Removal of Polymer for Nano-imprint Lithography using Atomic Hydrogen Generated by the Hot-wire Catalyzer

Akihiko Kono^{*}, Takeshi Maruoka^{*}, Yu Arai^{*}, Yoshihiko Hirai^{**} and Hideo Horibe^{***}

^{*}Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, 3-1
Yatsukaho, Hakusan, Ishikawa 924-0838, Japan

^{**}Department of Physics and Electronics Engineering, Graduate School of Engineering,
Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

^{***}The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki,
Osaka 567-0047, Japan
a.kono@neptune.kanazawa-it.ac.jp

We investigated the removal characteristics of an ultraviolet (UV) curable polymer for UV nano-imprint lithography (NIL) using atomic hydrogen, which was generated by the catalytic decomposition of H₂ molecules in H₂/N₂ mixed gas (H₂:N₂=10:90 vol.%) using a tungsten hot-wire catalyzer. The cured polymers were removed by atomic hydrogen without a residual layer. The removal rate of the polymer increased with rising catalyzer temperature. It was assumed that both enhanced reactivity between atomic hydrogen and polymer by the substrate temperature increase due to radiation heat of the catalyzer and increased atomic hydrogen concentration occurred as a result of the rise in catalyzer temperature. When the distance between the catalyzer and the substrate was 100 mm, the catalyzer temperature was 2400°C, and the initial substrate temperature was room temperature, the removal rate of polymers was 0.17 μm/min independent of exposure dose to the polymer. The removal rate of polymers was comparable to the removal rate of general *i*-line positive-tone novolak resist. The polymer adhering to the micro-asperity portion of the mold was removed without leaving a residual layer by grazing-incidence atomic hydrogen.

Keywords: Atomic hydrogen, Hot-wire catalyzer, Nano-imprint lithography,
Polymer removal, Mold cleaning

1. Introduction

Recently, nano-imprint lithography (NIL), proposed by Chou *et al.* [1], has received much attention from many industries because of the potential high throughput production of various nanostructure applications, such as electronic devices with a simple process and low cost. Thermal NIL [1, 2] using thermoplastic polymer and ultraviolet (UV) NIL [3, 4] using UV curable polymer have been performed. Figure 1 illustrates the UV-NIL process. First, the substrate is coated with UV curable polymer. Second, a quartz mold with a nano-size pattern is pressed onto the UV

curable polymer. Third, UV light is irradiated through the mold to cure the UV curable polymer. Fourth, after the polymer is cured, the mold is removed from the polymer. Finally, the residual polymer layer equivalent to convex portions of the mold is removed by oxygen reactive ion etching, and substrate etching is performed.

One problem with UV-NIL is that polymer adheres to the mold when the mold is removed [5, 6]. This leads to contamination of the mold and abrasion of the patterns transferred from the substrate. The molds are generally prepared by electron beam lithography, and those with high

Fig. 1. Schematic diagram of the UV nano-imprint lithography (NIL) process.

aspect ratio patterns are fabricated by the Lithographie Galvanoformung Abformung (LIGA) process using synchrotron radiation. These molds are quite valuable because they are difficult to fabricate. Thus, cleaning technology for removing the adhering polymer to reuse the mold is an elemental technology in UV-NIL. However, the polymer cured by UV irradiation is difficult to remove by conventional methods such as wet processes using chemicals.

In this study, we investigated removing UV curable polymer using UV-NIL by atomic hydrogen generated by catalytic decomposition of H_2 molecules using a tungsten hot-wire catalyzer [7-11]. This method is beneficial to the environment because it does not use chemicals such as sulfuric acid hydrogen peroxide mixture (SPM), ammonia hydrogen peroxide mixture (APM), and organic amine solutions. Moreover, it is expected that the nano-sized pattern on the mold will not be damaged by bombardment of high-energy ions because this method is plasma-free.

