Micron order patterning by a novel inkjet technology, SIJ

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Abstract

We introduce an ultra-fine inkjet system as a powerful tool for nanotechnology research that allows the arrangement of dots with a minimum size of less than one micron. Diverse materials, such as conductive polymers, fine ceramics, metal particles etc., can be used as inks. Using an nano metal paste as an ink material, we achieved the direct printing of metallic wires of only a few micrometers in width without any pre-patterning treatment of the substrate. Direct forming of three-dimensional structures anywhere on a substrate has also been demonstrated, and is possible by taking advantage of the rapid drying of the small volume droplets printed. The process is simple and the entire setup can be carried out on a desktop, in an ambient environment, and at room temperature.

Introduction

Many nano-scale functional materials such as nano-tubes, nano-particles, super-molecules, and biomaterials have been developed, and the functionalities of the materials are being enhanced with the further development of nanotechnology. In order to incorporate these active materials in devices, a precise "drop on demand" technique which deposits extremely small volumes of ink should be useful [1-3].

Inkjet printing has several prominent features. It is on-demand, efficient and the smallest amount of energy to position the ink. Each one of these features is attractive when considering possible applications of inkjet technology to manufacturing processes. For example, whereas electronic elements have hitherto been created through micro processing at a large-scale facility such as a semiconductor factory, the adoption of inkjet technology is making it possible to manufacture them using a simple apparatus the size of a desktop printer, which can position electronic element materials on a substrate the same way an inkjet printer positions ink on a page.

In this paper, we discuss the capabilities of an ultra-fine inkjet system which can be used as a powerful tool for nanotechnology research. The system can arrange dots with a minimum size of less than one micron. We also demonstrate several applications using nanomaterials and the super-fine ink-jet system, such as the direct printing of ultra-fine metal wiring of a few microns in width.

Experiments

Super-fine Inkjet system

As has been advertised elsewhere, conventional inkjet heads can eject droplets of 1 to 2 pL and are widely used as the main component of personal printers. Typical ink of 1 pL volume results in a droplet that is 13 μm in diameter while in flight, but once deposited on engineering substrates, such as glass, silicon, and ceramics, the droplet can spread to up to 100 μm in diameter. Achieving the high precision deposition of a smaller volume droplet involves the difficulty of adding sufficient kinetic energy to a smaller droplet. Our super-fine ink-jet system overcomes these difficulties, achieving true micron scale patterning of engineering materials. A custom developed super-fine ink-jet system has the ability to print materials with sub-micron scale resolution [1-7]. The typical nozzle diameter is about 1 μm and is mounted on a print head. Samples are placed on computer-controlled linear motor stages that are used for X-Y movement. The stage and head are controlled by a PC with a vector scan data file. As shown in Fig. 1, the prototype of our super inkjet system is a simple device compact enough to sit on a desktop. Since the prototype system is designed for laboratory use, the system has a single nozzle, however multiple nozzle systems are possible, and should be useful for semi production level applications.

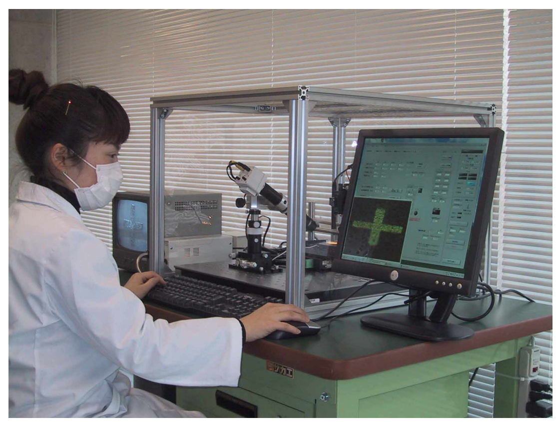

Figure 1 *Entire super-fine ink jet system.*

Materials

The trend towards industrial applications of inkjet technology has been further accelerated by ongoing progress in nanotechnology and other materials technology—in short, by the development of compatible inks with various functions. Different types of functional materials have been used as ink materials for our super-fine ink-jet system, including organic materials such as a conductive or semi-conductive polymers, fluorescent dyes, and sol-gel solutions of fine ceramics [1,2]]. As has been reported previously, we can use transition-metal nano-particles as catalyst-ink for carbon nano-tube growth, and patterned arrays of carbon nano-tubes were successfully obtained [2,3]. A field emission made from the patterned carbon nano-tubes has also been demonstrated [3].

