# Chapter 2
# Printing Technology

## 2.1 Printing Parameters

A wide range of printing methods have already been applied to conventional electronics fabrication. They include screen printing, inkjet printing, gravure printing, flexo printing, and offset printing. They are also applicable to many advanced PE products. Depending on the nature of the PE products, one must make a suitable choice regarding the of ink, substrate, designed device structure, pattern geometry, manufacturing speed, yield, quality, and production cost. The important printing parameters are as follows:

- Printing accuracy and resolution: display application for smart phone/tablets, among the finest applications today, requires fine patterning above 300 pixels per inch (ppi). A resolution of a few micrometers with ±5 μm position accuracy will be required. Multilayer printing accuracy is also a key factor.
- Uniformity from a few centimeters to more than 1 m in size area is required in combination with the designing ink composition and the drying process.
- Wetting control and interface formation: flatness within a few nanometers to several tens of nanometers is required for many OLED applications such as TV and lighting since the typical OLED layer thickness is less than 100 nm. Sharpness at pattern edges and bonding with substrates are strongly dependent on the underlayer (acceptance layer) material and its design.
- The compatibility of inks with printing components such as rollers, masks, doctor blades, and inkjet heads has a significant effect on yield and quality in mass production.
- Throughput and cost considerations: one of the great benefits of PE technology is its mass production at a reasonable cost. The high speed and high quality of printed patterns should be maintained for up to hundreds of printings.

Roll-to-roll printing is one of the active research areas in PE technology because it enables large-scale production by high-speed web handling. Roll-to-roll printing allows for large-scale production of such items as RFID antennas or keyboard

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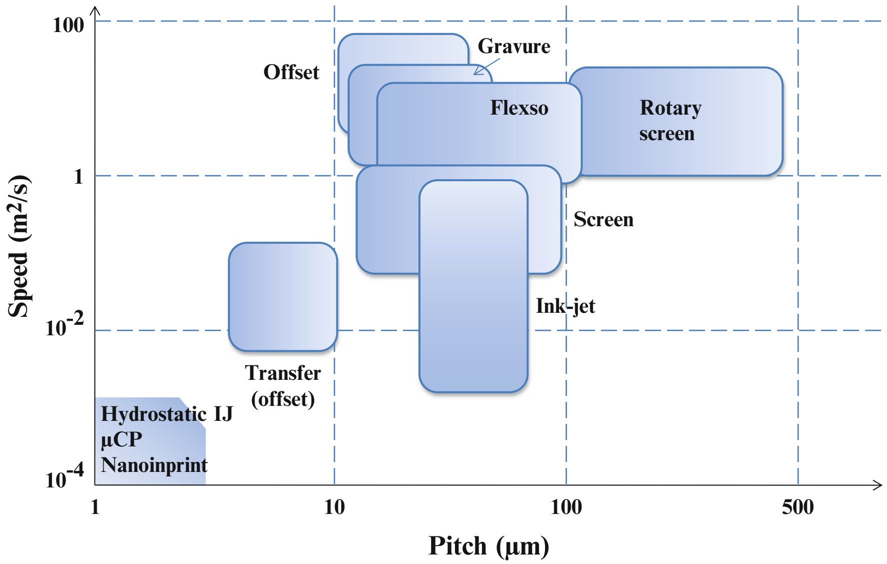



**Fig. 2.1** Throughput vs. fine pitch comparison for various printing methods (Adapted from ref. [1] by author)

membranes. Nevertheless, the roll-to-roll process is not mature enough to be applied to many areas where PE technology is used since adjustments among materials, printing methods with suitable web handling, accurate positioning, and inspection methods with definitions of defect criteria have not yet been established. Sheet-fed production is still a major printing method for most PE products. To shift from sheet-fed printing to roll-to-roll printing will require time to develop the printing technologies with suitable parameters including materials development. Figure 2.1 compares the throughput to fine pitch resolution among various printing methods [1] (Table 2.1).

The choice of printing methods is sometimes a major issue before launching research projects or before building up production lines. There is no single selection for one application. There are certain suitable matchings between inks and printers. A substrate may play a role in this choice. Not only the viscosity/surface tension of the ink but the device structures and whether the device line/layer is thin or narrow will affect the pattern quality obtained.

The cross-section profile of a printed circuit or a device has a distinctive shape. Figure 2.2 shows typical wiring cross-sectional shapes formed by printing. As wiring or as a device, a square cross section as in Fig. 2.2a is desirable to obtain certain electronics properties. Unfortunately, this does not happen with PE technology except with high-viscosity inks such as in screen printing. In wiring by inkjet printing, a low-viscosity ink droplet lands on a substrate, so that its cross section sometimes exhibits a coffee-ring effect, as shown in Fig. 2.2c, depending on the viscosity of the ink, its wettability on a substrate, and the vaporization uniformity of the solvent.

**Table 2.1** Feature comparison of printing methods

| Printing method | Ink viscosity (cP) | Line width (μm) | Line thickness (μm) | Speed (m/min) | Other feature |
|---|---|---|---|---|---|
| Inkjet | 10–20 (electrostatic inkjet: Approx. 1,000) | 30–50 (electrostatic inkjet: Approx. 1) | Approx. 1 | Slow (rotary screen: 10 m/s) | Surface tension: 20–40 dyn/cm<br>On demand<br>Noncontact |
| Offset | 100–10,000 | Approx. 10 | Several –10 | Middle—fast Approx. 1,000 | |
| Gravure | 100–1,000 | 10–50 | Approx. 1 | Fast Approx. 1,000 | |
| Flexo | 50–500 | 45–100 | <1 | Fast Approx. 500 | |
| Screen | 500–5,000 | 30–50 | 5–100 | Middle Approx. 70 | |
| Dispense | 1,000–$10^6$ | Approx. 10 | 50–100 | Middle | Single stroke |
| μCP | – | Approx. 0.1 | Approx. 1 | Slow | |
| Nanoinprint | – | Approx. 0.01 | Approx. 0.1 | Slow | |

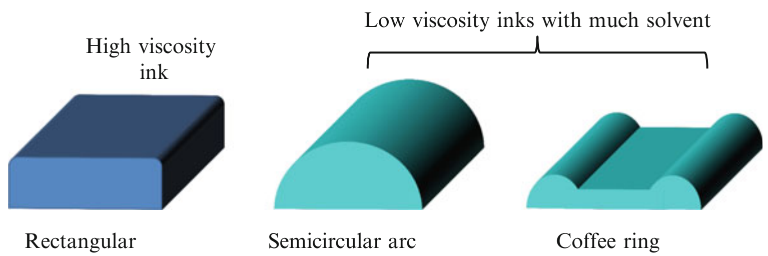



**Fig. 2.2** Typical cross sections of printed patterns

This shape is not appropriate in most cases because many defects are likely to form in the concave central area. Thus, the droplet shape must somehow be made flat. At the very least, a semicylindrical shape, as in Fig. 2.2b, is desired.

The wetting ability of liquid on a solid substrate is measured by a simple sessile drop method, as shown in Fig. 2.3a. The wetting angle can be a good index for wetting. Where the wetting angle θ is larger than 90°, it is called nonwetting, while at less than 90°, it is known as wetting. The wetting phenomenon is governed by the surface energies of the liquid and of the substrate and the interface energy as expressed by the inset Young's equation. In drying patterned ink droplets, the segregation of solute content toward the outside edge of a droplet sometimes occurs, as

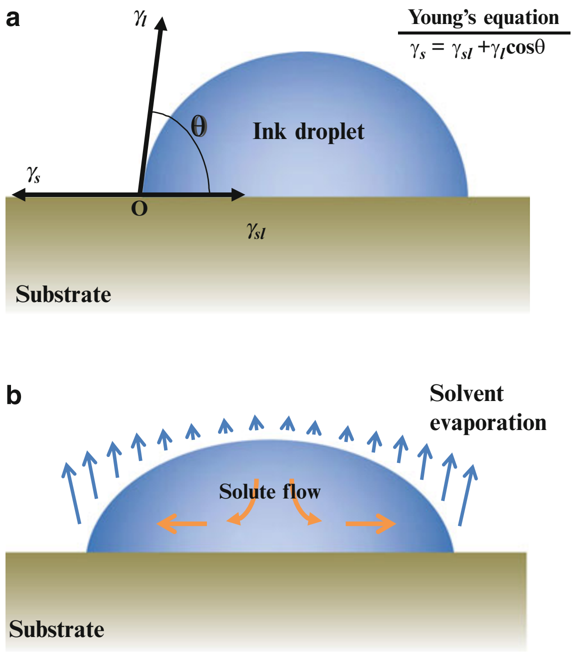



**Fig. 2.3** (**a**) Wetting of a droplet on substrate. (**b**) Mechanism of coffee ring effect

shown in Fig. 2.3b, which is known as the coffee-ring effect. The coffee-ring effect must be avoided (see subsequent discussion).