2. Experimental

2-1. Atomic Hydrogen Irradiation Apparatus and Conditions

Figure 2 schematically illustrates the atomic hydrogen irradiation apparatus. A tungsten wire (99.95% purity, 0.7mm in diameter, and 500mm in length) was used as a hot-wire catalyzer to generate atomic hydrogen. A 40mm-long, 10mm-diameter catalyzer was coiled into a helix with five turns.

Fig. 2. Schematic illustration of the atomic hydrogen irradiation apparatus.

The polymer-coated Si substrate and the mold with adhering polymer were attached just below the catalyzer. The distance between the catalyzer and the substrate was fixed at 100mm. The catalyzer was heated at 2000°C (current = 20.5A), 2100°C (22.2A), 2300°C (25.7A), and 2400°C (27.3A) using a direct current supply. The catalyzer temperature was measured using a two-wavelength (0.8 and 1.05 μ m) infrared radiation thermometer (Impac Electronic ISR12-L0). The working gas, H_2/N_2 mixed gas ($H_2:N_2 = 10:90$ vol.%), was introduced from the center nozzle into a fused silica chamber. To avoid explosion, N_2 gas was used to dilute the H_2 gas concentration. The gas flow rate was fixed at 300sccm using a mass flow controller. The H_2 partial pressure was fixed at 2.13Pa, and the initial substrate temperature (just below the atomic hydrogen irradiation) was fixed at room temperature (R.T.). The substrate temperature during atomic hydrogen irradiation was monitored using a K-type thermocouple attached to the back of the substrate.

2-2. Preparing Samples for Measuring the Removal Rate

UV curable polymer PAK-01 manufactured by Toyo Gosei Co. was used. The polymer was spin-coated onto a Si wafer (substrate) using a spin coater (MIKASA MS-A 100) at 4000rpm for 20sec. The polymer was exposed to UV (mercury lamp *i*-line, 365nm wavelength, 9nm half width, 0.10mW/cm² intensity) in N_2 at atmospheric pressure using a mask aligner (MIKASA M-1s). The exposure dose was controlled by changing exposure time. The film thickness of the polymer

was measured using a stylus surface-profile measurement instrument (ULVAC DekTak 6M). The residual layer of polymer was evaluated by observing the substrate surface using an optical microscope (Nikon ECLIPSE L150) and x-ray photoemission spectroscopy (XPS, SHIMADZU ESCA-3400) measurement of the substrate surface.

2-3. Preparing Samples for Evaluating Mold Cleaning Performance

UV curable polymer PAK-01 was used. Both the Si mold and the quartz substrate were cleaned with water, acetone (20min), SPM (sulfuric acid:hydrogen peroxide = 1:1, 40min), and UV ozone (5min). The polymer was spin-coated onto a quartz substrate using a spin coater at 1000rpm for 30sec. The mold was pressed onto the polymer, and the substrate was irradiated with UV light to cure the polymer. The samples (molds with polymer adhering) were prepared by the mold removal. The cleanliness of the mold was evaluated by observing the surface and cross sectional area of the mold using an optical microscope and a scanning electron microscope (SEM, Hitachi High-Technologies TM-1000), and XPS measurement of the mold surface.

3. Results and discussion

3-1. Using Atomic Hydrogen to Remove Polymer Coated onto the Si Substrate

Figure 3 plots the catalyzer temperature versus the polymer removal rate. The exposure dose to polymer was fixed at $100\text{mJ}/\text{cm}^2$ (recommended exposure for PAK-01). Removal rates were calculated by dividing the reduced film thickness by the atomic hydrogen irradiation time. The atomic hydrogen irradiation time was fixed at 30min. For catalyzer temperatures of 2000 to 2400°C , the polymer film thickness decreased with atomic hydrogen irradiation, confirming that atomic hydrogen can remove the cured polymer. Based on a report by Izumi *et al.* [12], who investigated removal characteristics of photo-resists using atomic hydrogen, it is speculated that atomic hydrogen decomposes polymer to $-\text{C}_x\text{H}_y$ and $-\text{OH}$ compounds. The N_2 molecules in the working gas do not contribute to the decomposition of polymer. The generation efficiency of the nitrogen atom by a hot-wire catalyzer is much lower than that of the atomic hydrogen. Umemoto *et al.* found that the atomic hydrogen concentration reaches 10^{14}cm^{-3} [13] at a catalyzer temperature of 1900°C and H_2 pressure of

Fig. 3. Relationship between catalyzer temperature and polymer removal rate with an exposure dose of $100\text{mJ}/\text{cm}^2$.

