Sub-100nm and a Large Area Patterning Process by using Hybrid Nanocontact Printing (HnCP)

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ABSTRACT

The hybrid nanocontact printing(HnCP) process is a technology for manufacturing an ultra violet(UV) imprinted silicon substrate from a master and then printing by letting it get in contact with a substrate coated with a metal thin film. In the HnCP process, a master with a pattern as already designed is prepared, and the resist is applied to the silicon substrate as manufactured through the UV nanoimprint lithography(NIL) process. Let the master, where the pattern is formed, get in contact with the resist surface, pressurize it at a given pressure and expose it to UV lights. After separating a master from the imprinted silicon substrate, cure the surface of the silicon substrate to which the resist has been applied at the room temperature or a high temperature. Then, the imprinted silicon substrate stamp gets to be completely manufactured. In order to print a pattern on the substrate as coated with a metal thin film such as Au and Pd, in the first place, ink the self-assembled monolayer on the surface of the imprinted silicon substrate stamp. After transferring the print pattern by letting the imprinted silicon substrate stamp get in contact with the metal thin film of the substrate on which the pattern is to be printed, take off the imprinted silicon substrate stamp. Then, the pattern is formed by the self-assemble monolayer on the surface of the metal thin film with which the substrate has been coated. In the substrate coated with the metal thin film to which the print pattern has been transferred, the self-assembled monolayer serves as a mask. Therefore, it is possible to etch a selected part, and obtain a substrate on which a metal thin film with a desired pattern is formed.

Keywords: Nanocontact printing, UV Nano Imprint lithography(UV-NIL), Hybrid Nanocontact printing(HnCP), SAM

1 INTRODUCTION

Ultraviolet-nanoimprint lithography (UV-NIL) is a promising nanoimprint method for cost-effectively defining nanometer scale structures at room temperature and low pressure[1]. This presents a new UV-NIL process for high throughput in which an element wise patterned stamp(EPS) and additional pressurization are employed to imprint a large-area wafer in a single step[2]. Soft lithography is the collective name for a set of lithographic techniques that has been developed as an alternative to photolithography and a replication technology for micro- and nanofabrication. Microcontact printing is a technical process for fabrication the same pattern as a master by manufacturing a PDMS (poly(dimethylsiloxane)) stamp, staining a pattern with functional ink, transferring it onto the substrate and transferring an etching process or vapor deposition process[3]. Nano stamp fabrication technology is a key technology for UV-NIL because fabricating a high resolution nano-stamp is the first step for defining high resolution nanostructures in a substrate[4][5].

In case the microcontact printing method is used, it is possible to embody a micropattern of upto 300nm, but its resolution is poor and there are many defects in it. And, it is almost impossible to embody a micropattern of 100nm or less. Further, in case it is manufactured in the multilayer form, there is also a problem that any mismatching is liable to take place in alignment due to any deformation of the pattern and any torsion of the structure in the lamination process[6]. In case the HnCP method, on which this study is conducted, is used, it enables the stamp manufacturing process to be shortened and optimized, because the nanoocontact printing process is conducted by using an imprinted silicon substrate stamp. Also, as a hard stamp is used, any error resulting from an ultra micro torsion and mismatching can be prevented in the multi-layering process, and since any deformation or defect is not brought about, the pattern’s resolution can be enhanced so that it is possible to embody a pattern of sub-100nm, and further it enables alignment for lamination to be more easily made in effect.

Inking and printing were conducted by using imprinted silicon substrate stamp and the self-assembled monolayer (SAM) solution. The imprinted silicon substrate stamp was pressed on the substrate surface of the wafer coated with Au and Pd by controlling time and a pressing force. Self-assembled alkanethiols made a compact and orderly mono-layer on the metal (Au and Pd), and it could be known that such self-assembled film was different in the size, depending upon a degree of staining the stamp with ink, adhesion, chemical reactivity, electric conductivity and a quantity of the substance migrating to the metal[7][8]. Also, we are seeking for its applicability to a biological electronic device, inorganic electronic device, a flexible electronic display and the like by optimizing the HnCP process, and having mono-dispersion metal particles and silica polymer particles selectively adhering and growing to the inside of a 2-dimensional pattern.