For wiring applications, conductive silver and gold-pastes (Nanopaste^{TM}) developed by Harima Chem. Inc. are used as metal ink [8, 9]. As has been reported elsewhere, the pastes comprise of single dispersion nano-particles which are very fine, about 5 nm [8, 9] and the inks shows both good sintering features and low viscosity. After ink-jet printing, a heat treatment of 250°C was carried out for sintering. A sheet resistance of a few µΩcm can be achieved.

Results

Micro patterning

The droplets ejected by the ink-jet head in commercial home-use ink-jet printers are a few picoliters (pico = 10^{-12}) in volume. Each droplet measures around 20 microns in diameter. When one of these droplets is deposited onto a substrate, the difference between the substrate and ink surface energy causes the ink to spread out to cover a circular area of anywhere from several dozen microns to about 100 microns in diameter. This range of variation is just smaller

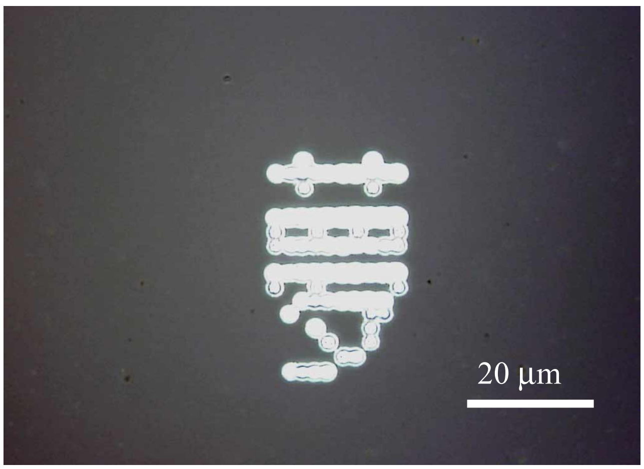

Figure 2 *A example of a printed micro character (dream) which is patterned by a super –fine ink-jet with silver Nanopaste™ ink.*

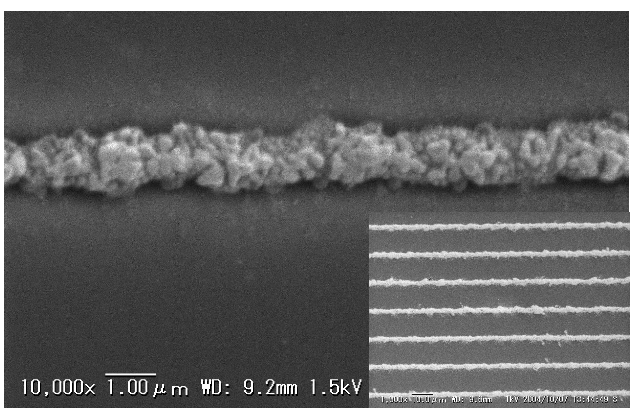

Figure 3 Optical microscope images of silver micro-wires which are patterned by super inkjet system on silicon substrate. The line width is about 1 µm. The inset shows low magnification image. (10 µm pitch)

than what can be discerned by the naked eye, however applications in the electronics field require a more precise patterning capability. Developing this capability has been a major issue in the advancement of inkjet technology. Figure 2 shows an optical microscope image of a micro character and Figure 3 shows a representative SEM (scanning electron beam microscope) image of both line and space patterns. In both figures, silver Nanopaste™ ink was printed on silicon substrates. As shown in these figures fairly fine printing could be achieved. The super-fine ink-jet printer is capable of emitting microscopic droplets of sub-femto liter volume (femto = 10^{-15}), which is less that 1/1,000 the volume of droplets ejected by today's inkjet technology. With this technology, it will be possible to create

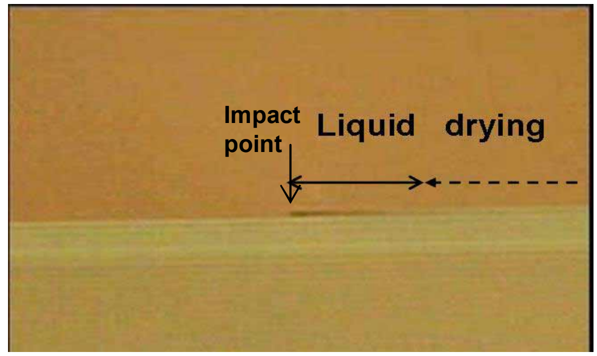

Figure 4 Still image of line pattern of silver Nanopaste™ on silicon substrate by using a super ink-jet with droplet size of 1µm and line pitch of 10 µm (a) and a normal droplet size of about 20µm. with line pitch of 50µm (b). Dark region denotes wetting area while bright region shows the ink drying

dots on a substrate that are less that one micron in diameter. With this development, precise processing that in the past would have been impossible without photolithography is now becoming possible at room temperature and atmospheric pressure conditions.

