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Application of Soft Lithography for Nano Functional Devices

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1. Introduction

Since photolithography method that is for producing minuteness electronic devices was developed, attempts against the new methods are progressing constantly as increasing demands for the electronic devices. Currently, because of the resolution required for the integrated element is decreased to below 100 nm, the lithography method using ultraviolet rays is developed as various methods like EUV(Extreme UV), X-ray, E-beam lithography. However, the methods mentioned previously are basically non-environmental friendly, and the development of photoresist that reacted on the source should be preceded. Also, it has limitations such as substrate and material selections, low throughput and high cost of methods.

To overcome these limitations and guarantee the high throughput, the soft lithography method is a new counter plan, so a lot of researches are executed. This indicates the producing technique that making patterns with mechanical method by using the master of polydimethylsiloxane (PDMS) stamp, so it has advantages to micro and nano structure patterning on the substrate that is not uniform than photolithography producing technique. Specially, it is useful to produce of optics, mechanics and heat fluid structure of MEMS/NEMS. The detail methods related to nano imprint lithography (NIL) and nano moldings, and each of them are effected on the producing structure that size of between 25 ~ 100 nm, 10 ~ 100 nm, respectively.

NIL is the technique that can effectively produce nano pattern that line width below 100 nm, the limitation of UV lithography, and nano contact printing method produces and uses the stamp with polymer such as PDMS by using patterned master by electron beam, and after transfer to the self-assembled monolayer (SAM) substrate that created by contacting of the stamp that has ink by arranging ink element on the stamp and substrate, use them in the wet etch mask to produce the structure.

So, we fabricated gas chamber that is for collecting gas diffused on the skin, optical waveguide, and pixel definition for polymer light-emitting diode (PLED) by using above mentioned methods and evaluated the possibilities.

Soft Lithography mentioned above can overcome the resolution limitation that photolithography method has, and the method is simple and it has advantages on cost saving. Also, like lens and optical fiber, it is available on the method in large area like non planar surface, so it can be applied to the not only cell biology industry but microelectronics, optics and display areas.

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2. Trend of research and development

In late 1960's and early 1970's, Gorden Moore, a founder of Fairchild Semiconductor and Intel, argued that the circuit integration of semiconductor is estimated to double its degree every eighteen months (Younan Xia & G.M. Whitesides, 1998). His prediction later becomes Moore's law (R.W. Keyes et al., 1992). Dr. Hwang in Korea published a "new memory growth theory" in 2002 asserting a Hwang's law, which argues that degree of integration of semiconductor doubles every twelve months. Samsung company demonstrated the doubling growth of integration degree that continued over a period of seven years, beginning from 256-mega in 1999 to 32-giga in 2006. Such accomplishment was possible thanks to the continuous advancement in photolithography technology that doubled its resolution every three years over the past thirty years, as many trends in semiconductor industry followed those laws. (Figure 1)

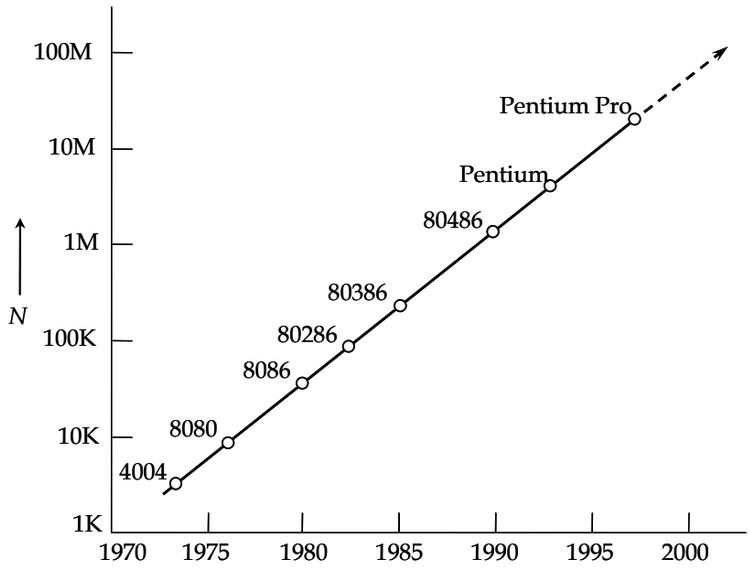

Fig. 1. The integration trend given by Moore's law, and how microprocessors manufactured by Intel have followed this law since 1973. N is number of transistors per chip. (C.R. Barret, 1993; R.F. Service, 1996).

This curve reflects the general trend of scaling technology that was made possible due to micro lithography which can also be applied to RAM, DRAM, micro processor, etc. Assuming that development of new short wavelength light source and photosensitive film continues following this trend, creating semiconductor with a so-called minimum line width of 100 nm can become possible.

However, creating chips that are small than 100 nm are extremely limited due to light diffraction, problems in creating light masks, lens resolution, etc. In fine processing technology, reducing the line width under 100 nm necessarily requires new approach.

The current photolithography technologies include EUV, soft X-ray lithography, e-beam writing, focused ion beam writing, proximal-probe lithography, etc (W. M. Moreau, 1998; R.F.W. Pease, 1992).

Even though these technologies can realize a very small chips, originalities are critical matters when is required when actually applying it to mass-producing technology that require mass production at low cost.

The photo lithography field for creating chips smaller than 100 nm is facing new technological challenge, and there is no guarantee that photolithography technology is the optimal technology. For example, in chemistry, biology, and materials science, reducing the size of an object requires high cost both in capital and operational manner. Moreover, patterning the non-uniform surface requires difficult technology and using in case of glass, plastic, ceramic, carbon-based materials that have great potential for next-generation technology is very limited.

Currently, a development of practical technologies that can produce structures smaller than100 nm is one of the most critical matters and the most challenging issues in micro-integration technology field. As a result, a variety of non-photolithography technologies are being introduced in creating high-quality micro structure and nanostructure chip, as is shown in Table 1.

Method	Resolution
Injection molding	10 nm
Embossing (imprinting)	25 nm
Cast molding	50 nm
Laser ablation	70 nm
Micromachining with a sharp stylus	100 nm
Laser-induced deposition	1 um
Electrochemical micromachining	1 um
Silver halide photography	5 um
Pad printing	20 um
Screen printing	20 um
Ink-jet printing	50 um
Electrophotography	50 um
Stereolithography	100 um
Soft Lithography	
Microcontact printing	35 nm
Replica molding	30 nm
Microtransfer molding	1 um
Micromolding in capillaries	1 um
Solvent-assisted micromolding	60 nm

Table 1. Non-photolithographic methods for micro- and nanofabrication (Younan Xia & G.M. Whitesides, 1998).

