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Fine pattern imprint lithography using dimpled mold

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Fine dots fabrication using dimpled mold is demonstrated with narrow gaps between neighboring dots. An inverted pyramidal dimpled mold is fabricated by the novel method utilizing the peculiarity of an anisotropic wet chemical etching to form narrow gaps. By this method, the nano-imprinting mold for a quantum dot array with narrow gaps is fabricated beyond the resolution limit of conventional lithography. The optimum imprinting conditions such as imprinting pressure, temperature, sequence, cooling procedure and surface treatment for the mold and substrate are investigated by preliminary experiments using the test mold, which has 2 to 10 μm square dot arrays. Based on the preliminary experiments, 250nm-pitched dot array is successfully fabricated by the fine mold with narrow gaps.
Keywords: imprint lithography, mold, dot, isotropic etching

1. Introduction

Nano-imprint lithography[1] is one of the fantastic candidates to compensate the low productivity of direct electron beam lithography, because the mold can be used repeatably once fine patterns are fabricated on the mold. Recently, various papers have reported this technology.[2-6] The nano-imprint lithography is expected to apply to not only VLSI's fabrication but also to optical devices. There are some problems to make this technology practical use for fabrication of advanced integrated circuits.

One of the problems is that the resolution is dominated by the mold pattern, which is generally fabricated by direct electron beam lithography. In electron beam lithography, narrow spaces are hard to fabricate by the proximity effect[7].

On the other hand, the nano-imprinting is mainly carried out using the projecting mold, which produces hole or space patterns. When nano-imprint lithography is applied to the fabrication of the single electron tunneling devices[7], dot patterns have to be placed keeping the gaps less than several nano-meter to induce a single electron tunneling between the quantum dots.

In this paper, fine dot pattern fabrication by dimpled mold with narrow gaps is demonstrated using dimpled mold with inverted pyramidal shaped patterns.

2. Mold Fabrication

The fabrication process of the dimpled mold with narrow gap patterns is shown in Figure 1.[9] The holes array pattern is fabricated by direct electron beam lithography. The holes are formed keeping the offset angle to the <110> crystalline axis on (100) plane surface. The primary gap size is determined by the electron beam lithography. Then, an anisotropic wet chemical etch is performed. After the anisotropic etch, inverted pyramid shaped holes with (111) plane surface are formed and the gap become narrower than the originally gap. After removing the resist, the mold pattern with narrow gaps is obtained, which is capable to induce a single electron tunneling. Figure 2 shows the resist pattern by direct electron beam lithography. The 100nm hole array with 100nm gap is patterned over 40 μm square area on Si substrate. The beam energy is 50KeV and the resist is 70nm thick PMMA (ZEP-5000). Figure 3 shows the fabricated mold pattern after anisotropic wet chemical etch by 22wt% TMAH

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(Tetramethyl ammonium hydroxide) at 40℃ for 90s. Fine dimpled pattern with narrow gaps around 10nm is fabricated.

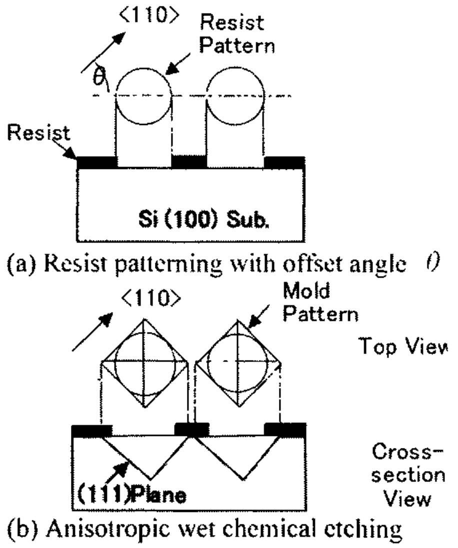


Fig.1. Mold fabrication process based on off-set angle method.

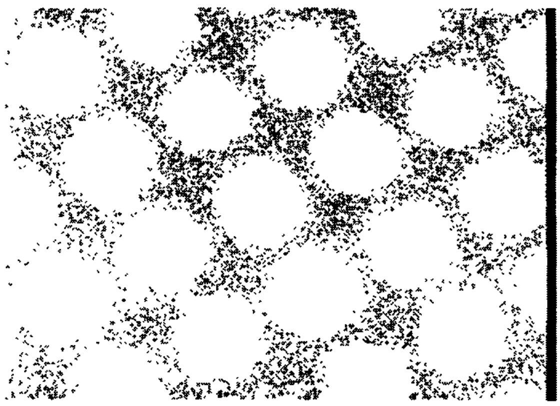


Fig. 2. 100nm hole array patten with 150nm space. Beam energy=50KeV, 160nm PMMA on Si.