2 PROCESS OF HNCP

The HnCP process is a technology for manufacturing an UV imprinted silicon substrate from a master and then printing by letting it get in contact with a substrate coated with a metal thin film. Figure 1 shows concept of the HnCP process. In the HnCP process, a master with a pattern as already designed is prepared, and the resist is applied to the silicon substrate as manufactured through the UV-NIL process. Let the master, where the pattern is formed, get in contact with the resist surface, pressurize it at a given pressure and expose it to UV lights. After separating a master from the imprinted silicon substrate, cure the surface of the silicon substrate to which the resist has been applied at the room temperature or a high temperature. Then, the imprinted silicon substrate stamp gets to be completely manufactured. In order to print a pattern on the substrate as coated with a metal thin film such as Au and Pd, in the first place, ink the self-assembled monolayer on the surface of the imprinted silicon substrate stamp. After transferring the print pattern by letting the imprinted silicon substrate stamp get in contact with the metal thin film of the substrate on which the pattern is to be printed, take off the imprinted silicon substrate stamp. Then, the pattern is formed by the self-assemble monolayer on the surface of the metal thin film with which the substrate has been coated. In the substrate coated with the metal thin film to which the print pattern has been transferred, the self-assembled monolayer serves as a mask. Therefore, it is possible to etch a selected part, and obtain a substrate on which a metal thin film with a desired pattern is formed.

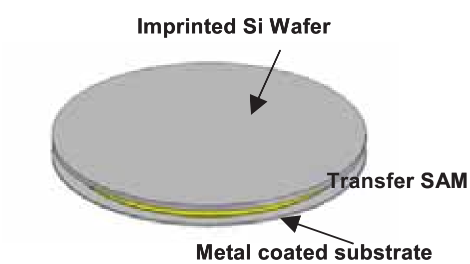


Figure 1: Concept of HnCP process

The nanostamp used in fabrication process of nano-pattern could be categorized into a PDMS stamp and an imprinted silicon substrate stamp, according to a pattern size and a fabrication method. Figure 2 shows fabrication process of nanopattern. The general process of microcontact printing, on which a microsize of pattern could be fabricated, was fabricated by using PDMS stamp[9]. The process of HnCP for the high fidelity pattern form of a nanosize is very different that of the microcontact printing, and it was fabricated by using the imprinted silicon substrate stamp.

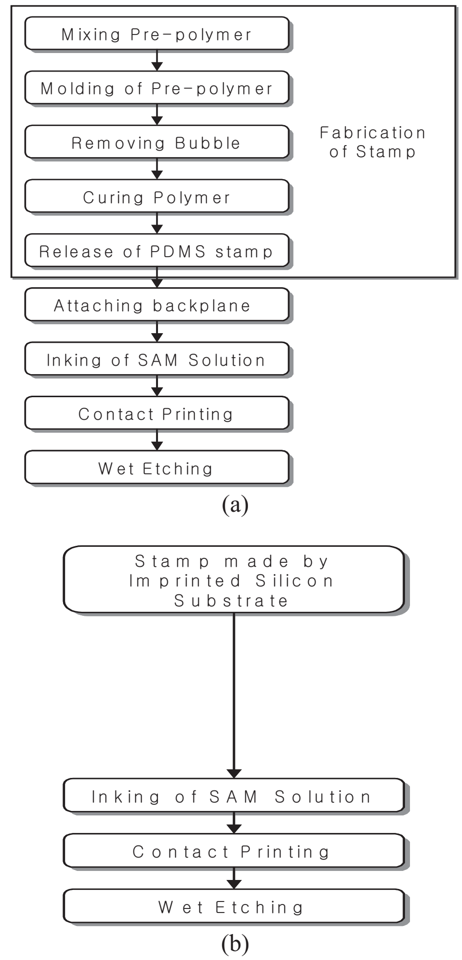


Figure 2: Process sequence diagram for the fabrication of nanopattern: (a) general process of microcontact printing and (b) new process of HnCP: (i) fabrication of imprinted silicon substrate master(don't etching), (ii) inking of SAM solution on imprinted silicon substrate stamp, (iii) contact printing of Au coated substrate, (iv) forming a SAM, (v) selective wet etching, and (vi) fabrication of nanopatterns

The pattern was transferred to a silicon substrate coated with Au(adhesion layer Cr) and Pd(adhesion layer Ti) in the form of a thin film by controlling a printing time and a force to press the stamp wet with the SAM solution. The SAM solution used in HnCP was manufactured by mixing ethanol (ethyl alcohol) with alkanethiols such as dodecanethiols(DDT), octadecanethiols(ODT), and hexadecanethiols(HDT) in consideration of inhibition of diffusion, implementation of a high-resolution pattern and excellent surface adhesive force to Au and Pd substrate. The printed pattern was embodied through the etching process so that it might be the same as the master's pattern, and nanostructures had a high resolution without any defect could be fabricated. The substrate surfaces of Au and Pd were cleaned by using a chemical method to put them in the piranha solution. A chemical etching was conducted for the post-process, and the printed pattern was measured and analyzed.