This chapter focuses on soft lithography technologies that are currently under research, such as microcontact printing (A. Kumar & G.M. Whitesides,1993), replica molding (Y. Xia et al, 1996), embossing, elastomeric stamp (X.-M. Zhao et al., 1996), mold, and micromolding in capillaries (MIMIC) (E. Kim et al., 1995). The name of soft lithography originates from the following facts. First, different from the photolithography, elastomeric stamp and mold play an important role as a board in transferring patterns. Second, it uses flexible organic device instead of rigid minerals.

Such soft lithography creates SAM thin film type fine patterns using contact printing or builds fine structure using embossing (imprinting) or replica molding. Figure 2 describes soft lithography in a technological general procedure that we call as “rapid prototyping. (Younan Xia & G.M. Whitesides, 1998)” The biggest strength of soft lithograph is that

cloning process is possible through creating master or mold without complicated process such as photolithography. Other advantages of the technology include relatively low investment cost and simple procedure which does not require special environment such as the clean room. Hence the research can be generally conducted in a normal lab and it is not affected by the diffraction of light or transparency. With these merits, the soft lithography is receiving increasing amount of attention as an alternative to the photolithography technology in creating structures smaller than 100 nm. Moreover, it opens door to a new approach to creating those that are hard to be created using the photolithography technology, such as a surface, optical structure, sensor, etc.
Therefore, this chapter explains the fundamental theory of soft lithography and patterning technology and presents the application research results.

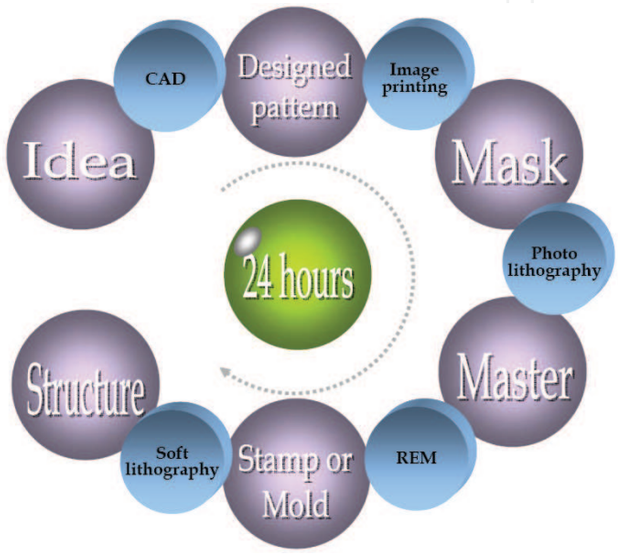

Fig. 2. The rapid prototyping procedure for soft lithography.

3. Method of soft lithography

3.1 Self-Assembly

Photolithography has been regarded as an extremely new approach in micro-integration technology as a technical challenge for 100 nm and lower resolutions. Through amazingly extensive contributions to the practical and conceptual aspects in chemistry and biology, it provided a new methodology in micro-integration area and many means for achieving smaller size and lower cost with conceptually new strategies. A representative example is self-assembly which has been most perfectly studied and actually implemented.
In a self-assembly, molecules or objects form continuous structures in stable form which are very well defined by non-covalent forces (J.-M. Lehn, 1990).
One of the key concepts of self-assembly is that the final structure is almost thermodynamically stable and often has a better system than non-self-assembly structure.
Studies on the technology of self-assembly have steadily developed and it has been applied to the integration of structures of two and three dimensions that include various levels from molecules to middle structures and large structures (J.-M. Lehn, 1988; C.A. Mirkin et al., 1996; A.S. Dimitov & K. Nagayama, 1996; A. Terfort et al., 1997).

3.2 Self-Assembly monolayers

SAM has been studied in most extensive areas and many developments have been achieved in the self-assembly systems of non-biological areas (C.D. Bain & G.M. Whitesides, 1989; J. Xu et al., 1995). It refers to the self-organization in a continuous form of functionalized organic molecules with chemical adsorption and long chains on the surface of an appropriate substrate. It is realized by soaking the substrate in a solution that contains ligands or exposing the substrate to a gas that contains reactive species. Table 2 lists various mechanisms known as SAM, and many studies are being conducted in new areas in addition to them (Younan Xia & G.M. Whitesides, 1998; P. Fenter et al., 1994).

Substrate	Ligand or Precusor	Binding
Au	RSH, ArSH (thiols)	RS-Au
	RSSR' (disulfides)	RS-Au
	RSR' (sulfides)	RS-Au
	RSO_2H	RSO_2-Au
	R_3P	R_3P-Au
Ag	RSH, ArSH	RS-Ag
Cu	RSH, ArSH	RS-Cu
Pd	RSH, ArSH	RS-Pd
Pt	RNC	RNC-Pt
GaAs	RSH	RS-GaAs
InP	RSH	RS-InP
SiO_2, glass	$RsiCl_3$, $Rsi(OR')_3$	Siloxane
Si/Si-H	$(RCOO)_2$ (neat)	R-Si
	$RCH=CH_2$	RCH_2CH_2Si
Si/Si-Cl	Rli. RMgX	R-Si
Metal oxides	RCOOH	RCOO-…Mon
	RCONHOH	RCONHOH…Mon
ZrO_2	RPO_3H_2	$RPO_3^{2-}…Zr^{IV}$
In_2O_3/SnO_2 (ITO)	RPO_3H_2	RPO_3^{2-}-…M^{n+}

Table 2. Substrates and ligands that form SAMs.

One example that best represents the characteristics of SAM is the reaction of Au and alkanethiolates $CH_3(CH_2)nS\ddot{y}$ (Figure 3) (P. Fenter et al., 1994). From liquid state, alkanethiols react with gold surface in continuous chemical adsorption and alkanethiolates are adsorbed as a result. Although there is no established theory related to the fracture of hydrogen atoms, it is assumed that this process occurs together with the loss process of dihydrogen. Sulfur atoms combine with gold by bringing alkali atoms near them to the gold surface. This approach of atoms is characterized by stabilized structural entropy and attainment of orderly structure.

