ヒートモードリソグラフィーによるZnS-SiO_2微細パターン形成技術

Nanometer-scale Patterning of ZnS-SiO_2 by Heat-mode Lithography

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要　旨

相変化型光ディスクの保護層として用いているZnS-SiO_2薄膜の特性を精査し，ナノメータスケールのパターン形成材料として用いる方法を見出した．本パターン形成方法では，簡便なレーザ加熱とウェットエッチング処理を用いるにもかかわらず，鮮明で滑らかなエッジのZnS-SiO_2パターンが形成できる．さらに，パターンサイズは，レーザビームスポットの1/4サイズまで縮小できる．本報では，ヒートモードリソグラフィーと呼んでいる，この低コストパターン形成方法を紹介する．

ABSTRACT

We investigated characteristics of ZnS-SiO_2 thin film used as a protective layer in phase-change optical disc and found that this thin film could be used for forming nanometer-scale patterns. In this method, ZnS-SiO_2 patterns with clear and smooth edge were formed even though using convenient laser annealing and wet etching treatment. In addition, the pattern size could be reduced to one-fourth the size of a laser beam spot. In this paper, we introduce this inexpensive patterning method that is calling heat-mode lithography.

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1. Introduction

Phase-change optical disc consists of a phase-change layer, such as AgInSbTe, $ZnS-SiO_2$ layers, and a metal layer. (1) The $ZnS-SiO_2$ layers are used as a protective layer, a reflectivity adjustment layer, and a thermal conductivity adjustment layer. Thus, $ZnS-SiO_2$ thin film is an important material in the phase-change optical disc. We investigated the wet etching characteristics and crystalline structure of $ZnS-SiO_2$ thin film and found that the $ZnS-SiO_2$ thin film could be patterned by laser annealing and wet etching treatment. (2) This patterning technique is based on a heat-mode recording technique for the optical disc, and we are calling it heat-mode lithography. In the field of optical disc, several authors have recently reported on the mastering methods for producing Blu-ray disc and next-generation optical discs by using heat-mode lithography, and this lithography technique is expected to become an inexpensive and high-throughput mastering method. (3-6)

In this paper, we introduce and describe the use of $ZnS-SiO_2$ thin film as a patterning material for heat-mode lithography. In other words, we present a new use for $ZnS-SiO_2$ thin film used as the protective layer in phase-change optical disc. In addition, we present a fabrication method of quartz master mold, which is skilful combination of heat-mode lithography and a dry etching process.

2. Wet etching characteristics

We describe the wet etching characteristics of the $ZnS-SiO_2$ thin film. Fig.1 shows a diagram of experimental procedure. The sample structure used in the experiment was Si substrate / ZnS (x%) - SiO_2 (100-x%) mixture thin film, and the ZnS mixture ratio (x%) was changed from 0% to 100%. The samples were annealed in a furnace and were dipped in a hydrofluoric acid (HF) solution after the annealing. Then, the etching rate and etching selectivity were calculated from the thickness changes of the ZnS (x%) - SiO_2 (100-x%) thin films.

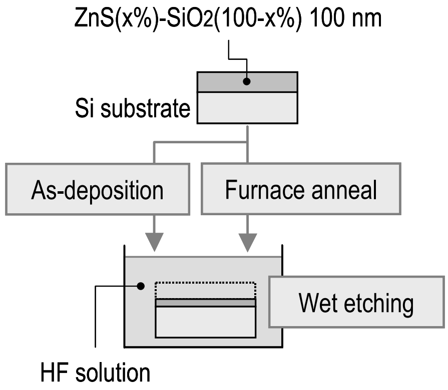


Fig.1 Experimental procedure for examination of wet etching characteristics.