To obtain the desired shapes for printed wires and devices, one must adopt a certain kind of wetting control on substrate faces, which can both promote and prevent the spread of printed inks. Basically, there are two ways to control wetting and spreading, which have been in use in the graphic printing industry for many years, i.e., chemical treatment and physical treatment. Figure 2.4 depicts these methods.

Making a low-/high-energy state of the surface is the basic idea behind chemical treatments. Table 2.2 summarizes the surface energy ranges for various types of polymer substrate. Thus, in addition to a substrate, the type of ink solvent is very important. Plasma cleaning of substrate surfaces usually creates a high-energy state on most surfaces, resulting in the promotion of wetting and spreading. $CF_4$ plasma treatment, in contrast, creates a fluorinated layer on the surface in a very low-energy state. Figure 2.5 shows a $CF_4$ treatment period on the contact angle of PEDOT/PSS (Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) droplets on substrates, a bank, and indium tin oxide (ITO). A $CF_4$ plasma treatment initially increases the contact angle very rapidly, and the increase slows down after 1 or 2 min. A selective hydrophobic treatment such as fluoridation can create a fine pitch pattern at widths of even less than 1 μm. Figure 2.6 shows an example of an extreme case of PEDOT/PSS fine patterning [2]. In this case, the first PEDOT line was inkjet printed and cured. Then, a $CF_4$ plasma treatment made the surface of PEDOT fluorinated low energy and the glass substrate high energy. Then the second PEDOT droplet flows off the low-energy first PEDOT surface, resulting in a very small gap formation between the two PEDOT lines.

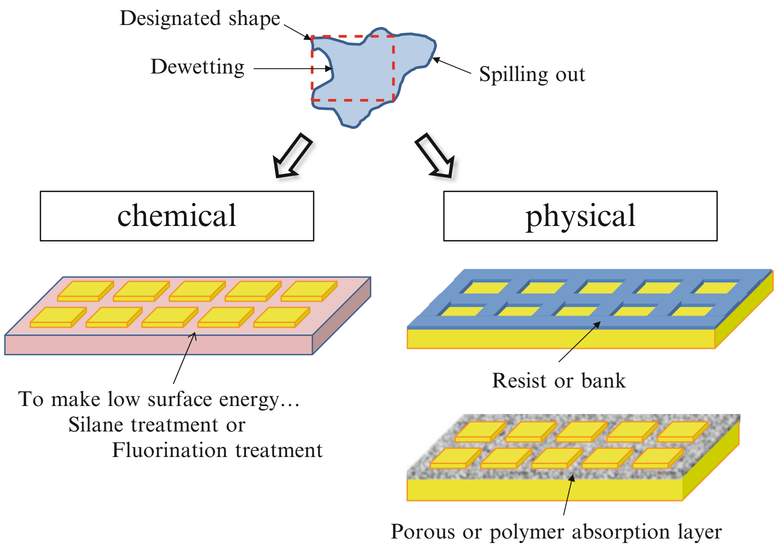



**Fig. 2.4** Various wetting control methods

**Table 2.2** Surface energies of various film substrates

| Surface energy (dyn/cm²) | Typical plastic | Properties |
|---|---|---|
| 10–20 | Silicone | Water repellent |
| | Fluorocarbon polymers | |
| 20–35 | Polyethylene | Hydrophobic |
| | Polypropylene | |
| 35–50 | Polyester | Polar |
| | Nylon | |
| | Epoxy | |
| | Acrylic resin | |
| | PET | |
| 50–60 | Polyvinyl alcohol | Hydrophilic |
| | Cellulose | |
| | Polyvinylpyrrolidone | |

Creating a bank or an absorption layer is a reasonable method of forming accurate patterns that can be adjusted for many types of ink solvent. Bank formation, which is commonly used for display pixels, is limited in resolution by its printing method. Screen printing is usually used for bank formation where the bank width is larger than 30 μm. Ink-absorption-layer formation has been widely used in graphic printing. There are two different choices of absorption layer, a porous layer type and a polymer type. The combination of ink, especially a solvent, and substrate plays a key role in the successful control of wetting and absorption for both types of absorption layer. Figure 2.7 shows an example of inkjet-printed Ag nanoink line formation on a porous surface layer made with a silica sol-gel coating on a PET film.

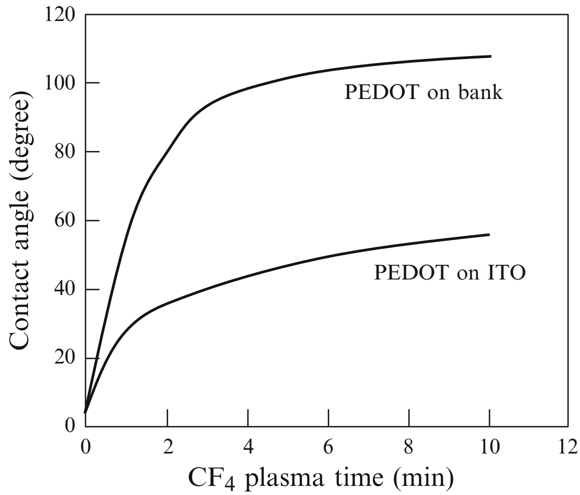



**Fig. 2.5** Gas bombardment effect of PEDOT wetting (Courtesy of Dr. James Lee, CDT)

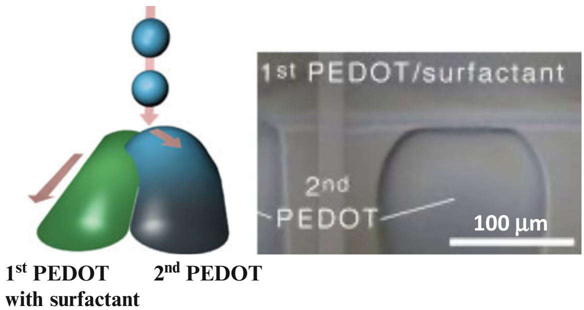



**Fig. 2.6** Fine gap formation using $CF_4$ plasma wetting control [2]

The solvent was organic. The wetting of the Ag ink on the PET film was so good that ink spreads unexpectedly over the PET film. In contrast, ink wetting on the silica-coated PET film was precisely controlled, as expected.

Not only wetting of ink on substrates but a drying condition is important. For many printing methods such as inkjet, offset-gravure, and flexo, the viscosity of inks, the concentrations of metallic nanoparticle inks are very low, which means those inks contain a large amount of solvent. Because of the presence of much amount solvents, the solvent must be evaporated to achieve suitable solid tracks. Depending on the evaporation process, such inks often produce a coffee-ring effect, as mentioned earlier and shown in Fig. 2.3b, thereby unexpectedly resulting in high electrical resistance. Figure 2.8 shows the influence of the coffee-ring effect on the resistivity of wiring using Ag nanoparticle ink [3]. By changing the line width, the resistivity of the lines narrower than 300 μm is much greater than those of wider lines, of which resistivity is $5\times10^{-6}$ Ω cm. The coffee-ring effect is caused by a convection flow from the center to the edge of droplets during the relatively slow

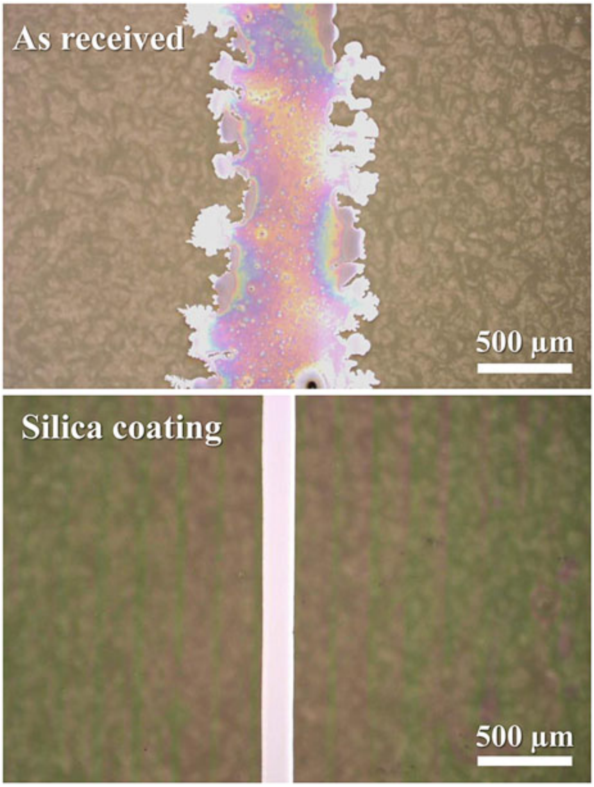



**Fig. 2.7** Surface control effect of PET film substrate with silica sol-gel coating. Ag nanoparticle ink was inkjet printed on PET with or without silica coating