3 EXPERIMENTS AND RESULTS

In the HnCP process for embodying high resolution, such parameters as the fabrication of the stamp, the inking method, printing tools, an etching time are very important factors[10][11]. The imprinted silicon substrate stamp for embodying a pattern form of a nano-size, a master designed and manufactured with quartz. Figure 3 is the imprinted silicon substrate stamp on 9 pattern zones as fabricated by UV-NIL process. The imprinted silicon substrate stamp has a pattern size ranging from 30nm to 100nm, and its printing zone is a large area of 4 inch. The imprinted silicon substrate stamp with a high resolution corresponds exactly to the master pattern, and could be replicated a pattern up to the size of sub-100nm.

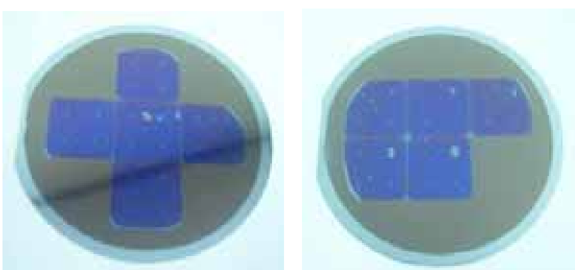
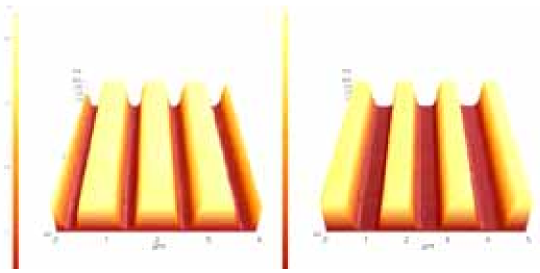


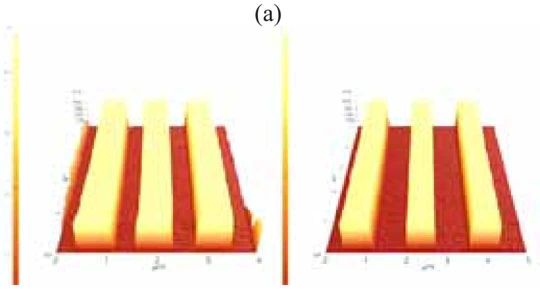
Figure 3: Photo image of UV nano imprinted silicon substrates stamp with various line patterns (the line widths range from 30nm to 100nm)

The surface characteristic and the thermo-chemical changing characteristic of the large area stamp as fabricated were measured and analyzed in the experiment process, and the characteristic of the SAM solution to the metal thin film substrate was measured and analyzed by conducting the large area printing experiment. The contact angle were measured and analyzed in the tests. It could be known that to the chain length of alkanethiol solutions were getting increased. The contact angles were increased into 102.2°(92.8°), 106.6°(93.4°), and 111.5°(95.4°) and adhesion force and friction force were decreased due to characteristic of hydrophobic surface.

Figure 4 shows the results of an accuracy of replication of the imprinted silicon substrate stamp, and analyzing them by using atomic force microscope(AFM). The imprinted silicon substrate stamp has a replicated pattern exactly corresponding to the master pattern and has a high accuracy of filling and releasing. Also, in the surface characteristic, as a result of measuring the wettability, it could be known that the imprinted silicon substrate stamp has the surface characteristic of the hydrophobic and surface energy of 102°. The adhesion force and the friction force were 12nN so that they were very low.



(a)