Fig.2 shows the etching rate and selectivity in the as-deposited and annealed samples. The etching rate of the $ZnS-SiO_2$ thin film decreases with an increase in the ZnS mixture ratio (x%). In the case of x=80%, the selectivity was much larger than other mixture ratios. Thus, there was a large difference in the etching characteristics of $ZnS-SiO_2$ thin film between x=80% and other mixture ratios. In addition, the etching selectivity of $ZnS-SiO_2$ thin film at x=80% was more than 10, which was large enough to be used as a patterning material when using HF solution.

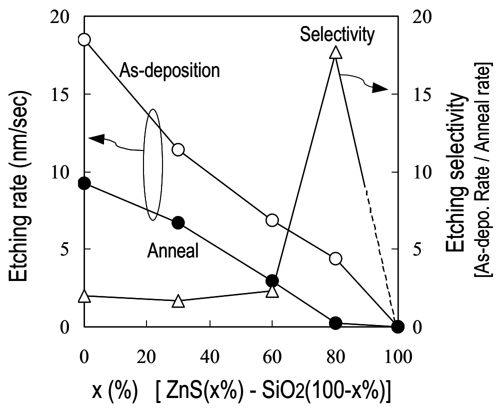


Fig.2 Etching rate and selectivity of ZnS (x%) - SiO_2 (100-x%) thin film.

3. Structural analysis

The ZnS-SiO_2 thin film at x=80% has a sufficiently large etching selectivity, which is an appropriate characteristic for the patterning material in heat-mode lithography. The structure of the ZnS-SiO_2 thin film and the structural change by annealing were investigated in order to determine the reason for the large etching selectivity.

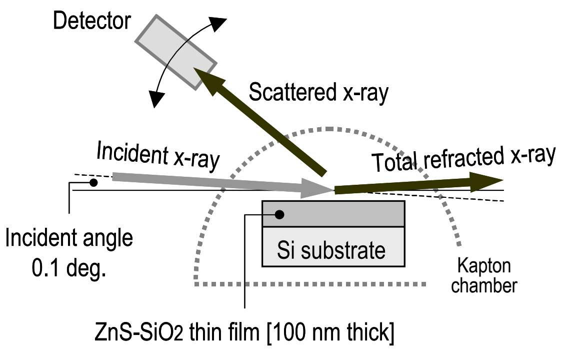


Fig.3 Grazing incidence x-ray scattering (GIXS) measurement method.

Synchrotron radiation measurement of the ZnS-SiO_2 thin film was performed at SPring-8. Grazing incidence x-ray scattering (GIXS) with a multi-axes diffractometer installed at BL46XU was used to examine the structures of the as-deposited and annealed thin film. Fig.3 shows a diagram of the GIXS measurement method. The sample was mounted in a chamber filled with He gas. The x-rays irradiated the sample surface at an incident angle of 0.1°. Only scattered x-rays from the thin film were selectively detected by irradiating the x-ray at such a low angle.

Fig.4(a) shows the x-ray scattering profile and (b) shows the radial distribution function (RDF) of the as-deposited thin film at x=80%. The RDF was derived from the x-ray scattering profile. (7) In the Fig.4(b), the horizontal axis represents the averaged atomic distances. The neighboring atomic distances in a tetrahedral network structure of the ZnS crystal are 2.3 Å and 3.8 Å, which correspond to the Zn-S and Zn-Zn distances,

