Developing Roll-to-Roll Manufacturing System for Flexible and Stretchable Electronics by Direct Stamping of Silver Nano-Ink

by

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Abstract

Direct stamping of silver nanoparticle based ink has been developed for cost-effective and process-effective manufacturing of flexible or stretchable electronic devices. Facile removal of residual layer from deposited silver nanoparticles (AgNPs) layer results in high fidelity of final silver electrode without further post-processes.

Scanning electron microscopy (SEM) images and energy dispersive x-ray spectroscopic analysis have revealed residue-free transfer of microscale inter-digitated capacitors onto flexible or stretchable substrates. Enhanced adhesion with viscous UV-curable adhesive enables perfect contact between the substrate and AgNPs in the patterned trenches. As a result, adhesion between them is maximized enough to transfer AgNPs from the trenches to the target substrates. The direct stamping also leads to densification of AgNPs in the patterned trenches by pressing force for contacting the substrate and the stamp. The densification results in lower annealing temperature (~130°C) of AgNPs than normally required annealing temperature (160°C) and better mechanical stability of resulting patterns than one from other ink-based printing techniques. SEM and atomic force microscopy show highly reduced number of pores and less roughness of the layer of AgNPs as it confirms densification of AgNPs. For further understanding of the densification in the microscopic view, simulation of the direct stamping has been performed as normal pressure is applied vertically to the stamp. The simulation reveals that by external pressure during direct stamping, the layer of AgNPs is compressed in the direction of the external pressure and is extended in the normal direction to the pressure. Extension provides room for AgNPs to move helping compression of the AgNPs’ layer by the external pressure. In addition, restoring force of the PDMS stamp enables further densification of AgNPs in the x-direction after removal of the pressure to the stamp.

Finally, a table-top roll-to-roll (R2R) manufacturing system has been also successfully built to demonstrate high throughput manufacturing of flexible and stretchable electronic devices by the developed direct stamping method. Strain sensors, touch pads and radio-frequency identification (RFID) tags have been fabricated for highly sensitive flexible and stretchable sensor applications by the R2R direct stamping with the maximum speed of
1 m/minute. The fabricated sensors are still operational even with 8 mm bending radius and after 10,000 cycles of bending. And the wireless and stretchable RFID tags have shown strain sensing behavior up to 7% of stretching strain.

Keywords: Flexible electronics; stretchable electronics; roll-to-roll fabrication; silver nano-ink; direct stamping;
Dedication

To my parents who always cheer me up even in the long distance. They are always by my side wherever I go and whatever I do. Dad and Mom, I give this thesis to you. I love you.

To my wife, you make me stand up again in the middle of any kind of failure and frustration. Please, take this thesis although it is not that much. I love you.
Acknowledgements

I really appreciate my senior supervisor, Dr. Woo Soo Kim who has accepted and supervised me for last three years. Without his guidance and patience, I would not have been successful during my Ph.D. at Simon Fraser University. His enthusiasm and sincerity toward research have always encouraged me to be awake for my study. I also would like to give special thanks to my supervisory committee members, Drs. Byron Gates and Behraad Bahreyni. Their productive comments on my thesis proposal contribute much to improvement of my thesis.

I should thank my colleagues in my lab, Stretchable Devices Laboratory (SDL). They have made my stay at the lab enjoyable. Kyle, he has been a good labmate and classmate of mine and has always given me his hand willingly whenever I asked. Rouzbeh, I really appreciate him that he kindly provided me with precious figures for my thesis. Mohamad, with him, I could try to figure out better stamping processes. Hyun-Woo, he was the second Korean after me in the lab having given me cultural comfort. Kimball, I would like to appreciate that he made a stretching apparatus for me. I also want to thank Kevin, one of co-op students in the lab for providing design of interdigitated capacitors. I want to mention the effort of Tina, another co-op student, to build the roll-to-roll stamping apparatus. I also appreciate Mr. Masih Hosseini and Dr. Carolyn Sparrey for helping me perform cycled bending tests for the touch pads with their electroforce bench machine.

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<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>AgNPs</td>
<td>Silver nanoparticles</td>
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<tr>
<td>PU</td>
<td>Polyurethane</td>
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<td>PET</td>
<td>Polyterephthalate</td>
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<tr>
<td>RFID</td>
<td>Radio-frequency identification</td>
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<tr>
<td>IC</td>
<td>Integrated circuit</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(3,4-ethylenedioxythiophene):p-tosylate</td>
</tr>
<tr>
<td>R2R</td>
<td>Roll-to-roll</td>
</tr>
<tr>
<td>LC</td>
<td>Inductor-capacitor</td>
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<tr>
<td>PI</td>
<td>Polyimide</td>
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<tr>
<td>SEM</td>
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Chapter 1. Introduction

1.1. Background and motivation

Realization of flexible or even stretchable electronic devices is in process by many researchers to improve convenience of life. This study will hopefully contribute to the way. This section will introduce flexible and stretchable electronics and the fabrication methods, especially focused on patterning of conductive media on flexible or stretchable substrates. And conductive metal inks used for the patterning technologies will be discussed.

1.1.1. Introduction to flexible and stretchable electronics

Our daily life is full of electronic devices. Electronic devices are rigid because main electronic components such as transistors, batteries, and circuitries are made of hard and brittle materials. In 1970s, integrated circuit (IC) chips were embedded into plastic cards by a French inventor, Roland Moreno. The card was thick to protect the embedded IC chip from being broken. These days, very thin IC chip is used so that you may put a smart card in a wallet and sit on it. Somehow it is working as a flexible electronic device although not expected to be so. But with this idea, we can learn how flexible electronic devices provide convenience for us. This concept has been even
evolved into electronic identification devices attached on the body so that we do not have to carry any plastic cards with us. This has become possible with the development of flexible electronics. Being flexible means being capable of being bent without breaking or damage by the dictionary definition. It certainly reminds us of rubber-like materials.

Most part of an electronic device is a substrate [1]. Thus, the substrate must be flexible to fabricate a flexible electronic device. Flexible electronics is a modern technology to fabricate flexible electronic devices by depositing electronic components on flexible substrates [2]. When the conventional substrate is replaced with a flexible substrate, many things related to fabrication of electronic devices must also be modified or newly developed. The most conventional method to fabricate an electronic device is the photolithography [3]-[8]. UV exposure, chemical etching, vacuum evaporation of metal and lift-off processes are usually included. Some of these processes can be applied toward flexible electronics [9]-[12], but they are still expensive, complex and harsh for substrates for flexible electronic devices. Flexible electronic devices are not aiming for high performance. They, however, are meant to be for high portability, low price, large-area, conformability and disposability [1], [13]-[20]. And high throughput fabrication is essential to realize those properties. For flexible electronics, continuous roll-to-roll (R2R) manufacturing is feasible because flexibility of substrate tolerates deformation during R2R fabrication processes so that unit price becomes very cheap [21]. Thus, development of high throughput fabrication methods for flexible electronic devices is of major importance.

Flexible electronics enables electronic devices to be bendable, rollable, foldable and even wearable. And those devices are by nature light-weight and extremely portable because the heaviest one of all parts of a device, a substrate is replaced into a light
material. This can be easily conceived by looking into the evolution of digital displays as shown in figure 1-1.

![Figure 1-1. Evolution of digital displays.](image)

As shown in figure 1-1, displays are getting thinner, lighter, cheaper, larger, and more portable. And these attributes are only possible with flexible electronics. Thus, flexible electronics can not only improve or replace conventional electronic devices but also open possibility to new applications. For illustration, in the near future you may read and also watch a newspaper in which flexible digital displays are embedded. It is not necessary to carry heavy equipment to watch TV or movies, but you just take a roll digital display anywhere and spread it wide. A TV monitor is a delicate and heavy item when you move out or travel, but the flexible display makes it easier. Leading digital
display companies such as Samsung have competitively presented prototypes of flexible large displays and mobile phones because they see a large potential market. Figure 1-2 shows many applications of flexible electronics such as displays [18], [22]-[25], batteries [26], [27], sensors [22], [28]-[36], solar cells [7], [16], [19], [37], and identification devices [15], [38]-[45].

Figure 1-2. Applications of flexible electronics [16], [18], [27], [28]. Reproduced with permission from ref. 16 (©2012 Wiley Periodicals, Inc.), 18 (©2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim), 27 (©2012 American Chemical Society) and 28 (©2012 Nature Publishing Group).
Electronic devices for identification are also one promising application. Barcodes on products at a grocery store may be replaced with flexible radio frequency identification tags (RFIDs), which can contain even more functions than barcodes [15], [46]. Flexible RFIDs attached to the products will enable to transmit their information to smart phones of customers and to make payment wirelessly passing through RFID readers without taking out the products from their carts. Flexible sensors, power system and electronic maps may also help soldiers to survive harsh situations and to perform their missions in warfare. Those flexible systems reduce weight and volume of combat gear which a soldier carries relieving restrictions on moving around. As you can see in the examples, flexible electronic devices provide clear benefits to enrich our daily life. Thus, the market for flexible electronics is also growing and the global market for flexible electronics is estimated US$ 26 billion by 2018 according to Global Industry Analysts, Inc.[47]

However, ability to be bent is not enough to satisfy every need. Stretchable electronics has been recently emerging although it is extended from flexible electronics. Stretchable refers to being able to be stretched out and be restored back without significant reduction in performance when it comes to stretchable electronic devices. Stretchable electronics is a technology to provide electronic devices with stretchability fabricating electronic devices on stretchable substrates. Stretchability of electronic devices overcomes restriction on applications for flexible electronics and provides even more options of applications since stretchability ensures electronic devices to be conformable to any curved surface, even to be wrapped around any irregularly shaped objects and to be attached onto a surface stretching out and restoring back regularly or irregularly [48]-[56]. Thus, stretchable electronics can have the best opportunity to be
applied on the human body although other applications are set aside. For example, stretchable sensors for biomedical applications have been attracting interest to have various sensing capability such as temperature, touch, electrocardiogram and motion detection [48], [51], [55], [57]-[65]. Stretchable electronic devices can also be attached to any organ in the body to monitor or assist functions of organs for health care as figure 1-3 shows examples.

Figure 1-3. Biomedical applications of stretchable electronics: (a) strain sensors [55], (b) an electronic eye [66], (c) a thin electric circuit pattern attachable to a brain [17], and (d) a temperature sensor attached to an expandable catheter [67]. Reprinted with permission from ref. 17 (©2010 Nature Publishing Group), 55 (©2011 Nature Publishing Group), 66 (©2008 Nature Publishing Group), 67 (©2010 Nature Publishing Group).

It is the application which is hardly achievable with conventional planar, rigid and brittle silicon-based electronic devices. Electrode array, for instance, has been attached on to the visual cortex of the brain to monitor electrical activity of that area [17], [68]. And
stretchable contact sensors fabricated on a catheter has been also delivered into the blood vessel to monitor the function of the heart [67]. Tattoo-like epidermal electronic system which is very thin and perfectly conformal to skin has been mounted onto the surface of the skin to measure electroencephalograms more conveniently [61]. Recently, Roger’s group introduced an electronic eye which adjusts thickness of lens and thus resembles operation of human eyes a lot by using stretchable electronics [66], [69]. Thus, benefits of stretchable electronic devices are clear. An important issue is on how to fabricate stretchable electronic devices. To be more specific, the crucial basis of fabrication is deposition of thin films of conductive media on stretchable or flexible substrates because they transmit signals and power connecting active components to function.

Much effort has been done to fabricate flexible or stretchable electronic connectors for the last several years [70]-[72]. One area is to develop materials that can withstand high strain because of their physical properties. Those materials are mostly conductive polymers [73], [74], graphene [35], [75], metal-coated fabric [28], [76] and conductive polymer composites with conductive fillers including conductive polymers [77], carbon nanotubes (CNTs) [55], [65], [78]-[83], metal nanowires [53], [84] and nanoparticles [85], [86]. Blending of poly(3,4-ethylenedioxythiophene):p-tosylate (PEDOT, conductive polymer) and polyurethane (PU) elastomer results in highly stretchable conductor with conductivity of 120 S/cm [77]. Fabric threads coated with silver have been sewn in clothes to demonstrate stretchable RFID devices [76]. PU has been doped with silver nanoparticles (AgNPs) by layer-by-layer assembly to make stretchable electrodes [85]. Conductive polymer composite has been also made by mechanically mixing melted polyethylene (PE) and polybutylene terephthalate (PBT) with
AgNPs [86]. Also, woven fabric fibers with many pores have been soaked with CNTs to be used as stretchable conductors for a super-capacitor [81]. Single wall carbon nanotubes (SWNTs) have been mechanically mixed with ionic liquid and fluorinated polymer and stretchable interconnection between organic transistors has been successfully demonstrated with the composite [54]. CNTs have been made gel with other various polymers such as anionic polysaccharide and polyvinyl alcohol [83] and also been embedded in elastic polymer such as polydimethylsiloxane (PDMS) [56], [65], [80]. For these composite materials, stretchability is excellent, but conductivity is very low. Super-aligned CNTs have been cross-stacked to achieve a stretchable and transparent conductor [82]. SWNTs [78] and graphenes [75] have been ink-jet printed to fabricate flexible electrodes. Nanowires embedded in PDMS have shown high conductivity and good stretchability [84]. High aspect ratio of nanowires and nanotube prevents them from losing contact upon stretching. Conductive polymer composites are basically collection of long polymer chains woven together so that they are hard to be disconnected upon strain. But the conductivity is too low to be used for well performing electronic devices. As presented in the previous examples, conductivity is usually 10 ~ 10^2 S/cm which is 10000 ~ 100000 times less than bulk metals as summarized in table 1-1.
They can be used for some applications, but cannot be widely used as conductors because of their low power efficiency. Polymer composites are usually drop-cast for patterning, but by this way, it is difficult to implement mass production. Metal nanowires have high conductivity, but are difficult to make ink formulation to deposit into a fine pattern because of their high aspect ratio. As a result, high throughput fabrication methods are not applicable for them. And also a film made of metal nanowires may show different conductivity according to direction of the current [85].

The other area is to design strain-relief patterns which modulate strain distribution over a device i.e. reduce actual strain applied to the active components on
an electronic device. Thin film is known to be more stretchable than bulk [70]. And also, thin film well attached on flexible substrates is more resistance to tensile strain than free standing film since strain is delocalized over the whole area [87]-[89]. It has been reported that copper was deposited as a film on a polyimide substrate by magnetron sputtering and the well-bonded copper film on the flexible substrate tolerated up to 10% of tensile strain [88]. Also, the film stood up to 30% of tensile strain with some disconnected cracks, which means to remain conductive. Thus, metal films which are well-attached on stretchable substrates as strain-relief patterns must show excellent stretchability. There have been trials on designing strain-relief patterns as shown in figure 1-4.

Figure 1-4. Examples of conductive metal film structures for stretchable electronics: (a) wavy [90], (b-d) serpentine [48], [51], [52], (e) off-plane [91], and (f) interlocking structures [28]. Reprinted with permission from ref. 28 ©2012 Nature Publishing Group, 48 ©2010 Nature Publishing Group, 51 ©2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim), 52 (©2013 Nature Publishing Group), 90 (©2005 IEEE), 91 (©2009 AAAS).
The wavy pattern has been introduced [90], [92], [93]. Thin metal film is deposited on a pre-strained substrate and wavy pattern on metal film is formed after removal of the strain. The wavy pattern lessens the actual strain on the film. Horseshoe patterns [51], [52], [94], [95] and interlocking structure [28] have been also introduced to be strain-relief patterns. Horseshoe patterns allow off-plane strain when it is stretched out so to reduce strain on the film. Meandering horseshoe metal interconnectors were demonstrated to link rigid and separate thin film transistors and light emitting diodes together. Interlocking structure switches external tensile motion into bending motion on the actual device and reduces strain and it was applied to a flexible strain sensor which attachable to human skin. In addition, three-dimensional, namely, off-plane connection has also been reported to help reduction of strain on the metal connection [91]. If these strain-relief patterned metal films connect electrically active components on a flexible or stretchable substrate, then the components are assembled to become a flexible or stretchable electronic device. Islands of active components which are connected via these strain-relief patterned metal paths are much less strained by external tensile strain since stretchable metal connectors overtake most of the strain [96]. The above-mentioned patterns have been mostly fabricated by vacuum based evaporation and photolithography. By these methods, one or two good working stretchable devices can be fabricated, but high-throughput manufacturing systems such as a R2R system is hard to be implemented to produce cheap and disposable electronic devices. Thus, before any excellent strain-relief design, there should be cost-efficient and polymer-substrate compatible methods to deposit metal patterns.
1.1.2. Patterning metal film on flexible or stretchable substrates

Basically materials used for electronics such as semiconductors and electrodes are really weak to tensile strain. Even ductile metal electrode is hard to stand more than 1% tensile strain even though it is made very thin [92]. As mentioned in the previous section, a thin metal film which is well attached to the substrate shows better stretchability because strain can be delocalized over the whole surface. Thus, robust thin film deposition on a substrate is crucial before any structural design of electrical connectors for stretchable electronic devices to ensure their flexibility or stretchability. And also, fabrication cost should be considered because mass-production is essential for flexible or stretchable electronic devices to be applied to real life.