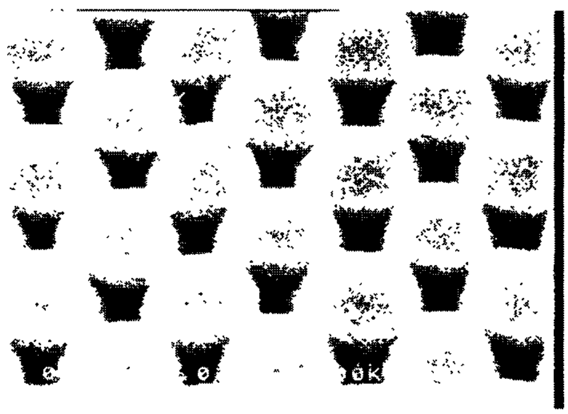


Fig.3. Mold pattern after anisotropic wet chemical etching. TMAH 90 s., 40℃. The gap among dimples is around 20nm or less.

3.Imprint Experiments

3.1. Imprinting Machine

For the imprinting process, there are some difficulties to complete perfect imprinting in nanometer scale. One of them is an imprinting machine. We modified the commercial available air press machine for imprinting. Figure 4 shows the photo of the modified hot-press machine for imprint lithography.

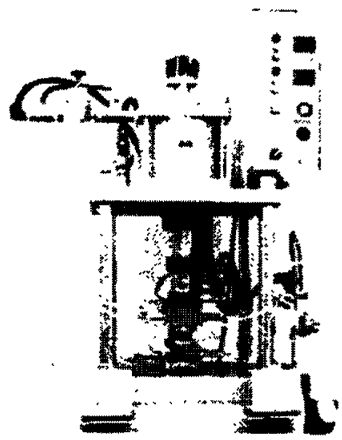


Fig. 4. Photo of the modified hot-press machine for imprint lithography. The maximum load is 1500Kgf and the stage temperature is controlled up to 200℃.

In the imprinting process, the mold should vertically press the resist on the substrate. One of the problems is surface flatness of the machine stage, which will affect the pressure uniformity in the imprinting field. Also, the mold should be put parallel to the substrate to keep the imprinting pressure to be uniform in the mold and to avoid lateral slipping of the mold. To solve these problems, the surface of the stage is finished by mirror polished and a spherical seat is placed upon the mold as shown in Fig. 5.

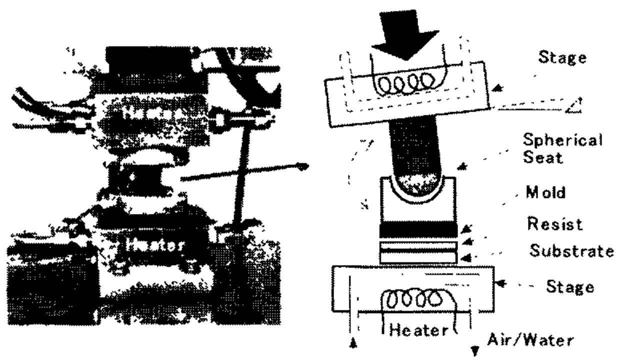


Fig. 5. Photo of the remodeled hot-press machine for imprint lithography.

The mechanical property of the resist is an another important factor for the specification of the machine. The rigidly of the resist polymer generally decreases over the glass transition temperature. In case of PMMA (poly methyl methacrylate), the shear modulus decreases to be less than 10 MPa over glass transition temperature (around 110℃), while it is around 1 GPa at room temperature[10]. This fact implies that imprinting is suitable over the glass transition temperature because the polymer becomes easy be deforme by mechanical force. So, the temperature of the stages is controlled up to 200℃.

3.2. Preliminary Experiments

3.2.1. Imprinting Process

Before examining the nano-meter scaled pattern fabrication using the above discussed molds, large patterns whose size are 2 to 20 μm squares and lines are examined in order to optimize imprinting conditions. This is because the larger mold is easy to fabricate by conventional photo lithography and also it is easy to evaluate the results by optical microscope or by scanning electron microscope.