In fine micro-patterning techniques, many patterning errors arise due to significant surface instabilities, creating unwanted bulge and bridge formation, as well as fragmentation [10]. Strong surface tension in the micro liquid creates a powerful driving force towards minimizing its surface energy, and therefore reducing its surface area, and results in these patterning errors. To avoid these patterning errors in practice, several kinds of approaches have been explored. One is the pre-patterning of substrates by using surface treatments of hydrophobic and hydrophilic coatings [11-12]. The other is a multi-pass patterning technique. In the former case, we would need to use the inkjet deposition technique in combination with another patterning process such as photolithography or laser patterning, and the ejected droplets will self align according to the pre-patterned surface due to the strong surface energy on substrates. This is a powerful and robust technique and is compatible with high throughput processing, however it cannot be considered complete direct patterning. In the latter case, the objective image is formed in multiple passes by superimposing discrete dots images, resulting in a much simpler and truly drop on demand process, free of pre-patterning. The weakness of this method is its low throughput, and its patterning resolution is limited by the droplet size.

In our SIJ, we have achieved precise printing without using both the pre-patterning nor multi pass (super imposing) technique. This is made possible due to the low volume of expelled droplets which rapidly dry, allowing accurate SIJ deposition.

Fast drying effect

Figure 4 shows an image of super fine droplets of 1 μm in diameter with 10 μm in line pitch. In this experiment, both the substrate and the nozzle are kept at room temperature. In this figure, dark regions (indicated by a solid line) denote a wetting area and bright regions (indicated by a dashed line) denote a dried area. The lifetime of the wetting area is only on the order of 0.1 seconds. The boiling temperature of tetra-decane (the solvent for our Nanopaste^{TM}) is about 250˚C. The drying rate of the liquid is strongly dependent on its specific surface area, so of the drying of SIJ droplets is much more rapid compared with that of a conventional ink jet droplet. Because of their extremely small size, the droplets ejected by super ink-jet technology more susceptible to drying. Because the SIJP droplet surface area to volume ratio is very high, their evaporative speed is extremely high. Even though the organic solvent we commonly use for ink materials made of silver Nanopaste^{TM} has a high boiling point of 250ºCelsius, nonetheless, when the ink droplets have a diameter on the sub-micron scale, they evaporate in an instant.

Since the inkjet process is a non-contact patterning process, inkjet printing could be done on an uneven substrate. Figure 5 shows a demonstration of a hill climb configuration by using the super ink-jet system with gold Nanopaste^{TM}. An insulator hill of light curing polymer is printed on a glass substrate as a first layer. After curing with light, interdigitated electrodes are printed on the hill by using the super ink-jet system. As shown in these figures, the inkjet lines are conformal to the hill. Due to the fast drying nature of the super fine droplets, droplets deposit at the position of contact without slipping down the slope.

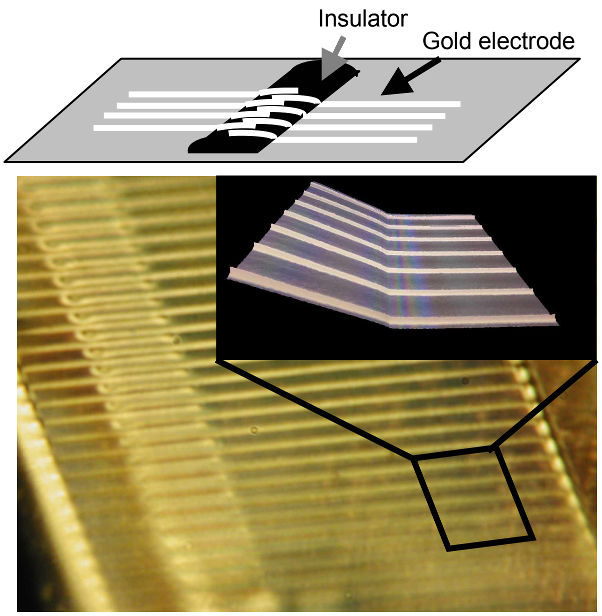

Figure 5 Upper image: A schematic view graph of the layout (upper figure) of Inter digitate layout comb-like electrode which is patterned on a gently sloping hill. Lower image: An optical microscope image of the inkjet printed gold electrodes. The inset shows a 3D image taken by a confocal laser microscope around starting point for a climb.