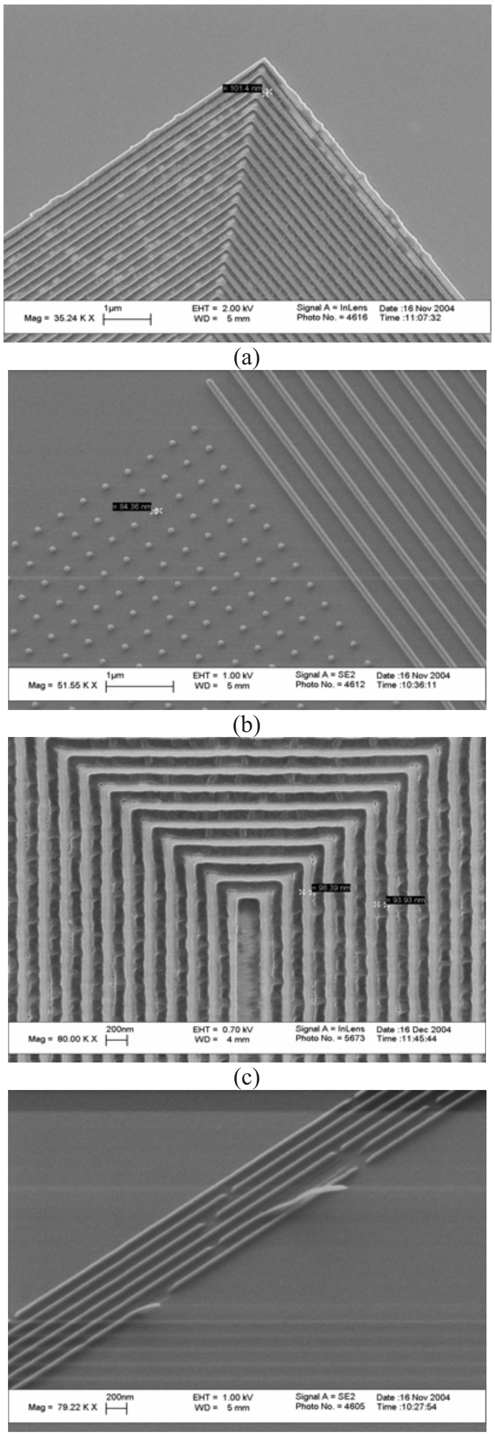


(b)

Figure 4: AFM image of fidelity comparison of the fabricated line patterns between (a) PDMS stamp and (b) imprinted silicon substrate stamp.

Since the imprinted silicon substrate stamp could maintain a higher precision of parallelism than the PDMS stamp, it could have a uniform pattern. And, as a hard stamp could be used, a pattern resolution could be enhanced. It was possible to fabrication a 100nm pattern without defect.

Figure 5 is a SEM image of nanopattern with variable line widths and the imprinted silicon substrate stamp of the pattern is 100nm, and 30nm, pattern space is 100 nm, and pattern depth is 200nm. As a result of comparing them, it could be known that the imprinted silicon substrate stamp was fabricated high filling resolution. In the HnCP experiment, a silicon substrate on which the Cr adhesion layer of 100Å and the Au etching layer of 500Å were deposited by using the DC sputter and a silicon substrate on which the Ti adhesion layer of 100Å and the Pd etching layer of 500Å were deposited in the form of a thin film, were manufactured, and a pattern was transferred to the substrates where to print by the imprinted silicon substrate stamp wet with the SAM solution. The pattern was etched with TFA/GE-8148 and TFP etching solution and nanostructures were fabricated.



(a) (b) (c) (d)

Figure 5: SEM Image of nanopatterns with feature of (a) 100nm V type lines, (b) dots and lines of 100nm, (c) 100nm U type lines, and (d) 30nm lines.

4 CONCLUSIONS

As a result of conducting HnCP, the defect-free imprinted silicon substrate stamp of sub-100nm and nanostructures could be manufactured respectively from a quartz master, and it could be ascertained that when the pattern was transferred to substrate on Au and Pd by the SAM solution, ink diffusion caused little change in the pattern size and the space between patterns. In the HnCP the following factors determined a success in the pattern transfer: fabrication of the imprinted silicon substrate stamp with a high resolution and conformal contact between the imprinted silicon substrate stamp and the surface of the silicon wafer coated with a metal thin film. It is thought that if studies are conducted on stamp materials and new processes for embodying a pattern of sub-100nm in the HnCP, it will be possible to fabrication a nanopattern with a high resolution.

It is thought that if this technology is well established, the HnCP process in place of the conventional photo lithography process can make an important contribution toward the semiconductor process, and the patterning process for the inorganic electronic and biological devices, and particularly, it will be very available for fabrication relatively simple structures of a single-layer which can be used for a sensor in NEMS and the applied optics field or a device of a nano analyzing system.

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REFERENCES

[1] Younan Xia et al, Chem. Rev. 99, pp. 1823-1848, 1999.

[2] Eung-Sug Lee et al, *Proc. of 1st Int. Sym. for Nanoscale Mechatronics & Manufacturing*, pp9~25, 2004.

[3] B. Michel et al, IBM J. Res. & Dev. Vol. 45, No. 5, pp.679-719, 2001.

[4] Jeongdai Jo et al, *Proc. of Int. Conf. OnAPCOT MNNT2004,* pp. 1018-1022, 2004.

[5] Jeongdai Jo, Jun-Ho Jeong, Kwang-Young Kim, and Eung-Sug Lee, Patents No. 2004-0005548, 2004.

[6] A. Bietsch, et al, J. Applied Physics, Vol. 88, No. 7, 2000.

[7] A. Biebuyck et al, IBM J. Res. & Dev., Vol. 41, No.1-2, pp.159-170, 1996.

[8] Hong-Wei Li, et al, Lamgmuir, LA0269098, 2002.

[9] Primin Hidber, et al, US Patent No. 6060121, 2000.

[10] Jeongdai Jo, et al, *Proc. of KSPE Conf.*, pp. 28-31, 2003.

[11] Jeongdai Jo, et al, *Proc. of 2nd Int. Conf. On NNT2003*, pp. 108-109, 2003.