Somehow, metal should be patterned on a substrate without any residual metal to be used for electronic devices. Patterned metal connects active components on a device for sending and receiving electrical signals [97]. Residual metal should be absent to prevent short-circuit and wrong operation of electronic devices. At first, conventional indirect patterning methods were introduced to achieve this requirement [4], [98]-[101]. Researchers have successfully made conductors patterned on conventional substrates such as silicon by photolithography combined with metal evaporation and metal lift-off process. However, these processes require special equipment and environment such as vacuum, chemical etching, and high temperature and pressure. Additionally, non-conventional substrates such as polymers usually do not tolerate the harsh environment associated with the above-mentioned patterning method. This could be an issue because metal must be well patterned on flexible or stretchable substrates before any nice idea is implemented to reduce strain on it. Especially, patterning of conductive
media directly on a substrate has attracted much interest to overcome restrictions of conventional indirect patterning methods since they have not well fit the non-conventional substrate with respect to cost and efficiency of fabrication and compatibility to the substrate [102]. Several patterning methods have been developed parallel to bypass or overcome disadvantages of the conventional technology.

Micro-contact printing (μCP) has been introduced first to make metal patterns on the conventional silicon substrate [99] and later was applied to plastic substrates [24].
Figure 1-5. Representative indirect stamping methods for patterning of metal thin film: (a) micro-contact printing (μCP) [24], (b) nano-transfer printing (nTP) [103], (c) transfer of patterns from a Si mold onto a flexible substrate [104], and (d) water-mediated nTP [105]. Reprinted with permission from ref. 24 (©2001 National Academy of Science, USA), 103 (©2002 AIP Publishing LLC.), 104 (©2011 IEEE), 105 (©2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).
The μCP uses a rubber stamp such as PDMS with patterns replicated from a master. The rubber stamp is re-usable and is easily replicated from the master many times preserving the master intact. The stamp is coated with alkane thiol molecules and the raised parts of the stamp conformably contact a polymer substrate which is covered with metal (usually gold) through metal evaporation to transfer alkane thiol molecules onto the metal-coated substrate. The substrate is immersed into an etching chemical solution and gold on the alkane thiol-free area is etched away leaving patterns because the alkane thiol molecules play a role as a protective layer against the etching solution. A flexible display has been demonstrated by this technology. Later, the μCP evolved into nano-transfer printing (nTP) technology [103]. For the nTP, a rubber stamp, instead of a substrate, is coated with gold by the metal evaporation technique. And gold on the raised parts of the stamp contacts a polymer substrate which is plasma-treated on the surface and chemical bonds formed by chemical reaction between gold and the polymer substrate ensure the transfer of gold from the stamp onto the substrate. This nTP technology is, thus, an additive method while the μCP is a subtractive one. The nTP removes etching procedures for the μCP for more simplicity. Another version of the nTP has been also reported using water as a capillary bridge and reaction catalyst to enhance conformal contact and chemical bonding between metal on the rubber stamp and the polymer substrate [105], [106]. On the other hand, another variant similar to the μCP, but closer to the conventional photolithography has been also tried [104]. That is, metal patterns are prepared first on a conventional brittle substrate and then are transferred onto a flexible substrate. A sacrificial or anti-adhesive layer is inserted on the conventional substrate before deposition of metal to facilitate the transfer of deposited metal patterns onto the flexible substrate.
However, these indirect patterning methods still include many steps which contain special equipment and environment although they have successfully made metal patterns on non-conventional substrates. They are not well fit into mass-production systems for flexible or stretchable electronics such as a R2R manufacturing system. Thus, direct ways to deposit metal patterns have been emerging.

1.1.3. Direct metal patterning

More direct ways to make metal patterns have been developed. Direct writing [42], [43], [91], [107]-[114], direct imprinting [115]-[117], and direct stamping [118], [119] are included. These methods use metal ink solution in common to enable metal-depositing directly on substrates. Their simple and straightforward procedures such as filling, depositing and annealing ink make them advantageous. Conventional metal evaporation methods are excluded.

Figure 1-6 shows various direct metal patterning methods which have been introduced so far.
A well-known direct patterning technologies is the ink-jet printing method. The ink-jet printing is originally for graphic arts including posters and regular documents. The ink-jet printing method for electronics uses conductive metal ink instead of conventional dye ink.
for graphic arts. It has advantage because it can print any pattern on demand on any substrate although the printing speed and the resolution should be improved. Other printing systems originally for graphic arts such as screen and gravure printing methods have also attracted interest of researchers finding fabrication methods for flexible electronics since those could be much faster for printing a large area than the ink-jet printing method. Three-dimensional printing has also been used to deposit conductive ink to connect a circuit off-plane.

Conductive ink based direct imprinting method was introduced in 2007 [115]. Direct imprinting method is similar to the nano-imprint lithography. Solution-based conductive ink on a substrate is imprinted against a stamp as photoresist is so. The conductive ink which is usually nano-sized silver crystals in a dispersing solvent is first patterned on a substrate by pressing a stamp against them on the substrate. Thus, the pattern is a replica of trenches of the stamp. Then, the patterned and dried ink is heat-cured to become a continuous and conductive metal film. Field effect transistors have been fabricated on a flexible substrate by this method. But this method requires high pressure and residual layer may still remain in the unwanted area of final products. Liquid-bridge-mediated transfer (LB-nTM) method was proposed by J.K. Hwang et al[118]. In this method, trenches of a rubber stamp are filled with the ink solution when the ink is sucked into the narrow trenches by the capillary force. And the dried ink inside the trenches is transferred onto a polymer substrate. Then, the transfer has taken advantage of the capillary force to force the dried ink out into the substrate. In more detail, inserted is a volatile organic solvent such as methanol between the stamp and the substrate so that dried ink is extracted out from the inside of the trenches by the capillary force due to evaporation of the solvent. Source and drain electrodes of organic
transistors were successfully fabricated by this technology. However, LB-nTM needs a specific substrate having a high surface free energy to achieve the capillary action strong enough to detach the dried ink out of the stamp, and the volatile solvent is demanding to deal with and need precise control because it evaporates so quickly. Additionally, the capillary force is difficult to appear to take out the dried ink when the patterns are a closed loop inside the stamp since evaporation of the volatile solvent is prevented.

The present study is to overcome the limitations of the previous direct patterning methods and to develop a new and facile direct patterning technology for flexible and stretchable electronics.

1.1.4. Conductive inks

Patterning metal is difficult because metal itself has very high melting point. Common electrode metals such as copper, silver and gold have a melting temperature of around 1000°C. Previously, soldering was used to deposit patterning metal on a substrate. And it was also applied to ink-jet printing system [123]. However, high temperature prevented its further development. Later, it has been reported that compared to the bulk metal, nano-sized metal particles have even lower melting temperature which is less than 200°C [124], [125]. For example, bulk silver has high melting point around 1200°C. However, melting temperature of silver is depressed as the size of particles reaches nano-scale [126]. This phenomenon is caused by high surface to volume ratio of nanoparticles. High surface to volume ratio means that cohesive energy of a surface atom becomes small compared to that of a bulk atom. The average cohesive energy per atom is expressed as follows [125].
\[ E_p = E_b \left(1 - \frac{d}{D}\right) \]  

(1-1)

where \( E_p \) is the cohesive energy of a nanoparticle, \( E_b \) the cohesive energy of bulk material, \( d \) the diameter of an atom, and \( D \) the diameter of a nanoparticle.

The cohesive energy is proportional to the thermal energy to lose an atom from the material. For example, bulk silver (Ag) has 289 kJ/mol of cohesive energy and the diameter of a Ag atom is 0.288 nm. So, when Ag becomes nano-sized, such as 5 nm, the cohesive energy of nano-sized Ag is reduced to 272 kJ/mol. And also surface energy of nano-sized material is much bigger than that of bulk one. Thus, a nanoparticle can free an atom from surface at lower temperature than bulk material can. And the depressed melting temperature is [127],

\[ T_m(r) = T_m(\infty) \left(1 - \frac{2\sigma_{sl}}{\Delta H_f(\infty)\rho_s r}\right) \]  

(1-2)

where \( T_m(\infty) \), \( \sigma_{sl} \), \( \Delta H_f(\infty) \), \( \rho_s \) and \( r \) are the bulk melting temperature, the solid-liquid interfacial energy, the bulk latent heat of fusion, the solid phase density, and the diameter of a nanoparticle, respectively.
Thus, significant depression of the melting temperature enables facile metal-patterning on a substrate. That is, nano-sized metal crystals are deposited and patterned on a substrate as they are dispersed in a solution and later, are fused together to become conductive by heat-annealing. The low annealing temperature also ensures applications on polymer substrates. Solution processed fabrication of metal nanoparticles were introduced and their use for a conductive ink was promising [128]. Because of its size, it is well dispersed as a solution and can be stored without precipitation for a month. Evaporated metal can also be used as a conductive ink as in the above-mentioned μCP or nTP, but it requires expensive and complex vacuum equipment. It cannot be prepared in advance for later use. Thus, it does not fit cost-efficiency fabrication of flexible or stretchable electronic devices. AgNP-based ink (Ag nano-ink) has been successfully applied to the ink-jet printing system to fabricate conductive patterns [108]. Silver is well known for its highest conductivity in a bulk state. Heat-annealed nano-sized silver crystals show almost similar conductivity to evaporated
silver. Annealing temperature is less than 200°C for silver. And silver is a noble metal so that it is more resistant to oxidation than copper which is also very conductive. Besides, silver is much cheaper than gold which is usually selected for evaporated electrodes because of inert property and good conductivity. Thus, out of other metal nanoparticles, AgNPs have been promising and extensively used for direct metal patterning methods.

1.2. Overview of this study

In this study, introduced is UV-curable adhesive-mediated direct stamping of metal nanoparticles. For the main idea of this novel method, UV-curable polyurethane (PU) pre-polymer was used as an adhesive layer to efficiently transfer patterns of AgNPs onto the target substrate. Viscous PU pre-polymer solution easily fills in trenches of a rubber stamp with AgNPs so that the PU layer makes a full contact with AgNPs. The full contact enhances detachment of AgNPs out of the stamp onto the substrate. This direct stamping method has been applied to fabricate sensors made of micron-thick inter-digitated electrodes without any residual layer.

Direct stamping provides enhancement with respect to annealing temperature of nanoparticles and mechanical strength of the final electrode. Stress distribution over AgNP layer during stamping procedure has been simulated to show compaction of AgNPs before annealing. Inter-digitated capacitors and inductor-capacitor (LC) based RFIDs have been fabricated using the developed direct stamping method.

A tabletop prototype of a R2R direct stamping apparatus has been also developed to show possibility of application of the direct stamping method to a
continuous manufacturing system. We have demonstrated facile fabrication of flexible strain sensors that have micro-scale thick inter-digitated capacitors with no residual layer by the R2R direct stamping. All steps of the direct stamping are adapted for a R2R process combined with spraying of Ag nano-ink. Filling the stamp with the nano-ink, removing the residual layer, stamping, and de-stamping proceed while the whole apparatus is run by several rolls and motors. This is the first demonstration of direct stamping of Ag nano-ink performed by an R2R apparatus.
Chapter 2. Development of direct stamping method

2.1. Direct stamping of metallic nano-ink

Direct stamping method has been developed using a solution of metal nanoparticles as a conductive ink which is called metallic nano-ink. Residue-free and clear transfer of metal patterns is successfully performed by the newly developed direct stamping method. All details about the method including materials, preparation of a stamp, preparation of silver nano-ink (Ag nano-ink) and stamping processes will be presented.

2.1.1. Materials

Polydimethylsiloxane (PDMS elastomer, Sylgard 184) and cross-linker were obtained from Dow Corning. Silver paint was purchased from SPI supplies. Silver acetate, hexadecylamine, phenylhydrazine, toluene, acetone, methanol and polyethylene glycol monomethyl ether acetate (PGMEA) were purchased from Sigma-Aldrich Inc for synthesis of silver nanoparticles (AgNPs). Urethane acrylate (EBECRYL 265 photo-curable resin) and photo-initiator (Irgacure 184) were obtained from Cytec Industries and CIBA, respectively. All the reagents were used as received.
2.1.2. Preparation of a stamp

2.1.2.1. PDMS stamps

PDMS has been used as a material for a stamp which transfers a pattern onto other substrates. It is viscous polymerized silicone and becomes rubbery when it is cross-linked. This cross-linked PDMS is called an elastomer which deforms under external force and restore to the original state when the force is removed. Si-O bonds constituting the backbone provide the elasticity as shown in figure 2-1.

![Figure 2-1. (a) Molecular structures and (b) a real image of PDMS.](image)

Its elasticity depends on the degree of cross-linking. And the cross-linked and solidified PDMS presents hydrophobicity on its surface. Hydrophobic methyl groups (\(-\text{CH}_3\)) along the chain of PDMS provide much hydrophobicity with PDMS. Thus, polar solvents such
as water cannot wet the surface of the PDMS. Thus, PDMS is used for surfactant and antifoaming agents in many commercial products such as in food, clothes, cosmetics and medicine. The surface energy of PDMS is around 20 mJ/m² of which value is quite low compared to polymer substrates such as polyethylene terephthalate (PET), polyethylene (PE), polyimide (PI), polystyrene (PS) and etc. as shown in table.

### Table 2-1. Surface free energy for common polymeric substrates

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface free energy (mJ/m²) at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72</td>
</tr>
<tr>
<td>Toluene</td>
<td>27.7</td>
</tr>
<tr>
<td>PET</td>
<td>44.6</td>
</tr>
<tr>
<td>PE</td>
<td>35.7</td>
</tr>
<tr>
<td>PS</td>
<td>40.7</td>
</tr>
<tr>
<td>PMMA</td>
<td>41.1</td>
</tr>
<tr>
<td>PI</td>
<td>46.5</td>
</tr>
<tr>
<td>PDMS</td>
<td>19.8</td>
</tr>
</tbody>
</table>

This hydrophobicity is an excellent property for a stamp material since patterns on the PDMS stamp are easily detached to makes an easy transfer of the patterns onto a substrate. There have been studies on modification of PDMS with fluorine in order to make the PDMS stamp more hydrophobic and to achieve more facile detachment from the stamp [129]. In this study, one of commercially available PDMS encapsulation kits, Sylgard 184, has been used. The kit includes PDMS base polymers and cross-linking agents. The ratio of the polymer to the cross-linking agent is chosen to be 10 to 1.
according to recommended instruction from the company. Cross-linking has been done by heating at 60 °C for one and a half hour. In this study, PDMS has been used as it is without any modification.

2.1.2.2. Fabrication of a master pattern

A master pattern from which PDMS stamps are replicated is fabricated on a silicon wafer by the conventional photolithographic method. The master pattern is made exactly same with the shape of the final product since the PDMS stamp has the inversed pattern of the master, that is, raised parts of the master pattern become lowered parts on the PDMS stamp. The ink filled in the patterned trenches of the stamp is transferred to leave the final pattern on the substrate. The processes of photolithography used in this study are briefly diagrammatized in figure 2-2.
Figure 2-2. Processes of preparation of a master pattern by photolithography.

Photolithography is a well-established fabrication method of micro- and nano-sized structures on a silicon wafer. It uses photoresists which interact with ultraviolet light to be cross-linked (negative) or be destructed (positive) through a patterned window called a photo-mask. Photoresist which is not cross-linked or destructed is later removed and the wanted patterns remain on the silicon wafer. In this study, negative photoresist polymer is dropped on a 10-cm diameter silicon wafer and is spun on a spin-coater. Then, the photoresist is pre-baked on a hot plate. The pre-baked photoresist on the silicon wafer is covered with a photo-mask with pre-patterned windows and is radiated by ultraviolet light.
for a short time. The radiated photoresist is post-baked on a hot plate to complete the
cross-linking process. Finally, the photoresist on the silicon wafer is dipped into an
etching solution which contains a solvent of the photoresist to wash away un-radiated
parts which are not cross-linked to leave only the wanted pattern, that is, the master
pattern on the wafer.

