Development of fabrication process for shape-controlled three-dimensional nanostructures

S. Fujinawa, F. Kato, and S. Sugiyama

Abstract

The fabrication process and technique for shape-controlled sub-micron structures by Synchrotron radiation X-ray lithography has been developed the technique also includes the structure-height control, therefore, a structure with high-aspect-ratio as high as 4 was achieved. The briefly introduced fabrication process is to deposit a PMMA (poly-methylmethacrylate) layer to a silicon substrate by spin coating. The layer is used as the X-ray resist. Subsequently, to expose SR onto the resist through an X-ray mask, then to develop the exposed resist. The principal shape-control is accomplished by optimizing each parameter influencing the resist formation, the exposed X-ray dosage, and development time. All mentioned above are the parameters determined from the fabrication of an arbitrary shape which is the main purpose in this paper. The targeted evaluation of fabricated structures is to provide the grating of 1μm pitch, 1.9μm line-height. The technique for optimization of the experimental condition varied by parameter influencing the fabrication process will be explained. The application of the targeted structure is mainly for optical elements e.g. lens, filter and a number of applications in device or system which requires sub-micron scale structures.

Department of Microsystem Technology, Graduate School of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

1. Introduction

High-aspect-ratio diffractive optical elements are expected for the application of multi-wavelength CD/DVD lens. The nano gratings have been on demand since the higher diffraction effects can be achieved from the higher aspect ratio structure and the structure-height corresponding to wavelengths used for the multi wavelength DOE. The diffractive gratings are typical passive elements for optical applications, e.g. high-resolution encoders, the spectroscopes, the hologram elements, and the switching elements. In Digital Versatile Disc (DVD) application, the shorter wavelength of the light allows a much smaller focused beam width. Future design soon to come is the Blue-Ray laser with a much shorter wavelength that will allow much greater data densities. The diffraction efficiency is great when the pitch becomes near the wavelength or when the aspect ratio is high, if the pitch and wavelength are away. The multi wavelengths pass through the DOE at once, the high-aspect-ratio structure is therefore, able to achieve a better diffraction efficiency. Consequently, a high-aspect-ratio nano diffraction grating will become more useful in the future. [1, 2]

At present, there are a number of techniques for fabricating diffractive optical elements including photolithography, the direct high-resolution printing, with diamond machine tools. These techniques are scales from tens to several microns. Other techniques using laser, UV, Electron Beam (EB) direct writing, Focused Ion Beam (FIB), and laser direct writing can fabricate sub-micron or nano scale structures. However, these processes do not have adequate throughput and difficult to accomplish the fabrication of high-aspect-ratio and controlled structure-height structures [3-5]. Contrary, X-ray lithography makes it possible to reach the high-aspect-ratio nanostructures. We, therefore fabricate the DOE based on X-ray lithography using PMMA (Poly-methylmethacrylate) as the X-ray resist. The processes including the discussion and the technique for structure-height control are provided in this paper.

2. Experimental Conditions

2.1 Fabrication Process

The fabrication processes are listed as in the following steps and schematically shown in Figure 1. At the first step, the interlayer is spin-coated onto the Si substrate with the use of silane coupling agent (APZ6633, Dow Corning Toray Co., Ltd) and following by PMMA resist (950 PMMA A11, MicroChem Corp.) spin-coated onto the interlayer. A 30μm-thickness spacer is then placed on resist to hold a gap of X-ray mask and the resist. The X-ray mask is finally placed upon the spacer. The X-ray mask made of 0.5 μm-thick Tantalum (Ta) absorber consists of submicron patterns. The 2.2 μm-thick silicon nitride (SiN) was used as the membrane. After an exposure by SR from the AURORA, the resist was then developed in the GG developer [6] at 37 ° C and following by the dipping the resist in the stopper liquid (80 vol% 2-(2-butoxy-ethoxy) ethanol, 20 vol% water) at 37 ° C. The resist was post-baked at 90° C for 30 min. after rinsed by pure-water at 37 ° C for 10 min.

