論 文 の 内 容 の 要 旨

論文題目　Novel Pattern Transfer Technique on Elastomeric Polymer Using Surface Modification by Self-Assembled Monolayer and Its Application
（自己組織化単分子膜を用いた表面特性の制御による微細金属パターンのフレキシブルポリマーへ転写技術の開発と応用）

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The purpose of this thesis is to establish direct transfer ways of metal micro-patterns, which are embedded in elastomeric polymers. In addition, micro-patterns of electronic components, such as metal electrodes, thin metal film of resistive, and PZT films, are applied as flat metal-embedded stamps for microcontact printing, micro-heaters with flexible substrate, and energy harvester, respectively.

Transfer of thin, micro metal patterns to polymeric substrates has not been fully established yet, although this method has several advantages compared to direct metal patterning on polymeric substrates. Micro-patterns of metal thin films can be released from the solid-substrate (or donor substrate) to polymer one by (1) etching a sacrificial layer between metal and base solid-substrate or (2) surface modification by self-assembled monolayers (SAM). Wet-etching the sacrificial layer (SiO_2, Au or Cr) may cause the chemical contamination of polymer substrates. On the other hand, if the surface properties of solid-substrates and metals are modified, polymers with metal patterns can be easily released (i.e. transferred) from the solid-substrate without any chemical contamination. However, it is difficult to control precisely the surface properties of substrates and metals, so that small metal patterns (e.g. line width < 10 μm) are difficult to transfer to the polymer substrate.

In this research, a dry peel-off process is developed to transfer the micro-patterns of metal thin films that involves modifying the surface properties of a donor substrate and metal patterns through SAMs treatment and peeling off the polymer with embedded metal layers. The surface properties of donor substrates and metals are precisely controlled with different SAMs, treatment methods, concentration and treatment time.

To achieve the successful transfer of metal micro-patterns to polymers, several different surface modifications with SAMs are carried out. Among selected SAM molecules, 3-mercaptopropyl-trimethoxysilane (MPTMS) plays the most important role. MPTMS has thiol and methoxy groups that can bind to metals and polymers, respectively. Thus, MPTMS can be used as a molecular adhesive (i.e. a linker molecule) between metals and polymers. The degree of bonding with respect to the concentration of SAMs, treatment time, and methods of deposition is investigated by a simple adhesion test. The results indicate that liquid deposition of MPTMS provides the strongest adhesion between Au and PDMS among the different deposition methods and the different linker molecules. The strong adhesion between metals and polymers enabled by liquid deposition of MPTMS facilitate the successful transfer as well as robust devices without exfoliation of metal films from the polymers.

On the other hand, the moderate adhesion is necessary in the interface between metals and donor substrates. Metal patterns should not be exfoliated from the donor substrate during the wet process (e.g. photolithography or wet metal etching), but should be released from the donor substrate during the transfer process. Therefore, the surface properties in the interface between the metals and the donor substrate should be precisely controlled. In this research, a vapor of MPTMS was treated on a Si substrate, and the adhesion between the metals and the substrate was precisely controlled with varying the treatment time. As the final step, the interface between the donor substrate and the polymers was treated with octadecyl-trichlorosilane (OTS) or perfluoro-decyltrichlorosilane (FDTS) as anti-adhesives to reduce the surface energy of the donor substrate.

The dry peel-off process, the method proposed in this thesis, includes only conventional photolithography, metal deposition and SAM treatment on the surfaces for the transfer the metal patterns to polymers over the full-wafers. Moreover, this method is simple with relatively short process time. As a result, Au patterns with 2 m width (both dots and holes shape) are successfully transferred to polymers, such as PDMS and polyimide.

As an application, PDMS embedding metal micro-patterns is used as a flat stamp for microcontact printing. Embedded metal patterns on a flat PDMS stamp act as a molecular transport barrier of SAM ink during the microcontact printing. The flat stamp avoids the mechanical deformation (e.g. lateral collapse and roof collapse) of the stamp tip, which is a crucial problem when printing the stamp onto a substrate.

As another application of the dry peel-off process, micro-heaters embedded in PDMS sheet are fabricated by a simpler and easier way compared to a conventional method (e.g. patterning a conducting composite of PDMS using a razor blade). Micro-heaters on a glass substrate are also fabricated for comparison with those embedded in PDMS. We cannot observe any degradation of the micro-heaters by thermal stresses that confirmed by repeatability (10 thermal cycle with a range of 25–89°C) and stability test (20 min at 90°C). The temperature of micro-heaters is simulated by finite element method (FEM), and the results are in good agreement with the experimental ones.

Finally, an energy harvester is fabricated by transfer of Au thin film electrodes with piezoelectric materials (e.g. lead zirconate titanate, PZT) to elastomeric polymers. PZT should be thermal treated above 600°C to form a perovskite structure which is crucial to piezoelectric properties. In this research, PZT with the perovskite structure is formed on a Si substrate, then it is transferred to polymers finally to avoid depolymerization of polymer by high temperature during thermal treatment of PZT.

In summary, the novel transfer technique of metal micro-patterns onto elastomeric polymers, a dry peel-off process, was established. Also, flat PDMS stamp for microcontact printing and micro-heaters embedded in PDMS were demonstrated as applications of the dry peel-off process for future flexible electronics. It is expected that micro-patterns with various materials can be transferred to various kinds of polymers using this dry peel-off process. Thus, it can be applied for various flexible devices, such as physical or chemical sensors, flexible micro-fluidic channels with micro-heaters, and so on. Moreover, the methods that control the surface properties of Si and metals using SAMs can be applied to not only the transfer technique, but also expected to solve the problems in conventional fabrication process for semiconductors or MEMS devices, such as exfoliation of thin films on any substrates.