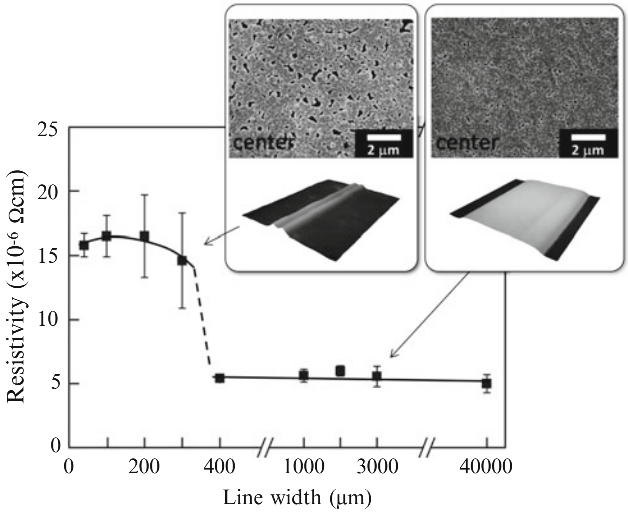



**Fig. 2.8** Influence of line width on measured resistivity [3]; low-viscosity ink sometimes forms coffee ring pattern

evaporation of solvent. This coffee-ring effect can be overcome by reducing the solute flow in a drying ink droplet. The formation of absorption layers of ink vehicles on pristine polymer films is one of the effective methods that leads to the fabrication of convex-shaped lines without the coffee-ring effect, even if a low concentration of commercially available ink is used.

## 2.2 Screen Printing

Screen printing is one of the most common printing methods and has been used for many years in electronics manufacturing. The most distinct feature of screen printing compared with other printing methods is the high aspect ratio of printed objects. The usual thickness of a screen-printed image is in the range of several tens of microns, but, especially when a thick screen mesh is used, the thickness can exceed 100 µm with a single pass of printing, which cannot be obtained by any other printing method. For other methods such as inkjet or flexo printing, the typical thickness is less than 5 µm. Figure 2.9 shows a high-aspect-ratio screen-printed line example.

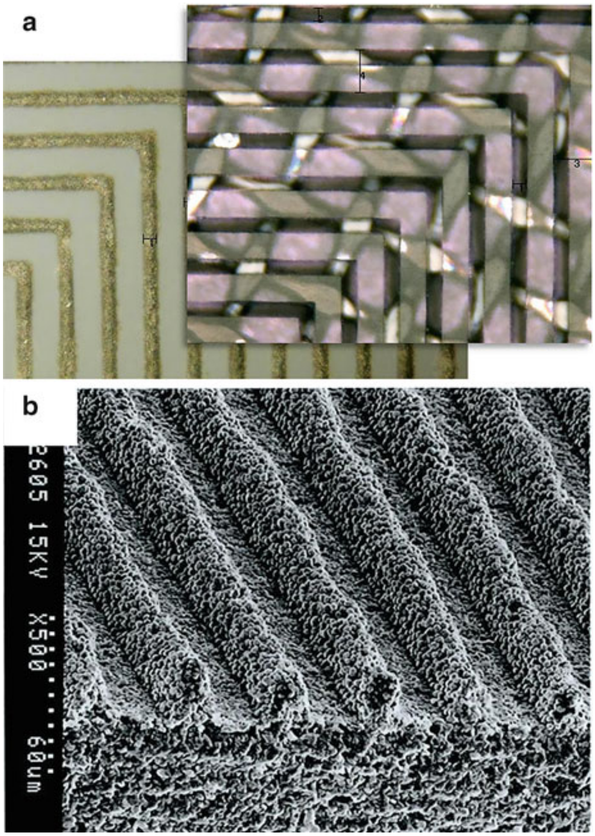



**Fig. 2.9** Fine line screen printing (Courtesy of Nakanuma Art Screen, Kyoto, Japan). (**a**) 8 m width Ag nanoparticle ink pattern and screen mask. (**b**) High aspect ratio: 19 µm height, Cu particle ink patterning with L/S = 20/20 µm

**Fig. 2.10** Screen printer for large-scale PDP panel manufacturing (Courtesy of Newlong Machine Works, Tokyo, Japan)

The printing of fine lines of line/space (L/S) below 10 μm/10 μm is possible at the laboratory scale. However, for mass production, current realistic screen printing provides a fineness of 50 μm in L/S production and is expected to reach 30 μm for L/S in the near future. On the other hand, thin printing or coating cannot be achieved in screen printing.

Large-scale screen printing, beyond widths of 2 m as shown in Fig. 2.10, has also been achieved in the industry, especially for plasma display panels, which, unfortunately, are no longer a part of standard TVs.

In screen printing, as schematically shown in Fig. 2.11, printing is performed at a low printing pressure using a screen mesh with a designed pattern of uniform thickness. A flexible metal squeegee or rubber squeegee is used for squeezing paste through the mesh. A polymer mesh, such as polyamide/polyester, or a stainless steel mesh can be used. A mesh pattern is formed by photolithography of an emulsion on the mesh. Instead of a mesh screen with an emulsion pattern, a metal screen can also be used.

Although screen printing is relatively slow, as shown in Fig. 2.1, rotary screen printing, which is used nowadays in large-scale mass production, is very fast, equivalent to other methods of high-speed printing. The resolution of rotary screen printing is, however, limited. Figure 2.12 shows a typical rotary printer with its printing mechanism.

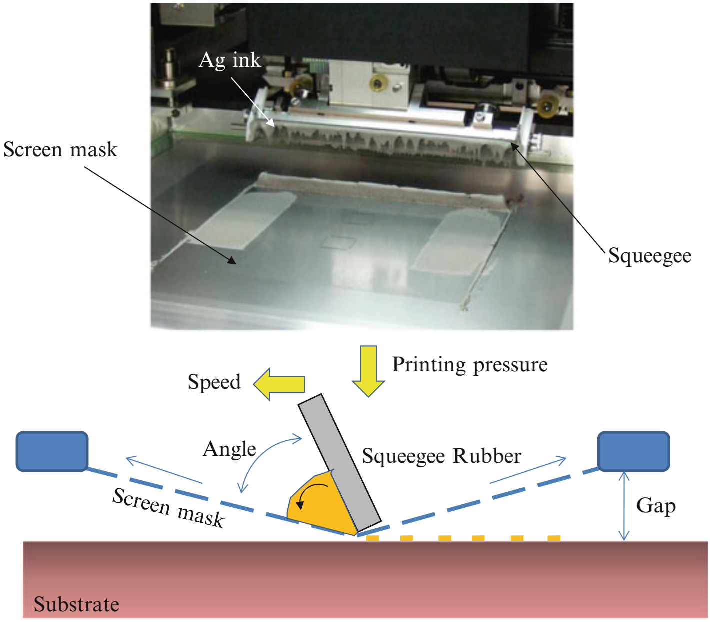



**Fig. 2.11** Parameters in screen printing

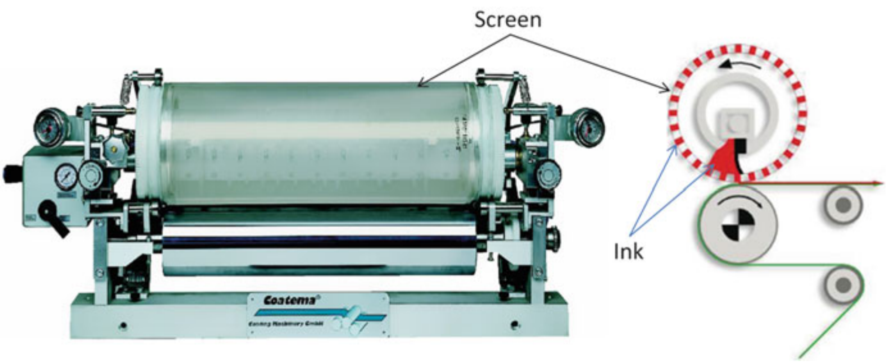



**Fig. 2.12** Rotary screen and its mechanism (Courtesy of Coatema Coating Machinery, Dormagen, Germany)

## 2.3 Inkjet Printing

A piezo drive inkjet has been widely applied to PE technology in a variety of inkjet methods because of its excellent compatibility with functional inks. Inkjet-printed display products have been available on the market. Inkjet technology, which has been around for many years, and its mechanism of droplet ejection are well understood. Figure 2.13 shows a cartoon of ink droplet ejection simulated by a

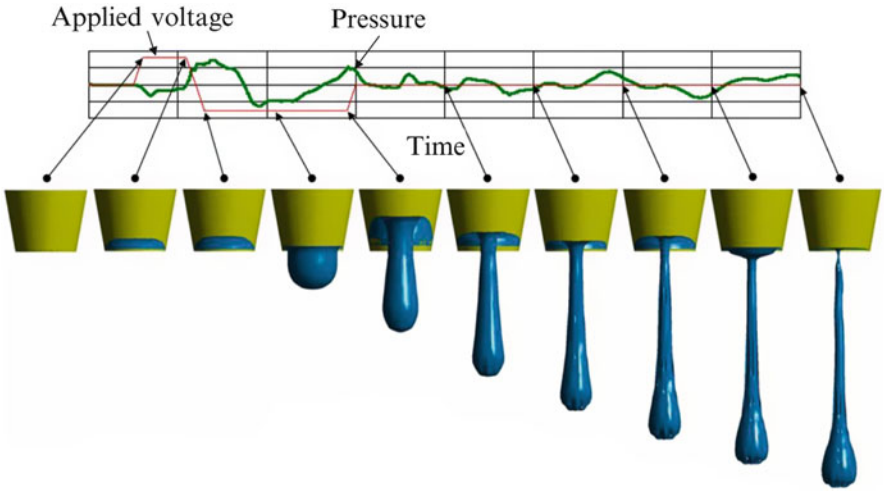



**Fig. 2.13** Inkjet droplet simulation by finite-element method (Ansys, Courtesy of Cybernet Systems, Tokyo, Japan)

finite-element method. To form a wiring homogeneous fine line, at each step, the inkjet parameters should be controlled for each nozzle.