Fig. 4. Substrate temperature change as a function of atomic hydrogen irradiation time. Catalyzer temperatures are 2000, 2100, 2300, and 2400°C .

5.6Pa ; however, the nitrogen atom concentration is only 10^{11}cm^{-3} [14] even at a catalyzer temperature of 2500°C and N_2 pressure of 100Pa .

The removal rate rapidly increased with rising catalyzer temperature (Fig. 3). This result is discussed in detail below. Figure 4 presents substrate temperature changes during atomic hydrogen irradiation. For all catalyzer temperatures, substrate temperatures rose with increasing atomic hydrogen irradiation time, and were saturated when the atomic hydrogen irradiation time was longer than 20min. The saturated substrate temperature increased with higher catalyzer temperature because the substrate is heated more by the radiation heat of hot-wire catalyzer as the catalyzer temperature rises. Therefore, the reactivity between atomic hydrogen and polymer is enhanced by the rise of catalyzer temperature, because the reaction

Fig. 5. Optical microscope images ($\times 50$) of the substrate surface (a) before polymer removal and (b) after polymer removal. The catalyst temperature is 2400°C , and the exposure dose to polymer is $100\text{mJ}/\text{cm}^2$.

Fig. 6. Wide scan XPS spectra of (1) the Si substrate surface before polymer coating, (2) polymer surface coated onto Si substrate, and (3) Si substrate surface after polymer removal. The catalyst temperature is 2400°C , and the exposure dose to polymer is $100\text{mJ}/\text{cm}^2$.

field temperature rises with catalyst temperature. Moreover, Umemoto *et al.* [13] and the authors [10] reported that the natural logarithm of the atomic hydrogen concentration is inversely proportional to the inverse of the absolute catalyst temperature, and the generation of atomic hydrogen by the hot-wire catalyst follows the Arrhenius law. The atomic hydrogen concentration increases with rising catalyst temperature because the atomic hydrogen dissociatively adsorbed onto tungsten dangling bonds of the catalyst surface easily desorbs at higher catalyst temperature. Based on the above, it is obvious that the reactivity between atomic hydrogen and polymer is enhanced and the atomic hydrogen concentration increases with a rise in catalyst temperature. Therefore, it is assumed that the removal rate rapidly increases with rising catalyst temperature.

Fig. 7. Relationship between the atomic hydrogen irradiation time and the polymer film thickness with various exposure doses. The catalyst temperature is 2400°C .

Figure 5 (a) presents an optical microscope image of the Si substrate surface before polymer removal (before atomic hydrogen irradiation), and Fig. 5 (b) presents that after polymer removal (after atomic hydrogen irradiation). The catalyst temperature was fixed at 2400°C , and the exposure dose to polymer was fixed at $100\text{mJ}/\text{cm}^2$. After atomic hydrogen irradiation, no residual layer of polymer was observed. This result was similar for the entire area of the substrate. Figure 6 presents XPS spectra of the Si substrate surface before polymer coating, the polymer surface coated onto the Si substrate, and the Si substrate surface after polymer removal. Results indicated that the intensity of the C_{1s} peak (284eV) in the Si substrate after polymer removal is approximately equal to that in the Si substrate before polymer coating. In addition, peaks of Si_{2s} (150eV) and Si_{2p} (100eV) were observed at the Si substrate surface after polymer removal. Thus, it is concluded that atomic hydrogen can remove cured polymer without leaving a residual layer.