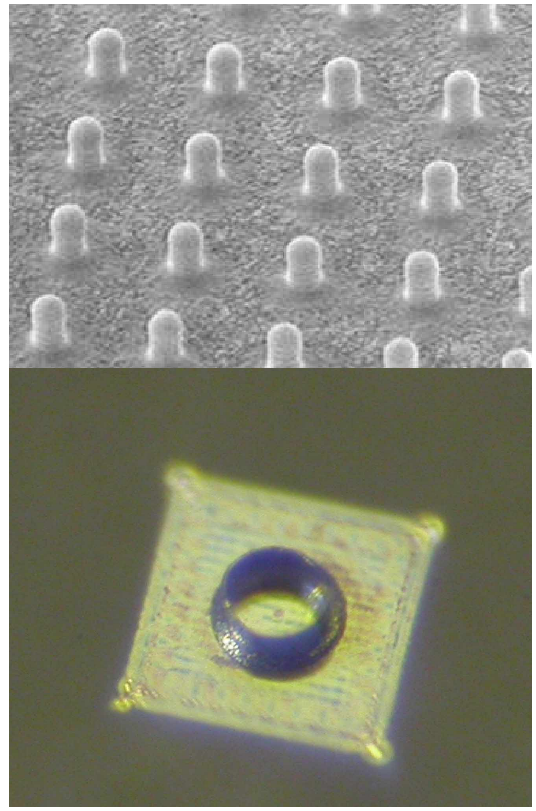

Figure 6 Upper photo: Scanning electron beam microscope image of gold micro bumps array formed by a super inkjet system with a silver Nanopaste^{TM}. The pitch is 50μm. Lower photo: Optical microscope image of cylinder formed by super inkjet system with a silver Nanopaste^{TM}.

Micro bumping and 3D capability

As has been discussed above, the high rate of drying can be used advantageously to build three-dimensional shapes on a substrate. Figure 6 shows a representative result of gold micro bumps formed by the super ink-jet system. Ink is dropped sequentially in exactly the same spot. The first droplet of ink instantaneously dries, so it can immediately be followed by subsequent drops to create a shape like that shown in the figure. The process is reproducible, and micro bump arrays have been formed.

In contrast, sequential deposition of ink-jet droplets of typical pico liter volume would only form a puddle of ink. A metal bump formed on a silicon wafer can be given a cone-shape with a high aspect ratio, all which is carried out at ambient temperature pressure. As has been reported previously, the height of pillar is almost linearly proportional to the ejecting period. A pillar with a high aspect ratio can be formed by simply ejecting super fine dropletsin the same location. By using this technique, pillars of sub-micrometer radius and a few tenth of micrometer heights could be formed.

Bumps of a diameter of ~5 μm is difficult to achieve by a conventional stud bumping techniques. We have checked the inner structures of the micro bumps by using a focused ion-beam technique and the results shows that the bump is uniform, from bottom to top. A typical bump pad requires at least a hundred micro-meters square footprint. Our micron scale bumps might be useful for high density ultrasonic bonding interconnection. The lower image of Fig. 6 shows a representative result of cylindrical shape which was formed by the super ink-jet system. The fast drying nature of the super fine droplets allow the formation of arbitrary 3D shapes by simply scanning the nozzle.

Microscopic parts that are currently manufactured using expensive vacuum apparatus can now be fashioned under normal atmospheric conditions. In addition to the enhancement of ordinary inkjet technology, these demonstrations of super ink-jet technology have enlarged the possibilities of direct drawing techniques which can overcome the limits of conventional printing , and is capable of micro processing as well.

Conclusion

We have developed a super-fine inkjet technology which enables fine pattern processing by super fine droplets measuring less than 1 micro meter. By using conductive ink which is based on super fine metal particles, we have demonstrated direct drawing of metal circuits having a width of just a few microns and direct fabrication of three-dimensional metal bump arrays, micro plugs and micro sockets.

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Author Biography

Dr. Kazuhiro Murata received the Ph.D. degree in material science from the University of Tohoku, Japan, in 1994. From 1994, he joined electorotechnical laboratory and worked on basic physics of conducting polymer and organic thin films. From 1999 to 2000, he worked on organic electronics in the Cavendish laboratory of Cambridge University as a Visiting Scholar. Since 2002, he has been team leader of collaborative research team of super inkjet technology. He has received awards such as Nanotech aword 2002 from International Nanotechnology Exhibition & Conference (Nano tech 2002), Best Paper of International Conference on Electronics Packaging (ICEP) in 2005.