2.1.3. Preparation of metallic nano-ink

AgNPs have been used for other many applications such as medical use [130]
and sanitization [131]. It has not been long since AgNPs were used for electronics [108].
Silver paste which is micro-sized silver particles is tried to make conductive pattern, but it
is mechanically weak and brittle because the silver particles are not fused together but
just physically contact one another. Thus, silver paste is not fit for use in flexible or
stretchable electronics. On the other hand, AgNPs can be sintered together to become
continuous conductive path at low temperature because of melting temperature
depression cause by their small size. Thus, conductive patterns made of AgNPs are
mechanically more robust. AgNPs for this study is easily synthesized by chemical
reduction in an organic solvent at low temperature. Silver salt is reduced into silver by a
reducing agent and the reduced silver grows into nanoparticles surrounded by surfactant
molecules.

2.1.3.1. Preparation of Ag nano-ink

AgNPs are synthesized by the similar recipe with the previous work [132]. The
processes of the synthesis are schematically shown with in figure 2-3.
At first, hexadecylamine which will cover AgNPs as surfactants is poured into a round bottom flask and the flask with hexadecylamine is put in a water bath at 60 °C. Toluene is added to the hexadecylamine. After all the hexadecylamine is completely dissolved, silver acetate is added into the solution. Then, phenylhydrazine, a reducing agent is added drop by drop to the solution. In this step, silver ions are reduced into silver, tiny silver clusters form, and they grow into AgNPs by continuous supply of reduced silver. As a result, the color of the solution changes. The solution is stirred and precipitated with a mixture of acetone solvent. The precipitated solution is filtrated through a filter paper to obtain the precipitate. The precipitate is washed two more times and then, is dried overnight in a vacuum oven at 35 °C. Then, AgNPs are dispersed in toluene for further use as Ag nano-ink.

2.1.3.2. Annealing of AgNPs

The synthesized AgNPs are covered with surfactants called hexadecylamine which has a melting point at 50 °C. Thus, annealing by heat energy is a necessary step to melt away surfactants. And higher temperature is required for fusing or sintering silver
nanoparticles which are separated from each other to make them contact. AgNPs become conductive through annealing by heat. To check the quality of the obtained AgNPs, several drops of Ag nano-ink are put on a glass slide and annealed on a hotplate at 160 °C for several minutes. The dark blue drop of Ag nano-ink on the glass slide turns to shiny and silvery color as shown in figure 2-4. The annealed layer of AgNPs shows high conductivity, 2.0~4.0 \times 10^4 \text{ S/cm}.

![Figure 2-4. Silver thin films on glasses after annealing of Ag nano-ink.](image)

### 2.1.4. UV-curable adhesive-mediated direct stamping of Ag nano-ink.

This direct stamping method is to facilitate transfer of AgNPs in a stamp onto a polymeric substrate by assistance of UV-curable adhesive. There have been trials to transfer patterns onto a substrate without the UV-curable adhesive layer. At first, Ag nano-ink is spread on a substrate and then a PDMS stamp is brought against the substrate with the Ag nano-ink.
Figure 2-5. Previous trials of stamping of Ag nano-ink – (a) a silver pattern imprinted by a stamp and (b) a transferred pattern by stamping without the adhesive layer.

It resembles the way to seal official documents in which a special pattern is embossed. However, it is not successful because first, too much amount of Ag nano-ink is spent and is wasted and second, AgNPs remain on unwanted area besides patterned area. This, so called residual layer of AgNPs affects the final product later by short-circuitry. Next, Ag nano-ink is wiped over a PDMS stamp by the edge of a small PET film to fill the trenches of the stamp and to remove excess of Ag nano-ink, which is similar to the way a doctor blade removes the excess ink in a rotogravure printing. There still remains the residual layer of AgNPs although the amount is less than the previous method. And the stamp is placed and is pressed against a substrate to transfer, but the AgNPs inside the trenches do not come out at all. The adhesion force between AgNPs and the substrate does not seem to be enough to overcome that between AgNPs and the trench. Thus, the adhesive layer has been inserted to facilitate transfer by fully contacting AgNPs inside the trenches and thus achieving force enough to take out AgNPs from the trenches.
Our direct stamping basically includes filling of Ag nano-ink into the patterned trenches of a PDMS stamp, removal of the residual layer on protruded surfaces of the stamp, transferring of the AgNPs onto a substrate and annealing of the patterned AgNPs. Figure 2-6 schematically describes main processes from removal of the residual layer to the annealing of AgNPs. The whole processes are discussed from the following section in detail.

![Diagram of direct stamping process](image)

**Figure 2-6.** (a) A schematic representation of processes of the direct stamping of Ag nano-ink and (b) a final silver electrode pattern fabricated on a PET substrate by the direct stamping method [119]. Reprinted with permission from ref. 119 ©2012 IOP Publishing Ltd.

### 2.1.4.1. Filling the trenches of a PDMS stamp

A flexible PDMS stamp is replicated from a silicon master patterned by the conventional photolithography as described in the previous section. Figure 2-6 shows the main steps of UV-curable adhesive-mediated direct stamping. First, a drop of silver nano-ink (40 wt% AgNPs in toluene; viscosity is about 25 cps.) is placed on a non-patterned area beside patterned trenches. The patterned trenches of the PDMS stamp
are filled with Ag nano-ink and excess of the Ag nano-ink is removed while it is doctor-bladed across the patterned trenches by the edge of a piece of PET film. Much of excess Ag nano-ink is wiped off, but there still remains Ag nano-ink on non-patterned area to be removed later. Alternatively, more diluted Ag nano-ink (5 wt% AgNPs in toluene) is sprayed over a PDMS stamp by an air sprayer with an air compressor. The stamp is placed 5 to 10 cm from the sprayer. Then, the silver nano-ink covers all the surface of the stamp including both patterned trenches and non-patterned area. The silver nano-ink on the non-patterned area is to be removed later. The spraying method fills the trenches more evenly but in longer time than the doctor-blade method. And doctor-bladed silver nano-ink needs a minute to dry for the next step while sprayed AgNP ink is dried right away when sprayed mist of silver nano-ink reaches the surface of PDMS stamp.

2.1.4.2. Removal of residual layers

Removal of residual layers of AgNPs is very important since any remaining AgNPs on non-patterned area adversely affect the final product. An adhesive film which is one of commonly used stationery such as a Scotch tape is placed on the PDMS stamp. The residual layer of AgNPs is attached on the adhesive film and is removed as the adhesive film is peeled off from the surface of the stamp. By this simple method, the unwanted, so called residual layer of AgNPs is perfectly removed. The blue stripes on the adhesive film in figure 2-6(a) schematically represent the unwanted residual layer of AgNPs attached from the protruded surfaces of the stamp. Only the unwanted AgNPs are easily attached on the adhesive film while the pattern of AgNPs inside the trenches of the stamp is left intact because PDMS material itself has an anti-sticking property due to its low surface free energy and decrease in volume of AgNPs after drying leaves a little more room between the adhesive film and the AgNPs in the trenches of the stamp.
The low surface free energy ensures the small adhesion force between AgNPs and the surface of the stamp so that AgNPs are even more adhering to the adhesive film than to the stamp. The patterned trenches of the stamp are physically lower than the rest of the stamp. This fact along with the volume decrease of dried AgNPs make sure that when the adhesive film is attached to the surface of the stamp, it contacts only the residual layer of AgNPs on the rest of the stamp but not the inside of the trenches. As a result, the layer of AgNPs on the unwanted area is taken off along with the adhesive film when the adhesive film is peeled off from the surface of the stamp. Figure 2-7 shows these processes clearly.

Figure 2-7. (Optical microscopic images) processes of the direct stamping. (a) A stamp is filled with AgNPs. (b) The residual layer of AgNPs is removed by an adhesive film. (c) A clear stamp after stamping and transferring. (d) The transferred silver pattern on a substrate.
The first image is taken right after filling of Ag nano-ink. AgNPs are shown not only inside the patterned trenches but also over the rest of the stamp. The second one shows an image taken after removal of the residual layer of AgNPs. AgNPs are only shown inside the patterned trenches.

2.1.4.3. Adhesive layer for easy transfer of AgNPs in the stamp trenches

Next, the UV-curable PU was used as an adhesive layer to enhance the perfect transfer of the AgNPs onto a flexible substrate. The yellow layer in figure 1(a) describes the PU layer spread between the PDMS stamp and the substrate. For the actual experiment, the PDMS stamp is spread with 0.1 ml of UV-curable polyurethane (PU) prepolymer (urethane acrylate 90 wt% and radical generating photo-initiator 5 wt% in PGMEA). The structure of UV-curable PU prepolymer is shown in figure 2-8.

![Acrylate Urethane Prepolymer](image)

Figure 2-8. A structure of UV-curable polyurethane prepolymer [133]. Reprinted with permission from ref. 133 ©2012 Elsevier.
By exposure of UV light, double bonds are open to cross-link other PU prepolymer together. The cross-linking process is completed in tens of seconds with 0.5 \text{ W/cm}^2. A substrate is conformably covered on the stamp on which the UV-curable PU prepolymer is applied. No additional pressure is applied when the substrate is placed on the PDMS stamp and afterwards. Viscous property of the PU prepolymer helps it to fill the small empty room above the AgNPs in the stamp and thus the conformal contact with the substrate is enhanced without any additional pressure or heat. The substrate starts to contact one end of the stamp and then consequently covers the whole surface of patterned area on the stamp as if it squeezes out the PU prepolymer to the other end. In this way, excess of the prepolymer is squeezed out and formation of bubbles is avoided. Presence of bubbles prevents perfect contact between the prepolymer and AgNPs in the trenches. Therefore, removal of bubbles is important because the poor contact leads to the poor transfer later. The whole stamp with the substrate on is then exposed to UV light at 3 \text{ mW/cm}^2 for 5 minutes with a Black-Ray B-100AP high intensity UV lamp with 365 nm wavelength. Afterwards, the substrate is peeled off from the PDMS stamp. A completely transferred pattern of AgNPs is left on the substrate as none of AgNPs remains inside the trenches. For the final step, the pattern of AgNPs transferred on the substrate is annealed at 160°C for 10 minutes.

2.2. Characterization of stamped nano-ink

For demonstration, a capacitor pattern with inter-digitated micro-scale electrodes is fabricated to confirm practicality of the direct stamping method. The inter-digitated capacitor has many separate fingers with a certain distance so that if just two adjacent
fingers of them become connected then the whole capacitor is out of order. Thus, it is important to obtain all separated fingers after stamping. In this aspect, this inter-digitated capacitor is a good example to demonstrate practicality of the UV-curable adhesive mediated direct stamping of AgNPs.

2.2.1. Confirmation of complete removal of residual layer and perfect transfer

The inter-digitated silver pattern fabricated by the newly developed direct stamping method is observed on a Strata DB235 Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) instrument after coating of gold on the sample. And elemental analysis of the inter-digitated silver pattern is performed by the EDS instrument. The SEM image in figure 2-9(a) clearly shows no silver residue between the inter-digital finger electrodes. And it is also confirmed by the EDS analysis that no silver is found between the finger electrodes (figure 2-9(b)). Other peaks between oxygen and Ag are from gold and silicon. First, the sample is coated with gold for conducting path for SEM imaging. Silicon is probably from the PDMS stamp because repeated use of the PDMS might cause the PDMS to wear out and its major component, silicon, to adhere to the sample. The layer of AgNPs is successfully transferred onto the substrate maintaining almost the same shape of the sensor designed on the silicon master. Originally designed dimensions are reduced by about 10%. This small reduction should be caused by the decrease of the volume of AgNPs after thermal curing during which surfactant molecules surrounding AgNPs are burned away and AgNPs are sintered to fuse together. In addition, the thickness of the PU layer is measured to be about 7 μm and that of the inter-digitated electrode made of AgNPs above the PU layer is about 28 μm.
2.2.2. Electrical conductivity

Electrical conductivity of silver electrodes fabricated by the direct stamping method is investigated with several variables such as temperature for heat annealing of AgNPs and stamping conditions. The stamping conditions include as-sprayed AgNPs inside the trenches, stamped AgNPs by the direct stamping, and stamped and annealed AgNPs with a stamp on. The first sample is later annealed inside the trenches of the stamp. The second one is annealed after the substrate is peeled off from the stamp. The last one is annealed with the stamp still on the substrate and after annealing, the substrate is peeled off from the stamp. This experiment is performed to see whether the direct stamping processes affect the quality of the final product.
The Ag nano-ink formulated for spraying (5 wt% in toluene) is sprayed on the surface of three identical PDMS stamps with an inter-digitated electrode pattern by using an air sprayer (IWA-4294, Iwata). One stamp with sprayed AgNPs is set aside as an as-sprayed sample. After short drying time with 30 s, other two PDMS stamps are brought to contact onto substrates. One of the two stamps is followed by peeling the stamp off from the substrate. The other stamp remains attached to the substrate. Finally, all three patterned silver samples are annealed at 130, 140, 150, and 160 °C for 5 min. Resistance of three samples at each annealing temperature is measured between two points which are around 500 μm away from each other on the electrodes by probes and a Keithley 4200 Semiconductor Characterization System. Those three samples are schematically shown around the graph in figure.
Figure 2-10. Resistance results from three different samples at increasing curing temperatures [34]. Reprinted with permission from ref. 34 ©2013 IEEE.

From the top of the graph, the first sample is prepared as AgNPs are sprayed into trenches of a PDMS stamp (as-sprayed). The second sample on the right side of the as-sprayed sample is prepared by transferring an AgNP electrode pattern onto a substrate by the direct stamping method (Stamped&Cured w/o Stamp). The third at the bottom of the graph is also fabricated by the direct stamping method, but the stamp stays and was pressed on contact with the substrate during annealing step (Stamped&Cured w/ Stamp). The results are shown as a graph in Fig. 1. Data points are obtained after measuring three times for each sample and taking average. The resistance of the as-sprayed sample is taken as a starting point in the graph. All three samples reach a certain resistance for final conductivity at 160 °C. The final conductivity is calculated to
be around $2.5 \times 10^3$ S/cm which is less than $2.0 \times 10^4$ S/cm for annealed AgNPs on a glass slide. This is because AgNPs and surfactants move more freely on a glass than on a UV-cured PU. Interestingly, two directly stamped electrodes (Stamped&Cured w/ and w/o Stamp) show much lower resistance than the as-sprayed one even before annealing of AgNPs. And the stamped samples reach lower resistances than the as-sprayed one until the samples are fully annealed at 160 °C. Even the Stamped&Cured w/ Stamp sample has the lowest resistance at a very low temperature, 130 °C. Pressure is continuously applied by the contact between the stamp and the substrate during the annealing process might enhance densification of AgNPs for the Stamped&Cured w/ Stamp sample, while there is no pressure applied during annealing for the Stamped&Cured w/o Stamp sample after detachment of the AgNPs from the stamp. Judging from the results of electrical conductivity, mechanical stamping affects annealing of AgNPs.

2.2.3. **Mechanical stability**

Inter-digitated capacitors are prepared on two different substrates in mechanical properties, brittle (GFR-hybrimer) and elastomeric (PDMS) to compare them on the substrates. An initial capacitance is measured to be around 3 pF which is reasonably high. Each capacitor is installed in a GUNT WP300 universal material tester and capacitance is measured in-situ by an Agilent E4980 precision LCR meter at 1MHz as the capacitor is stretched out uni-axially. Capacitance is registered up to 4% of strain for the PDMS substrate and 3% for the GFR-hybrimer. For bending test, capacitance is registered by the LCR meter at 1 MHz as the inter-digitated capacitor is placed on
cylinders having different radii from 38.5 mm to 2.5 mm. Capacitance is still measured with the smallest radius, 2.5 mm.

The inter-digitated capacitor is also loaded laterally on an electroforce testbench (Electroforce Dual 200 N, Bose). The testbench is set to bend the samples to 8-mm bending radius, and then, to be released to the original position for 10,000 cycles at 1 Hz. And capacitance is measured before and after the bending test. No significant change in capacitance has been found before and after the test. Subsequent multi-axis compression by the stamp as well as the capillary force during stamping of AgNPs leads to mechanically flexible silver electrodes. This result of cycled bending tests supports high mechanical flexibility of the conductive patterns fabricated by the direct stamping method.

2.2.4. **Morphological analysis of stretching by atomic force microscopy (AFM)**

For more detailed observation during stretching, a sample electrode is stretched on a stretching apparatus installed on AFM stage while taking AFM images on the same spot as shown in the upper schematic image of figure 2-11. AFM (NX-10, Park Systems) has been operated in the non-contacting tapping mode. As shown in the actual AFM images of figure 2-11, the electrode stretches up to 6.5% strain until cracks initiate while it is extended to 8% strain. And the electrode shows good conductivity up to 7% strain. Fewer pores lead to fewer cracks since pores usually become sites for cracks and connected pores result in a crack. Since average distance between neighboring AgNPs is reduced, strong connection between AgNPs is possible at relatively short annealing
time. Thus the direct stamping enhances mechanical stretchability, compared to other methods such as inkjet printing (~2.5%) [112] and screen printing techniques (~1.5%) [122].