Figure 7 depicts the relationship between the atomic hydrogen irradiation time and the polymer film thickness with various exposure doses. The catalyst temperature was fixed at 2400°C . Polymers with exposure doses of 50, 100, 150, and $200\text{mJ}/\text{cm}^2$ were removed by atomic hydrogen. The removal rates (= initial film thickness / polymer removal time) were $0.17\mu\text{m}/\text{min}$ independent of exposure dose. This removal rate is comparable to the removal rate of $0.1\mu\text{m}/\text{min}$ for generally *i*-line positive-tone novolak resist [10]. It may be that the polymer can be removed faster

Fig. 8. Optical microscope images ($\times 200$) of the mold surface before polymer removal ((a), (b)), and after polymer removal ((c), (d)). The catalyzer temperature is 2400°C . In photograph (a), polymer adheres to part of the mold. In photograph (b), polymer adheres to the entire area of the mold.

Fig. 9. Wide scan XPS spectra of (1) the mold (with micro-asperity) surface after polymer removal, and (2) the Si substrate surface after polymer removal.

because the maximum removal rate of the novolak resist can reach $2.5\mu\text{m}/\text{min}$ [7] by optimizing the atomic hydrogen irradiation conditions.

3-2. Removing the Polymer Adhering to the Mold Using Atomic Hydrogen

We investigated the removal characteristics of the polymer adhering to the mold, and estimated the mold cleaning performance of atomic

Fig. 10. SEM images ($\times 10000$) of (a) the mold surface after polymer removal, and (b) the cross sectional surface after polymer removal.

hydrogen. Figures 8 (a) and (b) present optical microscope images of the mold surfaces before the adhering polymer was removed (before atomic hydrogen irradiation), and Figs. 8 (c) and (d) present those after the adhering polymer was removed (before atomic hydrogen irradiation). The catalyzer temperature was fixed at 2400°C . In Figs. 8 (c) and (d), polymer adhering to a large area of mold was removed by atomic hydrogen. Figure 9 presents the XPS spectra of the mold surface and the Si substrate surface after polymer removal. Peaks of Si_{2s} and Si_{2p} were observed in the mold surface after polymer removal. Moreover, peak intensities of C_{1s} , Si_{2s} , and Si_{2p} were approximately equal to those in the Si substrate after polymer removal. Figure 10 (a) and (b) present SEM images of the mold surface (the cross sectional mold surface) after polymer removal. No residual polymer was observed even on the micro-asperity portion of the mold. Based on these results, we conclude that atomic hydrogen can remove adhering polymer from the mold and can clean the mold. In the following section, we explain how the polymer that adhered to the micro-asperity portion of the mold was removed, similar to the polymer coated onto the Si substrate without micro-asperity patterns.

When the velocity of atomic hydrogen follows

the Maxwell-Boltzmann distribution, the mean free path λ of atomic hydrogen is given by equation (1).

$$\lambda = \frac{1}{\sqrt{2}Qn}, \quad (1)$$

where Q is the collision cross section and is given by equation (2) for collisions of heterogeneous molecules or atoms.

$$Q = \pi(r_A + r_B)^2 \quad (2)$$

Here, r_A is the radius of the atom (or molecule), r_B is the radius of the other atom (or molecule), and n is the volume concentration of gas. In the following discussion, we consider the collisions between atomic hydrogen and N_2 molecules because N_2 occupies 90vol.% of the working gas. The radius of atomic hydrogen is 52.9pm, and that of the N_2 molecule is 189pm. The n is estimated by total pressure in the chamber (21.3Pa) and temperature. The temperature assumed is R.T., and the calculated λ is 0.75mm. This 0.75mm is much smaller than the distance between the catalyzer and the substrate (mold) (100mm). There are 130 collisions between atomic hydrogen and N_2 molecules when the distance between the catalyzer and the substrate (mold) is 100mm. From this estimate, it is assumed that the atomic hydrogen near the mold surface moves in various directions due to collisions with N_2 molecules. The atomic hydrogen penetrated obliquely into the mold and can attack a sidewall of micro-asperity patterns on the mold. Therefore, it is assumed that the polymer adhering to micro-asperity patterns on the mold was removed by atomic hydrogen.