The droplet size, shape, speed, and uniformity of an inkjet printer varies from one inkjet head to another, or perhaps from one nozzle to another, even in a single inkjet head. It is necessary to understand the characteristics of an inkjet head and printer algorithm. For instance, a piezo drive waveform, frequency, and amplitude define the initial droplet nature, i.e., shape, size, and speed. Upon droplet ejection, not only the viscosity of the ink and the wettability of the ink on the head material (orifice), but the size and shape of the nozzle tip also affect the amount and shape of the ejected droplet. The shape and direction of droplets during flight also vary greatly depending on ejection conditions. Thus, these ejection parameters should be precisely controlled for each nozzle.

Figure 2.14 shows a series of photographs of Ag nanoparticle ink droplets from the same nozzle where the piezo voltage was changed. In this example, the droplets change their form drastically. At higher voltage, droplets apparently split into two initially, the main droplet and the second satellite, but they coalesce when the second satellite catches up with the main droplet before landing.

The distance to a substrate to be printed from a nozzle tip is usually 1–2 mm, but during flight, air resistance will affect the droplet shape, and in addition, the evaporation of solvent will occur at the same time. When droplets land on a substrate, a droplet wets and spreads on it. Now let us consider the case of droplets of a 2 pl ejection. The diameter of the droplet is approximately 16 μm if it is sphere shaped. When the droplet lands, it will spread as a dot 30–60 μm in diameter depending on the wetting conditions.

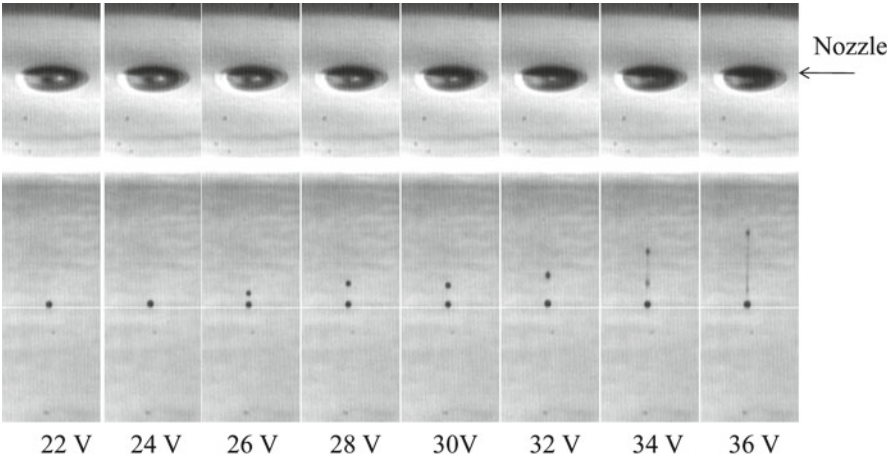



**Fig. 2.14** Influence of accelerating voltage on inkjet droplets (frequency: 2 kHz)

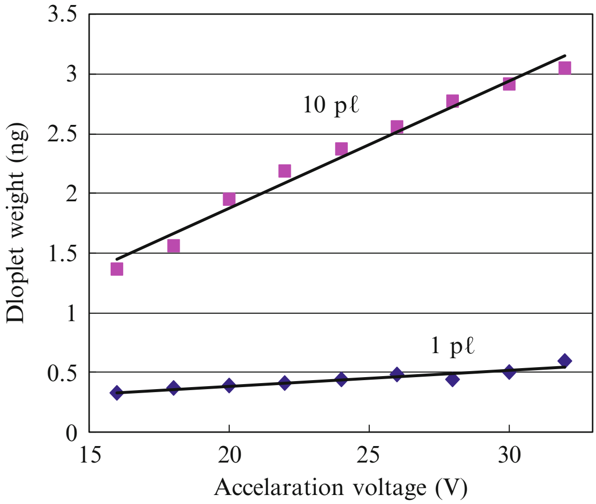



**Fig. 2.15** Weight of droplet as a function of acceleration voltage

Figure 2.15 shows the variation in droplet weight and velocity that occurs by changing the piezo voltage. Both the speed and weight of the droplets increase linearly with voltage. Thus, conversely, it is possible to reduce the pattern size even using the same nozzle by decreasing the applied voltage.

Controlling the algorithms of inkjet ejection and of stage motion with a substrate is also a key factor in achieving fine patterning. Figure 2.16 shows the applied voltage effect on inkjet patterns. A dot at a piezo voltage of 32 V exhibits an ellipse due to the long tail shown in the photograph, while that at a piezo voltage of 17 V shows a clear circle, as desired.

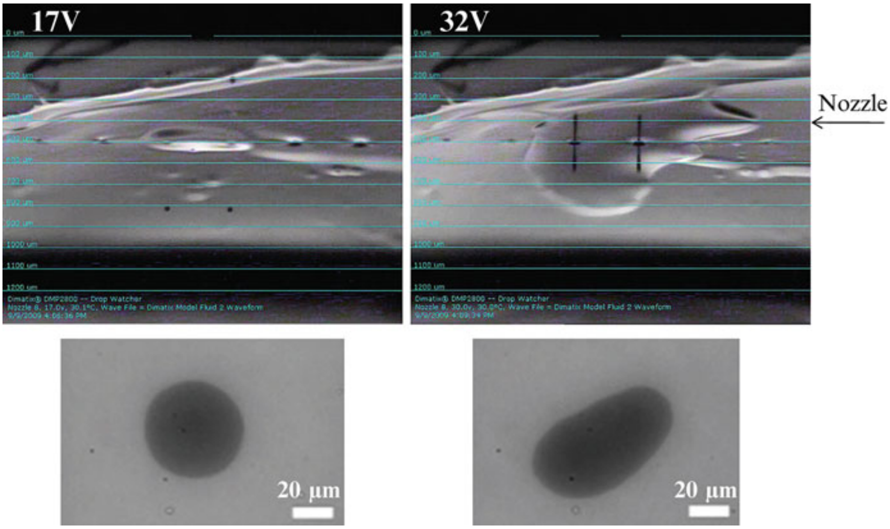



**Fig. 2.16** Effect of acceleration voltage on dot shape on substrate

Inkjet printing sometimes unexpectedly forms extra dots that spread out from main patterns, which should be taken into account as the limit of digital imaging technology. A modification must be made to the template for printing images, especially for angled or curved line/edge formation.

When all parameters are suitably controlled, the accuracy of inkjet printing is excellent. Figure 2.17 compares an OLED pixel image before and after adjustment. Because each nozzle has its own deviations, even in a single head, driving each nozzles should be precisely controlled individually. For mass production, an minimum line width/space for typical inkjet printers is 50 μm/50 μm. The accuracy of dots forming on a substrate can be controlled within ±5 μm.

## 2.4 Fast Printing: Flexo Printing and Offset-Gravure Printing

Flexo printing, which is a very fast relief printing method, has been widely used for flat panel display printing. The mechanism of flexo printing is shown in Figure 2.18, which is suitable for flexible substrates because of the lighter printing pressure involved. The viscosity of flexo printing inks is rather low as compared with those of screen and offset printing; thus, flexo printing has been applied in large-area thin and uniform coating.

