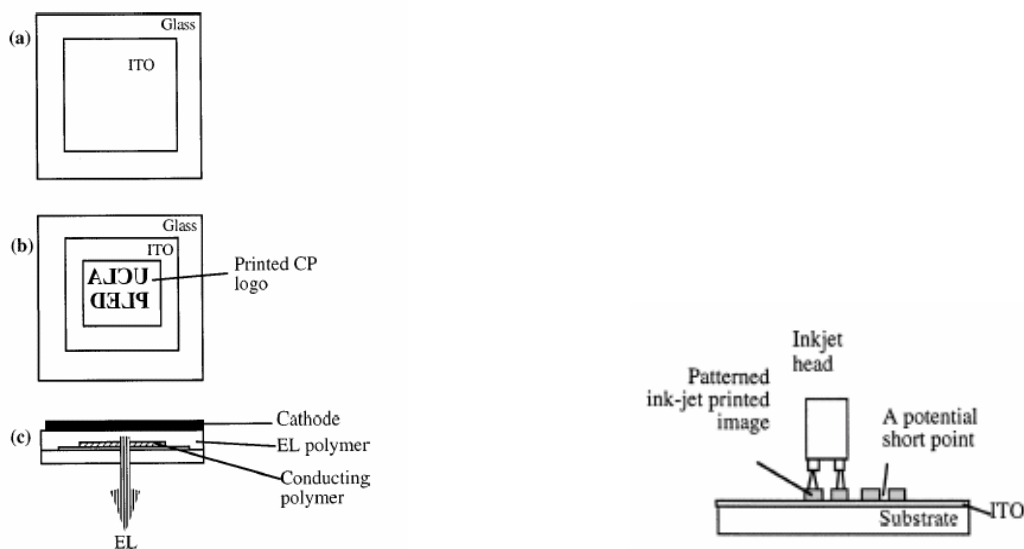

Fig. 4-1: *The polymer light-emitting logo fabrication process: a) preparation of the substrate; b) printing of the conducting polymer into desired pattern; c) deposition of the luminescent polymer and the cathode material[5].*

Table 3: *Four PLED/OLED devices fabricated using ink-jet printing [6]*

Devices fabricated	IJP material	Buffer material
Polymer light-emitting logo	Hole-injection layer: PEDOT[a]	EL polymer: MEH-PPV[b]
Dual-color PLED	Red-emission polymer: MPS-PPV (Diffusion of MPS-PPV into PPP buffer layer, energy transfer occurred)	Blue-emission polymer: PPP-NEt$_3$[c]
Multicolor OLED	Green emission organic molecule: Almq$_3$ Red-emission organic dye: DCM (Bilayer structure, no diffusion occurred)	Blue-emission polymer: PVK[d]
Pixelated PLED	Insulating polymer: PVA[e] is used as the insulating shadow mask for the patterning of cathode.	EL polymer: MEH-PPV

[a]PEDOT (3,4-polyethylenedioxythiophene-polystyrenesulfonate) [b]MEH-PPV: Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) [c]PPP-NEt$_3$$^+$: poly[2,5-bis[2-(N,N,N-triethylammonium) ethoxy]-1,4-phenylene-alt-1,4-phenylene] dibromide [d]PVK: poly-9-vinylcarbazole [e]PVA: polyvinylalcohol

