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Research paper

Vacuum ultraviolet light assisted bonding and nanoscale pattern transfer method for polydimethylsiloxane

Yuki Hashimoto, Katsuo Mogi, Takatoki Yamamoto *

Department of Mechanical Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

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ABSTRACT

This paper describes a method for transferring a nanoscale pattern from a cyclic olefin polymer (COP) mold to the surface of UV curable polydimetylsiloxane (PDMS) on a glass substrate. The PDMS is first deposited on the patterned mold by spin-coating and photocuring. Vacuum ultraviolet (VUV) radiation is then used to activate the surface of both the PDMS and the glass substrate before bringing them into contact. Once a bond has been formed, the COP mold is peeled away, leaving the patterned PDMS on the glass substrate. Bonding tests were first carried out to determine the optimum VUV irradiation dose to form a permanent bond. The effectiveness of the proposed method was then demonstrated by transferring a periodic nanoscale pattern. Microscopic examination of the original and transferred patterns revealed that successful reproduction was achieved. A spectroscopic analysis was also performed to clarify the mechanism involved in the bonding process. The results suggested that VUV irradiation caused oxidation of the PDMS surface and the formation of OH groups. When the PDMS and the glass substrate were brought into contact, a dehydration reaction took place which caused the formation of siloxane (—O—Si—O—) bonds between the two materials. The proposed method offers the advantages of being simple and allowing deformation-free transfer of very fine patterns. It can also be applied to a wide range of nanoscale fabrication tasks.

1. Introduction

Electromagnetic radiation with a wavelength less than 200 nm requires a vacuum in order to propagate due to strong absorption by nitrogen and oxygen in air. For this reason, it is referred to as vacuum ultraviolet (VUV) light. VUV light is of interest for photolithography since its wavelength is shorter than that of conventional light sources [1,2]. In addition, because of its high photon energy, it is used to promote photochemical reactions for cleaning [3,4], surface modification [5,6] and film formation on substrates [7,8].

One promising application of VUV irradiation is bonding of materials by activating their surfaces. This method can potentially avoid deformation of micro- or nanostructure on the surface, which is difficult using conventional bonding techniques such as adhesive bonding, thermal fusion bonding, and vacuum and atmospheric plasma bonding assisted by ion bombardment of active species [9]. In previous research, we succeeded in directly bonding polydimetylsiloxane (PDMS) and its analogs to glass substrates by VUV irradiation at a wavelength of 172 nm [10,11]. We also reported a UV-curable form of PDMS (UV-PDMS) which exhibited extremely low shrinkage after curing compared with conventional thermo-curable PDMS, and had potential applications for nanoscale fabrication [12–15].

In the present study, we invented and demonstrate an easy nanoscale patterning method by taking advantage of a combination of VUV bonding and a releasing agent free molding of PDMS using a cyclic olefin polymer (COP) mold master. This method has several advantages compared with the conventional close but not the same methods. The use of COP mold master does not require any releasing reagent to transfer PDMS-made nanostructures due to its low surface energy [16], so that the fabrication process was simplified and more accurate by excluding the releasing agent layer on the surface of mold master. Furthermore, the flexible COP mold master will be available for roll-to-roll printing process preferable for large-area mass production, which is difficult by the use of conventional hard-type mold master. It also simplifies the fabrication process in bonding between PDMS-made nanostructure and glass substrate just by irradiating vacuum-ultraviolet. The PDMS shows comparable or better performance than conventional optical polymers in terms of optical transparency [17], weather resistance and resistance to chemical corrosion [18,19], etc. On the other hand, the fabrication using deformable COP mold master will realize a method for fabricating nanostructures on curved surfaces. Hence, one of the killer application of this method will be to realize optical nanostructures on curved surfaces, such as anti-reflection moth-eye structures on optical lenses, glasses, curved display panels, curved solar cells, etc., to improve

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* Corresponding author.
E-mail address: yamamoto@mes.titech.ac.jp (T. Yamamoto).

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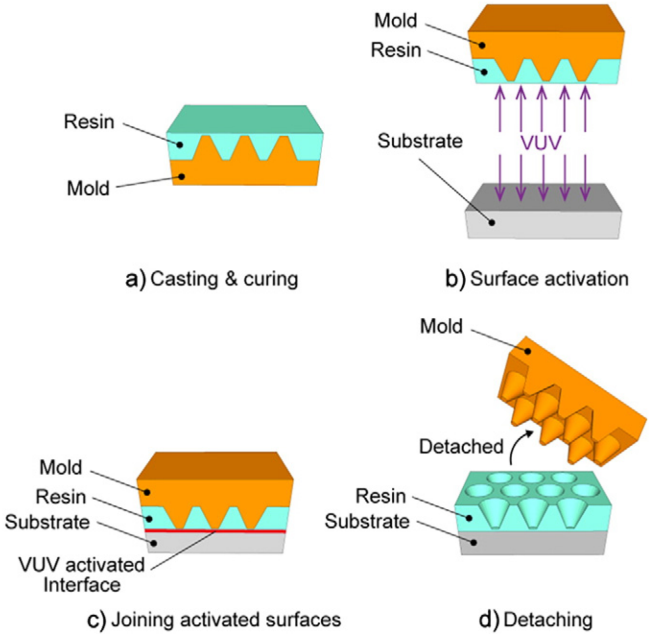

Fig. 1. Schematic diagram of VUV assisted direct transferring process: (a) casting and curing of resin on master mold, b) surface activation by VUV irradiation, c) joining activated surfaces, d) detaching mold master from resin.

the transmittance or the absorption of light [20], which are difficult to be realized by conventional nanoimprint technology using hard-type mold master.