In the case of about 20 carbon combinations, the degree of interaction of molecules in SAM increases in accordance with the molecular density on surface and the length of alkali backbone. Only alkanethiolates with n>11 form a close, solid structure, and two-

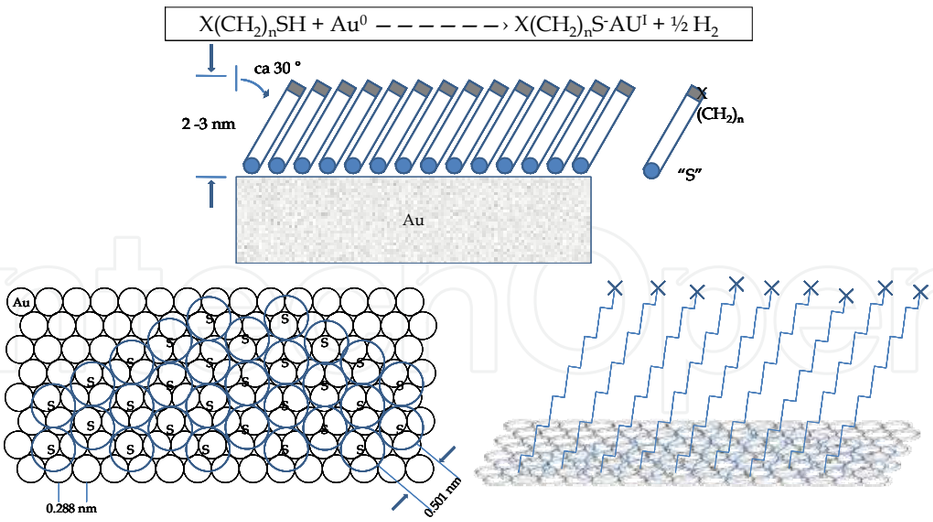

Fig. 3. Representation of a highly ordered monolayer of alkanethiolate formed on a gold surface. The sulfur atoms form a commensurate overlayer on Au(111) with a (√3×√3)R30 degree structure, whose thickness is determined by the number of methylene groups (n) in the alkyl chain. The surface properties of the monolayer can be easily modified by changing the head group X. The alkyl chains $(CH_2)_n$ extend from the surface in a nearly alltrans configuration. On average they are tilted approximately 30 degrees from the normal to the surface to maximize the van der Waals interactions between adjacent methylene groups.

dimensional organic quasi-crystals necessarily sustain the form supported by gold, which is the most useful case of the application of soft lithography in SAM (E. Delamarche et al., 1996).

The orderly structure formed on gold starting from alkanethiols exhibit relatively fast progressing speed. In this way, the structure in which hexadecanethiolates are very orderly aligned on gold can be fabricated by soaking a gold substrate in ethanol solution containing hexadecanethiol for a few minutes. It is formed for a few seconds during mCP. The ability to form an orderly structure in a short period of time is one of the factors that mCP can be implemented as a successful process.

As can be seen from the before mentioned alignment of alkanethiolates on a gold substrate, the structure and characteristics of SAMs have been experimented using various techniques (Table 3). (G.E. Polner, 1997; C.A. Alves et al. 1992; M.R. Anderson et al., 1996; N. Camillone et al., 1996; W.B. Caldwell et al., 1995; L. Strong & G.M. Whitesides, 1988; M.A. Bryant & J.E. Pemberton, 1991; Q.Du et al., 1994; J.P. Folkers et al., 1992; L.H. Dubois et al., 1990; Y. Li et al., 1992; C.D. Brain & G.M. Whitesides, 1988; C.D. Brain et al., 1989; T.W. Schneider & D.A. Buttry, 1993; M.D. Ward & D.A. Buttry, 1990; S. Li & R.M. Crooks, 1993; X.-M. Zhao et al., 1996)

In general, sulfur atoms have been known to form R30 degree overlayer on the Au(111) surface (Figure 3), and recent STM studies revealed that these systems consist of heterogeneous, complex structures. Alkyl chain forms a superlattice on single film surface which is different from the symmetrical hexagonal lattice formed by sulfur atoms at the bottom. This result indicates that the top part of SAM is not affected by sulfur atoms which are directly attached to the gold surface and strongly depends on the intra-molecular interactions between alkyl backbones.

Alkanethiolates SAM on gold explains the reasons that self-assembly system is an excellent technology: easy fabrication, low defects for wide applications, stable characteristics in laboratory environment, technical applicability, and the possibility of variation of characteristics by the adjustment of the system interface characteristics (physical, chemical, electrochemical, biological).

Consequently, SAM provides excellent models for studies in various areas such as wet, adhesive, lubricating, and erosive, nuclear-structural methods, usage of protein absorption, and cell attachment method. Furthermore, it is also an appropriate technique and basis for horizontal unit pattern in the range from nanometer to micrometer, as well as structural and integrated devices.

Patterning SAMs in the plane of the surface has been achieved by a wide variety of techniques (Table 4) (J.L. Wilbur et al., 1994; Y. Xia et al., 1996; T.P. Moffat & H. Yang, 1995; Y. Xia et al., 1995; P.M. St. John & H.G. Craighead, 1996; J. Huang & J.C. Hemminger, 1993; J. Huang et al., 1994; K.C. Chan et al., 1995; E.W. Wollman et al., 1993; A.C. Pease et al., 1994; W.J. Dressick & J.M. Calvert, 1993; J.A.M. Sondag-Huethorst et al., 1994; M. Lercel et al., 1993; M.J. Lercel et al., 1996; G. Gillen et al., 1994; K.K. Berggren et al., 1995; K.S. Johnson et al., 1996; C.B. Ross et al., 1993; N.L. Abbott et al., 1992; A. Kumar et al., 1992). Each technique has advantages and disadvantages. Only micro-contact printing will be discussed in this review since it is the one that seems to offer the most interesting combination of convenience and new capability.

3.3 Contact printing, replica molding and embossing

Contact printing is the most efficient pattern transfer method. The biggest benefits of this printing are simplicity and convenience (A. Voet, 1952). Once a stamp is available, it is possible to produce repeated patterns. Moreover, it minimizes the waste of materials and

Property of SAM	Technique
Structure and order	Scanning probe microscopy
	STM, AFM, LFM
	Infrared spectroscopy
	Low-energy helium diffraction
	X-ray diffraction
	Transmission electron diffraction
	Surface Raman scattering
	Sum frequency spectroscopy
Composition	X-ray photoelectron spectroscopy (XPS)
	Temperature programmed desorption (TPD)
	Mass spectrometry (MS)
Wettability	Contact angle
Thickness	Ellipsometry
Coverage	Quartz crystal microbalance (QCM)
Degree of perfection	SAW device
	Electrochemical methods
Defects	STM and AFM
	Wet etching

Table 3. Techniques for characterizing SAM of alkanethiolates on gold.

Technique	SAM	Resolution
Microcontact printing (uCP)	RSH/Au	35 nm
	RSH/Ag	100 nm
	RSH/Cu	500 nm
	RSH/Pd	500 nm
	RPO_3H_2/Al	500 nm
	Siloxane/SiO_2	500 nm
Photooxidation	RHS/Au	10 um
Photo-cross linking	RHS/Au	10 um
photoactivation	RHS/Au	10 um
	Siloxane/glass	10 um
Photolithography /plating	Siloxane/SiO_2	500 nm
E-beam writing	RHS/Au	75 nm
	RHS/GaAs	25 nm
	Siloxane/SiO_2	5 nm
FIB writing	RSH/Ag	10 um
Neutral metastable atom writing	RSH/Au	70 nm
	Siloxane/SiO_2	70 nm
SPM lithography	RSH/Au	10 nm
Micromachining	RSH/Au	100 nm
Micropen writing	RSH/Au	10 um

Table 4. Techniques that have been used for patterning SAM.

has potential for large-area patterning. Contact printing is optimized for the production of two-dimensional devices and provides the advantage of extending its application to three-dimensional structures through a process that uses metal plates, etc (P.O. Hidber et al., 1996).