Nowadays there are extensive developments and advances of pixel ink-jet printing for organic displays applications [7, 8, 9]. Many companies including Cambridge Display Technology, Seiko-Epson, DuPont Displays, and Toshiba have demonstrated full-color emissive-polymer display prototypes ranging in size from several to 40 in., in which the polymeric color pixels and hole injection layers were deposited. In such applications, ink-jet technology is used to pattern the red, green, and blue emissive polymers, as well as charge injection and transport layers, into the photolithographyically pre-defined pixel locations, respectively. Fig. 4-2 is such a schematic of the RGB multicolor PLED display fabricated by Seiko-Epson, while Fig. 4-3 is from DuPont Displays.
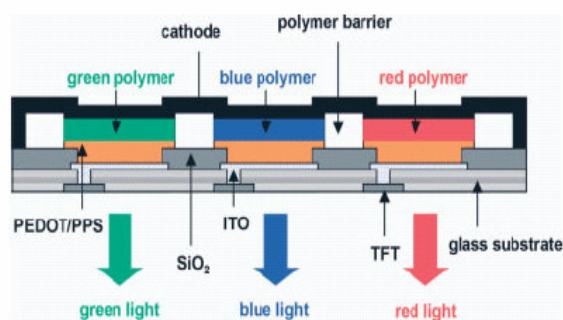

Fig. 4-2: *Schematic of a RGB multicolor PLED display fabricated by Seiko-Epson Co.; Green, blue, and red light-emitting polymers are printed between polymer barriers, on top of a conducting polymeric PEDOT/PSS layer. Each pixel is addressed individually with a thin film transistor (TFT) [8].*
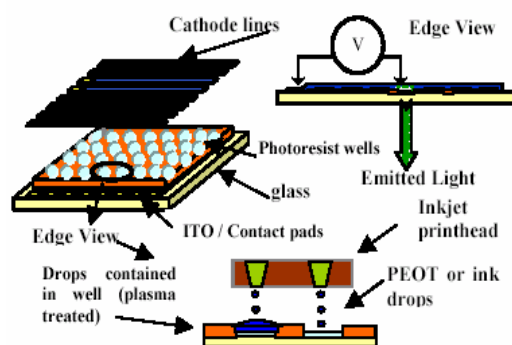

Fig. 4-3: *Schematic illustration of PLED structure, fabricated by DuPont Co. [9].*

§ 4.1.2 Ink-Jet Printing of Electron Donor/Acceptor Blends: Towards Bulk Heterojunction Solar Cells

A typical solar cell structure using organic bulk heterojunction (BHJ) materials looks such as the one shown in Fig. 4-4a. For device fabrication the photoactive layer is usually deposited on a transparent bottom electrode, such as indium tin oxide (ITO) located on a carrier substrate, covered with a conducting polymer layer such as polyethylenedioxy-thiophene:polystyrene sulfonate (PEDOT: PSS). PEDOT: PSS is a hole conducting material, which improves both device stability and performance. On top of the photoactive layer, an additional thin layer (~ 10Å) such as lithium fluoride (LiF) is used to improve the device performance; an aluminum electrode is deposited on top to complete the solar cell. The asymmetry of the work functions between the cathode and the anode creates an internal electric field such that the holes move toward the ITO layer and the electron towards the aluminum cathode. By externally connecting the electrodes a current can be generated. There are some drawbacks related to the traditional spincoating technique such as solution wastage [5]. Moreover, finding the most favorable donor/acceptor ratios and the determination of their optical properties is highly time consuming.

There are a number of BHJ materials researchers have tried in order to print organic solar cells. Those commonly used and reported are [10]:

1) MDMO-PPV: poly (2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene), and [6,6]-PCBM (6,6-phenylC$_{61}$-butric acid methyl ester).

2) Poly (3-hexylthiophene) in its regio-regular form as electron donor and fullerene ([6,6]- Phenyl C$_{61}$ – butyric acid methyl ester) as electron acceptor.