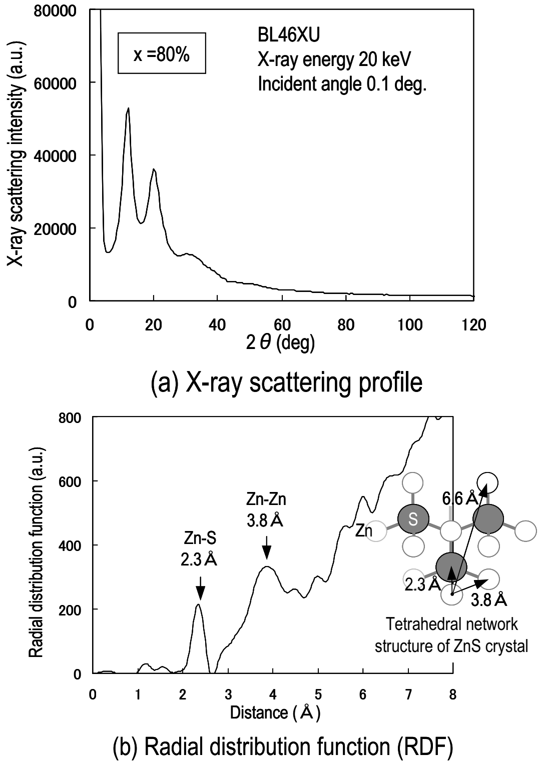
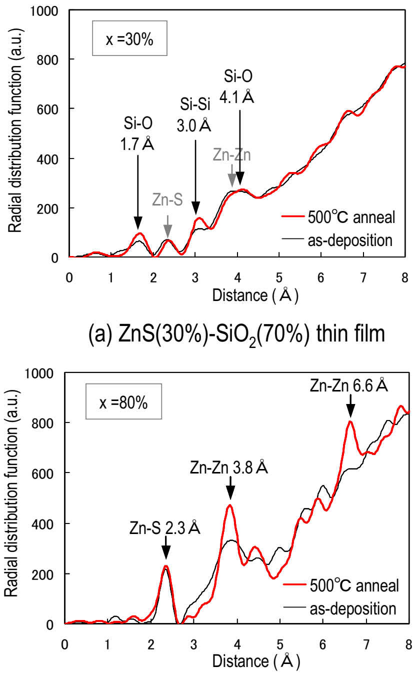


Fig.4 GIXS measurement of as-deposited ZnS (80%) - SiO_2 (20%) thin film.

respectively. The RDF shows that the tetrahedral network structure like ZnS crystal exists in the as-deposited ZnS-SiO_2 thin film.

The wet etching selectivity of the ZnS-SiO_2 thin film strongly depended on the ZnS mixture ratio (x%), and the selectivity of x=80% was much larger than that of x=30%, as shown in Fig.2. So, the RDF of each thin film was compared. Fig.5 shows a comparison of the RDF between the as-deposited and annealed ZnS-SiO_2 thin films. Even after annealing, the RDF of x=30% did not changed, as shown in Fig.5(a). On the other hand, the RDF of x=80% was notably changed by the annealing, as shown in Fig.5(b). The peaks at 3.8 Å and 6.6 Å correspond to the Zn-Zn distances in the tetrahedral network structure of the ZnS crystal. The change of the RDF profile suggests that the ZnS grains in the ZnS-SiO_2 thin film at x=80% were crystallized by annealing.



(a) ZnS(30%)-SiO_2(70%) thin film

(b) ZnS(80%)-SiO_2(20%) thin film

Fig.5 Comparison of RDF between as-deposited and annealed ZnS-SiO_2 thin film.

Fig.6 illustrates a model for the structural change of ZnS-SiO_2 thin film caused by the annealing, which was derived from the GIXS measurement. The ZnS-SiO_2 thin film is consisted from a ZnS grain and a SiO_2 grain. In the case of x=30%, the ZnS grains are dispersed in a matrix that is composed of SiO_2 grains. We assume that the SiO_2 grains isolate the ZnS grains, because there is more SiO_2 grain content than ZnS grain content. On the other hand, the ZnS grains are in contact with each other in the ZnS-SiO_2 thin film at x=80%. The closed ZnS grains are grown by the annealing, and the grown ZnS grains surround the SiO_2 grains. In the wet etching process, the HF solution dissolves the SiO_2 grains, and a lift off of ZnS grains occurs in the matrix. In the case of x=80%, the ZnS grains grow enough to surround the SiO_2 grains during the annealing process, and the grown ZnS protects the SiO_2 grains from the HF solution. Therefore, the etching tolerance of ZnS-SiO_2 thin film at x=80% is increased by the annealing. Thus, the crystallization of the ZnS grains by the annealing is the reason of the large wet etching selectivity in the as-deposited and annealed thin film.