Figure 2-11. A schematic representation of measurement of AFM as a stamped Ag electrode is elongated in the direction of the length and the resulting AFM images [134]. Cracking is found from 6.5% of strain. (Scan size for each image is 25 µm by 25 µm. 5 µm-bar corresponds to all images.)
2.3. Summary

Patterned silver film has been successfully fabricated on stretchable or flexible substrates by the newly developed direct stamping method of Ag nano-ink with UV-curable adhesive layer. The direct stamping method includes several steps, 1) filling the patterned trenches of the PDMS stamp, 2) removal of residual layers, 3) applying UV-curable adhesive layer 4) stamping and transfer onto substrate and 5) heat-annealing of patterned AgNPs. Residue-free and clear transfer of AgNPs from the PDMS stamp onto the substrates is made possible. Anti-sticking property of the stamp material, PDMS lowers the adhesion of AgNPs to the surface of the PDMS stamp. Thus, simple adhesive film is enough to remove the AgNPs between patterned trenches of the PDMS stamp. Viscous UV-curable adhesive layer ensures perfect and conformal contact of AgNPs inside the patterned trenches of the PDMS stamp to the substrate and facilitate easy and clear transfer of AgNPs onto the substrate. Micro-sized inter-digitated capacitor patterns are fabricated as demonstration. By SEM and EDS, it is confirmed that there is no residual layer between inter-digitated finger electrodes. And, also, no AgNP is left on the PDMS stamp after stamping. Pattern transfer has been successfully performed. Annealing behavior of AgNPs has been investigated. Silver patterns fabricated by the direct stamping method reach higher conductivity more quickly than those by drop-casting. It is suggested that densification of AgNPs by stamping pressure affect positively the annealing behavior although it will be discussed in detail in the next chapter. The inter-digitated capacitors fabricated by the direct stamping method show decent mechanical stability. The capacitors are still operational after 10,000 bending cycles; bending radius is 8 mm. And they stretch out up to 7% of tensile strain. Cracks on the silver pattern start around 5% of tensile strain from observation by AFM.
Chapter 3. Mechanical analysis of the direct stamping

3.1. Clean and facile transfer onto a substrate

3.1.1. Perfect removal of residual layer

When silver nano-ink (Ag nano-ink) is doctored off or sprayed on the polydimethylsiloxane (PDMS) stamp, AgNPs fill the trenches of the stamp and also remain on unwanted surfaces of the stamp between patterns. Clean transfer of AgNPs in a stamp onto a substrate starts from complete removal of the residual layer of AgNPs. This unwanted residual layer of AgNPs can be perfectly removed by an adhesive film as shown in the previous chapter. Only the unwanted AgNPs are easily attached on the adhesive film while AgNPs inside the patterned trenches of the stamp are left intact because PDMS material itself has an anti-sticking property due to its low surface energy and reduction in volume of AgNPs after drying results in an empty room between the adhesive film and the AgNPs in the trenches of the stamp. The small empty room might prevent the adhesive film from sticking to the AgNPs inside the trenches. Thus, AgNPs in the trenches do not come out with the adhesive film when it is peeled off.

The adhesive film is basically a pressure sensitive adhesive. Light pressure is required to make proper bond between the adhesive material and the target adherend.
The adhesion results mainly from van der Waals force between the adhesive and the adherend. The van der Waals force initiates formation of a bond when the adhesive material comes in proximity to the adherend. Then, pressure enlarges the contact area between them which subsequently increases the van der Waals force to ensure proper bond. The adhesive film used in this study is composed of an acrylic polymer adhesive and a backing polymer film. The acrylic polymer on the adhesive film has much higher surface free energy than the PDMS. Thus, AgNPs on the surface on the PDMS stamp willingly expand contact area with the adhesive film so that the van der Waals force to the adhesive film becomes much bigger than that to the PDMS stamp. Consequently, putting on and peeling off the adhesive film result in clear detachment of the residual layer of AgNPs. For the same reason, it is important for the adhesive film not to touch AgNPs inside the trenches, or they are also detached along with the adhesive film.

3.1.2. Analysis of adhesion between a stamp, a substrate and ink particles

UV-curable polyurethane (PU) is used as an adhesive layer to enhance the perfect transfer of the AgNPs onto a flexible substrate. UV-curable PU is viscous and is cross-linked by UV exposure to become a solid film. Although no additional pressure is applied, the viscous property of the UV-curable PU helps it to fill the small empty room above the AgNPs in the stamp and thus the conformal contact with the substrate could be enhanced without any application of additional pressure or heat.

The same discussion about the van der Waals force from the previous section is applied to adhesion between the UV-curable PU and the AgNPs, too. In a microscopic view, adhesion becomes an important interaction for contact between two objects.
Provided there is no special interaction when two solids contact, adhesion is dependent on the surface free energy and the real contact area between two different solids [135]. Clear transfer of AgNPs from a stamp onto the substrate is possible if adhesion between AgNPs and the substrate is higher enough than that between AgNPs and the PDMS stamp. When a hard sphere of AgNP and a flat elastic surface make contact, the elastic surface deforms since van der Waals force between them pushes the hard sphere down on the elastic substrate as shown in figure 3-1.

![Figure 3-1. A schematic representation of deformation of an elastic material when a hard sphere contacts it by van der Waals forces.](image)

The real contact area is determined by this deformation. The van der Waals force can be calculated by equation (3-1) [136] and is high enough to deform the PDMS stamp by one AgNP’s radius since PDMS has a low elastic modulus.

\[
F_{vdw} = 3.2 \times 10^{-15} \frac{hd}{z_0^2} + 6.4 \times 10^{-15} \frac{ha_0^2}{z_0^3} \quad \text{(N)} 
\]  

(3-1)
where $h$ is the van der Waals constant in eV, $d$ is the particle diameter in μm, $z_0$ is the adhesion distance in Å and $a_0$ is the radius of the adhesive contact area in μm which induced by the first force term, and the first term is the van der Waals force caused before any contact and the second is the additional van der Waals force caused by deformation which the force of the first term makes.

This high van der Waals force might enable the PDMS stamp to maximally contact one AgNP by about a half surface area of it. However, when it comes to multiple AgNPs together, the full contact becomes impossible because the elastic restoring force of PDMS due to intramolecular bonds does not allow PDMS to flow and fill the gaps between the AgNPs as schematically shown in figure 3-2.

Figure 3-2. Formation of real contact area when a hard sphere (the upper image) contacts an elastic material which represents the PDMS stamp, and formation of real contact area when multiple hard spheres (the bottom image) contacts the PDMS stamp.
Thus, the real contact area between PDMS and AgNPs remains much smaller than the sum of individual AgNP’s contact area. On the other hand, viscous UV-curable PU can easily flow and fill the gaps between AgNPs to make full contact between the PU layer and AgNPs before the PU prepolymer layer is cross-linked into a solid film by UV. As shown in figure 3-3, real contact area for one particle has no difference between in one particle case and multiple particles’ case.

![Figure 3-3. Formation of real contact area when a hard sphere (the upper image) contacts a viscous liquid which represents the UV-curable PU prepolymer layer and formation of real contact area when multiple hard spheres (the bottom image) contacts the PDMS stamp.](image)

Afterwards, the PU layer is UV-cured into a solid PU film and the real contact area between them remains maximal. Surface free energy of PU (~25 mJ/m²) and PDMS (~20 mJ/m²) are similar, but the PU adhesion layer has much larger real contact area than the PDMS stamp does, which leads to much difference in adhesion force. As a result, adhesion force between the UV-cured PU layer and AgNPs becomes much bigger than that between the PDMS stamp and AgNPs. As a result, clear transfer of
AgNPs in the trenches of the PDMS stamp onto the substrate can be made successful with the UV-curable PU adhesive layer. If it were not for the PU layer, AgNPs directly contact the substrate, and then AgNPs might fail to make full contact with the substrate, and as a result, clear transfer of AgNPs from the stamp is not feasible. For example, the direct stamping of Ag nano-ink has been performed on three substrates including glass-fiber reinforced hybrimer (GFR-hybrimer), polyethylene terephthalate (PET) and PDMS. GFR-hybrimer and PET have much harder than PDMS (Young’s modulus is ~10 GPa for GFR-hybrimer and ~2.5 GPa for PET but ~2 MPa for PDMS.), so the van der Waals force does not deform GFR-hybrimer and PET as much as PDMS. Thus, for GFR-hybrimer and PET substrates, the real contact area becomes much smaller and the adhesion force also becomes smaller. Subsequently, this makes transfer of AgNPs even harder onto the bare GFR-hybrimer or the bare PET substrate. On the other hand, clear transfer has been successfully done by the direct stamping of Ag nano-ink on those three substrates. Thus, the UV-curable PU layer is very helpful for clear transfer of AgNPs onto any substrate as it induces full contact.

3.2. Enhancement of electrical and mechanical properties of stamped electrodes

From the results from the previous chapter, annealing behavior of AgNPs is influenced positively by the direct stamping and the resulting silver electrodes show certain degree of mechanical stability compared to free standing or ink-jet printed silver electrodes. It is suggested that these results are caused by densification of the layer of AgNPs during the direct stamping processes. In this section, densification of AgNPs
inside the trenches of the stamp due to the direct stamping and the effects on the final products are discussed.

### 3.2.1. Densification of AgNPs by the direct stamping

AgNP layers as drop-cast and directly stamped, respectively, have been compared by morphological investigation with scanning electron microscopy (SEM, Strata DB235 FESEM) and atomic force microscopy (AFM, Park Systems NX10). The SEM is used to observe the surface morphology of AgNPs before and after the direct stamping process. Root-mean square roughness of the AgNPs’ layer is measured by the AFM. The directly stamped AgNPs reveal smoother surface than the drop-cast ones as shown in SEM and AFM images of figure 3-4. As shown in the SEM image, large porosity in the layer of AgNPs which is visible in the drop-cast sample becomes mostly invisible in the direct stamped one. Therefore, roughness of directly stamped sample measured by the AFM is much smaller than that of drop-cast one as shown in figure 3-4(b). Roughness of the former is 22 nm while that of the latter is 136 nm. The large reduction in roughness after the direct stamping may come from compaction of AgNPs by compressive force which is induced during the direct stamping. And the reduction in roughness infers removal of pores between neighboring AgNPs. This result demonstrates that the densification actually happens during the direct stamping. The compressive force should be induced when the stamp contacts the substrate among the direct stamping processes because that is the only moment when the external pressure is applied.
3.2.2. Simulation of pressure distribution on Ag nano-ink layer

Compressive stress applied to the layer of AgNPs during the direct stamping is suggested to help densification of AgNPs which positively affect annealing temperature of AgNPs and mechanical strength of the final electrode. This section is aiming for numerical simulation and analysis of the stress distribution over the layer of AgNPs during the direct stamping process for better understanding about Ag nano-ink’s
behavior. Furthermore, for experiments including micro or nano-sized components, it is really difficult to see what is happening down there. In those cases, simulation helps us to have better understanding and new insight. The finite element analysis (FEA) is one of well-known and good tools for engineering simulation. It is a way to find approximate solutions by dividing a complex system into much smaller subdomains called elements. The direct stamping process is simulated by Ansys which is a simulation software using the FEA algorithm.

3.2.2.1. One trench Simulation of stamping process by Ansys

A simulation of stress distribution inside a trench of a PDMS stamp is performed by the Ansys ver. 14.5 simulation software. According to the direct stamping process as schematically shown in figure 3-5(a), simulated is stress distribution on the layer of AgNPs inside a stamp trench when a substrate is pressed against the stamp.
Simulation parameters are shown in figure 3-5(b) from the cross-sectional side and the top views. A stamp with a trench which is 30 μm in depth, 100 μm in width and 500 μm in length is drawn and is assembled with one layer of AgNPs in the trench. The substrate is covered on the side of the opening of the trench. Mechanical properties of the materials involved in the direct stamping are inserted for simulation. For PDMS and PET,
their actual physical values are in use while estimated values are applied for PU and AgNPs because PU is a viscous liquid and collective mechanical properties of AgNPs are not known. High bulk and low shear moduli are used and Poisson’s ratio is 0.5 for PU taking account of incompressibility of liquid. Table 3-1 shows the values of properties of materials used in the simulation.

Table 3-1. Mechanical properties of materials included in the simulation

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus</th>
<th>Shear modulus</th>
<th>Bulk modulus</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al foam</td>
<td>6 Gpa</td>
<td>2.7 Gpa</td>
<td>2.5 Gpa</td>
<td>0.1</td>
</tr>
<tr>
<td>PDMS</td>
<td>2.7 Mpa</td>
<td>0.89 Mpa</td>
<td>43.3 Mpa</td>
<td>0.49</td>
</tr>
<tr>
<td>PET</td>
<td>3.5 Gpa</td>
<td>1.3 Gpa</td>
<td>5.3 Gpa</td>
<td>0.39</td>
</tr>
<tr>
<td>PU</td>
<td>30 pa</td>
<td>10 Pa</td>
<td>2.2 GPa</td>
<td>0.5</td>
</tr>
</tbody>
</table>

For AgNPs, the mechanical properties of aluminium foam are applied for the simulation since it is porous and has small Poisson’s ratio. No-separation and no-friction mode is chosen for boundary conditions of all components. The bottom surface of the stamp is fixed. Mesh size is 7 μm for the layer of AgNPs. Smaller size than that is not available for successful execution. External pressure from 5 to 50 kPa is uniformly applied over the substrate to simulate the direct stamping process. This amount of pressure corresponds approximately to the pressure as a finger is gently pressed against a hard flat surface. Thus, external pressure by direct stamping is expected to be included in the pressure range. Then, stress distribution at a cross-section in the middle of the layer of AgNPs along the length is analyzed by Ansys as the thickness of the Ag nano ink layer varies.
from 3 to 21 μm which corresponds to 10 ~ 70% of the total thickness of one trench as shown in figure. And table 3-2 summarizes combination of parameters for simulation. In total, 28 pairs of external pressure and AgNP layer’s thickness have been simulated.

<table>
<thead>
<tr>
<th>External pressure</th>
<th>Thickness</th>
<th>3 μm</th>
<th>6 μm</th>
<th>9 Mm</th>
<th>12 μm</th>
<th>15 Mm</th>
<th>18 μm</th>
<th>21 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 kPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 kPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 kPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 kPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Combination of parameters for simulation |

Distribution of normal stresses in x- and y-directions is obtained, respectively because the stress in those directions is the most significant to compaction of AgNPs in the trenches. The x-direction is the normal direction to the external pressure applied to the substrate during direct stamping. The y-direction is the same direction with the external pressure and is normal to the layer of AgNPs.

The y-direction normal stress distribution for the layer of AgNPs with thickness of 15 μm which is a half of the trench is shown in figure 3-6 as 20 kPa of external pressure is applied. 20 kPa is a slightly higher than a gentle touch. The top image of figure 3-6 shows the stress distribution with colours. Values of stress from the top, middle and
bottom of the cross-section are obtained and presented in the left bottom image of figure 3-6 as a graph.

Figure 3-6. The y-direction normal stress distribution at the top, middle and bottom parts on a cross-section of Ag nano ink layer with 15 μm in thickness when 20 kPa of pressure is externally applied to the stamp. The y-direction is the direction of the external pressure and the x-direction is the normal direction to the external pressure.

The black dashed lines of both images represent the profile of the stamp trench with depth of 30 μm and width of 100 μm. Stress is up and down around 20 kPa which is the externally applied pressure while higher pressure is found at both ends. Even though
there is fluctuation, mostly compressive (negative) stress is found in the y-direction. Thus, as anticipated, the AgNPs in the trench is compressed down in the y-direction. The graph in figure 3-6 is asymmetric although it is supposed to be symmetric since the external pressure is homogeneously applied to the substrate. The asymmetry might come from the fact that the generated meshes on the AgNPs’ layer and the stamp for the simulation is not symmetric. Later results in this chapter also show asymmetry in their corresponding graphs. Elongation can be induced by Hooke’s law.

\[ S = E \varepsilon = E \frac{\Delta L}{L} \]  

(3-2)

where \( S \) is stress, \( \varepsilon \) strain, \( E \) Young’s modulus, \( \Delta L \) deformation by stress and \( L \) original length.