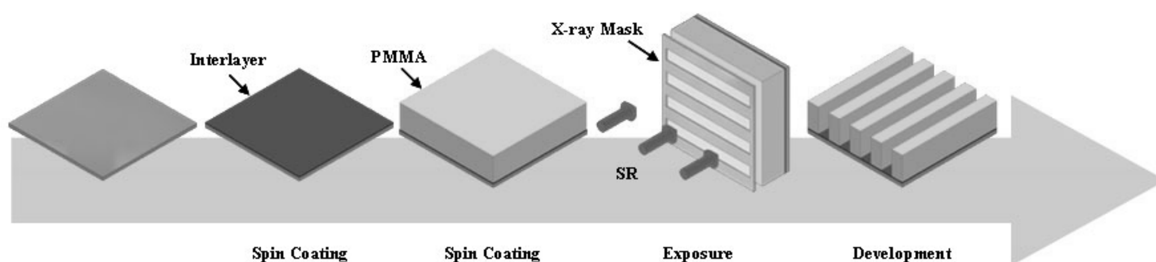


Fig. 1 fabrication process flow

2.2 Process Improvement

The improvement method of line-height is described in Table 1. The possible factors for an improvement of the line-height with their effects are shown below.

Table 1 list of improvement factors and influences

Improvement factor	Influence
Type of the substrate	Secondary exposure line bottom by secondary electrons
Type of the photoresist	Minimum line width of pattern
Resist thickness	Resist thickness must be thicker than the desired pattern height
Mask and resist gap (Proximity gap)	Light intensity distribution by diffraction after mask transmit
Mask contrast	Selected ratio of absorber and membrane
Exposure dosage	Influence of etching rate by developing
Type of the developer	Influence of etching rate and pattern shapes
Developing method	Influence of etching rate and pattern shapes
Developing time	Influence of etching rate and pattern shapes
Developer temperature	Influence of etching rate and pattern shapes

As referred to the above principle, the pitch and the line-height are important. However, structure pitch is depended on x-ray mask since the structure pitch of the x-ray mask is sufficient with 1.000μm. Therefore, from viewpoint of the structure, the line-height is consequently the most important. List of the selected influence is described in Table 1. In the improvement factor list, possible factors influencing the line-height are; resist thickness, exposure dose amount, and developing time. Other factors are not influencing the line-height. In our experiment, the following three experimental parameters were used. The resist thickness was optimized by controlling the spin-coating condition, exposure dosage and the development was optimized by the dipping time.

A control method of the specific line-height has been improved and is explained as following;

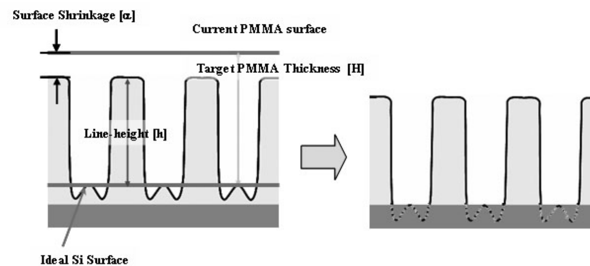


Fig. 2 Improvement method by controlled line-height

$$H = h + \alpha \quad (1)$$

Figure 2 shows the improvement method where H is the target PMMA thickness, h is the line-height, and α is the surface shrinkage. The structure spaces must be developed until reaching the interlayer. The reason is from the experimental result that undesired small-structures were formed at the bottom of spaces by the influence of Fresnel diffraction. The influence was controlled by exposure dose amount and developing time. It is noted that, PMMA thickness before exposure is to be controlled. The reason that PMMA thickness reduced after exposure through Ta absorber is understood by Eqs. 1, the target PMMA thickness needs a consideration of surface shrinkage.

2.3 Experimental Method

The experimental methods are classified into five phases.

2.3.1 Phase 1

The spin-coater speed for desired PMMA thickness has been indicated as Phase 1. The PMMA thickness was measured by using a thin-film measuring equipment (FILMeasure, Filmetrics, Inc). The experimental conditions were designed for 2 groups with six samples each varying by the spin-coater speed. For experimental group 1, the samples were spin-coated from 1500 rpm and stepping up by 500 rpm until 4000 rpm. Contrary, for the experimental group 2 the samples were spin-coated from 4000 rpm and stepping down by 500 rpm until 1500 rpm.

2.3.2 Phase 2

The dose amount and developing time for the desired line-height have been indicated as Phase 2. The developing time was controlled by dipping time in GG developer. The cross-section of the fabricated PMMA structure was measured by using a Field Emission Scanning Electron Microscopy (JSM-6700F, JEOL Ltd.,). In this experiment, the exposure dose amount was controlled from 0.0020 A.h. and stepped up every 0.0002 A.h. until achieving 0.0030 A.h. The developing time is varied from 6 min. and increased every 2 min. until 12 min. for each dose amount. Therefore, totally 24 samples have been experimented. It is noted that the all the samples were spin-coated with PMMA resist at 1500 rpm.