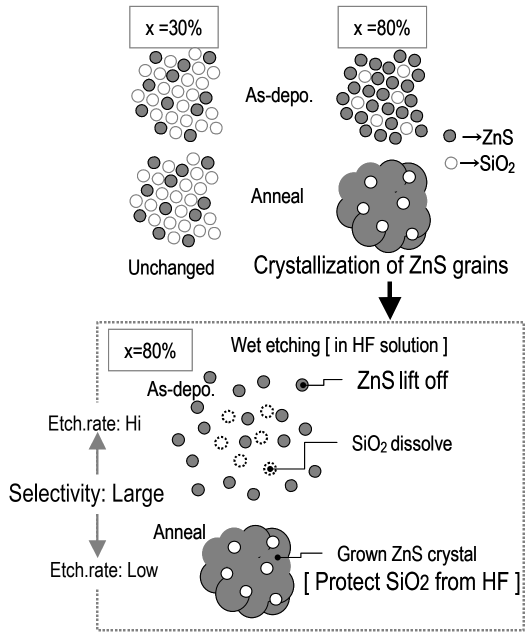


Fig.6 Model of structural change by annealing and etching characteristics of ZnS-SiO_2 thin film.

4. Patterning of ZnS-SiO_2

We estimated the ZnS-SiO_2 thin film at x=80% could be appropriately used as a patterning material for the heat-mode lithography by examining the wet etching characteristics and the structural analysis. So, we investigated the performance of this thin film as a patterning material. The ZnS-SiO_2 thin film at x=80% was compared with other mixture ratios in the viewpoint for clearness of pattern edge.

Fig.7 shows the patterning method for the ZnS-SiO_2 thin film, which is based on the laser annealing and wet etching treatment. The structure of this sample was a polycarbonate substrate / lower ZnS-SiO_2 layer (50nm) / AgInSbTe layer (20nm) / upper ZnS (x%) - SiO_2 (100-x%) layer (45nm). The ZnS mixture ration (x%) was changed from 30 to 100%. In this structure, the AgInSbTe layer was used as an optical absorption layer, and the upper ZnS-SiO_2 layer as a patterning layer. Fig.7(b) shows the laser annealing process. An optical disc tester was used, and the optical pickup consisted of a 405-nm laser diode (LD) and an objective lens with a 0.85 numerical aperture (NA). When a focused beam was irradiated onto the sample, the structure of the ZnS-SiO_2 thin film changed with a heat transmission from the AgInSbTe layer. Fig.7(c) shows the wet etching process. After laser annealing, the upper ZnS-SiO_2 layer was removed by the etching in the HF solution. Fig.7(d) shows the sample structure after the wet etching. The laser-irradiated part of the upper ZnS-SiO_2 layer remained, even after the etching. The convex patterns of the ZnS-SiO_2 were formed by this method.

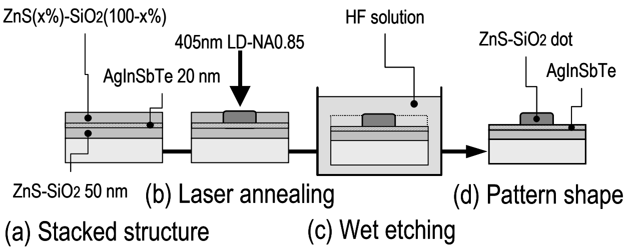


Fig.7 Patterning method of ZnS-SiO_2 thin film by heat-mode lithography.