Replica molding is to replicate the shape, form, structure and other information of the master, and can accept formative information of materials in a wider range than photolithography. Furthermore, it allows the replication of three-dimensional morphology through only one processing step, which is impossible in photolithography. Replica molding has been used for mass production of objects that have stable surface structures such as diffraction grating (B.L. Ramos & S.J. choquette, 1996), holograms (M. Nakano, 1979), CD [(H.C. Haverkorn et al., 1982), and microtools (D.A. Kiewit, 1973). Replica molding that uses appropriate materials can replicate reliably down to nanometer unit even materials with very complex structures in a simple, cheap method. The excellent replication property of replica molding is determined by Van der waals interaction, wet method, and dynamic factors used for filling the mold. Due to this physical interaction, replica molding enables more accurate replication in the smaller sizes than 100 nm which cannot be done with photolithography because of its limitation by diffraction.

Embossing is another technique for stamping thermoplastic materials and has advantages in terms of price to performance ratio and high yield. For example, the technique for stamping polycarbonate using Ni master is used as a basic technique for CD production, and the technique for stamping SURPHEX photopolymer (Du-Pont) using a master with melted

quartz is used as a basic technique for producing holograms (Sing H. Lee, 1993). In recent years, embossing technique has rapidly developed as it is used in semiconductors, metals, and micro electronic circuits. Chou group demonstrated the possibility of forming 25 nm-class patterns on silicon with embossing technique, and reported on its potential. This potential indicates that patterning techniques can develop through new materials and technical approaches. In particular, merging self-assembly technique with various soft lithography techniques such as elastic stamp, mold, mask, etc. will enable more innovative developments than any others (S.Y. Chou et al., 1995).

These technical fusions can complement the limits of photolithography, and provide new opportunities for micro- and nano-unit structures or integrated devices. We are extending the capability of these patterning techniques by bringing new approaches and new materials into these areas. In particular, a combination of self-assembly (especially of self-assembled monolayers) and pattern transfer using elastomeric stamps, molds, or masks constitutes the basis of soft lithographic methods. It complements photolithography in a number of aspects and provides a wide range of new opportunities for micro- and nanofabrication (X.-M. Zhao et al., 1997)

3.4 Elastomeric stamps and molds

The technique for separating after contacting of elastomeric stamp, mold, and mask with surface is a core technique in soft lithography (X.-M. Zhao et al., 1997). The use of elastomeric stamp and mold is based on the technique for forming a pattern by applying liquid prepolymer that is contrary to the characteristics of mater to the surface and removing it which is used in replica molding (Figure 4). Typical materials used for this purpose include PDMS Sylgard 184 series from Dow Corning, polyurethanes, polyimides, and cross-linked Novolac resin (a phenol formaldehyde polymer) (J.L. Wilbur et al., 1994; 1996; A. Kumar et al., 1994; Y. Xia et al., 1998).

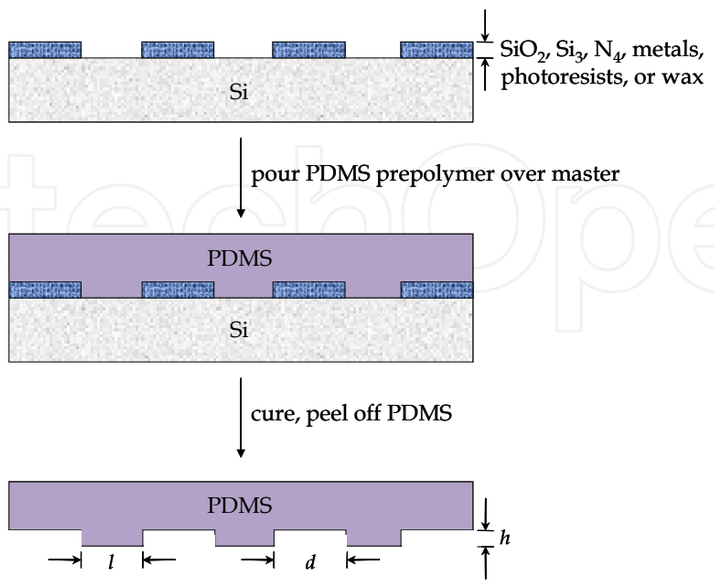

Fig. 4. Schematic illustration of the procedure for casting PDMS replicas from a master having relief structures on its surface.

The reason that soft lithography can produce high quality patterns and structures is because it has many excellent characteristics of PDMS.
Firstly, PDMS is an elastomer, and highly adhesive to substrates in relatively wide area of the surface even in micrometer unit, which allows conformal contact. Furthermore, its elastic property facilitates attachment to and detachment from even the surface of complex, brittle structures. Secondly, PDMS is free from the surface in terms of energy and chemically inactive; so polymers can be easily attached to or detached from the surface of mold-shaped PDMS. Thirdly, PDMS is homogeneous, isotropic, and optically transparent to the wavelength range of 300 nm, so it allows the UV cross-linking of prepolymers even in mold form (J.L. Wilbur et al., 1996).
Therefore, it is used in photomasks which are used in UV photolithography and contact phase-shift photolithography and in elastic optical instruments which are used in adaptive optics. Fourthly, PDMS has excellent durability and its functions do not degrade even after 100 or more repeated works for several months. Fifthly, the surface characteristics of PDMS can be easily changed through plasma treatment using a SAM method. Various surface interactions can be generated by freeing the surface energy through this treatment (Figure 5). (G.S. Ferguson et al., 1991)

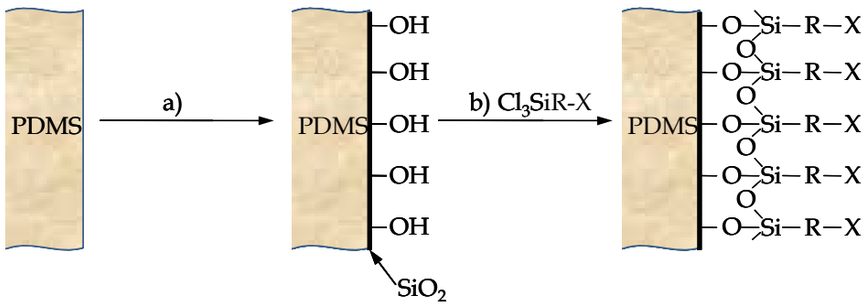

Fig. 5. Schematic procedure for the modification of the PDMS surface. (a) Treatment with an O_2 plasma, (b) reaction with silyl chloride vapor.

