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
aspect ratio patterns are fabricated by the Lithographie Galvanof ormung 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. 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 1.05μm) infrared radiation thermometer (Impac Electronic ISR12-L0). The working gas, H\(_2\)/N\(_2\) mixed gas (H\(_2\):N\(_2\) = 10:90vol.%), 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-A100) at 4000rpm for 20sec. The polymer was exposed to UV (mercury lamp i-line, 365nm wavelength, 9nm half width, 0.10mW/cm\(^2\) 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

Fig. 1. Schematic diagram of the UV nano-imprint lithography (NIL) process.
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 100mJ/cm² (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 –CₓHᵧ and –OH compounds. The N₂ 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 10¹³ cm⁻³ [13] at a catalyzer temperature of 1900°C and H₂ pressure of 5.6Pa; however, the nitrogen atom concentration is only 10¹¹ cm⁻³ [14] even at a catalyzer temperature of 2500°C and N₂ 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
field temperature rises with catalyzer 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 catalyzer temperature, and the generation of atomic hydrogen by the hot-wire catalyzer follows the Arrhenius law. The atomic hydrogen concentration increases with rising catalyzer temperature because the atomic hydrogen dissociatively adsorbed onto tungsten dangling bonds of the catalyzer surface easily desorbs at higher catalyzer 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 catalyzer temperature. Therefore, it is assumed that the removal rate rapidly increases with rising catalyzer temperature.

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 catalyzer temperature was fixed at 2400°C, and the exposure dose to polymer was fixed at 100mJ/cm². 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 catalyzer 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 catalyzer temperature was fixed at 2400°C, and the exposure dose to polymer was fixed at 100mJ/cm². 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 catalyzer temperature was fixed at 2400°C. Polymers with exposure doses of 50, 100, 150, and 200mJ/cm² were removed by atomic hydrogen. The removal rates (= initial film thickness / polymer removal time) were 0.17μm/min independent of exposure dose. This removal rate is comparable to the removal rate of 0.1μm/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 (×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.

because the maximum removal rate of the novolak resist can reach 2.5μm/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 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 $\lambda$ of atomic hydrogen is given by equation (1).

$$\lambda = \frac{1}{\sqrt{2Qn}} \tag{1}$$

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

$$Q = \pi(r_A + r_B)^2 \tag{2}$$

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 90 vol.% of the working gas. The radius of atomic hydrogen is 52.9 pm, and that of the $N_2$ molecule is 189 pm. The $n$ is estimated by total pressure in the chamber (21.3 Pa) and temperature. The temperature assumed is R.T., and the calculated $\lambda$ is 0.75 mm. This 0.75 mm is much smaller than the distance between the catalyster and the substrate (mold) (100 mm). There are 130 collisions between atomic hydrogen and $N_2$ molecules when the distance between the catalyster and the substrate (mold) is 100 mm. 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 catalyster. The cured polymers were removed by atomic hydrogen without leaving a residual layer. The removal rate rapidly increased with rising catalyster temperature because of enhanced the reactivity between atomic hydrogen and polymer and increased atomic hydrogen concentration due to a rise in catalyster temperature. When the hydrogen partial pressure was 2.13 Pa, the catalyster temperature was 2400°C, the distance between the catalyster and the substrate was 100 mm, and the initial substrate temperature was R.T., polymers with exposure doses of 50 to 200 mJ/cm$^2$ were removed at a rate of 0.17 µm/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 catalyster and the substrate was 100 mm, 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