2. Materials and methods

2.1. Fabrication by VUV assisted nanoscale pattern transfer

A schematic of the proposed fabrication process is shown in Fig. 1. A UV-curable PDMS was first spin-coated onto a master mold with a nanoscale surface pattern, and was then cured by applying light (Fig. 1a). Both the PDMS and glass substrate surfaces were then exposed to VUV irradiation (Fig. 1b), and brought into contact with each other (Fig. 1c). Finally, the master mold was detached from the resin (Fig. 1d). In order to demonstrate this method, a cyclic olefin polymer (COP) was used for the master.

2.2. Bonding strength

In order to optimize the bonding conditions, the bonding strength was evaluated using the setup shown in Fig. 2. A slab of PDMS with dimensions of 75 mm × 5 mm × 1 mm bonded to a glass substrate (S9111, Matsunami Glass Co., Ltd.) was bent by 90° and then pulled directly away from the glass substrate. The force was measured using a force gauge (Z2-200N, Imada Co., Ltd.). The UV-PDMS material was commercially available UV-curable PDMS (X-34-4184, Shin-Etsu Silicone Co. Ltd.), which exhibits much lower shrinkage during curing than conventional thermally curable PDMS, and is thus suitable for nanoscale fabrication [13–15]. The UV-PDMS slab was cured using a UV lamp (PM25C-135, Ushio Co. Ltd.) with an exposure dose of 2000 mJ/cm^2 at a wavelength of 365 nm. The VUV source for bonding was a water-cooled dielectric barrier discharge excimer lamp filled with xenon gas (UVS-1000SM, Ushio Co., Ltd.), which emitted incoherent light at a wavelength of 172 nm. Irradiation was carried out in air at room temperature at an intensity of approximately 12.5 mW/cm^2, with a distance of 3 mm between the lamp surface and the specimen.

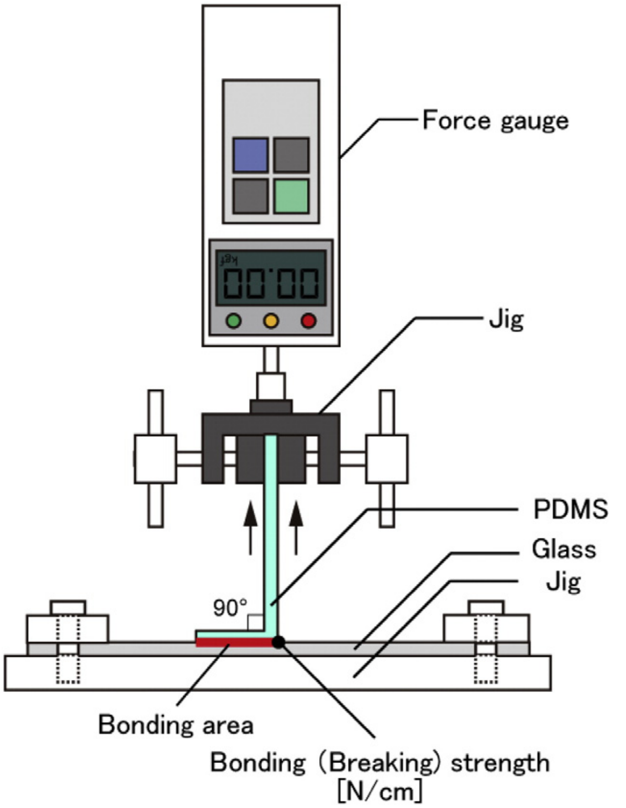

Fig. 2. Schematic image to evaluate bonding strength. A PDMS slab is bonded to a glass substrate and pulled directly away from the substrate during the test.

2.3. Surface analysis

The chemical changes occurring on the PDMS following VUV irradiation were investigated using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet iS5, Thermo Scientific Co., Ltd.) with a diamond ATR prism. The spectra were recorded in the wavenumber range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The ATR angle of incidence was 40°.

The surface morphology of the COP mold and the pattern transferred to the PDMS was observed using atomic force microscopy (AFM; Dimension Icon, Bruker Co., Ltd.).

2.4. Fabrication

Nanoscale pattern transfer was carried out using the following procedure. A COP master mold was fabricated by thermal nanoimprinting using a silicon-made template, on which a nanoscale pattern had been produced by electron beam lithography and dry etching [21]. The thermal nanoimprinting process was performed by applying the pressure at

Table 1
Bonding results for PDMS and glass for different VUV irradiation doses.

Irradiation dose [mJ/cm^2]	Result	Bonding (breaking) strength [N/cm]
0.0	Not bonded	0.00
62.5	Bonded a little but detached	1.43
125.0	Broken	(4.12)
250.0	Broken	(4.51)
500.0	Broken	(3.73)
1000.0	Broken	(3.92)
2000.0	Broken	(4.31)