The PDMS has most serious technical problems that must be solved before soft lithography can be used in forming complex patterned structures (Figure 6). First, gravity, adhesion and capillary forces (T. Tanaka et al., 1993) exert stress on the elastomeric features and cause them to collapse and generate defects in the pattern that is formed (E. Delamarche et al., 1977). If the aspect ratio of the relief features is too large, the PDMS microstructures fall under their own weight or collapse owing to the forces typical of inking or printing of the stamp. Second, when the aspect ratios are too low, the relief structures are not able to withstand the compressive forces typical of printing and the adhesion between the stamp and the substrate; these interactions result in sagging. Third, achieving accurate registration without distorting the multilayer fabrication process is substantially more difficult with a flexible elastomer than with a rigid material. Therefore, these problems must be improved to technique by material, design and configuration for nano/micro structure application.

3.5 Micromolding in capillaries (MIMIC)

There was the trial that a capillary phenomenon applies to lithography of nano-scale 15 years ago. In 1995 Prof. George Whitesides in Havard university reported MIMIC process which is representative lithography method using a capillary phenomenon (E. Kim et al., 1995; D. Myers, 1991).

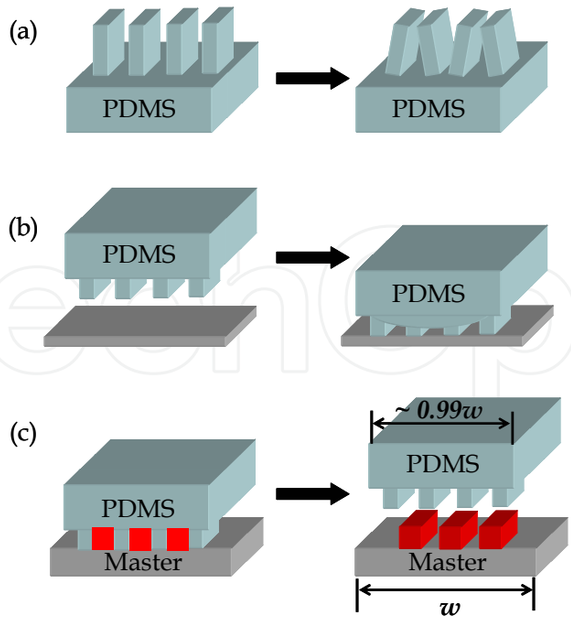

Fig. 6. Schematic diagram of possible deformations and distortions of microstructures in the surfaces of elastomers such as PDMS. (a) pairing, (b) sagging, (c) shrinking.

The capillary is natural phenomenon we can see easily when liquid like water go through a narrow tube, it goes up or down because of the Laplace pressure. The pressure is canceled out by the gravity, we can predict a rising or falling height of liquid based on Young-Laplace equation. When a glass tube is submerged under water or mercury, water causes the capillary rising because a contact angle is smaller than 90 degree and mercury causes the capillary falling because a contact angle is more than 90 degree. In these cases, Young-Laplace equation is

$$\Delta P = \frac{2\gamma}{r}\cos\theta,\ h = \frac{2\gamma}{\rho g r}\cos\theta \tag{1}$$

in which ΔP is Laplace pressure because of the curvature, γ is the surface tension, r is the radius of tube, θ is the contact angle, ρ is the density of liquid, g is the acceleration of gravity. If a tube is tetragonal not round, the curvature decreases and so a numerator in the Laplace pressure changes 2 to 1. To explain a MIMIC phenomenon physically, we use the mathematical modeling shown in eq. 2

$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z} \tag{2}$$

Here, R is value that the area of fluid flowing into hydraulic radius divides into the parameter of area, η is the viscosity of liquid, z is the path fluid flowed in. Three surface tensions are values that affect on the surface between liquid and vapor, solid and vapor, solid and liquid. It can be easily acquired that the length of channel is proportional to the square root of time, and reported it is accorded with the experimental results.
The trial that a capillary applies to the photolithography is reported as a form of MIMIC process in 1995, it is shown in figure 7.

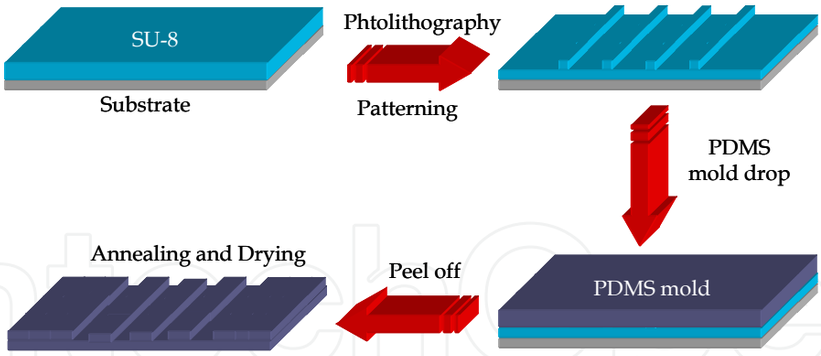

Fig. 7. Fabrication process of PDMS channel.

When we actually perform MIMIC process, patterns are made in the elastic mold PDMS using soft-lithography and contact with the Si wafer or glass surface. When this time, general contact can be achieved without external pressure because PDMS is an elastomer. And due to the small surface tension of about 21 $mJ/m^{2,}$ stable surface can be achieved. From a simple line to complicated structure can be fabricated easily using the MIMIC process and applicable to polyurethane, polyacrylate, poly(methylacrylate) etc, and if materials can be hardening by heats or ultraviolet, MIMIC can be applied to almost all materials (Figure 7).

It is very encouraging the MIMIC process is in the spotlight and applies to display devices or optic device fabrication but there are some limits because of intrinsic characteristics.

First of all, because making the network-structure connected each other is necessary to fill the vacant space of a channel, so it is impossible to make the dot-type structure isolated each other. Secondly, it is difficult for bio-fluid and water to flow in the channel because PDMS is hydrophobic. Lastly, it is often seen a fluid flowing in the vacant space of the channel stops its flowing. It can be a reason that one side of channel is closed, but mostly roughness of surface and other external factor is main reason.

To overcome these problems, applying the vacuum condition to the channel is tried and it showed better characteristics. But when length of the channel is shorter than 1 μm, the resistance increases and capillary movement of flowing in the side direction shows limit. Especially the movement has an unusual sensibility to molecular weight of materials melted in the fluid, limits of the structure using MIMIC is mostly micro-level.

The next section will describe the studies on devices manufactured using various methods mentioned above and examine their characteristics.