20 kPa can generate \( 0.33 \times 10^{-5} \) of strain with Al foam’s Young’s modulus of 6 GPa. The strain corresponds to \( 0.05 \) nm of compressive deformation with a 15 µm-thick layer of AgNPs. However, actual AgNPs are covered soft surfactants and are separated from each other and thus actual bulk modulus is supposed to be even smaller than that of Al foam. Accordingly, 20 kPa or less stress is enough to compress the layer of AgNPs. For example, if 1/2000 Young’s modulus (3 MPa which is similar to that of PDMS) is considered, then deformation becomes 100 nm which reflects the amount of reduction in roughness. As previously presented with AFM results, it changes from 136 nm to 22 nm after stamping. The stress from the bottom shows more fluctuation than that from the top and middle. It is because the bottom is more affected by deformation of the stamp which is made of an elastic polymer than others. For all three modes, relatively high stress appears between 40 and 60 µm along the x-direction. And local maximum is found at
around 50 μm which is the center position of the trench. The bottom surface of the trench is anticipated to be raised up in convex because of the Poisson effect when an empty trench is pressed with the same 20 kPa. This convex movement of the bottom surface of the trench which contacts the layer of AgNPs may cause relatively high stress and the local maximum around the center area along the x-direction.

Figure 3-7 shows simulated distribution of normal stress in the y-direction on the layer of AgNPs in the trench for various thicknesses of the layer of AgNPs, 3, 6, 9, 12, 15, 18 and 21 μm.

Figure 3-7. (One trench) The y-directional normal stress distribution at the middle part on the cross-section of Ag nano ink with various thicknesses from 3 to 21 μm (external pressure is 20 kPa).
A dashed line also represents cross-sectional profile of the stamp trench. 20 kPa of pressure is also applied evenly over the substrate. And around 20 kPa of compressive (negative) stress is distributed over the layer of AgNPs in the trench as shown in the graph regardless of thickness of the layer. The thinnest layer (3 μm) fluctuates much especially in the range of 20 μm from both ends. The thinnest one is more affected by the contacting surface of the bottom of the stamp trench which is raised up in convex. However, compressive pressure to the layer of AgNPs is applied for other thicknesses. This induced compressive pressure helps densification of the layer of AgNPs in the y-direction before annealing. On the other hand, pressure difference induces proportional changes in only value of stress while the shape of graph does not change at all.

Normal stress distribution along x-direction is also obtained simultaneously with y-directional normal stress and is shown in figure 3-8.
Figure 3-8. (One trench) The simulated x-direction normal stress distribution inside the trenches of a PDMS stamp during attachment and transfer of dried AgNPs onto a substrate (in the top, the middle and the bottom cross-section of the layer of AgNPs).

The figure representatively shows stress distribution when 20 kPa of external pressure is applied and the layer of AgNPs is 9 μm in thickness. As the normal stress distribution of the y-direction, values of stress from the top, middle and bottom of the cross-section of the layer of AgNPs are obtained. Unlike the case of the y-direction normal stress, mostly, tensile (positive) stress is found in the x-direction normal stress. This phenomenon is natural since the stamp is compressed in the y-direction and should be stretched in other directions because of Poisson’s effect and PDMS has Poisson’s ratio of 0.5 which means no volume change. As shown in the figure 3-8, the normal tensile stress in x-direction is the highest at the bottom and is the lowest at the top of the layer of AgNPs.
Normal stress in the x-direction on the layer of AgNPs in the trench is investigated also for various thicknesses of the layer of AgNPs, 3, 6, 9 and 12 μm and the result is presented as a graph in figure 3-9.

![Graph showing stress distribution](image)

**Figure 3-9.** (One trench) The simulated x-direction normal stress distribution inside the trenches of a PDMS stamp during attachment and transfer of dried AgNPs onto a substrate (with various thicknesses of the layer of AgNPs).

A dashed line also represents cross-sectional profile of a stamp which has one trench. The normal stress in the x-direction decreases as the thickness of the layer of AgNPs increases. It is because the cross-sectional area increases with the thickness although the force is same in the direction. As shown in figure 3-9, high normal stress over 50 kPa in x-direction is found compared to the external pressure which is 20 kPa. It is different than the case of the y-direction normal stress distribution which shows similar stress value to the external pressure. This relatively high stress in the x-direction compared to
the normal stress in y-direction is also attributed to the small cross-sectional area. Because of the tensile stress in the x-direction, the layer of AgNPs is expected to elongate in the x-direction. Therefore, when the external pressure is applied to the PDMS stamp in the y-direction, it is compressed in y-direction while it is stretched in other direction such as the x-direction because of Poisson’s effect. Poisson’s ratio for PDMS is almost 0.5 which means there is little change of volume under the external pressure so that dimension changes in other directions. 50 kPa stress can extend the layer of AgNPs by 1.852 μm in the x-direction by Hooke’s law as Young’s modulus of PDMS (2.7 MPa) is applied; the layer of AgNPs cannot hold tension since they are separated so that they move along with the PDMS.

Simulation is done without the layer of AgNPs to verify how the trench is changed. At first, layers of both AgNPs and PU are removed from the previous simulation design. And the external pressure of 20 kPa is applied as previous. The simulation software provides schematic representation of resulting cross-sectional profiles of the stamp trench while the pressure is applied. Figure is the schematic simulation result which shows that the bottom of the trench of the PDMS is raised in convex as it is elongated in the x-direction.
This convex movement of the bottom surface of the trench causes the local maximum of the normal stress in the y-direction as previously presented.

Next, the layer of PU is added to the simulation. The bottom of the trench of the PDMS is also raised in convex as it is elongated in x-direction as shown in the figure 3-11.
However, in this case, the upper part of the trench is elongated less. This phenomenon may be caused by restriction by the PU layer. Although elastic modulus of the PU layer is smaller than the Al foam which stands for the layer of AgNPs, the PU layer covers the whole top surface of the stamp. The restriction by the PU layer may be quite large to prevent the upper part of the stamp trench from stretching out. Thus, actual tensile stress is applied less as it goes up to the upper part of the trench as shown in the previous results of stress distribution in the x-direction.

Lastly, all components are inserted again and the result is shown in figure 3-12 which is similar to the result without the layer of AgNPs except that more restriction seem to be applied from the upper part of the trench to the boundary of the PU layer and the layer of AgNPs.

Figure 3-12. (One trench) Simulated cross-sectional profile of a stamp trench with all other components – the PU layer and the layer of AgNPs.
This may be due to contact resistance at the boundary of the PU layer and the layer of AgNPs. In conclusion, provided that the layer of AgNPs is inserted in the trench, again, then it is compressed in the y-direction but is elongated in the x-direction.

3.2.2.2. Multi-trench simulation

Previously, only one trench is taken into consideration for the simulation. However, multi trenches are more practical. Thus, two more trenches, thus, three trenches in total are simulated. Simulation of stress distribution over the layers of AgNPs inside three trenches trenches of a PDMS stamp is also performed by the Ansys ver. 14.5 simulation software. The PDMS stamp with three trenches which are all same in dimensions, 30 μm in depth, 100 μm in width and 500 μm in length is drawn and is mated with one layer of AgNPs at each trench. The distance between two adjacent trenches is 50 μm so that the three trenches span 400 μm in total as shown in figure 3-13.
Figure 3-13. (Three trenches) A schematics of parameters for simulation (x is thickness of Ag nano-ink layer).

The substrate is covered on one surface of the stamp where there are the openings of the trenches. Then, pressure is uniformly applied over the substrate to simulate the direct stamping process. Then, stress distribution at a cross-section in the middle of the layers of AgNPs along the length and the thickness is analyzed by the Ansys.

Figure 3-14 shows simulated distribution of stress on the layers of AgNPs in the trenches of the stamp during stamping.
A dashed line represents a cross-sectional profile of a stamp which has three trenches with depth of 30 µm and width of 100 µm. 20 kPa of pressure is applied evenly over the substrate. Compressive (negative) normal stress in the y-direction fluctuates around 20 kPa corresponding to the external pressure just as in the case of one trench. However, stress on the layer of AgNPs in the trench which is placed at the center shows an average less than 20 kPa which is lower than that at other two ends. This induced stress causes densification of the Ag nano ink layer before annealing.

As done in one trench, normal stress distribution in the y-direction is investigated over various thicknesses of the layer of AgNPs, 3, 6, 9, 12, 15, 18 and 21 µm. The results are shown in figure 3-15.
Figure 3-15. (Three trenches) The simulated y-direction normal stress distribution inside the trenches of a PDMS stamp during attachment and transfer of dried AgNPs onto a substrate (with various thicknesses of the layer of AgNPs) [134].

A dashed line also represents cross-sectional profile of a stamp which has three trenches. Compressive normal stress in the y-direction also fluctuates around 20 kPa corresponding to the external pressure, as in the case of one trench, regardless of thickness of the layer. That is, normal stress in the y-direction changes little even though the thickness of the layer of AgNPs increases or decreases. As mentioned above, stress on the layer of AgNPs at the center trench shows lower values than that on the other two ends for all the thicknesses.

For three trenches, distribution of normal stress in the x-direction is also obtained simultaneously with y-directional normal stress and is shown in figure 3-16.
As in the y-direction normal stress distribution, values of stress from the top, middle and bottom of the cross-section of the layer of AgNPs are obtained. The figure representatively shows stress distribution from the middle of the cross-section when 20 kPa of external pressure is applied and the layer of AgNPs is 9 μm in thickness. As in the case of one trench, x-direction normal stress is mostly tensile stress. This phenomenon is natural since the stamp is compressed in the y-direction and should be stretched in other directions with Poisson’s ratio of 0.5. As in the case of one trench, the normal tensile stress in the x-direction is also the highest at the bottom and is the lowest at the top of the layer of AgNPs. However, for the three trenches, the layer of AgNPs in the middle trench experiences much less tensile stress in x-direction than those in both
ends do. It is different from the stress distribution in the y-direction which shows almost same stress over the trenches.

Normal stress in the x-direction on the layers of AgNPs in the trenches is investigated also for various thicknesses of the layer of AgNPs, 3, 6, 9, 12, 18 and 21 μm and the results are presented in figure 3-17.

![Figure 3-17](image.png)

*Figure 3-17. (Three trenches) The simulated x-direction normal stress distribution inside the trenches of a PDMS stamp during attachment and transfer of dried AgNPs onto a substrate (with various thicknesses of the layer of AgNPs).*

A dashed line also represents cross-sectional profile of a stamp which has three trenches. The normal stress in the x-direction decreases as the thickness of the layer of AgNPs increases as in the case of one trench. It is because the cross-sectional area
increases with the thickness although the force is same in the direction. Only thickness increases so that the area increases in proportion to the thickness and the stress is also linearly but inversely proportional to the thickness. For example, when the thickness increases from 3 μm to 6 μm, the stress drops from 100 kPa to 50 kPa at the middle trench. And when the thickness changes from 6 μm to 12 μm, the stress also decreases from 50 kPa to 25 kPa at the middle trench. As shown in figure 3-18, relatively high normal stress in the x-direction is found compared to the external pressure which is 20 kPa. It is different than the case of the y-direction normal stress distribution which shows similar stress value to the external pressure. This relatively high stress in the x-direction compared to the normal stress in y-direction is also attributed to the small cross-sectional area. And one more thing to mention is that difference in stress on the layer of AgNPs between in the middle trench and in other two trenches at both ends is large for the thin layers of AgNPs. But for 15, 18 and 21 μm, there is little difference in stress between the middle trench and other two trenches at both ends.

3.2.3. Analysis of densification process of the layer of AgNPs

According to the simulation, the layer of AgNPs is stretched in the x-direction while it is compressed in the y-direction. This combination is beneficial for packing. When AgNPs are doctor-bladed or sprayed into the trenches, AgNPs are randomly packed in multi layers in the confined trenches as schematically shown in the left image of figure 3-18.
Figure 3-18. (a) A schematic representation of densification of the layer of AgNPs by the x- and y-direction normal stress induced by the direct stamping [34]. Reprinted with permission from ref. 34 ©2013 IEEE.

The x-directional elongation of the layer of AgNPs provides a little more room for AgNPs to move when multi-layered AgNPs are compressed down by the normal stress in the y-direction. Thus, compaction of AgNPs becomes easier. Also, when the external pressure is removed, PDMS restores and the restoring force induces compression to the layer of AgNPs in the x-direction and subsequently more compaction of AgNPs in the direction. As a result, the layer of AgNPs is compressed in both x- and y-directions by the direct stamping. This compression helps densification of AgNPs and reduction of pores between AgNPs. In conclusion, it is suggested that stress which is induced inside the trenches of the stamp results in close packing and enhances contacts of AgNPs as schematically shown in figure 3-18. This densification of AgNPs results in positive effects on annealing behavior of AgNPs and mechanical stability of the final product.
3.2.3.1. Theoretical analysis of annealing behavior of AgNPs by densification

From the results, densification occurs to the layer of AgNPs by the direct stamping [1]. Thus, porosity of the silver electrode decreases and its density increases. A good thing about this densification is that it is not caused by an additional step but is a part of the direct stamping method. To see how the densification affect annealing behavior and temperature of AgNPs, percolation theory is taken into consideration. It is a mathematical theory about possibility of long-range connectivity in randomly distributed particles. One long and continuous chain of particles forms when concentration of particles in a system increases and reaches a certain value which is called percolation threshold. The classical power law for the electrical conductivity of a material is the following equation [85].

\[ \sigma = \sigma_0 \left( V_f^0 - V_c^0 \right)^s \]  

(3-3)

where \( V_f^0 \) is the volumetric fraction of conductive fillers, \( V_c^0 \) is the volumetric fraction of conductive fillers at percolation threshold and \( s \) is a fitting exponent.

Percolation threshold for electrical conductivity is a volumetric fraction of conductive fillers where conductivity radically increases; where an electrical pathway made of connected conductive fillers starts to form. \( V_c^0 \) is constant and thus conductivity increases according to the above equation as fillers’ volume fraction increases. The increase in density of the layer of AgNPs means that the volumetric fraction of fillers - AgNPs for this study - \( V_f^0 \) increases. And the increase in \( V_f^0 \) leads to increase in conductivity according to the above equation. The denser the layer of AgNPs gets, the
larger the probability to pass the percolation threshold becomes. Only some AgNPs are fused together at low annealing temperatures. Therefore, a denser layer of AgNPs has bigger possibility to reach the percolation threshold at low temperature. The same discussion is applied to higher annealing temperatures until the temperature reaches a point where all the AgNPs are fused together. Thus, densification of the layer of AgNPs during the direct stamping helps to achieve high conductivity at relatively low annealing temperature and short annealing time. To be concluded, it is suggested that the pressure-induced densification helps the directly stamped AgNPs to exceed percolation limit at lower temperature (130 °C) and reach the lowest resistance before the required temperature for normal annealing of AgNPs (160 °C) where all the AgNPs are sintered to get connected.

3.2.3.2. Enhancement of mechanical stability

When AgNPs in the Ag nano-ink are deposited on the surface, the capillary force is one natural driving force to gather AgNPs as the solvent evaporates. However, AgNPs loosely stack with certain amount of porosity as they are dried. And the density of AgNPs may not be uniform over the film because of coffee-ring effect [20] (figure 3-19).
Figure 3-19. (a) A real image of coffee-ring effect. It is shown by the enlarged image that particles stack more around the edge [137] (b) a schematic representation of mechanism of the coffee-ring effect [138]. Reprinted with permission from ref. 137 (©2011 Nature Publishing Group), 138 (©2013 IOP Publishing Ltd.).

Solvent flows to the edge of the ink drop as the ink dries. This flow makes particles in the ink solution stack more around the edge than around center. Thus, it could be expected that some parts of the silver film are mechanically weak and vulnerable to cracks. On the other hand, it is highly possible to be even more packed for the deposited AgNPs with certain porosity if there is any additional compressive force to it. It has been reported that the increased sintering pressure on AgNPs lead to highly condensed silver films [139]. Compressing force enhances densification of AgNPs and increases active contact area of neighboring AgNPs so that empty space between them is significantly reduced. The direct stamping of AgNPs includes a normal compressing force in both x- and y-direction of the AgNP layer when the stamp is pressed to contact the substrate. The x-directional elongation during compression helps packing process even more as discussed previously. Therefore, in addition to the capillary force, the compressive force results in more densely packed AgNPs during the direct stamping process and thus mechanically more robust final products.
Inkjet printing has many advantages to fabricate electrodes on flexible substrates. However, since low concentration of the conductive ink is jetted on a substrate, it is difficult to avoid coffee ring effect which results in irregular thickness and low density of the electrode pattern after the ink dries out weakening the resulting electrodes [110]. And also, no pressure on the deposited and dried ink is involved in the printing process. As a result, relatively low conductivity and low mechanical strength usually can be obtained from inkjet printing. In contrast, the direct stamping has advantages over inkjet printing: First of all, the coffee ring effect can be avoided because Ag nano-ink is sprayed and dried in a confined stamp trench. In addition, pressure is automatically applied to the dried ink during the stamping processes. The layer of AgNPs is densified by the stamping pressure ahead of annealing. As a result, conductivity and mechanical strength are enhanced to be useful for stretchable electronic devices.