The test patterns for the preliminary experiments are shown in Fig. 6. The trial mold size is 5mm square and the offset angle θ is zero. Figure 7 shows the imprinting sequence. The mold and the resist on the substrate are pre-heated. The mold is pressed upon the resist and held. After cooling the stage, the mold is released. All processes are performed in air ambient.

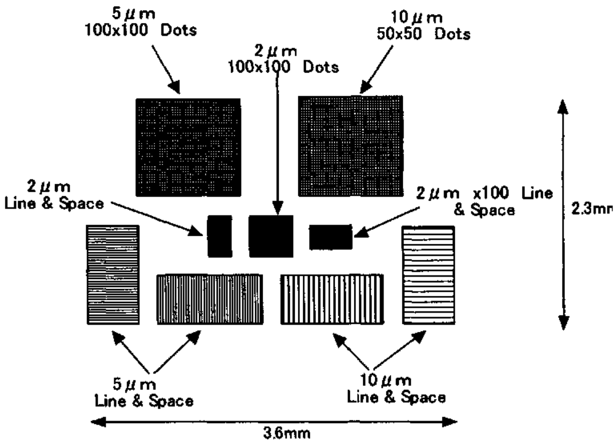


Fig.6. The trial mold pattern for preliminary experiment.

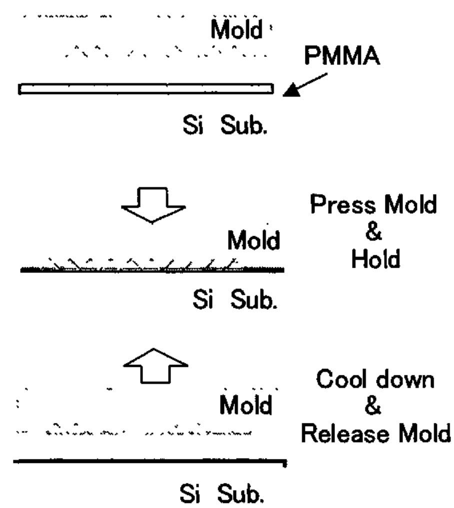
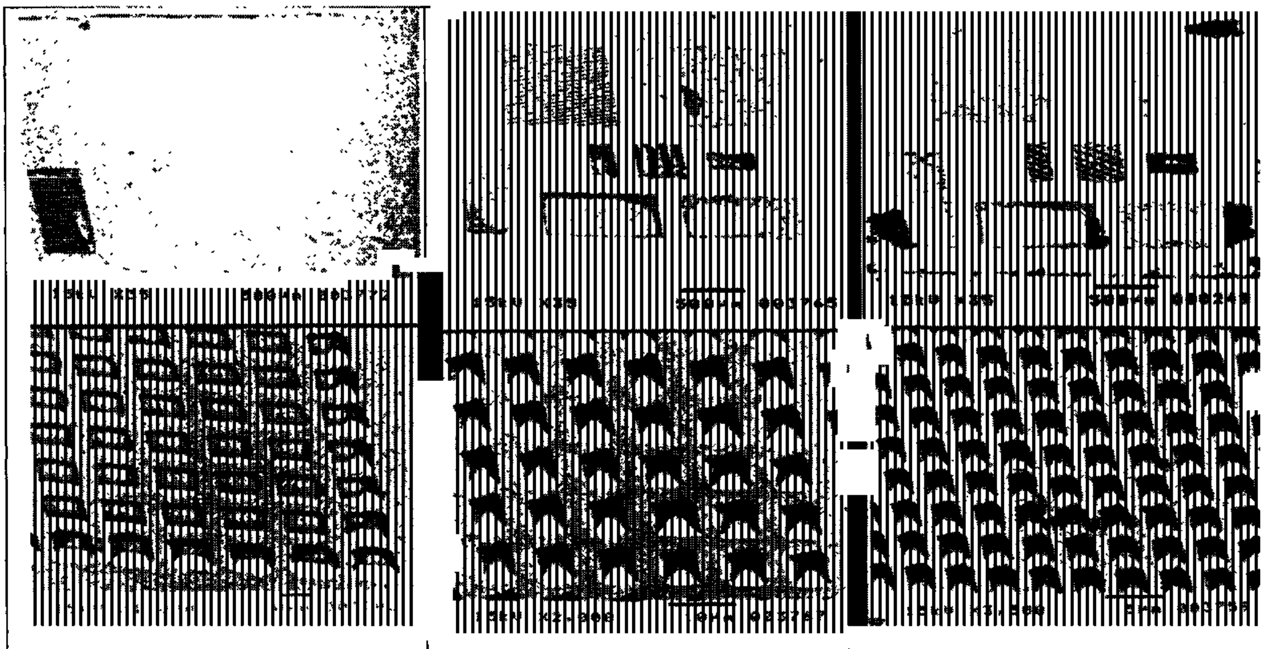