Offset-gravure or gravure printing also has an outstanding feature for high-speed mass production. The mechanism of this kind of printing is schematically illustrated in Fig. 2.19. First, ink is placed on a gravure roll of metal and the excess ink is

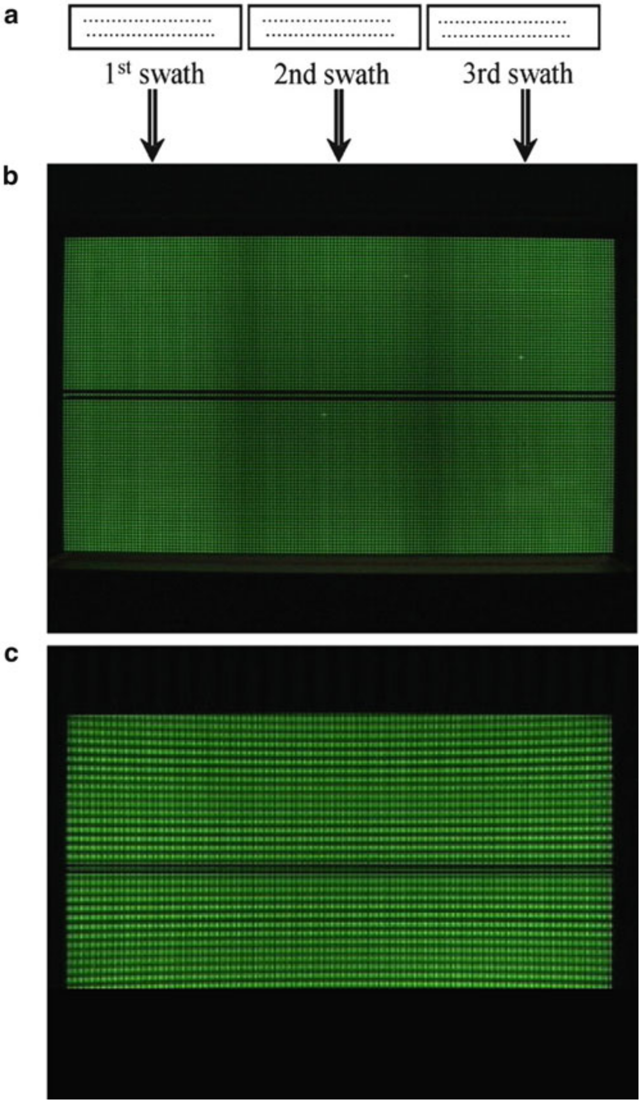



**Fig. 2.17** Influence of droplet volume control of each nozzle on OLED pixel images (Courtesy of EPSON, Nagano, Japan). (**a**) Arrangement of heads, (**b**) before adjustment, and (**c**) after adjustment

scraped off with a doctor blade. In the offset process, ink is transferred to a transfer roll, and then ink is finally printed on a substrate under a given pressure. It is possible to accumulate wiring several microns in height depending on its relief depth at very high speeds of up to 1,000 m/min. Because of the softness of the rubber layer on the transfer roll, offset-gravure printing is also very suitable for printing patterns on three-dimensional surfaces with high height steps.

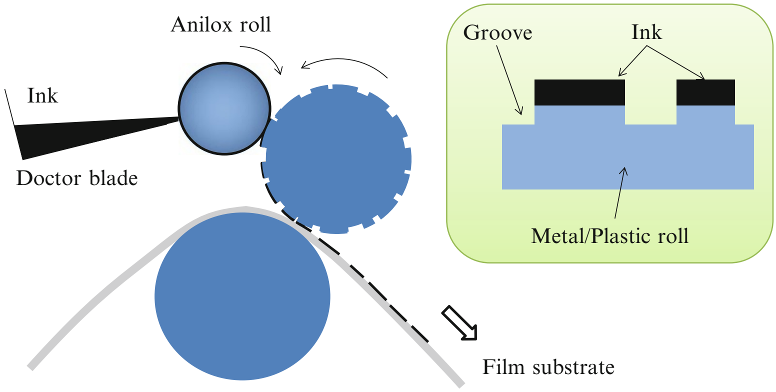



**Fig. 2.18** Mechanism of flexographic printing

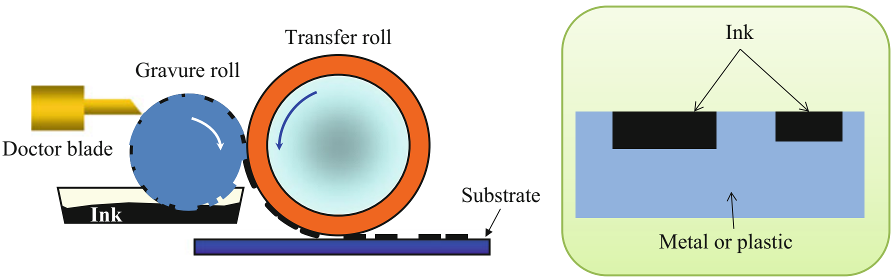



**Fig. 2.19** Offset-gravure printing

Figure 2.20 is an example of a gravure plate, withAg nanoink on the plate and Ag printed lines on a substrate. For a preparation of gravure plates, etching is usually performed by photolithographically multiplying copper plating or chromium coating on the roll. In the configuration of the gravure plates, a hard coating like diamondlike carbon (DLC) is frequently applied to surfaces to confer abrasion resistance.

Ideally, in printing, all of the ink on the flexo/gravure plate should be ultimately transferred onto the substrate surface. How this is done is determined by various parameters. Some of the key parameters are listed as follows (Fig. 2.21):

- Materia-l and state of roll/plate: affinity with inks, swelling, hardness
- Ink characteristics: type of solute and its content, viscosity, solvent type/volatility/amount, absorption by silicone, bubbling
- Depth and pattern/shape of relief
- Wetting and affinity between each roll and ink, surface state of substrate
- Contact pressure of print and transfer roll: push depth (roll deformation), rotational speed of each roll
- Materials and hardness state of plate and doctor blade

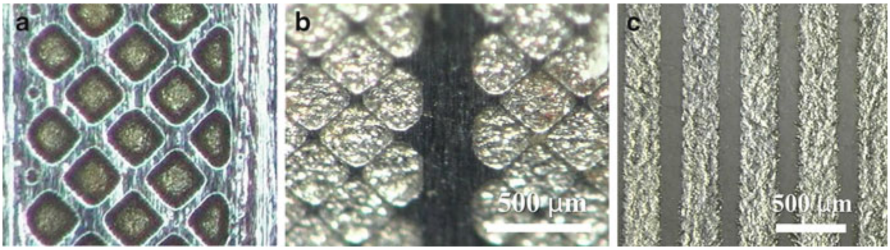



**Fig. 2.20** (**a**) Gravure pattern on a roll. (**b**) Ag ink on plate. (**c**) Printed Ag line on paper substrate

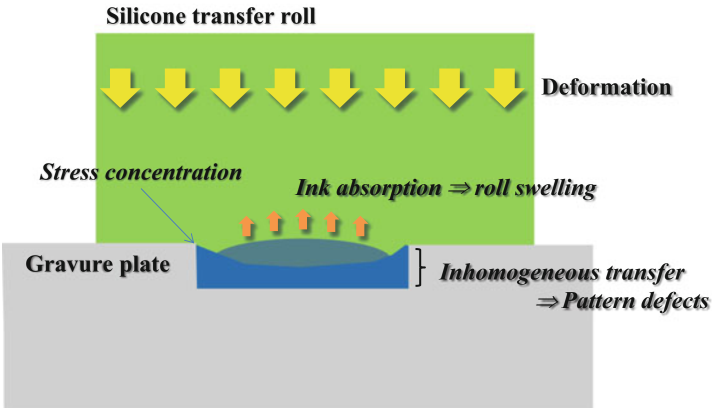



**Fig. 2.21** Influencing factors on quality of printed patterns in gravure printing: uniformity of ink, contact of transfer roll under applied pressure, swelling of rubber

For example, in gravure printing, the ink solvent and viscosity, tacking property, applied pressure, and material of the transfer roll significantly affect the ink transfer. Figure 2.21 shows a schematic illustration of the factors to consider in sound printing practices. In particular, an organic solvent is usually used for gravure and offset-gravure printing. The solvent may cause swelling of the silicone transfer roll, such as a permeate silicone blanket, after multiple printings, which will distort the printing quality considerably. Swelling easily occurs when an ink solvent has the same polarity as silicone. The evaporation of the ink solvent also has an influence. Figure 2.22 shows an example of the holding time of ink on a transfer roll [4]. Ink transfer is ideal when enough holding time has passed for solvent evaporation. This shows that the temperature of rolls and plates must be controlled to maintain uniform printing quality.

In mass production, the degradation of a doctor blade that comes from scraping off extra ink causes printing defects and damages plates and transfer rolls. Figure 2.23 shows the doctor blade degradation effects on the formation of many satellite spots. These materials must be selected with great care, especially for mass production.