4. Research and application

4.1 OLED device

4.1.1 Stamp method

We proposed the stamp method using soft lithography method to define the PLED's color pixel (W.J. Cho et al., 2006). This is subjected to using the merits of a spin-coating method or an Ink-jet printing method applying the roll-to-roll method (T. Zyung et al., 2005). This method requires a very simple process compared with the current spreading method and has a lot of merits can easily fabricate the uniform thickness of the respective pixel materials, surface uniformity and pattern's shape that brings on problems when we fabricate the fine patterns according to the form of the stamp (P.W.M. Blom & M.J.M. de Jong, 1998). On the

other hand, the surface uniformity of the patterns is a critical point when the polymer ink is hardened. To solve it, we used the PDMS, which is elastomeric material.

As shown in Figure 8 (a), this study first forms a mold using the soft lithography process, and then uses this mold to manufacture a stamp to define polymer light emitting pixels. The master used as the mold in this study is formed by laying a highly viscous SU-8 with a negative PR on a glass 100 um thick (C. Thibault et al., 2006). Then the pixel pattern is defined through the photolithography method. After forming the master, Sylgard 184A PDMS and 184B (Dow Corning Company, USA) hardener are diluted in a ratio of 10:1, and sprayed on the upper part of the master. To remove the bubbles which promote unevenness in the lower surface, the study uses a vacuum processing method under an atmosphere of 25 mmHg while manufacturing the stamp. Then the stamp goes through a heating process for 40 minutes at 120°C. In order to make the stamp easily separate from the polymer substances, an O_2 plasma process is also applied (P. Yimsiri & M.R. Mackley, 2006; W.P. Hsu, 2005).

The device fabricated in this study has a four-layer structure of anode, HIL, EML and cathode. A 170 nm thick ITO sputtering with a sheet resistance of 15 Ω/□ is used to pattern the anode. EML, polymer ink, is stamped by using soft-lithography after making an easy hole-injection with spin-coated PEDOT (Poly(3,4-ethylenedioxythiophene)) on the ITO patterned by photolithography. Finally, the device is completed with aluminum deposition (100 nm) by using a thermal evaporator. Figure 8 (b) shows the process of manufacturing the PLED device.

In order to define the EML layer of the PLED device with a four-layer structure, a stamp patterning system was designed as shown in Figure 9. This system can 1) simplify the overall process, 2) run the process at room temperature, 3) define the pattern consecutively and 4) resolve the shortcomings of the previous methods of defining PLED. The designed system is divided mainly into a device JIG part, a stamp location coordination part and a stamping controller. In order to move the light emitting device into an accurate position, an x-z stepping motor (Sigma Koki Co., Ltd., Japan) is used in the stamp location coordination part. In addition, the manufactured stamp is installed in stage z to adjust the stamping pressure and to define the light emitting pattern. In order to control the location accurately, software (SGTERM Ver. 1.20) from Sigma Koki Co., Ltd. is used.

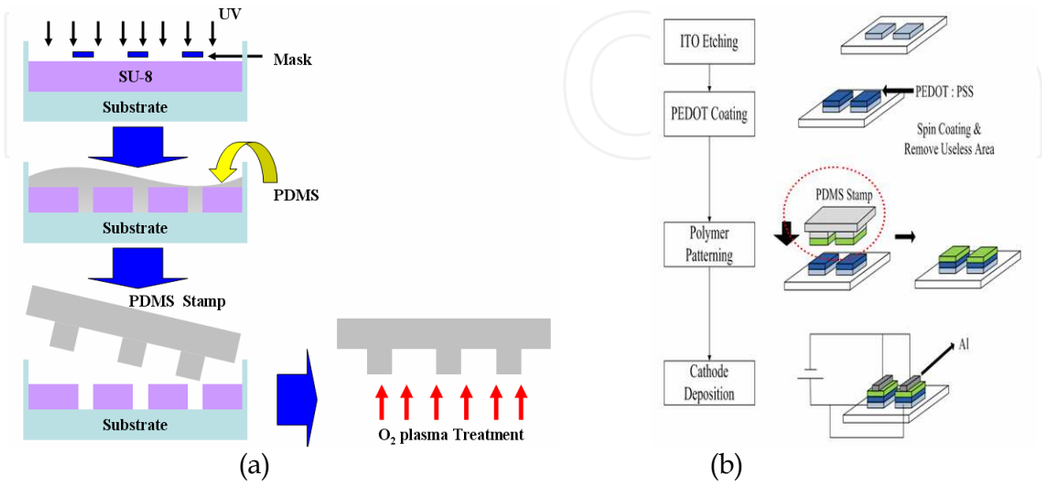

Fig. 8. Schematic diagram of stamp fabrication for pixel definition.

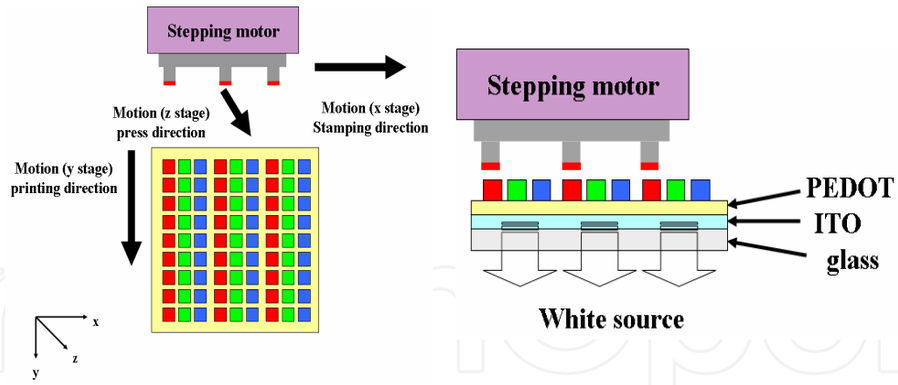

Fig. 9. Process of unit pixel definition using fabricated stamp.

4.1.2 MIMIC process

It can be a simple process to fabricate the PLED using the MIMIC process because we can form the emitting layer just drop the polymer solution to the channel (E. Kim et al., 1995). We used masks for MIMIC process in figure 10. There are cathode and organic channel, respectively.

Fig. 10. Masks of device fabrication by MIMIC process.

To make the 4 inch master structure, we formed the SU-8 2007 (Microchem Inc.) on the silicon wafer by spin-coating and defined channel pattern using photolithography. The height and width of fabricated channel of master structure are 7 μm and 600 μm, respectively. We fabricated the PDMS channel using made master structure, formed emitting layer by dropping the polymer solution to the substrate which anode has formed on the surface and finally confirm characteristics of the polymer light emitting diodes. The fabricated PLED showed about 50 cd/m^2 luminance and 0.2 cd/A efficiency characteristics.
In the experimental process, when the polymer material which has over 45,000 molecular weights is dissolved with over 0.7 wt% concentration, it is not flown in the PDMS channel.
Both molecular weight and concentration affect to viscosity of the polymer material, so it interrupted the capillary phenomenon of polymer material and eventually polymer material cannot be injected to the channel.
But we confirmed MIMIC process can be used to define line pattern but also unit pixel of PLED.