Fig.7. Sequence of the imprinting



(a) Sample 1 (50MPa)	(b) Sample 2 (110MPa)	(c) Sample 3 (160MPa)

Fig.8. SEM photo of the pre-experimental results by the test mold fabricated by photo lithography (1.6μm PMMA on Si, Press temp.;170℃, Release temp.;60℃ by air cooling for 30 minutes)

The examined conditions are shown in Table 1. The 1.6 μm thick PMMA is spin-coated on Si substrate and baked at 170℃ for 30 minute. The imprinting pressures are varied from 50 MPa to 160 MPa. The imprinting process sequence is shown in Table 2. As the rigidly of the resist changes around the glass transition temperature Tg, the resist is pressed above Tg and it is released below Tg.[9]

Table 1. Conditions for preliminary experiments

Sample No.	Pressure MPa	Press Temp. ℃	Cooling
1	50	170	Air
2	110	170	Air
3	160	170	Air
4	110	140	Air
5	110	170	Water

Table.2 Imprint sequence and conditions

Process	Conditions
1. Press	:50～160MPa,140～170℃
2. Hold	:5min
3. Cooling	:Air/Water in Press
4. Release	: at 60℃ after 5min hold

3.2.2. Imprinting Pressure

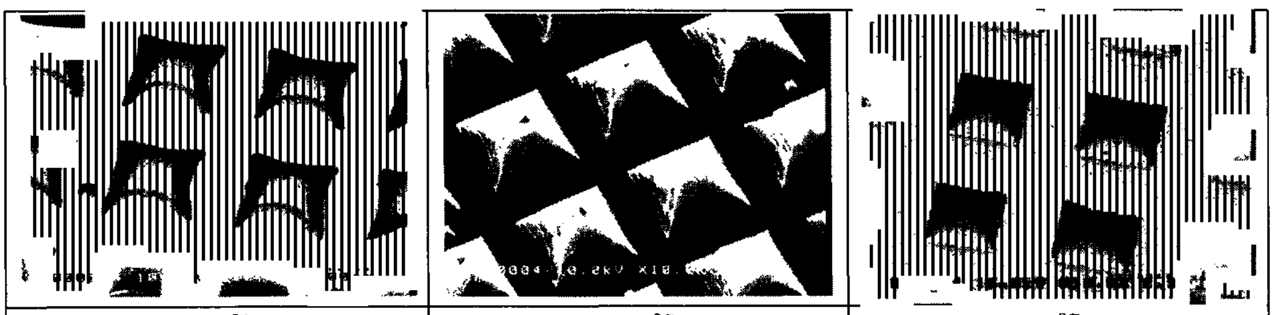
Figure 8 shows the experimental results by the test mold for various imprinting pressures. The upper shows over-view of the imprinted resist patterns and the lower shows the enlarged photo for typical pattern. When the mold is pressed at 50MPa, only a part of the pattern is transferred, and the imprinted pattern is not perfect as shown in Fig.8 (a). At 110MPa, the dot array patterns are clearly transferred. Fine pyramidal array patterns are fabricated, but the lines patterns are partially transferred and a part of the dot array patterns peel from the substrate. At 160 MPa, the resist peels much more. These results indicate that the mold patterns can not be sufficiently transferred to the resist at low pressure. However, the imprinting by high pressure causes peeling off the resist from substrate. In this case, the suitable pressure for imprinting is between 110 to 160 MPa. Those values are relatively higher than those of other reports. Since those have been imprinted mostly by the projecting mold, the pressure is concentrated at the tip portions of the mold.

3.2.3. Imprinting Temperature and Cooling

Figure 9 shows the dependency of resist profiles upon the imprinting temperatures and cooling procedures. When the imprinting is performed at 140℃as shown in Fig.9 (a), the mold patterns are incompletely transferred. The imprinting temperature at 140℃ is not enough for imprinting because the rigidly of the resist is not sufficiently low for large deformation. The cooling procedures are also evaluated. We compared air cooling and water cooling. It takes 40 minutes to cool from 170℃ to 60℃ by air cooling and 3 minutes by water. The resist profile by water cooling is the as same as the profile by air cooling.