2.3.3 Phase 3

The dose amount and developing time to achieve the desired line-height have been determined as Phase3. Although in the experiment of Phase2, an exposure dose amount and a developing time were controlled, in this phase, exposure dose amount and development time are restricted from the result of Phase2 whilst the surface shrinkage is determined in addition. It is important to determine the surface shrinkage before the PMMA has been exposed under Ta absorber. The measurement equipment for PMMA thickness is the same as that of Phase 2. Six samples were experimented by six conditions as followings; exposure dose amount was 0.0025 A.h and developing time was 11 min and 12 min for samples No.1 and No.2 respectively. Exposure dose amount was 0.0028 A.h and developing time was 9 min and 10 min for samples No.3 and No.4 respectively. Exposure dosage was 0.0029 A.h and developing time was 6 min and 8 min for samples No. 5 and No.6 respectively.

2.3.4 Phase 4

The desired PMMA thickness before exposure has been determined as Phase4. Although in Phase1, the spin-coater speed has been taken into account, the desired PMMA thickness was also included according to the surface shrinkage acquired from Phase3. A spin-coater speed range was narrowed down from Phase1. Two experimental groups were conducted as followings. The experimental group 1 is the magnification of the experiment in Phase 1. The samples were spin-coated from 1500rpm and stepping up every 100 rpm until 2000rpm. The experimental group 2 is then improved from that of group 1. The samples were spin-coated from 1750 rpm and stepping up every 50 rpm until 1900 rpm

2.3.5 Phase 5

The desired L&S structure is eventually concluded in Phase 5. The PMMA thickness, the dose amount and the developing time, optimized from the results of the experiment in Phase 4 and Phase 3 respectively were collected (spin-coater speed of 1800 rpm, exposure dose amount of 0.0028 A.h, and development time is 10 min). We measured the sizes of L&S structure in the dimensions of radius on upper surface of lines, radius on bottom surface of lines and taper angle other than line-height and line-width.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Phase 1

As the purpose of Phase 1, indicator of spin speed for PMMA thickness has been considered. The experimental results indicating PMMA thickness is shown in Figure 3.

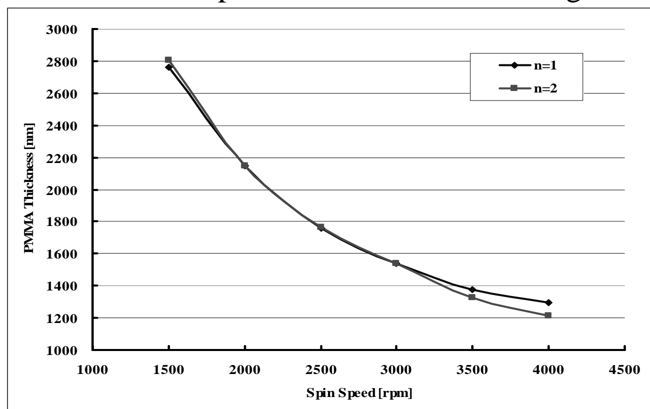


Fig. 3 The results from spin-coater speed VS PMMA thickness

Figure 3 shows the experimental data of PMMA thickness. The PMMA thickness of both experiments is in a uniform tendency as the spin speed is increased. The desired PMMA thickness was in the range of controllable spin-coater speed. It is noted that, the PMMA thickness has been decreased from the beginning. The possible reason is from the influence of solvent atmosphere around the spin-coater. This phenomenon is suppressed by spin coating PMMA on a dummy wafer in order to cover the spin-coater by PMMA solvent atmosphere. This result can be improved and discussed at Phase 4.

3.2 Phase 2

The purpose of Phase2 is to indicate the dose amount and development time for achieving the desired line-height. The experimental results are shown in Figure 4.