3.3. Summary

Adhesion between AgNPs, the PDMS stamp and the substrate is estimated by calculation of the van der Waals force between them. Clean removal of the residual layer is possible because low surface free energy of the stamp material, PDMS makes the van der Waals force between the PDMS surface and AgNPs small so that the adhesive film easily take AgNPs with them. Clear transfer is also possible in the similar way. The viscous UV-curable adhesive layer reaches inside the patterned trenches and fully contacts AgNPs that the contact area is maximized between the substrate and AgNPs and the van der Waals force between them is so after UV-curing of the layer. On the
other hand, AgNPs do not fully contact the trench surfaces because elasticity of PDMS does not allow its filling between particles when multi-particles are on it. As a result, adhesion between AgNPs and the substrate with the UV-cured adhesive layer is much stronger than that between AgNPs and the trenches of the PDMS stamp. Clear pattern transfer, thus, is possible by the direct stamping.

Densification of AgNPs after the direct stamping is confirmed by reduction of pores and roughness which are analyzed by SEM and AFM. Simulation presents that the layer of AgNPs inside the patterned trench experiences compressive stress in the y-direction which is normal to the layer and tensile stress in the x-direction which is parallel to the layer when pressure by the direct stamping is applied normally to the substrate. As a result, the layer of AgNPs is compressed in the y-direction and is extended in x-direction at the same time. Extension in the x-direction provides room for the AgNPs to squeeze into themselves when they are compressed. And after removal of the external pressure, the layer of AgNPs is also compressed in the x-direction because of PDMS restoring. This densification of AgNPs lowers annealing temperature of AgNPs because denser AgNPs have more possibility to pass percolation threshold than less dense ones. The densification also positively affects mechanical strength of the final silver pattern because of removal of pores which are the sites for crack-initiation.
Flexible or stretchable electronic devices are expected to be cheap because cheap materials such as plastic substrates and organic semiconductors are used. And the low price is a real advantage for commercialization of flexible or stretchable electronic devices. However, in order to mark truly cost-effective fabrication, fabrication processes should be simple and thus, compatible with high throughput continuous manufacturing system. Conventional lithographic techniques include many complicated steps, harsh conditions and special instruments which prevent the techniques from being applied for high throughput continuous fabrication. Conventional graphic art printing methods such as flexography, gravure, offset lithography and ink-jet printing have been tried to find application for printing electronic devices as graphic inks are replaced with electronic inks such as metal nanoparticle based inks. Except ink-jet printing, other printing methods are based on a roll-to-roll or reel-to-reel (R2R) printing system which is high throughput continuous printing technology. Figure 4-1 shows the rotogravure printing system as an example.
An R2R system uses rollers and webs. Ink is transferred from a stamp roller onto the webs as the webs are rolled in or out during rotation of rollers. Thus, the R2R system can be fit in a small room and allow for high speed ink transfer. For example, the rotogravure printing method for press reaches the speed of several hundred meters per minute. Any of these printing techniques are not confirmed to be the best for fabrication of flexible electronic devices so far although the rotogravure printing method appears to be promising. These graphic art printing technologies transfer ink onto a substrate from
small cells which form an image collectively. Thus, the printed image is a collection of tiny dots which are separated as shown in figure. This is a disadvantage for electronic devices because the final printed electrode may not be conductive. Thus, continuous patterns should be transferred. In this respect, conventional printing methods are not easily adapted to fabrication of flexible or stretchable electronic devices.

The direct stamping method is similar to the gravure printing technology but uses a rubber stamp. The direct stamping method ensures highly defined transfer of features on a flexible or a stretchable substrate without residual layers while previously mentioned ink-based printing methods suffer from bulging of ink and formation of the coffee ring after the ink is transferred onto a substrate. These can cause limited resolution and high failure rate of devices. The direct stamping method is also reasonably compatible with the R2R fabrication system to achieve high throughput production of flexible or stretchable electronic devices. Thus, the direct stamping method is expected to overcome short-comings of ink-based printing techniques and to be a promising printing method for flexible or stretchable electronics.

In this study, the direct stamping method is adapted to a high throughput R2R system for cost-effective and process-effective manufacturing of functional nano/micro structures for flexible or stretchable electronics. Continuous and high throughput fabrication of flexible or stretchable nano/micro-electronic devices on polymeric substrates is very important for keeping the production cost down. It has been reported that an R2R process is applied for the nano-imprint lithography [142]. Nano-scale gratings of epoxy-silicone were fabricated on PET by the R2R processing. However, further processes are required to produce electronic devices. Thus, if aforementioned direct stamping of silver nano-ink (Ag nano-ink) is adopted for the R2R fabrication
system, then a whole electronic device can be fabricated faster with lower cost. When only material cost and labor are considered, one unit of the inter-digital strain sensor is roughly estimated to be 50 cents. This is the first demonstration of the direct stamping of Ag nano-ink which is operated by an R2R apparatus.

4.1. Design of a table-top R2R direct stamping apparatus

For demonstration of a R2R system of the direct stamping, a tabletop prototype of a R2R direct stamping apparatus is developed [143]. We have demonstrated facile fabrication of flexible strain sensors that have inter-digitated capacitors with no residual layer by the R2R direct stamping. A conceptual R2R apparatus is originally designed by a computer aided design (CAD) software called SolidWorks as shown in figure 4-2.

![Figure 4-2. A conceptual design of an R2R direct stamping apparatus drawn by SolidWorks [119]. Reprinted with permission from ref. 34 ©2012 IOP Publishing Ltd.](image-url)
All steps of the direct stamping are adopted for the R2R fabrication system combined with spraying of Ag nano-ink. Filling the stamp with the Ag nano-ink, removing the residual layer by an adhesive film, stamping and transferring by the UV-curable adhesive layer, and de-stamping proceed while the whole R2R apparatus is operated by several rollers which revolve by an electrical motor. A polydimethylsiloxane (PDMS) stamp is fixed on the upper web as it faces up. The stamp is sprayed with Ag nano-ink by a sprayer above the upper web. The upper web carries the stamp to the left and meets the adhesive roller which is placed on the left above the upper web. The residual layer of AgNPs is removed as the adhesive on the adhesive roller contacts the stamp and the upper web moves carrying the stamp to the left. Then, the stamp turns down counter clockwise toward the stamping place at the center to meet a substrate which has UV-curable adhesive spread. Two small rollers at the center ensure perfect contact between the stamp and the substrate as the two rollers hold down the upper web tightly. The black equipment between and above the two holding rollers is a UV light source. The UV-curable adhesive is exposed to the UV during stamping and transferring silver nanoparticles (AgNPs) onto the substrate. De-stamping occurs as the upper web moves up with the stamp and the substrate with the final product moves to the right. All these processes are continuously performed by rotation of rollers to continuously fabricate the products.

The conceptual design is modified to build a prototype R2R direct stamping apparatus which is also designed ideally by the CAD software because the previous conceptual design does not include frames to support the whole R2R system as shown in Figure 4-2. Thus, actual components to be three dimensionally printed are again
designed with some modifications and are assembled in the software as shown in Figure 4-3.

![Figure 4-3](image)

Figure 4-3. (a) A schematic representation of R2R apparatus assembled from the parts to be three dimensionally printed. (b) An actual R2R direct stamping apparatus with an electric motor attached [143]. Reprinted with permission from ref. 143 ©2013 Cambridge University Press.

The components to be three dimensionally printed include rollers with gears, frames, chains and a stamping stage. The size of rollers is reduced for actual fabrication of them. The software enables visualization of what the R2R apparatus look like and how it operates. The upper web with a stamp rotates clockwise this time unlike the conceptual design and Ag nano-ink is sprayed on the stamp. And a flat stage for stamping is inserted to help perfect contact during the stamping process. That is, the bottom pressing roller from the conceptual design is replaced with a height-adjustable and flat stamping stage under the bottom web substrate so that the stamping pressure can be adjusted. The adhesive roller wrapped with adhesive film is removed from above the upper web and is placed below the upper web to include the adhesive roller into the system. Now, the adhesive roller is located between the stamping stage and the upper
right roller. The size of the whole system is designed to be 100 cm long, 30 cm wide and 40 cm high.

All the parts such as rollers with gears, frames, a stamping stage and chains are three dimensionally printed with acrylonitrile butadiene styrene (ABS) polymer by a Stratasys Dimension SST 1200es 3D printer. Eight rollers are made in total. Four rollers are to roll the webs as the upper web where a stamp is attached moves on the two rollers and the bottom web which is a substrate moves on the other two rollers. Other two of the eight rollers are used as adhesive rollers which remove residual layers. Unlike the design, one more adhesive roller is added to the actual system to ensure complete removal of the residual layer. The two adhesive rollers are designed to be detachable for replacement. The last two rollers are to press and hold the upper web with a stamp for stamping against the stamping stage. Gears are built in at both ends of the rollers to connect all the rollers via chains. More detailed explanation of the R2R processes will be discussed in the next section. And all the three dimensionally printed parts are assembled into a R2R apparatus as shown in Figure 4-3(b). The tabletop R2R direct stamping apparatus is 100 cm long, 30 cm wide and 40 cm high when all the parts are assembled. Three dimensionally printed chains are assembled into one long and closed loop. The R2R apparatus is operated by fitting the assembled chains into gears at one end of each roller and connecting an electric motor (Midwest Motion Products) to the right one of two rollers on which the upper web moves. The electric motor (the maximum rate of 11 rpm) attached to the right upper roll rotates the upper stamp web at maximum speed of 1 m/min, which is comparable to those of other R2R apparatuses as table 4-1 presents printing speed of some prior studies.
Table 4-1. Fabrication speeds of prior R2R systems

<table>
<thead>
<tr>
<th>Method</th>
<th>Fabrication speed</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESSENCIAL</td>
<td>0.6~1.2 m/min</td>
<td>Active layer of solar cells</td>
<td>[38]</td>
</tr>
<tr>
<td>Nano-imprinting</td>
<td>0.28 ~ 0.84 m/min</td>
<td>Optical film</td>
<td>[145]</td>
</tr>
<tr>
<td>Nano-imprinting</td>
<td>1 m/min</td>
<td>Gratings</td>
<td>[144]</td>
</tr>
<tr>
<td>Gravure</td>
<td>5 m/min</td>
<td>RFID tag</td>
<td>[39]</td>
</tr>
<tr>
<td>Self-aligned imprint lithography</td>
<td>0.5 ~ 5 m/min</td>
<td>Active matrix transistor backplanes</td>
<td>[146]</td>
</tr>
</tbody>
</table>

The assembled chains link the upper web and the bottom substrate web together at the rollers shown in Figure 4-3(b), and move them at the same speed. The web speed is important to achieve high throughput. Larger gears may allow the web speed to increase further. Polyethylene (PE) film with 15 cm in width is used as the web. The upper web supports and carries a stamp when the R2R apparatus is in operation as it turns clockwise. The bottom web is used as a substrate on which the AgNPs in the stamp is transferred and it carries the transferred products. And the bottom web is covered with the UV-curable adhesive polyurethane (PU) layer which later contacts the stamp and is cured for the clear pattern transfer. The bottom web moves from the right to the left as the left bottom roller rolls up the bottom web while the upper web turns clockwise. Thus, both webs moves to the same direction (to the left) when they meet on the stamping stage. And the upper web is designed to obliquely go up to the left from the stamping stage so that de-stamping occurs automatically right after stamping.
4.2. Demonstration of table-top R2R apparatus

A thin PDMS stamp is replicated from a master pattern which is a shape of interdigitated capacitors fabricated by the conventional photolithographic method. Then, the thin PDMS stamp is attached on the upper web by an adhesive film as shown in figure 4-4 (a).

Figure 4-4. An R2R direct stamping process (a) a PDMS stamp right after sprayed with Ag nano-ink, (b) removal of the residual layer by two subsequent adhesive rolls, (c) the stamp contacting the substrate on the stamping stage, (d) revelation of silver patterns on the substrate as the stamp moves upward to be separated from the substrate [143]. Reprinted with permission from ref. 143 ©2013 Cambridge University Press.
Ag nano-ink is prepared and sprayed to fill the PDMS stamp on the upper web by an air sprayer. Two rollers are wrapped with adhesive films to prepare adhesive rollers for removal of residual layers from the stamp and are placed between the upper right roller and the stamping stage. The two adhesive rollers are detachable so that they can be taken out to replace the used adhesive films on them. A Black-ray high intensity UV-lamp is used to cure a UV-curable PU prepolymer, which is used as an adhesive layer between a PDMS stamp and a substrate.

Figure 4-4 shows each step of the R2R direct stamping processes which are performed by the assembled table-top R2R apparatus. The PDMS stamp sprayed with Ag nano-ink moves to the right and rotates down clockwise. Figure 4-4(a) shows the stamp covered with Ag nano-ink right after spraying. Then, the PDMS stamp faces down and meets two adhesive rollers in a row. The residual layer other than the pattern is well removed onto the adhesive roller. One more adhesive roller which is added to the apparatus later works well for better removal of the residual layer on the stamp. The adhesive rollers are more than 30 cm away from the spraying place so that the nano-ink on the stamp have time to dry up. The process of removal of the residual layer is shown in Figure 4-4(b) as the stamp passes on the subsequent adhesive rollers. The residual layer is clearly removed from the stamp after the stamp goes through the two subsequent adhesive rollers. Figure 4-4(c) shows that the stamp on the stamping stage is clear of the residual layer. Even at the maximum speed of 1 m/min, residual layer is completely removed from the stamp. The adhesive films wrapped over the rollers become less sticky after removal of the residual layer. Thus, to maintain proper adhesiveness to remove the residual layer, several rollers had better switch in rotation while the used adhesive film is replaced. The stamp contacts the substrate on the
stamping stage as shown in Figure 4-4(c). The stamping stage is raised up to ensure perfect contact. Then, the UV-curable PU prepolymer between the stamp and the substrate are exposed to the UV lamp. The stamp is peeled off from the substrate as the upper stamp web proceeds to the left upward as shown in Figure 4-4(d). The stamp moving to the left upward rotates clockwise and returns to the original location to be re-used.

The inter-digitated silver pattern is successfully transferred onto the substrate as shown in figure 4-5.

![Image of successfully fabricated inter-digitated capacitors](image)

Figure 4-5. The successfully fabricated inter-digitated capacitors by the R2R direct stamping apparatus [143]. Reprinted with permission from ref. 143 ©2013 Cambridge University Press.

There is no difference in the transferred inter-digitated pattern than manually transferred one [119]. The length (l) and width (w) of the finger electrode, the overlapping length (v) and gap (g) between two adjacent fingers are measured to be 500, 80, 400, and 40 μm, respectively. And the thickness of the electrodes is around 2 μm. There are 200 finger
electrodes in total. The silver inter-digitated pattern on the substrate is annealed to be highly conductive silver electrode. The inter-digitated capacitor fabricated by the R2R direct stamping apparatus works greatly as a capacitive sensor that shows the initial capacitance of about 3 pF at 1 kHz.

4.3. Summary

A newly developed R2R direct stamping apparatus has been demonstrated to fabricate flexible electronic devices. All the necessary steps of the direct stamping of Ag nano-ink is successfully adapted into the R2R process. A prototype of the R2R direct stamping apparatus is designed by SolidWorks. And then, all the three dimensionally printed parts are assembled into a table-top R2R apparatus which is 100 cm × 30 cm × 40 cm in size. The apparatus is operational up to the web speed of 1 m/min by an electric motor. The subsequent adhesive rolls are enough to remove residual layer from the stamp covered with Ag nano-ink. Fabricated inter-digitated capacitor sensor shows around 3 pF in capacitance and works well to detect capacitance change during bending and finger-touching.
Chapter 5. Applications of direct stamping

5.1. Strain sensors

Strain sensors are an electronic device which measures strain on an object by transmitting electrical signals which are changed responding to mechanical strain. The electrical signals representatively include resistance and capacitance. Strain gauges are a well-known strain sensor device. Patterned metal foil is supported by an insulator and the whole device is attached to a target object on which strain is measured. Electrical resistance of the metal foil changes when the target object deforms and the deformation induces bending or stretching of the strain gauge. The strain gauge is often applied in civil engineering to monitor cracks or deformation of buildings and bridges. But strain sensors can be used for many other applications. One of them is an intelligent tire sensor which monitors tires of a car. Durability is required for the intelligent tire sensors because they are exposed to harsh environment like repeatable, irregular and abrupt deformation. However, conventional strain gauges are not appropriate because they do not stretch enough. Thus, flexible or stretchable strain sensors are demanded. For example, a flexible tire sensor has been fabricated by photolithography with metal lift-off [5].