3) Inorganic-organic hybrid dispersion of Cadmium selenide (CdSe) nano-rods in poly (3-hexylthiophene) in its regio-regular form.
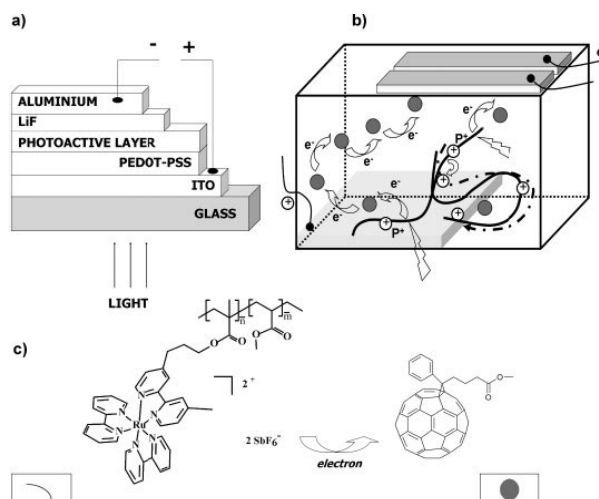

Fig. 4-4: *a) General layout of a solar cell device for polymeric materials; b) schematic principle in a bulk heterojunction solar cell; c) donor/acceptor pair under investigation (RuPMMA-PC60BM)[11].*

A recent work done by Veronica Marin et al. described the ink-jet printing of different electron donor/acceptor compositions for potential applications in bulk heterojunction solar cells by the preparation of thin-film libraries on photoresist patterned glass [11]. The electron transfer from RuPMMA copolymer to PC$_{60}$BM and C$_7$-V derivatives was screened in a fast manner utilizing a UV-vis/fluorescence plate reader. Best quenching performance has been observed for the PC$_{60}$BM case. Preliminary studies by AFM on the RuPMMA/ PC$_{60}$BM blends spin-coated from ODCB on PEDOT:PSS covered glass revealed formation of homogeneous structure. Their further efforts are focusing on the optimization of the printing of thin PEDOT:PSS films on photoresist patterned glass substrates in order to fabricate solar cell test devices by

ink-jet printing process.

§ 4.1.3 All-Polymer Field-Effect Transistor Fabricated Using Ink-jet Printing Technique

The advantages of conducting polymers over conventional materials, such as silicon and germanium, include low cost and ease of processing. Organic or polymer-based semiconductors have been applied to fabricate field-effect transistors (FETs). Since the first reported organic FET in 1983 [12], there have been many on-going efforts to form organic or polymer-based FETs. Organic or polymer based transistors have already found application in smart pixels such as radio frequency identification (RFID), electronic luggage tags, sensors, and active matrix light-emitting polymer displays, etc. [13–16]

A variety of approaches have been used to deposit conducting polymer or organic semiconductors based on the nature of those materials. The various techniques commonly employed include solution-processed deposition, such as spin coating and printing, electro-polymerization, and vacuum evaporation etc. Other techniques (soft lithography, self-assembly, and Langmuir-Blodgett) have also been applied to the fabrication of polymer-based FETs. Various printing techniques, including screen-printing, micro-contact printing, and Ink-jet printing (IJP), are attracting more and more attention. Among these printing techniques, IJP is very promising because polymer devices fabricated by an IJP technique have the advantages of simplicity of fabrication, compatibility with various substrates, availability of non-contact, no-mask patterning, etc [17].

For the previously reported all-polymer FET fabricated using an IJP technique [13-15], only the gate (G), source (S), and drain (D) electrodes were printed, while other components, such as the dielectrics and active layers, were still deposited by spin coating and patterned by lithography. The operation voltage of those polymer-based FETs was also relatively high, which is not appropriate for the logic gate circuit applications that require low-voltage operation. An Ink-jet-printed insulating layer of a polymer-based FET has seldom been reported, mainly because it is difficult to print out the insulating polymers, which are insoluble or soluble but easily clog the printer nozzles [18-20].