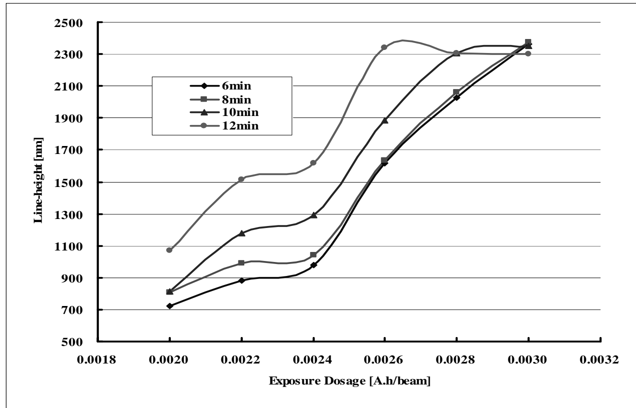


Fig. 4 The results from dose amount and developing time for a desired line-height

Figure 4 shows the experimental data of dose amount and developing time for a desired line-height. The height resulted from all experiments in this phase is in uniform tendency as the exposure dosage and developing time are increased. The desired line-height is in the range of controllable exposure dose amount and developing time. Therefore, this result can be improved and discussed at Phase3.

3.3 Phase 3

The purpose of Phase 3 is to optimize the dose amount and developing time for a desired line-height. The results are shown in Figure 5.

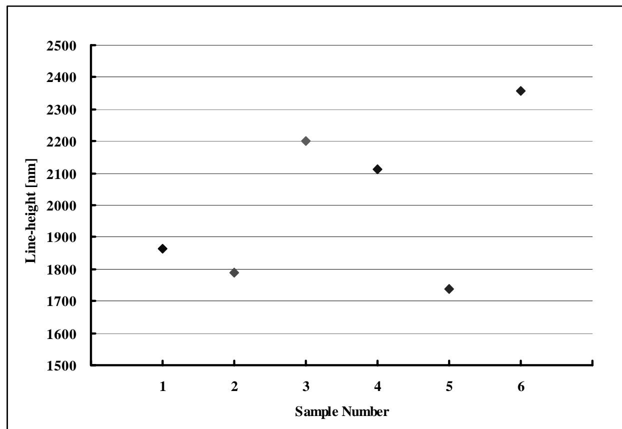


Fig.5 The results from dose amount and development time for a desired line-height

Figure 5 shows the experimental data of optimized dose amount and developing time for a desired line-height obtained from magnification of the experiment in Phase 2. Two considering points have been realized from this result; a taper degree and a surface shrinkage. The exact conditions of dose amount and developing time were investigated for minimizing the taper degree. The result before optimization showed that the exposure dose amount was too much, so called “over-dose”. Therefore, the optimized experimental condition becomes exposure dose amount of 0.0028 A.h and development time of 10 min. Moreover the surface shrinkage was considered to be 450 nm by the optimized condition. Thus, the desired PMMA thickness becomes 2350 nm (1900+450). These results can be used further at Phase 4 and Phase 5.

3.4 Phase 4

The purpose of Phase 4 is to optimize the spin speed for a desired PMMA thickness. The result of Phase 3, the optimized thickness is 2350 nm. The results are shown in Fig 6. In Figure 6(a), the desired PMMA thickness was achieved by spin-coater speed of about 1800 rpm. In Figure 6(b) the finer step of increasing spin-coater speed was used and the result confirms that the speed of 1800 rpm is optimum.

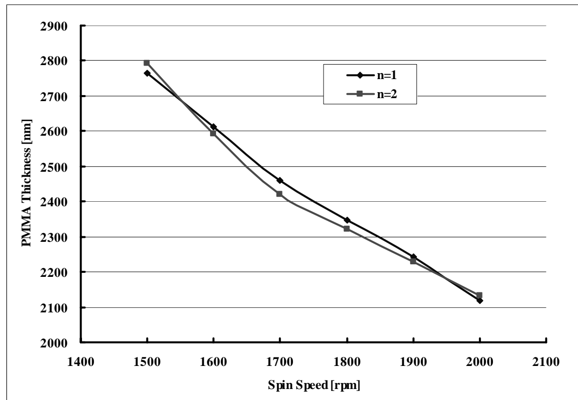


Fig.6 (a) The experimental data of PMMA thickness VS spin-coater speed improved from conditions in Phase 1
(n: number of experimental condition group)