Fig.8 shows SEM images of ZnS-SiO_2 dots. The ZnS-SiO_2 thin film at x=30% could not be patterned and the upper layer was completely removed, as shown in Fig.8(a). The ZnS-SiO_2 thin film at x=60% could be patterned, as shown in Fig.8(b). However, the edges of ZnS-SiO_2 dots were unclear. The ZnS-SiO_2 thin film at x=80% could be patterned and the edges of ZnS-SiO_2 dots were clear and smooth, as shown in Fig.8(c). And, the thin film at x=100% that was only ZnS was not a bit etched in the HF solution. Thus, the patterning of ZnS-SiO_2 thin film was markedly related to the ZnS mixture ratio (x%), and we could form ZnS-SiO_2 dots with clear and smooth edges by optimizing the mixture ratio for x=80%. There is an optimum ZnS mixture ratio for patterning ZnS-SiO_2 thin films, because the SiO_2 grains control the crystallization of ZnS grains, as shown in Fig.6.

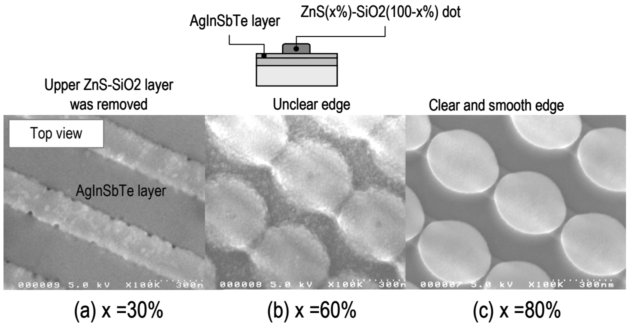


Fig.8 SEM image of ZnS-SiO_2 dot pattern.

Fig.9 shows an SEM image of the convex ZnS-SiO_2 pattern, which was formed by making adjustments to the taper profile of the convex pattern. The sample structure was a polycarbonate substrate / lower ZnS-SiO_2 layer (50nm) / AgInSbTe layer (20nm) / upper ZnS (80%) - SiO_2 (20%) layer (200nm). The taper profile of the convex ZnS-SiO_2 was almost perpendicular, as shown in Fig.9. The height of the convex ZnS-SiO_2 was approximately 200nm, which was nearly equal to the as-deposited thickness of the upper ZnS-SiO_2 layer. Thus, the taper profile of the convex ZnS-SiO_2 was very steep. This is a feature of the ZnS (80%) - SiO_2 (20%) thin film used as a patterning material.

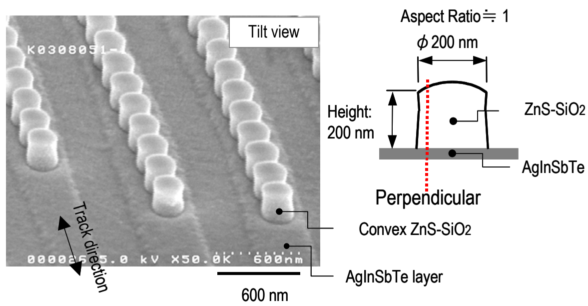
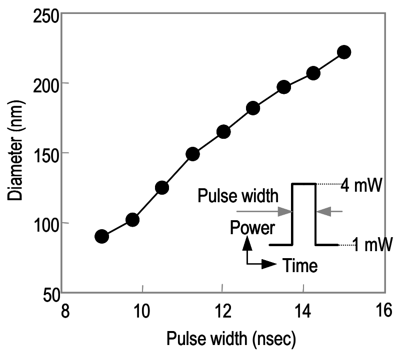


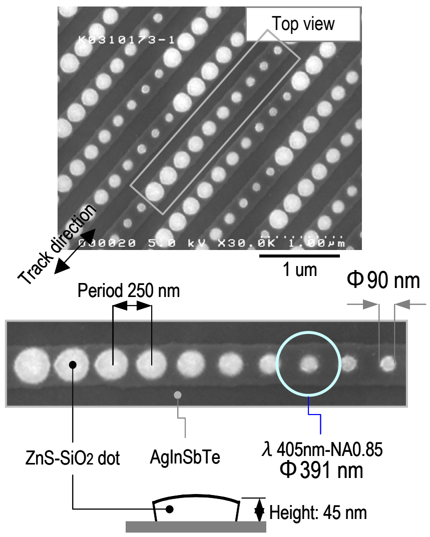
Fig.9 SEM image of convex ZnS-SiO_2 pattern. Convex ZnS-SiO_2 with perpendicular taper profile was formed.