4.2 Optical transcutaneous pCO_2 gas sensor

In this study, the proposed system is an optical system that detects the selected wavelength in the range of mid-IR radiated from a light source without using prism or diffraction

grating by NDIR method (A. Verdin, 1973). This optical system is composed of a light source which provides a mid-IR and an optical reaction chamber to make a vibration energy level of the sample gas changed in this part, a detector which detects an intensity of light and a signal processing circuit to amplify a micro signal. Then, the optical reaction chamber is designed by a 1 mm optical path length and 64 μℓ volumes as considering that a very small amount of CO_2 gas is exhausted from a skin (D.E. Kim et al., 2005).

Figure 11(a) and 11(b) show a fabricating process of the optical reaction chamber, respectively. Si-based optical reaction chamber is fabricated by photolithography with etching and bonding process. To make 1 mm optical path length, two Si substrates are etched up to 300 μm through wet etching. Then, Si supporting layer is bond between two Si substrates. In this case, however, this process makes a surface of Si substrate roughen and results in decrease of IR transmittance rate. Therefore, LiF glass, which is used for a material of a prism is used to fabricate optical reaction chamber because it has very high optical transmittance compared to Si substrate. This LiF-based optical reaction chamber has 1 mm optical path length by soft-lithography method which results in short fabricating process time. Also, the surface of LiF glass isn't rough because this soft-lithography method doesn't need etching process. It means that LiF-based optical reaction chamber is used to increase process efficiency and detecting efficiency. Also, LiF-based optical reaction chamber is used by thermally and chemically stable acetal stamp master to define the 1 mm optical path length by soft-lithography method. These two types of the fabricated optical reaction chamber and unification style are shown in Figure 11(inset image) (D.E. Kim et al., 2005; H.Y. Bang, 2007).

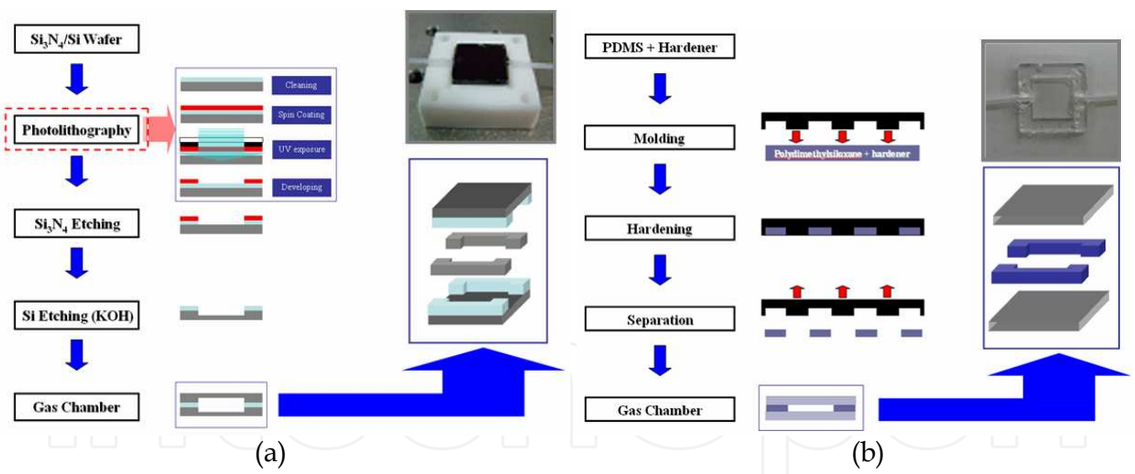

Fig. 11. Fabrication of optical reaction chamber. (a) is the Si optical reaction chamber and (b) is the LiF optical reaction chamber.

The IR transmittance of the two types of the fabricated optical reaction chamber was measured by using FT-Infrared Spectrophotometer (Mattson Instruments, Inc., Galaxy 7020A) and appeared to Figure 12. This figure shows that LiF-based optical reaction chamber has approximately 70 % IR transmittance comparing with Si-based optical reaction chamber of 35 % IR transmittance in the 4.26 μm ranges. Figure 13 shows the absorbance according to the concentration of CO_2 gas. This figure exhibits the absorbance in the arterial pCO_2 concentration region, 0 ppm ~ 5,000 ppm, after blowing CO_2 gas into each optical

reaction chamber by using MFC (Mass Flow Controller, P.J KODIVAC, Japan). The variation result of the absorbance is 3.78 × 10^{-6} absorbance/ppm and 6.50 × 10^{-6} absorbance/ppm in the arterial pCO_2 concentration region. As a result, LiF-based optical reaction chamber has more efficiency increased by 65 % comparing with Si-based optical reaction chamber.

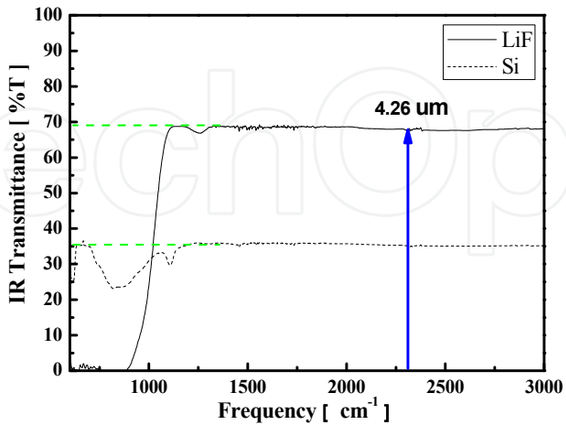

Fig. 12. IR transmittance of the fabricated optical reaction chamber.

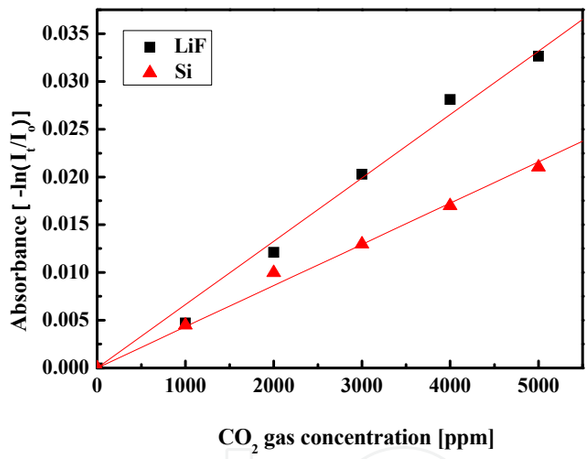

Fig. 13. Absorbance according to the concentration of CO_2 gas in each optical reaction chamber.