To overcome this problem, the approach described here [21] is to use a water-soluble insulating polymer solution that can be easily printed out without clogging the nozzles. Since the charge in the polymer-based FET is proportional to both the dielectric constant and the gate voltage, the material with a higher dielectric constant allows the necessary charge to accumulate at much lower voltages. Poly(vinyl pyrrolidone) K60 (PVP-K60), a water-soluble insulating polymer with a high dielectric constant of 60, meets the above requirements. As the schematic shown in Fig. 4-5 below, combining the printed poly(3,4-ethylene-dioxythiophene) / poly(styrene sulfonic acid) (PEDOT / PSS) as the source/drain/gate electrodes, and printed polypyrrole (PPy) as the active layer, all-polymer transistors have been successfully synthesized using an all-IJP technique, and characterized.
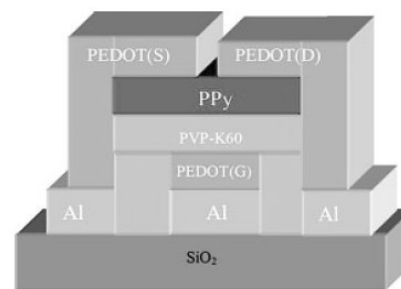

Fig. 4-5: Schematic of the all-polymer FET [21].

Thanks to the dielectric polymer with a high dielectric constant, the all-polymer FET operates at a low voltage. Since the printed active layer, PPy, is doped and much thicker than that using other deposition methods, this FET has a reversed gate effect conductivity. A mechanism based on the channel thickness and doping charge components has been proposed to explain the new phenomena. As far as I know, this is the first report of an all-Ink-jet printed all-polymer FET with a low operation voltage. This advance can make a great contribution to the fabrication of practical polymer microelectronic devices and circuits using a simple all Ink-jet printing technique.

§ 4.2 Ink-Jet Printing of Biological Microarrays

The DNA Microarray is a powerful tool for the high-throughput identification and quantification of nucleic acids. Among other uses, array analysis has become a standard technique in the molecular biology laboratory for monitoring gene expression. Arrays can be made either by the mechanical spotting of pre-synthesized DNA products [22] or by the *de novo*[3] synthesis of oligonucleotides on a solid substrate, usually a glass slide. As the sequences for *de novo* synthesized arrays are stored electronically rather than physically in frozen DNA libraries, the costs and the potential for errors in amplification, storage, and retrieval are eliminated.

Piezoelectric ink-jet oligo-array synthesis as proposed by Blanchard and Hood [23] is a particularly flexible method that allows the rapid construction of oligonucleotide arrays containing any desired sequence. By dispensing DNA monomers from a multi-channel Ink-jet print head, large numbers of sequences can be chemically synthesized in parallel. Development of a prototype Ink-jet system was continued in the private sector [24,25]. Work by Rosetta Inpharmatics (Seattle, WA) and Agilent (Palo Alto, CA) resulted in an industrial-scale ink-jet oligo-arraying system and a catalog of commercially available arrays. However, there has been virtually no access to the Ink-jet synthesis instrumentation in basic, academic research laboratories, and high set-up fees still deter the production of specialized arrays in small batches.

When compared with the rapid acceptance of the pin-spotting microarrays [26-29], the lack of access to oligonucleotide microarray synthesizers has hampered the

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[3] In Biochemistry, *de novo* synthesis refers to the synthesis of complex molecules from simple molecules such as sugars or amino acids, as opposed to their being recycled after partial degradation. For example, *de novo* synthesis of nucleotides, as opposed to the salvage pathway.

development of new uses for this technology. The early release of the pin-spotting arrayer design [22] also spurred commercial development of high-quality microarrays, which led to the availability of numerous models at competitive prices. Despite the problems and errors associated with collection of DNA libraries, the widespread availability of pin-spotted microarrays led to acceptance and standardization of protocols, terminology, data storage, and analysis techniques [30-32]. Several laboratories have modified commercial ink-on-paper printers for use in spotting microarrays. These printers were usually based on 'bubble jet' print heads containing tiny heating elements that rapidly vaporize a water-based solution in a capillary to eject a droplet containing protein or DNA, onto a solid support [33-35]. These printers, however, are difficult to clean and are not suitable for high-throughput production of oligo-arrays or the parallel *de novo* synthesis of oligonucleotide arrays. Like pin-spotting microarrayers, they also require libraries of known nucleic acid reporters before arrays can be made.