Recently, flexible and stretchable mechanical strain sensors for biomedical applications have been emerging to have extracorporeal sensing capability such as
motion detection [28], [55]-[61]. The mechanical strain sensors for biomedical applications have been developed to help disabled people in need and athletes in game. For example, applications are found in real-time monitoring of athletes in play to protect them from severe damages and improve them in performance [45], [58], [144]. However, conventional strain sensors do not conform to curved and soft human body. Stretchable or flexible strain sensors are also required for these applications.

The direct stamping method has been applied to fabricate a flexible and stretchable strain sensor made of micron-thick inter-digitated electrodes without any residual layer [119]. A strain sensor with inter-digitated electrodes is chosen for application of the direct stamping technique to demonstrate the advantage of our direct stamping technique. The sensor design is shown in figure 5-1(a).
Figure 5-1. (a) Design of an interdigitated strain sensor, \( l \): length of each interdigitated finger electrode, \( v \): overlapping length between two adjacent electrodes, \( w \): width of each electrode, \( g \): gap between two adjacent electrodes, \( n \): total number of electrodes. SEM images of an interdigitated strain sensor fabricated by the direct stamping (b) from the top view and (c) from the tilted view [119]. Reprinted with permission from ref. 119 ©2012 IOP Publishing Ltd.

The length \( l \) and width \( w \) of the finger electrode, the overlapping length \( v \) and gap \( g \) between two adjacent fingers and the thickness of the electrodes are 500, 80, 400, 40 and 40 \( \mu \text{m} \), respectively. The total number of pairs of two adjacent fingers \( n \) is 200.

The working principle of the strain sensor is simple. Each pair of adjacent finger electrodes can be considered as a capacitor [145]. Deformation of the sensor changes the overlapping length and the distance between those two adjacent finger electrodes. As a result, the sensor's capacitance varies [5]. For the strain sensor to work properly, it is very important to remove the residual layer of AgNPs between the finger electrodes because a contact between any pair of adjacent fingers will short-circuit the whole device. The SEM images in figure 5-1(b) and (c) clearly shows the absence of silver residue between the inter-digitated finger electrodes, which is also confirmed by EDS analysis. The thick layer of AgNPs is successfully transferred onto the substrate maintaining almost the same shape of the sensor designed on the silicon master. Originally designed dimensions (figure 2(a); \( l = 500, \ v = 400, \ w = 80, \ g = 40, \ t = 40 \mu \text{m} \)) are reduced by about 10\% \( (l_{ss} = 450, \ v_{ss} = 350, \ w_{ss} = 70, \ g_{ss} = 35, \ t_{ss} = 35 \mu \text{m} \) where \( l_{ss} \) is length of each finger electrode of the stamped strain sensor, \( v_{ss} \) overlapping length between two adjacent electrodes, \( w_{ss} \) width of each finger electrode, \( g_{ss} \) gap between two adjacent electrodes and \( t_{ss} \) thickness of each electrode). This small reduction should be caused
by the decrease of the volume of AgNPs after thermal curing, during which surfactant molecules surrounding AgNPs are burned away and AgNPs are sintered to fuse together.

The inter-digitated strain sensor is designed to obtain a high capacitance within a small area and a uniform distribution of strain over the capacitor area when the sensor is under tensile stress. Stress is uniformly distributed over the sensor as shown by the tensile simulation of figure 5-2(a) when the sensor is stretched out at both ends.
Figure 5-2. (a) Tensile-simulated deformation result which shows uniform distribution of stress over the strain sensor. For tensile stress, the left end is fixed and ~1mN of tensile load is applied to the right end. (b) Conventional tensile tester with the strain sensor sample loaded. (c) Relative capacitance versus tensile strain for flexible strain sensors fabricated on PDMS and GFR-hybrimer substrates [119]. Reprinted with permission from ref. 119 ©2012 IOP Publishing Ltd.

Capacitance decreases under the tensile stress as the overlapping length of two adjacent finger electrodes is reduced and the gap between the adjacent finger electrodes increases. The reduction of the overlapping length is caused by the Poisson’s effect which describes the change in length perpendicular to an applied load. This Poisson’s effect accounts for the substrate dependency of the sensor because the Poisson’s ratio is different from material to material. The direct stamping allows for successful fabrication of the strain sensors on the two different substrates, polydimethylsiloxane (PDMS) and GFR-hybrimer. PDMS is hydrophobic and stretchable while GFR-hybrimer is hydrophilic and brittle. As expected from the working principle of the inter-digitated strain sensor, capacitance is decreased according to elongation of the sensor on the tensile tester. Relative capacitance changes are calculated from the registered capacitance changes divided by the initial capacitance of the sensor to make comparison of the two substrates reliable. Tensile test of the stamped strain sensors can be easily performed on a conventional tensile tester. The installation of the sensor is shown in figure 5-2(b) and the results are plotted in figure 5-2(c). Gauge factors (GFs) which represent the sensitivity of a strain sensor to strain are obtained from the slopes of the graphs of figure 5-2(c) as −3.07 and −0.391 for PDMS and GFR-hybrimer, respectively. The GF was much larger for the strain sensor on PDMS than on GFR-hybrimer because the brittle GFR-hybrimer has a low Poisson’s ratio of ~0.1. Although
change in the distance between the adjacent finger electrodes is the same for both 
substrates because the change is in the same direction as the tensile strain, the 
reduction of overlapping length between the electrodes varies because the Poisson's 
ratio is different in each substrate. Also, the number of pairs of inter-digitated finger 
electrodes benefits the GF of the strain sensor due to the Poisson’s effect. For example, 
the total change of overlapping length between adjacent electrodes increases two times 
when the number of electrode pairs doubles – thus, the more the adjacent electrode 
pairs, the larger the change of capacitance. This might help to reliably detect small strain. 
A strain sensor does not work reliably if an absolute capacitance change is not large 
enough to be registered as compared to noise, even though the relative capacitance 
changes according to strain are the same in two different strain sensors. Thus, the UV-
curable adhesive-mediated direct stamping method has enabled us to fabricate many 
more pairs of inter-digitated electrodes in a small length. Accordingly, a reliable, 
sensitive, small and cost-effective strain sensor could be fabricated.

Bending test has been also performed to see how the stamped strain sensor 
works when it bends, as bending should be another mode for a strain sensor. Bending 
simulation in figure 5-3(a) shows uniform distribution of stress over the region where the 
strain sensor bends.
The strain sensor is wrapped around a cylinder as shown in figure 5-3(b) and capacitance is measured as the radius of the cylinder decreases. As shown in figure 5-3(c), capacitance remains almost constant down to a certain radius of curvature (~10 mm) at which the capacitance starts to decrease due to the increase of the gap between adjacent fingers. The initial distance between two adjacent fingers is 35 μm (from the SEM image) which is much smaller than the radius of curvature under the bending test. So, at the relatively large radii (>10 mm), the gap between the adjacent
fingers remains relatively small, and the change in capacitance is not large enough to be registered. When the radius of curvature becomes even smaller, the sensor capacitance starts to decrease. As capacitance is inversely proportional to the gap, change in capacitance is high at first and then decreases as shown in the graph.

The directly stamped strain sensor has properly responded to strain under both tensile and bending stresses. Thus, the reported direct stamping overcomes restrictions of other direct metal patterning methods and opens a way to direct patterning of a metal on a flexible or stretchable substrate in ambient environment without any complex processes.

### 5.2. Touch pads

For another application, we have fabricated highly sensitive capacitive touch sensing pads on transparent cellulose fiber paper substrates by the direct stamping of AgNPs [34]. Five pairs of inter-digitated electrodes are fabricated by single direct stamping to make a touch-sensing pad. They are electrically connected in parallel to constitute the touch pad. Then, the change in capacitance of the touch pad is measured with and without finger touching by a precision LCR meter (E4980A, Agilent) at 1 kHz. The same right index finger is used through the experiment at ambient temperature (24 °C) in a short time period. Touch sensors are loaded laterally on an electroforce testbench (Electroforce Dual 200 N, Bose). The testbench is set to bend the samples to 8-mm bending radius, and then, to be released to the original position for 10,000 cycles at 1 Hz. And change of capacitances is measured before and after the test.
Figure 5-4 shows the working principle and a real image of the touch sensing pad which consists of inter-digitated capacitors connected in parallel.

![Schematic representation of the working principle of an interdigitated capacitive touch sensor.](image)

**Figure 5-4.** (a) Schematic representation of the working principle of an interdigitated capacitive touch sensor. (b) Picture of the touch sensors fabricated on a paper substrate. The inset shows a scanning electron microscopic image of the specified part on the sensor. IDE capacitor electrode has 50 μm width and 30 μm in height. Also, total sample size is 1 mm in width and 30 mm in length [34]. Reprinted with permission from ref. 34 ©2013 IEEE.

A finger can be seen as an electrolyte covered with skin, and thus, capacitances appear between the finger and the IDEs ($C_{ft_1}$ and $C_{ft_2}$) when the finger touches the IDEs as presented in Fig. 3(a). Capacitances ($C_{ft_1}$ and $C_{ft_2}$) in series by the finger add up to the initial capacitance of the IDEs ($C_t$) in parallel so that the resulting total capacitance increases while impedances from the finger ($Z_{finger}$) and body ($Z_{body}$) might affect the increment in capacitance. On the contrary, when the finger is removed, the original capacitance of the IDEs is recovered. The initial capacitance of one capacitor
is about 5 pF and the touchpad shows initial capacitance as 25 pF as it is composed of five arrays of IDE capacitors. As a result, the touch pad shows significant change in capacitance from 25 to 1000 pF in figure 5-5(a).
When touch sensors are repeatedly touched with constant pressure, the capacitance change also remains consistent as shown in Fig. 5-5(b).

Bending tests are done to see the mechanical flexibility of the touch sensors. Changes in capacitance of the touch sensors are measured before and after the finger touching in different radii of curvature. There remained still high sensitivity to the finger touching for the touch sensors up to 8 mm of bending radius. Also, the touch sensors are loaded on a Bose electroforce testbench for cycled bending tests as shown in the inset picture of figure 5-6.
The touch sensors are repeatedly bent to 8 mm of bending radius at 1 Hz for 10,000 cycles. No significant change in sensitivity of each touch sensor has been found before (blue bars) and after (red bars) the test as shown in the graph of figure 5-6. The difference before and after the bending test is about 25%. However, by finger-touching, the touch pad changes in capacitance around 40 times, and thus, 25% of capacitance change is not considered significant for operation of the touch pad. Subsequent multiaxis compression by the stamp as well as the capillary force during stamping of AgNPs leads to mechanically flexible silver electrodes. This result of cycled bending tests supports high mechanical flexibility of the touch pad fabricated by the direct stamping method.

In conclusion, we have fabricated highly sensitive and mechanically flexible touch sensors by the direct stamping of AgNPs on a paper substrate. With highly bent touch sensor with 8-mm bending radius, there is no significant decrease in sensitivity. Even repeated bending stroke test after 10,000 cycles, there is no significant change in the sensitivity.

5.3. Radio frequency identification (RFID) tags as strain sensors

Additionally, RFID tags are also demonstrated by the direct stamping method since they are composed of a simple circuit, but they have huge significance to our life
as a wireless identification tag. As a wireless data acquisition technique, RFID has been significantly spotlighted and widely utilized for various commercial product identifications [39], [113], [146]. An RFID tag has a great potential to become a future barcode because it has a longer-range communication, ability of automation and data update, simultaneous identification of many products, and low fabrication cost [42], [147], [148]. A typical RFID system consists of three major components including a reader, which transmits and receives wave signals with particular frequencies, an RFID tag, which has identification information and a software system that can encode the captured information to identify objects [46]. There are two types of RFID tags, passive and active ones, with respect to inclusion of operating power sources. A passive RFID tag which does not include expensive batteries has much lower fabrication cost when compared to an active RFID tag [149]. Besides, a passive and chipless RFID tag can be fabricated on flexible substrates by printing technologies using conductive inks because it does not include bulky chips but only a metal pattern as an antenna so that fabrication cost goes much further down [150], [151]. Meanwhile, printability of the tags on stretchable substrates is also desired to enable the RFID tag to be conformable to any surface [152].

Flexible and stretchable mechanical sensors for biomedical applications have been emerging to have extracorporeal sensing capability such as motion detection [28], [55]-[61]. These sensors have been developed to help disabled people in need and athletes in game. For example, applications are found in real-time monitoring of athletes in play to protect them from severe damages and improve them in performance [45], [58], [144]. To achieve this purpose, wireless communication such as the RFID is essential. A system consisting of both mechanical sensors and RFID tags can be considered so that the mechanical strain is changed into electrical signals by the sensor and the electrical
signals are transmitted to the reader by the RFID tag simultaneously. However, this system is bulky for the attachable application to the body and it may restrict motion of the athletes. On the other hand, a stretchable RFID tag can perform both roles as the sensor and the antenna. Thus, a stretchable RFID tag can sense the mechanical strain and at the same time transmit the information wirelessly. And also, multiple tags attached to the body can provide more information about the player such as how much strain each part of the body experiences. Therefore, the stretchable, passive and chipless RFID tag is well fitted into the sensing applications for real-time motion detection.

Direct stamping of silver nano-ink (Ag nano-ink) is utilized to fabricate a stretchable, passive and chipless RFID tag with a simple inductor-capacitor (LC) resonator antenna stamped on flexible and stretchable substrates [134]. While the stretchable RFID antenna have been demonstrated by liquid metal injection [60], silver nanowire embedding [153], ink-jet printing [43] and electro-spinning [154], the direct stamping method is also simple to be applied for high throughput R2R fabrication with the aforementioned advantages [119]. Passive RFID tag layout is based on an LC circuit with a particular resonant frequency for sympathetic oscillations [155]. In this study, the pattern structure of tags is designed and optimized to meet the operating frequency range requirement of the measurement system. The resonant frequencies of a single tag, multiple tags, and stretchable tags are located through wave signal measurements. Therefore, the design, fabrication, and testing of tag’s resonant frequencies in different conditions are discussed here.

LC antenna patterns are fabricated on flexible substrates (PET and PDMS) by the direct stamping method as previously reported elsewhere [119]. Briefly, A PET film is cut into a pre-designed layout of a tag with a laser cutter (Universal Laser System
VLS3.60), the layout film is attached onto a piece of Plexiglas and it is used as a master later on. Then, an elastomeric PDMS stamp with a tag pattern layout trenched on the surface is replicated by casting liquid PDMS on the master pattern. The prepared Ag nano-ink is sprayed on the surface of the PDMS stamp with an LC antenna pattern. After short drying time with 30 seconds, the PDMS stamp are covered with polyurethane (PU) prepolymer as an adhesive layer and are brought to contact onto the substrates. The PDMS stamp is pressed from the bottom of the substrate to ensure perfect contact. Then, the PU prepolymer are exposed to UV light with 1 Watt from the bottom of the stamp through the paper substrate, followed by peeling the stamp off from the paper substrate. Finally, the patterned silver nanoparticles (AgNPs) on the substrate are annealed at 160 °C for 5 minutes to give the final LC antenna pattern. AgNPs are annealed at 160 °C instead of 130 °C to ensure complete curing of AgNPs.

The prepared LC RFID tag is placed in 20 cm away from wave-guide of a ZVB4 vector network analyzer (VNA, Rohde&Schwarz) with a horn antenna connected through coaxial cables to transmit the wave signals with frequencies ranged from 1.12 to 1.7 GHz through the waveguide. While frequencies are sweeping, the frequency corresponding to the resonance frequency reflected from the RFID tag and its strength are registered by the VNA. For the stretching test, the RFID tag on a PDMS substrate is stretched by a stretching apparatus and is placed as previous at each strain up to 4% and each resonance frequency and the signal strength are registered at each strain.

The proposed RFID tag pattern design is based on the sympathetic oscillation of an LC circuit because it has an advantage with respect to coupling and efficient energy transfer [156]. The design consists of a single turn rectangular coil inductor and an inter-digitated capacitor connecting to each other as shown in figure 5-7.
Figure 5-7. A schematic representation of an RFID tag design based on an LC circuit and an RFID system operation system consisting of a horn antenna with a vector network analyzer connected [134].

A resonance frequency of the RFID tag is approximated the same way as for an LC circuit by

\[
F = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \left(\frac{R}{L}\right)^2}
\]  

(5-1)

where \(F\) represents the resonance frequency, \(L\) represents the inductance, \(C\) the capacitance and \(R\) the resistance of the inductor wire.
Inductance \( (L) \) of a single turn and thin planar coil inductor is determined by the following equation [157].

\[
L = 4 \left[ l_a \ln \left( \frac{2A}{a(l_b + l_c)} \right) + l_a \ln \left( \frac{2A}{a(l_a + l_c)} \right) + 2[a + l_c - (l_a + l_b)] \right] \text{ (nH)} \tag{5-2}
\]

where \( l_a \) is outer height, \( l_b \) outer width, \( 2a \) turn width, \( A \) outer area of the rectangular inductor in Fig. 1, \( l_c = \left( l_a^2 + l_b^2 \right)^{0.5} \), and units are all in cm.