We tried to find the minimum size of the ZnS-SiO_2 dots, as shown in Fig.10. The sample structure was a polycarbonate substrate / lower ZnS-SiO_2 layer (50nm) /

AgInSbTe layer (20nm) / upper ZnS (80%) - SiO_2 (20%) layer (45nm). The relationship between the laser pulse width and the diameter of ZnS-SiO_2 dots is shown in Fig.10(a). The diameter of the ZnS-SiO_2 dots was modulated by changing the laser pulse width, and the diameter changed in proportion to the laser pulse width. Fig.10(b) shows SEM images of the ZnS-SiO_2 dot pattern. The period of ZnS-SiO_2 dots was 250nm, with a maximum diameter of 220nm and minimum diameter of 90nm. The edges of the ZnS-SiO_2 dots were clear and smooth, as shown in the SEM images. The minimum diameter was about 90nm, which was approximately one-fourth the size of a laser beam spot from a 405-nm LD with a 0.85 NA objective lens.



(a) Relation of laser pulse width and diameter of ZnS-SiO_2 dot



(b) SEM images of ZnS-SiO_2 dot

Fig.10 Modulation for diameter of ZnS-SiO_2 dot by changing laser pulse width.

From the viewpoint of minimum size and the edge clearness of the formed patterns, we believe that ZnS-SiO_2 thin film could be used as a patterning material for forming nanometer-scale patterns.

5. Fabrication of quartz mold

Quartz is a useful material as a master mold for light assist imprinting processes, because of its high-transparency. Therefore, the ZnS-SiO_2 pattern was applied to a hard mask for the dry etching process, and quartz molds with dot and line patterns were fabricated. We describe the fabrication process for the quartz mold and the shape of quartz patterns.

Fig.11 shows the fabrication process of the quartz mold. The ZnS-SiO_2 thin film was patterned by heat-mode lithography, as shown in Fig.11(a). The convex pattern of the ZnS-SiO_2 was used as the hard mask for the dry etching process, as shown in Fig.11(b). Finally, the hard mask was completely removed by wet etching in an acid solution, as shown in Fig.11(c). The shape of the ZnS-SiO_2 pattern was transferred onto a quartz substrate using this method, as shown in Fig.11(d).

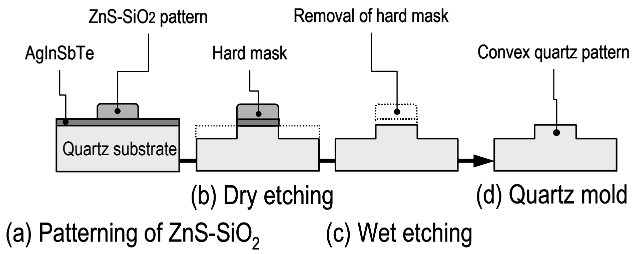


Fig.11 Quartz mold fabrication process.

Fig.12 shows an SEM image of a convex quartz pattern. The pattern height was 220nm and the period was 400nm. The top of the convex pattern was flat and the edge was very steep. This pattern shape proves that the ZnS-SiO_2 hard mask has a sufficient etching tolerance for the dry etching process. Fig.13 shows an SEM image of the quartz pattern in which the sizes were modulated by changing the laser pulse width during the laser annealing process noted in Fig.7(b). The minimum size of the quartz dot was 90nm in diameter. This size was approximately one-fourth the size of a laser beam spot from a 410-nm laser with a 0.9 NA objective lens.