4.3 Optical waveguide

The polymer waveguide presents several advantages including easy fabrication process, wide bandwidth and control of refractive index, high optical coefficient, and low cost compared to inorganic waveguide such as LiNbO (C. Bulmer & W. Burns, 1983), III–V compound semiconductor (C. Glingener et al., 1995), and glass substrate (C.C. Lee & R.W. Chuang, 2004). For these reasons, the polymeric waveguide has been widely applied to optical switch (K. Chen et al., 2005), modulator, optical interconnection device (H.-D. Bauer et al., 2000), etc. Recently, optic devices using polymers such as PMMA, polyimide, SU-8 and PDMS have been reported. Especially, PDMS is an optically clear, biocompatible and easily sealed so as to produce waveguides and micro/nano fluidic channels. In this paragraph, optical waveguide fabrication with soft-lithography method is presented.

In our experiment, SU-8 photoresist (Microchem Inc.) and PDMS were used as the mold and waveguide, respectively. SU-8 photoresist, is commonly used to the MEMS application, has advantages such as optical and thermally stability, high solidity, and simple fabrication with high resolution so it suitable to apply the mold formation in soft-lithography. Procedure of fabricating SU-8 is similar to the normal process of photolithography in semi-conductor fabrication. First, the SU-8 polymer was spin-coated on the substrate – glass or Si wafer. This step can define the thickness of the mold. Specification, was stated at Microchem Inc., of the spin speed versus thickness was shown in Figure 14 (http://www.microchem.com). Second, soft baking and exposure process was performed. Then, post exposure baking was performed before the develop process. This process which is one of the important fabrications to form the SU-8 mold functions the acid-initiated, thermally driven epoxy cross-linking. Finally, SU-8 master was formed after develop process. The example of the SU-8 mold fabrication is shown in Figure 15.

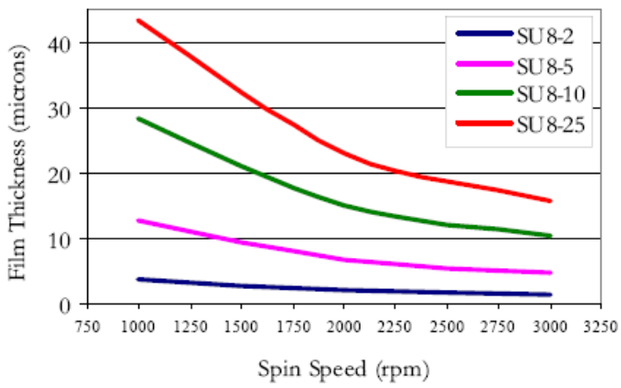

Fig. 14. Spin speed versus thickness

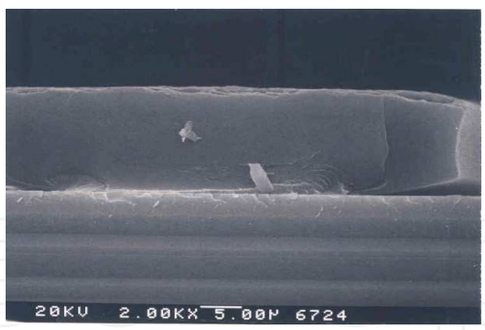

Fig. 15. SEM image of fabricated SU-8 master.

Next step is forming the PDMS waveguide. First, PDMS elastomer and curing agent were mixed in proper ratio. When mixing elastomer and hardner, refractive index of the PDMS waveguide could be changed with mixing an additive such as hexane (Jack Sheng Kee et al., 2008). Then, premixed PDMS solutions were poured on the pre-fabricated SU-8 master. After that, excess surface PDMS was scraped off with razor edge to form waveguides and PDMS was baked at 150 °C for 60 min. Then, PDMS was poured over cooled water to form optical substrate. Finally, substrate and waveguides peeled from SU-8 master. Waveguided photograph of fabricated PDMS waveguide was shown in Figure 16 (Su-Won Jang et al, 2006).

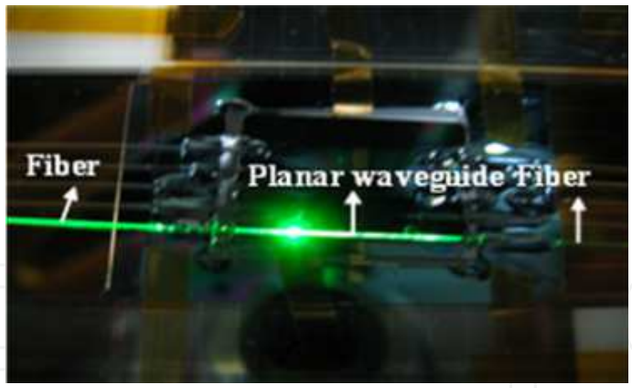

Fig. 16. Photograph of planar waveguide using PDMS.

5. Conclusion

The continued growth of the semiconductor industry is a direct result of the capability to transfer smaller and smaller circuit patterns onto semiconductor wafers or other substrate. Currently, the photolithography field for creating chips smaller than 100 nm is facing new technological challenge, and there is no guarantee that photolithography technology is the optimal technology. To create devices that are small than 100 nm is extremely limited due to light diffraction, problems in creating light masks, lens resolution, etc. So, vast majority of photolithographic equipment is optical system.

To overcome these limitations and guarantee the smaller electric devices, the soft lithography method is a new alternative plan, so a lot of researches are executed. Soft Lithography mentioned above can overcome the resolution limitation that photolithography method has, and the method is simple and it has advantages on cost saving. Also, like lens and optical fiber, it is available on the method in large area like non planar surface, so it can be applied to the not only cell biology industry but microelectronics, optics and display areas.

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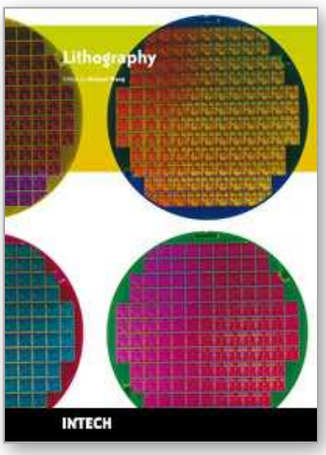

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Lithography, the fundamental fabrication process of semiconductor devices, plays a critical role in micro- and nano-fabrications and the revolution in high density integrated circuits. This book is the result of inspirations and contributions from many researchers worldwide. Although the inclusion of the book chapters may not be a complete representation of all lithographic arts, it does represent a good collection of contributions in this field. We hope readers will enjoy reading the book as much as we have enjoyed bringing it together. We would like to thank all contributors and authors of this book.

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