Capacitance \( (C) \) of the inter-digitated capacitor can be deduced by the following equation [44].

\[
C = \varepsilon_0 \varepsilon_r t \left( a - d \right) \left( \frac{2n - 1}{g} \right) + nC_p \text{ (F)} \tag{5-3}
\]

where \( \varepsilon_0 \) is vacuum permittivity, \( \varepsilon_r \) relative permittivity of the substrate, \( t \) thickness of the electrode, \( n \) number of fingers, \( C_p \) parasitic capacitance in farad, \( a \) finger length, \( d \) a gap from a finger to the main bar, \( g \) a gap between two adjacent fingers, and units are in m.

Thus, the resonance frequencies of RFID tags are adjusted by changing the feature sizes (width, height and turn width of the inductor and finger length and number of the capacitor, etc.) of the RFID pattern. For example, reduction of turn width of the inductor increases inductance or addition of number of fingers to the inter-digitated capacitor increases capacitance so that the resulting resonance frequency decreases according to the equations. By modifying the values of capacitance and inductance, we
can precisely control the resonance frequency range of tags to match the operating frequency range of the measuring device. The proposed RFID measuring system is constituted of three components as schematically shown in figure 5-7; a horn antenna (the right schematic image) through which radio waves emitted from the source and reflected from the RFID tag pass, the RFID tags, and a vector network analyzer (VNA). When the system operates, the VNA generates wave signals with sweeping frequencies. The horn antenna connected with the VNA through coaxial cables will transmit the wave signals with frequencies ranged from 1.12 to 1.7 GHz through the waveguide inside. The RFID tags existing in the detection zone, which is from about 20 cm away from waveguide, receive the wave signals, and modify the signals based on their sympathetic oscillations at specific frequencies. The modified signal is recaptured by the horn antenna, and is sent back to the VNA for analyzing and recognizing.

Fig. 5-8(a) shows schematics and actual images of the fabrication steps and successfully fabricated tags. Spraying and drying of Ag nano-ink occurs at the same time to lead to uniform deposition over the stamp.
Figure 5-8. (a) Schematic illustration of Chipless RFID tag fabrication process by Ag nano-ink spray technique (b) Simulated stress distributions inside the trenches of a PDMS stamp during attachment and transfer of dried Ag nano-ink onto a substrate [134].

Relatively large pattern is transferred well onto the substrate as shown in Fig. 5-8(a). Afterward, the Ag nano ink inside of a PDMS stamp is annealed at 160°C for 10 min after removal of residual layer by method described in the reference 120. Fully fabricated silver pattern layout inside the trenches of the stamp shows great conductivity ($1.5 \times 10^4$ S/cm). Meanwhile, when the PDMS stamp is bent back and forth or stretched up to 7% strain, the silver pattern remains in good conductivity. This is because of enhancement of mechanical stability by densification of the layer of AgNPs by the induced stress to the layer during the direct stamping as discussed in the previous chapter.

In order to analyze the fabricated RFID tags, the resonance frequency of the LC resonator based chipless RFID tag is identified by monitoring the abrupt changes of induced voltage gain on the VNA instrument. Figure 5-9 shows the field trial results to determine resonance frequency for two stamped RFID tags on flexible PET substrates.
Tag #1 and tag #2 have different coil inductor turn width and outer diameter length (tag #1: 1.0 mm turn width and 30 mm diameter length, and Tag #2: 1.5 mm turn width and 30 mm diameter length), and inter-digitated capacitor finger numbers and length (tag #1: 7 fingers, 3.8 mm finger length, 0.7 mm finger width, 1.0 mm gap width, and tag #2: 6 fingers, 4.9 mm finger length, 0.7 mm finger width, 1.2 mm gap width). With the feature sizes, inductances and capacitances are calculated to be 80.09 nH and 0.177 pF for tag #1 and 70.56 nH and 0.169 pF for tag #2. Hence, theoretically by equation (5-1), resonance frequencies are determined to have 1.33 GHz and 1.45 GHz, respectively for tag #1 and #2; the second term in the square root of equation (5-1) is ignorable because resistance of the stamped electrode is very small (the first term is an order of $10^{20}$ while
the second term is an order of $10^{15}$. Both tags are placed about 20 cm away from the waveguide. When tag #1 is put in the detection zone, we get the blue curve of figure 5-9 from the VNA, which clearly shows the abrupt change of voltage gain at around 1.31GHz. Similarly, when tag #2 is placed at the same position, we get the green curve of figure 5-9 from VNA, which also shows abrupt change of voltage gain at around 1.44 GHz. Based on the abrupt voltage gain change of the signal curves, we can successfully locate the resonance frequencies of tag #1 and tag #2 at 1.31GHz and 1.44GHz, respectively, which agree well with theoretically determined values of 1.33 GHz for tag #1 and 1.45 GHz for tag #2 although there is a small discrepancy between the values because of parasitic capacitance. Then, when we align the two tags together (separation distance: ~15 cm) in the detection zone, we get the red curve of figure 5-9 from the VNA, which shows two peaks of abrupt voltage gain changes at around 1.33GHz and 1.43GHz. Compared with the resonance frequency value for each tag, the resonance frequency values from two tags at the same time case are closely matched. Hence, resonance frequencies of the single tag and multiple tags can be readily determined through VNA wave signal test, and the measurement results show that the proposed tag can operate with good performance in practice.

The stretching test is also performed for the chipless RFID tag on the stretchable PDMS substrate, and the result is shown in figure 5-10.
Figure 5-10. (a) The stretchable RFID strain sensor on the stretching apparatus (b) Stretching behaviors of a chipless RFID tag on a stretchable substrate and the tag's resonance frequency changes (c) Comparison of the theoretical and the measured changes in the resonance frequency by stretching the RFID tag (d) calculation of the gauge factor from the measured values [134].

This stretchable RFID tag consists of a coil inductor with turn width 0.9 mm and outer diameter 30 mm, and the inter-digitated capacitor with 5 fingers, 4.2 mm finger length, 0.9 mm finger width and 0.9 mm gap width. Hence, theoretically, the unstretched PDMS RFID tag has 82.58 nH inductance, 0.110 pF capacitance, and 1.673 GHz resonance frequency. Varied resonance frequencies are registered as the tag is stretched out by
1%, 2%, 3% and 4% elongation on the stretching apparatus which shown in figure 5-10(a). The red curve of figure 5-10(b) represents the feedback signal from the VNA at the unstretched state and the abrupt change of voltage gain occurs at 1.613 GHz which is the original resonance frequency for the stretchable PDMS RFID tag. As the tag stretches with different incremental elongation, we can see the shift of abrupt voltage gain on the frequency spectrum towards left; resonance frequencies are registered to be 1.608 GHz for 1%, 1.593 GHz for 2%, 1.590 GHz for 3% and 1.541 GHz for 4%. As the RFID tag is stretched out in the direction along with the width of the inductor, the width of the inductor and the finger length of the capacitor increase and the increase results in the change in the resonance frequency. It is supposed that the horizontal length of the inductor and the finger length of the capacitor increase by the same ratio as the tensile strain and lengths in other directions decrease according to Poisson’s ratio (~0.5 for PDMS), and the change in the resonance frequency is theoretically estimated and is compared to the measured values in one graph. Figure 5-10(c) shows theoretical and experimental results, together. The slope of each graph is 1.18 GHz for the theoretical and 0.829 GHz for the measured if the last value which drops suddenly is excluded, respectively. The discrepancy might come from the measuring error by hand. The gauge factor (frequency shift/strain) for the RFID tag is calculated to be 0.51 as shown in figure 5-10(d). The GF could be improved by modification of the LC circuit design such as more turns of the inductor. Hence, we can decrease the resonance frequency of the tag by stretching it under the conductivity tolerable range. It could be possible to predict the strain of the stretchable RFID tag by analyzing the shifts of resonance frequency. Therefore, there is a possibility of applying this stretchable PDMS RFID tag to stain sensing tasks as well as identification tasks.
5.4. Summary

Applicability of this direct stamping technique has been confirmed by fabrication of highly sensitive and cost-effective strain sensors on stretchable or flexible substrates like PDMS and GFR-hybrimer for the intelligent tire sensor. The directly stamped strain sensor has properly responded to strain under both tensile and bending stresses. Thus, the reported direct stamping overcomes restrictions of other direct metal patterning methods and opens a way to direct patterning of a metal on a flexible substrate in ambient environment without any complex processes. Furthermore, a continuous R2R process is expected to be easily applicable to the direct stamping for high-throughput fabrication of electronic devices. For another demonstration of the direct stamping, we have also fabricated highly sensitive and mechanically flexible touch sensors by the direct stamping of AgNPs on a paper substrate. With highly bent touch sensor with 8-mm bending radius, there is no significant decrease in sensitivity. Even repeated bending stroke test after 10,000 cycles, there is no significant change in the sensitivity. We also successfully fabricate flexible and stretchable LC-resonator-based chipless passive RFID tags by using the direct stamping method with Ag nano ink, and the design of the tag pattern layout is based on sympathetic oscillations of an LC circuit at its resonance frequency. The single tag and multiple tags identifications are achieved by identifying the abrupt changes of voltage gain at each tag’s resonance frequency. Theoretically calculated resonance frequencies well agree with the measured ones. The stretchable tags maintain good conductivity up to 7% of elongation. The measurement results show that the proposed tags features good readability and robustness in the detection zone. The LC resonator based chipless RFID tag can also be potentially utilized in a flexible,
stretchable, or wearable identification system which performs strain sensing at the same time in future to help protection and performance of athletes.
Chapter 6. Summary and Future works

6.1. Summary

Flexible or stretchable electronics is an emerging technology to enrich our life because it enables extremely portable, light-weight, large-area, conformable or disposable electronic devices. However, deposition of electronic components, especially, conductors on flexible or stretchable substrates are not feasible by conventional fabrication methods for electronic devices on rigid substrates. Novel fabrication methods should be introduced. For the purpose, the UV-curable adhesive assisted direct stamping of silver nano-ink (Ag nano-ink) has been developed in this research.

In chapter 2, the newly developed direct stamping method for fabrication of flexible or stretchable electronic devices is introduced in detail.

The direct stamping method includes simple steps – filling ink, stamping, transferring, and annealing. Residue-free and clear transfer of silver nanoparticles (AgNPs) from the polydimethylsiloxane (PDMS) stamp onto the substrates is made possible. Simple adhesive film is enough to remove the residual layer between patterned trenches of the PDMS stamp. Viscous UV-curable adhesive layer is applied between the stamp and the substrate to ensure conformal contact of AgNPs inside the patterned trenches of the PDMS stamp to the substrate. After curing of the adhesive layer, AgNPs
in the trenches are easily taken out along with the cured adhesive onto the substrate. By SEM and EDS, it is confirmed that there is no residual layer between patterns. And, also, there is no AgNP in the trenches after stamping. The direct stamping is performed well on several different substrates including GFR-hybrimer (brittle), PET (flexible) and PDMS (stretchable). Silver patterns fabricated by the direct stamping method reach higher conductivity more quickly than those by drop-casting. The inter-digitated capacitors fabricated by the direct stamping method are still working even after 10,000 bending cycles with 8 mm of bending radius. And they stretch out up to 7% of tensile strain.

In chapter 3, advantages of the direct stamping method and theoretical analyses for the advantages are presented.

The van der Waals force between AgNPs, the stamp and the substrate is considered to understand the clean removal of the residual layer and the clear transfer of silver patterns. Low surface free energy of the stamp material, PDMS makes the van der Waals force between the PDMS surface and AgNPs small so that the adhesive film easily take AgNPs with them. The viscous UV-curable adhesive layer helps maximize the contact area between the substrate and AgNPs and thus do the van der Waals force between them after UV-curing of the layer. This van der Waals force overcomes adhesion between the trench and AgNPs in it. As a result, clear pattern transfer is possible by the direct stamping. Low annealing temperature of AgNPs and mechanical stability of the resulting product is caused by densification of AgNPs. The external pressure induced during the direct stamping makes AgNPs dense. Densification is suggested to occur in both x- and y-directions by FEA simulation.
In chapter 4, a prototypical roll-to-roll (R2R) manufacturing system including the direct stamping method has been demonstrated.

A tabletop prototype of an R2R direct stamping apparatus has been developed. The prototype is about 100 cm long, 30 cm wide and 40 cm high and is operational up to the web speed of 1 m/min. While upper rolls carry a web with a patterned stamp on it clockwise, a sprayer on top of the R2R apparatus dispenses the nano-ink to fill in the stamp. Two other rollers with adhesive films completely remove the residual layer on the stamp. Final products remain on the substrate after de-stamping in which the web rolls up and the substrate moves to the further right. This R2R direct stamping apparatus demonstrates high throughput and material efficiency for fabrication of flexible micro- and nano-electronic devices. Fabricated inter-digitated capacitor sensor shows around 3 pF in capacitance and works well to detect capacitance change during bending and finger-touching.

In chapter 5, strain sensors, touch pads and radio-frequency identification (RFID) tags which are fabricated by the direct stamping method are demonstrated.

Applicability of this direct stamping technique has been confirmed by fabrication of highly sensitive and cost-effective strain sensors on stretchable or flexible substrates like PDMS and GFR-hybrimer. The directly stamped strain sensor has properly responded to strain under both tensile and bending stresses. Highly sensitive and mechanically flexible touch pads are also tried by the direct stamping on a paper substrate. Sensitivity of the pads does not change significantly even with 8-mm bending radius and after 10,000 cycles of bending stroke tests. Flexible and stretchable LC (inductor-capacitor)-resonator-based chipless RFID tags have been also fabricated by
the direct stamping with Ag nano ink. By the stretchable RFID strain sensors, wireless strain sensing is demonstrated with a gauge factor of 0.51. Multiple encoded identifications with combination of double tags and stretching behavior of fabricated tags are also demonstrated. This stretchable RFID sensor is promising for biomedical applications such as real-time monitoring of motion detection.

In conclusion, the newly developed UV-curable adhesive assisted direct stamping of Ag nano-ink is a facile fabrication method of flexible or stretchable electronic devices. High throughput R2R manufacturing system is also adaptable to the direct stamping method. Thus, applicability of the direct stamping method is promising for high throughput fabrication of flexible or stretchable electronic devices.

6.2. Future works

For improvement of the direct stamping methods, there are some recommendations to do in the future.

For better filling of Ag nano-ink, doctor-blading or spraying has been used in this research. As a result, much portion of AgNPs is removed from the residual layers. Smarter ways to use only small amount of AgNPs should be considered for the direct stamping process. Also, in this study, only UV-curable polyurethane (PU) prepolymer is used as a UV-curable adhesive to enhance conformal contact between AgNPs and the substrate. Cured PU becomes a little brittle polymer layer so that there seems to be restriction for stretching applications (we demonstrate it about 7% of tensile strain). If stretchable material is used instead of the current PU in the study, then, even better
stretchability can be expected by the direct stamping. Adhesion between contacting components is important for clear transfer of AgNPs onto the substrate. So, it would be good to investigate the adhesion systemically by adjusting the hydrophobic property of PU using chemical modification and thus, the adhesion.

And surfactants surrounding silver nanoparticles have not been taken into account in this study. For later research, effect of surfactants on adhesion is also recommended to be considered. And the internal or cross-sectional structure difference in the layer of silver nanoparticles before and after direct stamping could be much beneficial for more detailed investigation of densification by the direct stamping method. Simulation has been done with one and three trenches. For more reality, more trenches are suggested to be considered for simulation. For example, in three trenches, the middle trench has less normal stress in the x-direction than other two trenches at both ends do. Simulation results from more trenches are proposed to provide better insight for the reason.

For demonstration of the R2R direct stamping apparatus, we used plastics for initial demonstration. The frames and other parts of the prototype have been three dimensionally printed with curable plastics. Thus, intrinsically, they are deformed much. And some parts such as chains are under high tension during operation of the apparatus thus they are not durable. Thus, frames and some parts, which are deformed under tension, are recommended to be replaced with more rigid materials such as stainless steel for actual manufacturing applications. And adhesive power of the adhesive rollers decreases after several uses in the current prototype. As a result, adhesiveness becomes not enough to remove residual layers later than few tens stamping. Therefore,
methods to use adhesive rollers repeatedly without losing adhesiveness should be investigated for high throughput manufacturing.
References


Contributions during Doctoral Study at Simon Fraser University

Referred Journal Articles (Key Publication Highlighted)


Referred Conference Proceedings


### Presentations


### Patents

1. W.S. Kim* and **J. Kim**, “Direct Stamping of Silver Nanoparticle Inks for Thick Electrode” US Provisional No. 61/672,156