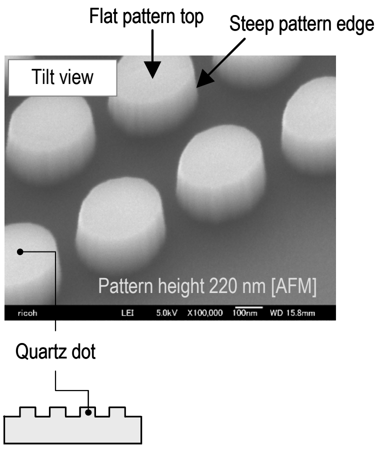


Fig.12 SEM image of convex quartz pattern.

Fig.14 shows SEM images of the line patterns. The shape of the quartz line and that of the replicated pattern were examined. A photo-polymerization (2P) method was used for the replication process, and the line pattern was replicated onto a 2P resin by using the quartz pattern as a master mold. The groove width of the quartz pattern was about 100nm, and the land width of the replicated pattern was about 100nm. It should be noted that the edge of the quartz line was smooth and that of the replicated line was also smooth.

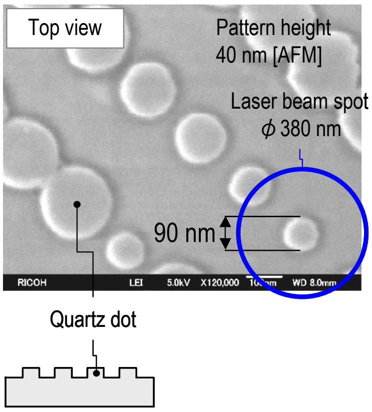


Fig.13 SEM image of quartz dot pattern.

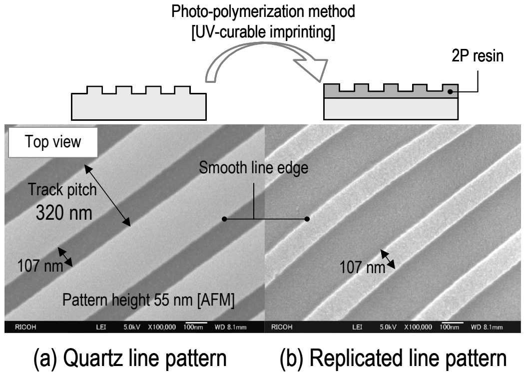


Fig.14 SEM image of quartz line and replicated line pattern.

Thus, the ZnS-SiO_2 pattern was used as the hard mask for the dry etching to fabricate the quartz molds. The minimum size of the quartz dot pattern was approximately one-fourth the size of the laser beam spot, which was the same as the minimum size of ZnS-SiO_2 pattern, and the line edge smoothness was maintained even in the replicated pattern.

6. Summary

The crystallization of the ZnS grains by annealing was the cause of the large wet etching selectivity in as-deposited and annealed ZnS-SiO_2 thin film. This characteristic was used to form ZnS-SiO_2 patterns. Optimizing the ZnS mixture ratio for 80% helped to form a convex ZnS-SiO_2 pattern with clear and smooth edges. The minimum pattern sizes were approximately one-fourth the size of a laser beam spot from a 405-nm laser diode. Furthermore, the ZnS-SiO_2 pattern was used as the hard mask for forming quartz molds using the dry etching process, and we fabricated quartz molds with clear and smooth pattern edges.

The edge quality of a pattern such as clearness and smoothness is very important for optical discs, because it markedly affects the quality of the readout signal. Therefore, the ZnS-SiO_2 thin film is useful as a patterning material for producing master molds of optical discs. In addition, the quartz molds will be widely used as master molds for light assist imprinting processes to fabricate luminescence and optical devices composed of nanometer-scale patterns.

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