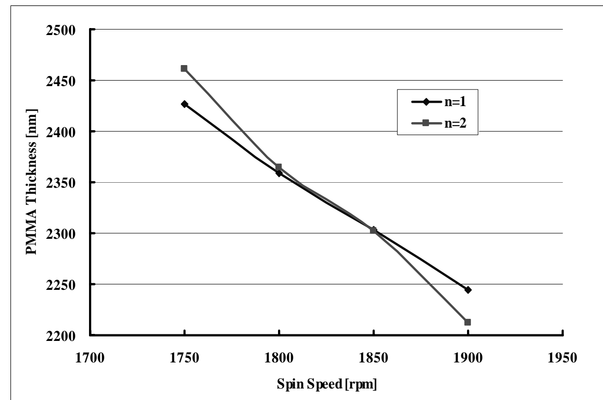
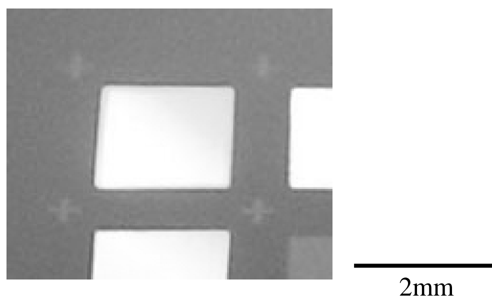


Fig.6 (b) The experimental data of PMMA thickness VS spin-coater speed magnified from the result in Fig.8(a)
(n: number of experimental condition group)

3.5 Phase5

The purpose of Phase 5 is to achieve the 500nm-L&S structure. The overall image of fabricated L&S structure in the 2 x 2 mm^2 section is shown in Figure 7 (a) with its close-up image shown in Figure.7 (b). The experimental results from each group indicated by parameter size are shown in Figure 8.