The first successful technique for *de novo* oligonucleotide synthesis on a chip was developed by Affymetrix (Santa Clara, CA) using photolithographic techniques borrowed from the semiconductor industry. By using photomasks and UV-catalyzed base de-protection, large numbers of oligonucleotide arrays can be synthesized with a high feature density. Chips are now being made that contain all the genes predicted to be in the human genome. However, coupling chemistry using photolabile monomers is less efficient than standard phosphoramidite chemistries, resulting in arrays consisting of short oligonucleotides (25 mers) that require multiple features for the unambiguous identification of each gene. In addition, the design and construction of new arrays is slow and expensive because new masks need to be cut for each base changed in the array.

De novo oligonucleotide synthesis using a piezoelectric Ink-jet oligo-array synthesizer overcomes several of the problems inherent in the pin-spotted arrays and the conventional photolithographic mask arrays. First, as soon as the genomic DNA or expressed sequence tag (EST) library is even partially sequenced, oligonucleotide reporters, including intergenic regions, can be designed and synthesized on arrays without having to clone and store large libraries. Second, the use of standard phosphoramidite chemistry for oligo-array synthesis allows longer reporters to be synthesized, decreasing the number of reporters required for confident identification of the target molecules.
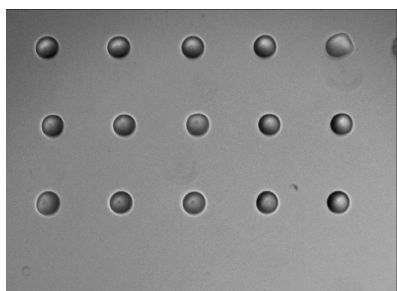

Fig. 4-6: Magnified surface of a printed slide for oligonucleotide microarray by using POSaM platform [36].

The POSaM (piezoelectric oligonucleotide synthesizer and microarrayer) platform described here [36] utilizes a low-cost piezoelectric print head with six fluid channels; four channels deliver phosphoramidite precursors and one delivers an activator (ethylthio-tetrazole), leaving one channel available for an optional linker or modified base. The piezoelectric jets can deliver a wide range of nonvolatile solvents in volumes as low as 6 pl. Piezoelectric jetting, highquality motion controllers and standard phosphoramidite oligonucleotide synthesis chemistry allow users to synthesize arrays of any nucleic-acid sequence at specific, closely spaced features on suitable solid substrates. Fig. 4-6 shows the magnified surface of a printed slide for oligonucleotide microarray.

The POSaM platform can produce multiple unique microarrays, each with 9,800 different reporter sequences, on modified glass microscope slides. Synthesis is inexpensive and rapid; new arrays can be ready for hybridization the same day that they are designed. These arrays are suitable for a wide range of biological investigations including the study of gene expression, alternative splicing, chromatin immunoprecipitation techniques (Chip-to-Chip), and single nucleotide polymorphism (SNP) detection. In addition, the covalent linkage of the oligonucleotides to the substrate is sufficiently robust to allow for re-use of individual oligo-arrays without a detectable change in the signal-to-noise ratio.

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Chapter 5:

Summary and Prospects

There are a growing number of applications that require the delivery of small quantities of functional materials with specific electrical, optical, chemical, biological, or structural functionalities into welldefined locations on a substrate. In many cases, these materials are most suitably processed from a liquid solution, dispersion, or melt, rather than from the vapor phase. Many functional materials, such as polymers or large biomolecules, are not amenable to vacuum deposition techniques. The need for solution processing may also be dictated by the nature and properties of the substrate; the need to distribute the materials over a large substrate area, or only to certain locations of the substrate and not to others (e.g., to induce a local chemical reaction); or simply to keep the material in a liquid environment at all times, such as for some biological applications.