3.2.4. Surface Treatments

The adhesion properties of the resist to the substrate are also examined. The resist should strongly stick to the substrate, but not to the mold. Table 3 shows the adhesion yield of the resist for various surface treatments. Before spin coating of the resist, the surface of the substrate is treated by Hexa methyl disilazane (HMDS) for replacement of active hydrogen by sililation. In the case of PMMA, spin coating of the HMDS is effective beside vapor treatment. On the other hand, the mold surface is hydrogen terminated by diluted HF etch for preventing of the resist adhesion to the mold. The experimental results



(a) Sample 4 (140℃/Air cooling) (b) Sample 2 (170℃/Air cooling) (c) Sample 5 (170℃/Water cooling)

Fig.9. SEM photo of the pre-experimental results by the test mold fabricated by photo lithography (1.6 μm PMMA on Si, Imprinting pressure:110 MPa, Release temp.;60℃)

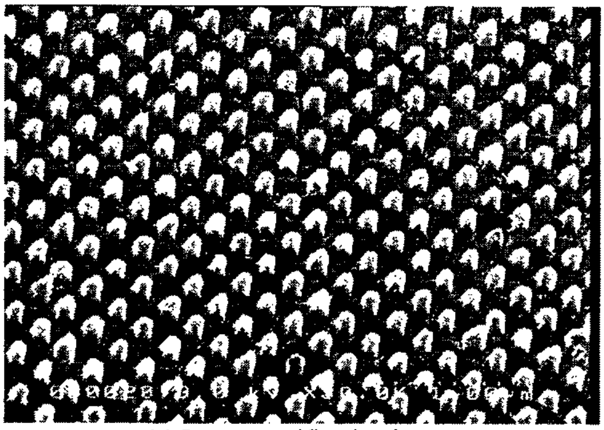
show that HF etch is effective for mold treatment to prevent sticking of the resist.

Table3. Adhesion yields for various surface treatments of the substrates before resist coating

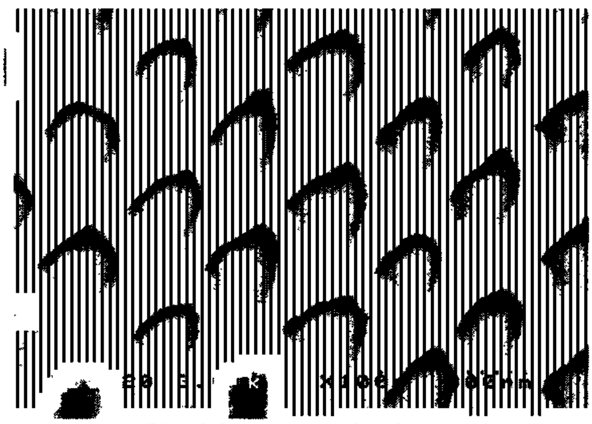
Mold surface treatment	Spin coating	Dipping	Exposing in Vapor
Diluted HF etching	50~80%	0%	0%
Non (Native oxide)	~30%	0%	0%

3.3 Nano Imprinting using Fine Mold

Based on the preliminary experiments, the imprinting using fine dimpled mold as shown in Fig.3 is performed at 160 MPa, 170°C. There are 25 patterns in the 5mm square mold. Each pattern is 40μm square field. Figure 10 shows the imprinted patterns.



(a) Low magnification image



(b) High magnification image

Fig.10. High resolusion SEM images of the imprinted dot patterns (250nm pitch, 70nm PMMA on Si, at 110 MPa, 170°C, Air cooling down to 60°C).

250nm pitched dot array pattern is successfully fabricated for 40μm square area. But the pattern profile is not completely pyramidal shape and the gaps are larger than the mold pattern.

4. Conclusions

Imprint lithography of dot pattern is studied using a pyramidal dimpled mold. The hot-press imprint machine is newly assembled with a spherical seat to keep the mold parallel to the substrate. Optimum imprinting conditions such as imprinting pressure, temperature and sequence are found by the preliminary experimental studies using several micron patterns. Based on the preliminary studies, pyramidal dimpled array pattern having 250nm pitch is imprinted to the PMMA resist and fine dot array pattern is successfully fabricated. However, the mold profile is not perfectly transferred to the resist.

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