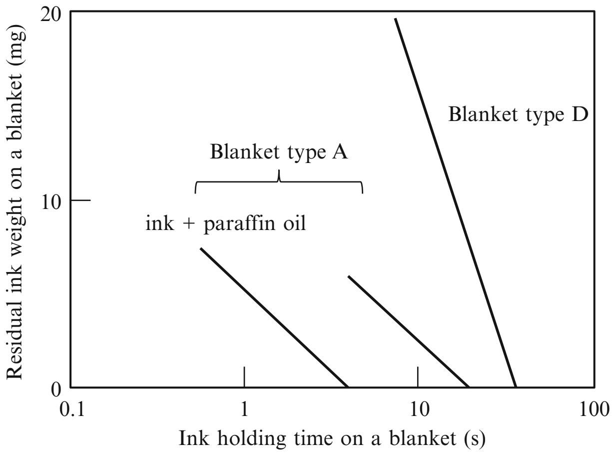



**Fig. 2.22** Influence of ink holding time on a transfer roll on residual ink weight on roll blanket [4]. Panels a and d are different types of blanket; the ink contains ceramics particles

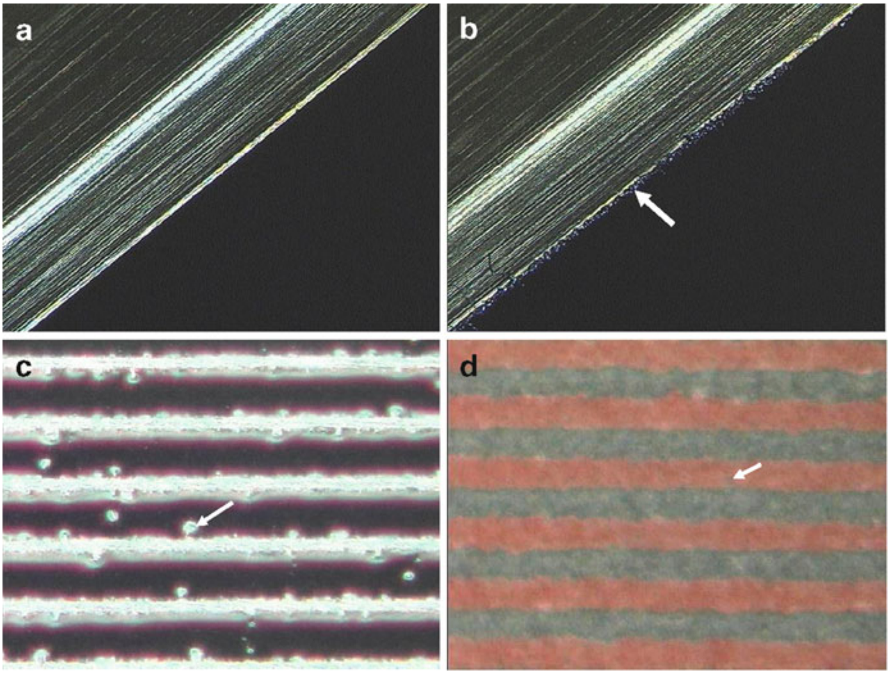



**Fig. 2.23** (**a**) Edge of initial doctor blade. (**b**) Edge of degraded doctor blade. (**c**) Ag ink on gravure roll with splash formed by degradation of doctor blade. (**d**) Printed Ag line with satellite spots

## 2.5 Fine Pattern Printing: Nanoimprint, µCP, and Electrostatic Inkjet

Among fine printing methods, several allow for L/S to be realized even below 1 µm. They include µCP (microcontact printing), nanoimprinting, and electrostatic inkjet printing.

The µCP method is a printing technology that can be applied to fine structure formation down to approximately 100 nm. Kumar et al. first applied µCP in 1993, forming Au wiring with a polymeric flexible stamp [5]. It is known as soft lithography, in imitation of Si photolithography. Figure 2.24 shows a typical process flow of the µCP method. First, the resolution of the patterns is highly dependent on the template [6]. A master template is prepared by photolithography. Polydimethylsiloxane (PDMS, silocone) is commonly used. Thiol is used as a self-assembled monolayer (SAM) that attracts metallic elements such as Au or Ag as in the case or that repels PEDOT or Ni as seen in Fig. 2.24d.

Figure 2.25 shows a fine pattern of Ag nanoparticle ink obtained by National Institute of Advanced Industrial Science and Technology (AIST, Ibaraki, Japan). On flexible plastics such as polycarbonate (PC) or polyethylene naphthalate (PEN), L/S less than 1.0 µm is possible on an area of 15 cm$^2$. Currently, the µCP method is being used in bio-related technology, such as printing DNA. Unfortunately, even

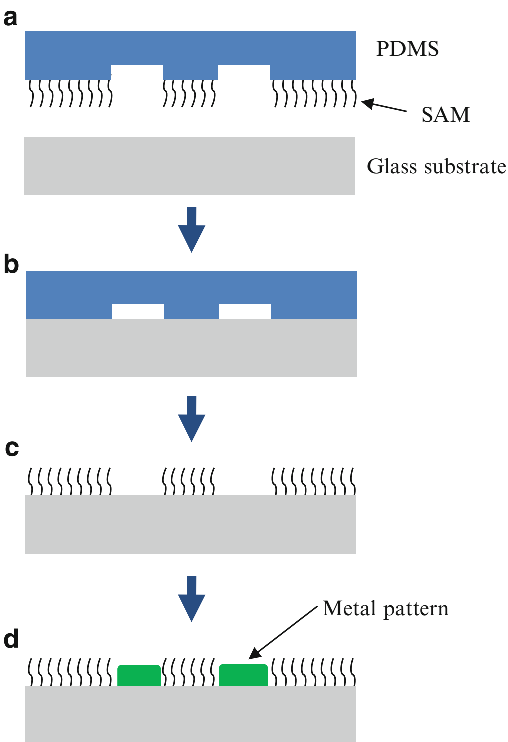



**Fig. 2.24** Typical µCP process for forming metal wiring on a glass substrate

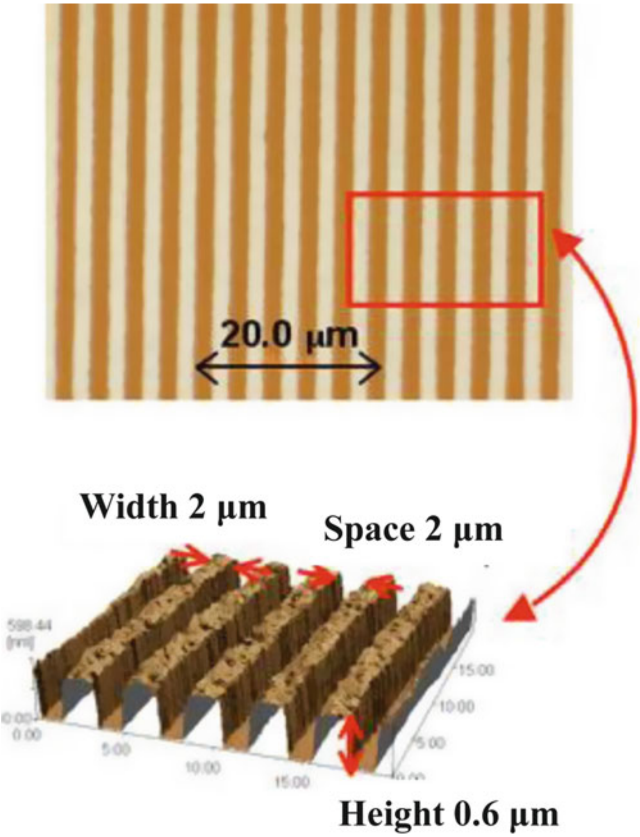



**Fig. 2.25** Fine patterns with Ag nanoparticle ink formed by μCP printing (Courtesy of AIST). The *bottom* photo was taken by Atom force microscope (AFM)

though the application expectation is greater in large-area patterning of organic electronic devices, the μCP method cannot meet requirements related to speed and yield in the mass production of PE technology.

Nanoimprinting is also expected to provide submicron pattering, as was first reported by Chou et al. in 1995 [7]. Figure 2.26 show the mechanism of nanoimprinting. This method has been applied to the mass production of hard disk drives (HDDs) and optical films, such as light-guiding or light-scattering plates, but not for the precise patterning of PE technology.

The electrostatic inkjet method is another option for fine patterning, but for a single stroke like dispensing. An ink droplet is driven by kinetic energy in the electrostatic field between nozzle and substrate, as shown in Fig. 2.27. Because the ink is drawn by an electrostatic field in response to voltage applied, it forms a Taylor cone at the tip of the nozzle. A tiny droplet with a high-viscosity ink can be formed without being constrained to the diameter of the nozzle tip. For example, fine lines less than 1 μm in width can be drawn on a substrate by a nozzle with a diameter of 20–100 μm when a high-viscosity ink is used [8].