2mm

Fig.7 (a) A photo of 1μm -pitch L&S pattern

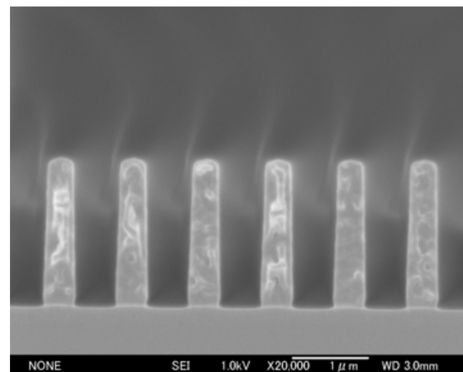


Fig.7 (b) SEM micrograph of 1μm-pitch sectional L&S for sample No. 4

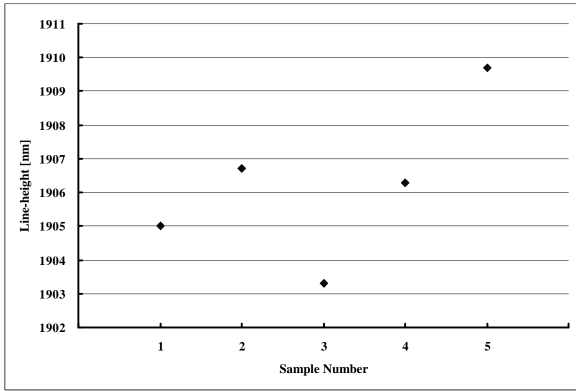


Fig.8 (a) Experimental results indicating line-height

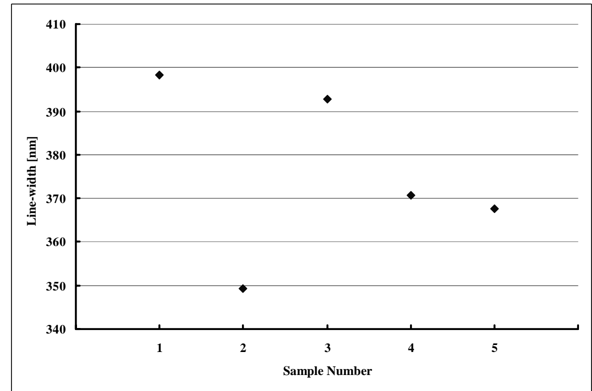


Fig.8 (b) Experimental results indicating line-width

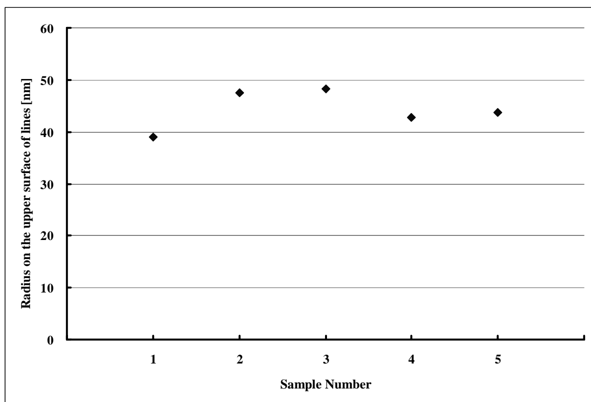


Fig.8 (c) Experimental results indicating radius on the upper surface of lines

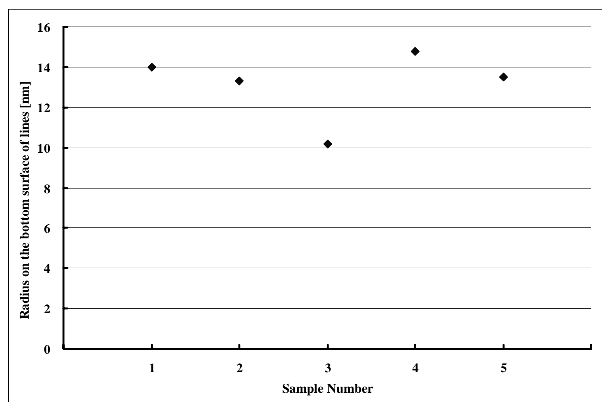


Fig.8 (d) Experimental results indicating radius on the bottom surface of lines

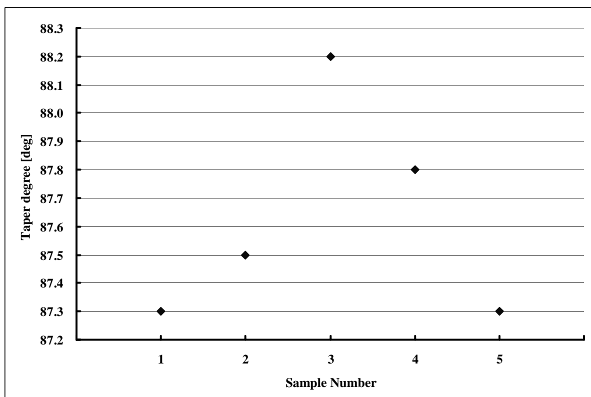


Fig.8 (e) Experimental results indicating taper degree

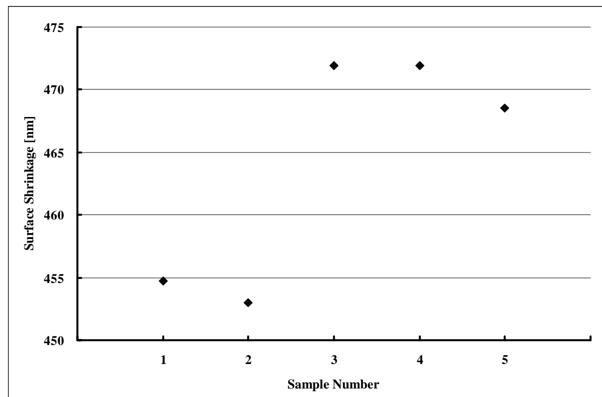


Fig.8 (f) Experimental results indicating surface shrinkage

The results in Figure 8 show that the L&S was fabricated with the actual height more than 1900 nm and the error was 0.5% of the desired height (Figure 8 (a)). The average line-width at 375 nm was fabricated which is narrower than the desired line-width. The effect was

caused due to the influence of proximity gap (Figure 8 (b)). The average radius on upper surface of lines was 44.3 nm (Figure 8 (c)). The average radius on bottom surface of lines was 13.2 nm (Figure 8 (d)). The average taper degree was 87.6 degree (Figure 8 (e)). The average surface shrinkage was 465nm (Figure 8 (f)). Consequently, these data have fulfilled the desired L&S size.

5. Conclusion

In this work, new fabrication process and experimental method for achieving controllable shape and dimensions of L&S structure has been developed based on SR lithography technique. Especially, to control the line-height, the following three parameters; spin-coater speed, exposure dose amount and developing time and the surface shrinkage have been realized and considered. The deformed structure resulted after the fabrication caused by Fresnel diffraction was suppressed. The experimental condition conducting the desired line-height was investigated empirically by optimizing the surface shrinkage of PMMA under Ta absorber and the taper angle of structure, and desired PMMA thickness before an exposure. We have tried to adjust the experimental conditions based on the possible influences to the fabrication. As the result, the fabrication of 1μm-pitch of PMMA L&S structure has become possible with 375 nm line-width and 1.9μm line-height which fulfilled the desired size. The error of line-height was found at 0.5%.

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