4. Conclusion

We investigated the removal of UV curable polymer using UV-NIL by atomic hydrogen, which was generated by the catalytic decomposition of H_2 molecules in H_2/N_2 mixed gas ($H_2:N_2=10:90$ vol.%), using a tungsten hot-wire catalyzer. The cured polymers were removed by atomic hydrogen without leaving a residual layer. The removal rate rapidly increased with rising catalyzer temperature because of enhanced the reactivity between atomic hydrogen and polymer and increased atomic hydrogen concentration due to a rise in catalyzer temperature. When the hydrogen partial pressure was 2.13Pa, the catalyzer temperature was 2400°C, the distance between the catalyzer and the substrate was 100mm, and the initial substrate temperature was R.T., polymers with exposure doses of 50 to

200mJ/cm² were removed at a rate of 0.17μm/min regardless of exposure dose. The polymer, which adhered into micro-asperity patterns on the mold, was removed by atomic hydrogen. When the distance between the catalyzer and the substrate was 100mm, it was assumed that the atomic hydrogen obliquely penetrates into the mold due to approximately 130 collisions with N_2 molecules. Therefore, the polymer that adhered to micro-asperity patterns on the mold was effectively removed by atomic hydrogen.

References

- [1] S. Y. Chou, P. K. Krauss, and P. J. Renstrom, *Appl. Phys. Lett.*, **67** (1995) 3114.
- [2] Y. Hirai, *J. Photopolym. Sci. Technol.*, **15** (2005) 475.
- [3] M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt, and C. G. Wilson, *Proc. of SPIE* **3676** (1999) 378.
- [4] N. Sakai, *J. Photopolym. Sci. Technol.*, **22** (2009) 133.
- [5] Y. Hirai, S. Yoshida, A. Okamoto, Y. Tanaka, M. Endo, S. Irie, H. Nakagawa, and M. Sasago, *J. Photopolym. Sci. Technol.*, **14** (2001) 457.
- [6] N. Fujii, T. Tanabe, T. Hirasawa, H. Kawata, N. Sakai, and Y. Hirai, *J. Photopolym. Sci. Technol.*, **22** (2009) 181.
- [7] M. Yamamoto, H. Horibe, H. Umemoto, K. Takao, E. Kusano, M. Kase, and S. Tagawa, *Jpn. J. Appl. Phys.*, **48**(2) (2009) 026503.
- [8] M. Yamamoto, T. Maruoka, Y. Goto, A. Kono, H. Horibe, M. Sakamoto, E. Kusano, H. Seki, and S. Tagawa, *J. Electrochem. Soc.*, **157**(3) (2010) H361.
- [9] H. Horibe, M. Yamamoto, E. Kusano, T. Ichikawa, and S. Tagawa, *J. Photopolym. Sci. Technol.*, **21**(2) (2008) 293.
- [10] M. Yamamoto, T. Maruoka, A. Kono, H. Horibe, and H. Umemoto, *Appl. Phys. Express.*, **3**(2) (2010) 026501.
- [11] T. Maruoka, Y. Goto, M. Yamamoto, H. Horibe, E. Kusano, K. Takao and S. Tagawa, *J. Photopolym. Sci. Technol.*, **22**(3) (2009) 325
- [12] A. Izumi, and H. Matsumura, *Jpn. J. Appl. Phys.*, **41** (2002) 4639.
- [13] H. Umemoto, K. Ohara, D. Morita, Y. Nozaki, A. Masuda, and H. Matsumura, *J. Appl. Phys.*, **91** (2002) 1650.
- [14] H. Umemoto, *7th Cat-CVD Kenkyukai Koenyokosyu*, (2010) 66 [in Japanese].