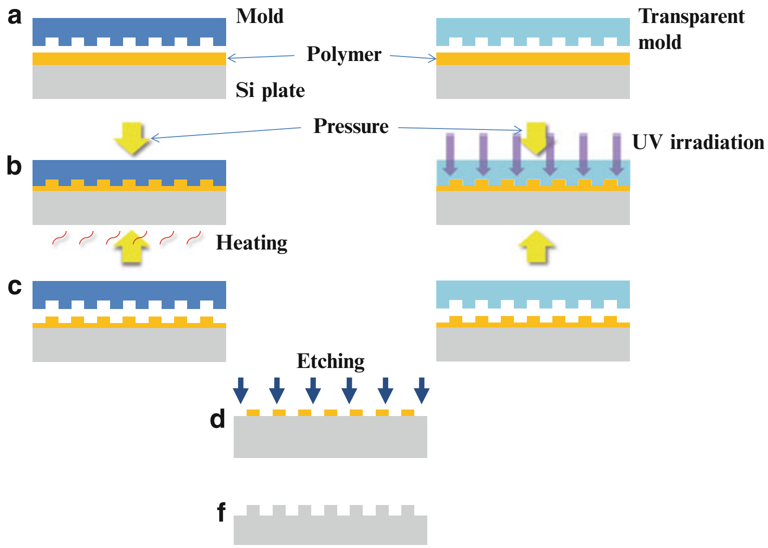
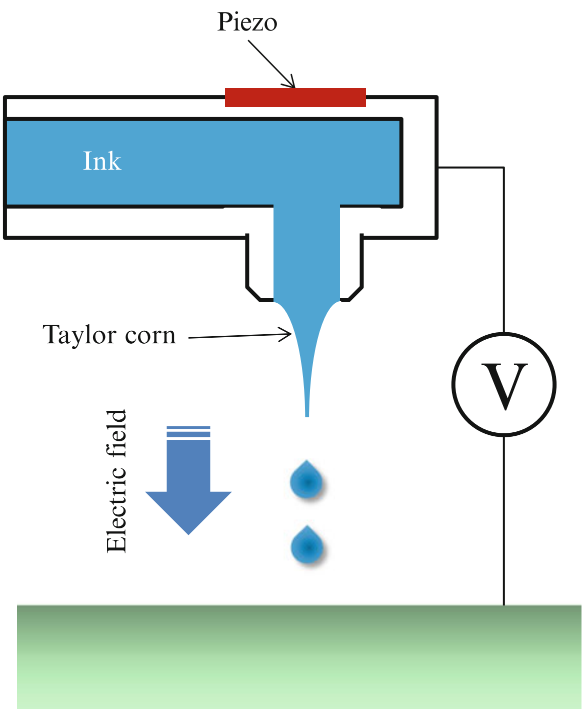



Fig. 2.26 Two different processes of nanoimprint

Fig. 2.27 Electrostatic inkjet printing mechanism. A piezo driver is not necessary



## 2.6 Laser-Induced Forward Transfer

Laser-induced forward transfer (LIFT) utilizes a metal ablation phenomenon by high-power laser irradiation developed in 1986 [9]. An object film on an optically transparent support is transferred to a substrate by a high-energy focused laser pulse, as schematically shown in Fig. 2.28. The resolution depends on the focus of the laser beam and can be on the order of a few microns. A successful example of the use of this method is shown in Fig. 2.29 [10]. Using the LIFT method, a polymer light-emitting device of a Polymer light emitting diode (PLED)/Al cathode bilayer (poly 2-methoxy-5-2-ethylhexyloxy-1,4-phenylenevinylene, MEH-PPV/Al) was transferred to a silica substrate directly without suffering any damage [10]. The device is uniform and has a very sharp edge. Thus, the LIFT method allows for noncontact, direct-multilayer printing in a solvent-free single step, without

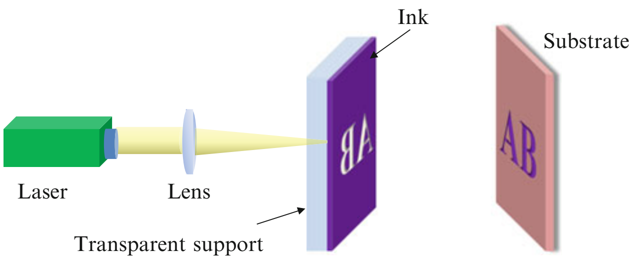



**Fig. 2.28** Typical setup for LIFT

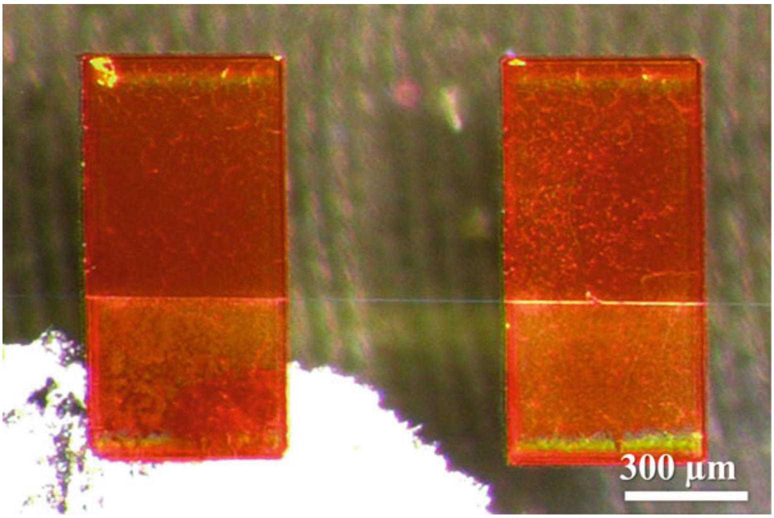



**Fig. 2.29** View of two pixels through ITO substrate formed by LIFT [10]

requiring any shadowing mask or vacuum installation. The LIFT method is also versatile and can be applied with a variety of donor materials such as metals, organic polymers and monomers, oxide/inorganic compound/Si semiconductors, and even sensitive biomaterials.

## 2.7 Posttreatment Process

After printing, as shown in Fig. 1.8, printed circuits or devices should be dried or cured before the next step, especially in multiple printing. Drying can be performed with an oven or curing with a UV lamp, both of which are conventional postprinting processes in the printing industry. Functional inks in PE technology have unique requirements in addition to drying. In particular, many metallic and inorganic inks require relatively high temperatures for their densification or crystallization to obtain the desired functional performance. For instance, metallic wiring with Ag and Cu nanoparticle inks requires temperatures exceeding 200 °C to achieve a resistivity of $5 \times 10^{-6}\ \Omega$ cm. Cu nanoparticle ink further requires an inert atmosphere to prevent severe oxidation. Si nanoparticles or oxide nanoparticles require much higher temperatures, above 300 °C. Such high-temperature treatment will distort the printing process flow and certainly damage most plastic substrates. Instead of high-temperature heating, one should employ certain specific treatments, of which there are several. They are listed as follows:

- Laser curing
- Flash lamp curing
- UV curing
- Plasma treatment
- Microwave curing
- Mechanical forming (cold working)

Direct laser sintering of metal powders is a well-known process involving rapid prototyping technologies [11]. Especially for PE technology, laser curing/sintering is a direct curing or sintering method for ink objects on a substrate. Using the heat energy of a laser, the irradiated pattern increases temperature in a very short time. By adjusting the laser beam size and intensity, one can obtain patterning several microns wide on a heat-sensitive substrate. Figure 2.30 shows an example of laser sintering of a source/drain with Au nanoparticle ink on a Si substrate [12]. As shown in the sequence, first, Au nanoparticle ink was inkjet printed in a wide-track pattern of approximately 100 μm. Then a focused laser was irradiated. The remaining unsintered nanoparticles were washed out, exposing two Au fine lines. A gap between the two lines forms a transistor channel of approximately 4.5 μm.