Ink-jet printing has become one of the most widespread printing techniques in the home and office desktop printing market. Since the original observation by Lord Rayleigh in 1878 that a liquid stream is unstable and tends to break up into individual droplets, a large number of ink-jet technologies have been developed.

The application of ink-jet technology to the delivery of functional materials poses a range of important challenges in terms of ink formulation, print head and print system design, substrate choice and preparation, and control of solvent evaporation. The inks need to be formulated in a narrow viscosity range compatible with the specific print head used. In many cases, the additives that are routinely used in graphic arts printing to modify, for example, ink viscosity, cannot be used for functional materials, as they will adversely affect the materials' performance. It is necessary to ensure that the ink does not in any way chemically interact with or dissolve any of the components inside the print head or the ink feed system. Nor should the ink's properties degrade under the high mechanical shear of a piezoelectric head or the high-temperature conditions of a thermal ink-jet head. The ejection of droplets from the array of nozzles needs to be stable and reliable. Nozzles can become clogged by the evaporation of ink on the nozzle plate or the presence of particulates in the ink. Fluctuations in droplet volume can lead to undesirable variations in the amount of material deposited onto the substrate. For many applications, the velocity and direction of the droplets ejected from the array of nozzles must be highly uniform in order to ensure highly accurate positioning of a large number of droplets in well-defined substrate locations. For many nontraditional ink-jet applications, the requirements for droplet positioning accuracy are significantly more demanding than for graphic arts printing. Finally, the spreading and drying of ink droplets on the substrate must be carefully controlled in order that the droplets arrive at the desired position and the desired structure and profile of the material on the substrate are achieved.

Solving these challenges through the design of specialized print heads and ink formulation is not made easier by the fact that ink-jet technology is still regarded by many experts in the field as 'black magic'. Although several groups have attempted to model theoretically the hydrodynamical processes occurring in the ink chamber and at the nozzle plate, in many cases ink formulation and print head design are still based on empirical experience and trials. A better theoretical understanding of the ink-jet process would be of great help to print head designers and ink formulators. Similarly, a theoretical understanding of the process of spreading and drying of a micro-liquid deposited onto a substrate is challenging because a micro-liquid exhibits specific size effects arising from its high surface-to-volume ratio, such as different drying kinetics, that are not observed for bulk liquids.

This article is devoted to the emerging non-graphic-arts uses of ink-jet printing as a technique for depositing and patterning functional materials in the liquid phase. The topics of this report have been selected to provide a representative, but in no way comprehensive, overview of important applications in the field of organic/polymer electronics, and biological microarrays (DNA chips), etc. Meanwhile, the author addresses some of the key challenges that face the broad scientific and industrial community as it attempts to apply a mature and well-developed graphic arts printing technique to the deposition of functional materials. Other interesting application areas such as textile printing, printing of photoresist layers, patterning of printed circuit boards, and the delivery of liquids to induce local chemical reactions had to be omitted due to the limitation of length. All of these above constitute important fields of research and development and provide a broad spectrum of interesting scientific challenges for a wide range of functional materials.

Recently, the development of printed organic/polymer semiconductors is approaching the final stages before commercialization, with prototypes printed on industrial equipment. This review involves industries that have the potential to use printing as a manufacturing tool, such as the energy (Solar Cells), display industries (PLEDs & OTFTs), and smart tagging devices (RFID). But questions still remain about which markets will deliver revenue and which printing techniques will be used. And as the first printed displays are commercialized, where else in the electronics industry are there printing opportunities, and who will benefit? Such an indepth strategic overview of this article will help us get some clues of its current status and the driving forces behind that.

Similarly, due to space limitations of this paper, no attempt has been made to include alternative, viable printing techniques capable of controlled delivery of small fluid volumes to well defined locations. Techniques such as micro-dispensing, screen, offset, and gravure printing, and spray and aerosol coating using small nozzles, have many attractive attributes that rival those of ink-jet technology and make them viable alternatives for many applications.

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