Flash lamp sintering/curing, which is also called photosintering, utilizes a strong pulsed light irradiation on objects on a heat-sensitive substrate. Figure 2.31 illustrates the mechanism of flash lamp sintering. A strong pulsed light from a controlled Xe lamp through a filter can be absorbed only by an ink object, but not by an optically transparent substrate. Then, only the ink temperature increases without

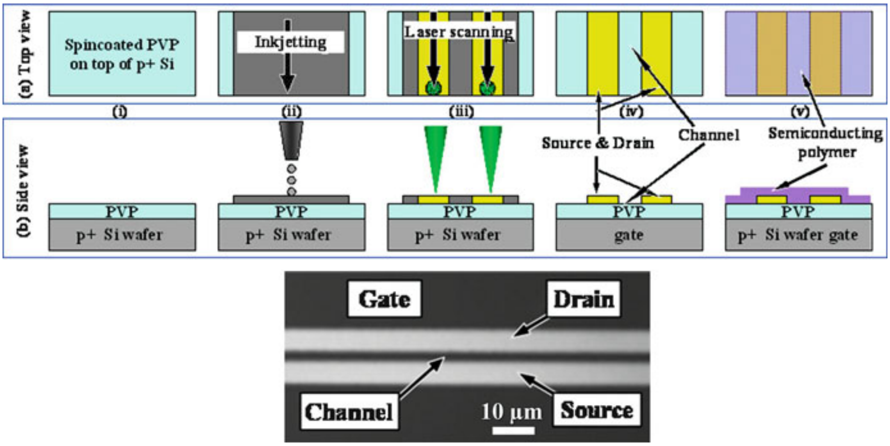



**Fig. 2.30** Laser curing of Au nanoparticle ink wiring on Si substrate [12]

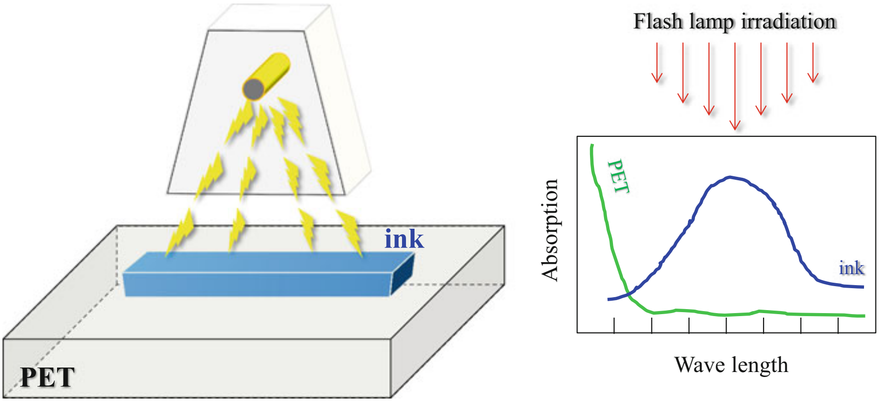



**Fig. 2.31** Flash lamp sintering

damaging the substrate. The benefits of this method are the treatment capabilities of a uniform and wide area, its very short run time, and the fact that there are no requirements for a specific atmosphere control such as a vacuum. Even Cu nanoparticles, which are susceptible to oxidation on heating, can be effectively sintered without an inert atmosphere. Figure 2.32 shows the sheet resistance change as a function of Xe flash lamp energy [13]. It is obvious that, as the light energy increases, the sintering of Cu nanoparticles effectively proceeds. Cu nanoparticles are usually covered by a thin oxide layer. In this process, it is likely that the Cu oxide is reduced, absorbing the light energy. In addition to the self-reduction of Cu oxide, a Polyvinylpyrrolidone (PVP) layer covering the Cu nanoparticles greatly influences the sintering, as shown in Fig. 2.33. There is a minimum resistivity in the PVP/Cu

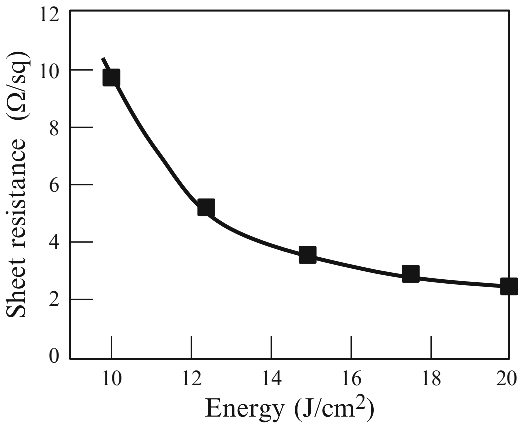



**Fig. 2.32** Sheet resistance of flashlight-sintered Cu nanoparticles as a function of irradiation energy on a polyimide substrate [13]

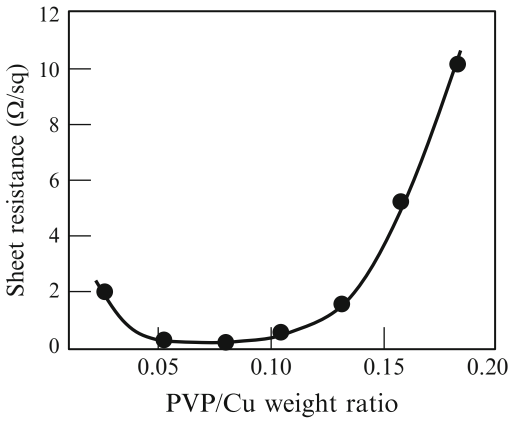



**Fig. 2.33** Sheet resistance of flashlight-sintered Cu nanoparticles as a function of PVP/Cu weight ratio [13]

weight ratio range, i.e., from 0.05 to 0.10. The reoxidation of Cu in the low content of PVP has been attributed to this slight increase in sheet resistance. With a higher content of PVP, the resistivity again increases sharply. Flash lamp sintering is also effective in nanowire networks, which will be discussed in the following chapter.

Like flash lamp sintering, UV curing with LED lamps is expected to be effective with PE technology. UV curing has many benefits, such as the absence of infrared in the spectrum, uniform radiation across the exposure width, low cost and long service life, low-voltage operation, instant on/off, and compact size. However, one must keep in mind that the wavelength range in UV curing is in the absorption range for plastic films, which may damage such films.

Plasma treatment is another selective sintering method for metallic inks that uses low-pressure argon plasma. This process shows a clear evolution starting from a sintered top layer into the bulk material, as shown in Fig. 2.34 [14]. Resistivity decreases as the plasma treatment time increases, and the final value is

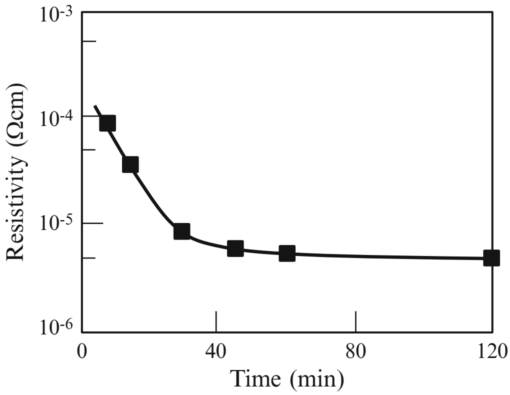



**Fig. 2.34** Resistivity change in Ag nanoparticle ink track as a function of plasma treatment time [14]

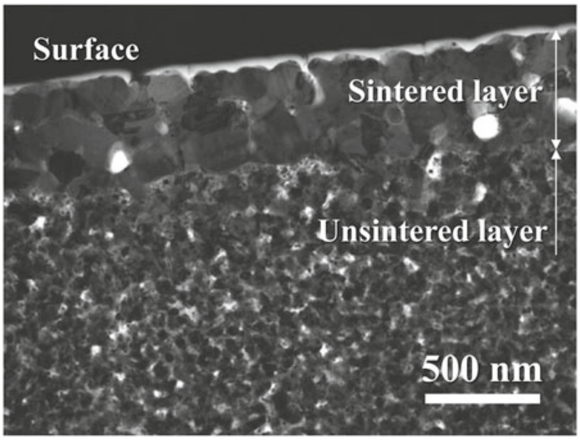



**Fig. 2.35** Transmission electron microscope (TEM) of surface of printed Cu nanoparticle ink treated by plasma (Courtesy of Prof. R. Izumi, Kyushu Institute of Technology, Fukuoka, Japan)

approximately three time higher than that of the bulk Ag. Plasma treatment is limited to objects of a certain thickness, which can be correlated to the penetration depth of the plasma into the objects. Figure 2.35 shows a typical example of a cross section sintered by plasma treatment.

The use of microwave radiation is also effective in sintering metallic/inorganic materials. Figure 2.36 shows conductance change as a function of microwave treatment time [15]. The conductance sharply increases after 100 s and almost saturates beyond 100 s. This treatment time shortening is a great advantage of microwave heating. However, metals have a very small penetration depth; the penetration depth of 2.45 GHz microwaves for metal powders of Ag and Cu is 1.3 μm and 1.6 μm, respectively [16]. The conductance or resistivity attained, $3 \times 10^{-5}\ \Omega$ cm, is approximately 20 times higher than that of bulk Ag.

Mechanical forming is another cost-effective method of PE technology. This will be introduced in the last part of the next chapter.

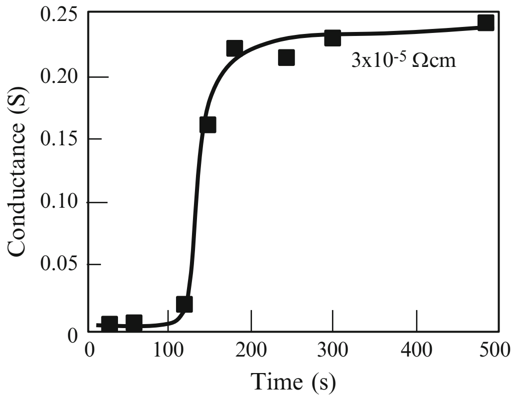



**Fig. 2.36** Conductance of printed Ag nanoparticle ink track as a function of microwave treatment time [15]

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