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Formation of High Contrast Periodic Corrugations by Optimizing Optical Parameters of Photoresists in 325nm Laser Holographic Exposure

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Formation of high contrast periodic corrugations by using laser holographic exposure is investigated. This paper first describes optical parameters of several positive acting photoresists extracted from UV spectra analysis. Conventional g-line photoresists have high values in the parameters and might not be suitable for this purpose. Next, corrugation-shapes are simulated using other optical parameters as well as developing process properties in three typical g-line photoresists. Both s- and p-polarized plane-wave difference and substrate dependence are also considered. As a result, the corrugation-shapes mainly depend on γ values of the photoresists. High contrast corrugations and highly reproducible process are expected if optimum photoresist are selected. Finally, we fabricate high contrast periodic corrugations with a period of 255 nm, which is in good agreement with the theoretical estimation.

1. Introduction

Formation of periodic corrugations is very important for integrated optic devices. In most cases, since the period of the corrugations required is of the order of a micrometer or less, conventional photolithography could not be applied. Hence, one most widely used technique is laser holographic exposure. In general, however, the corrugation there has just sinusoidal shape in cross-section and therefore is of low contrast. Also, the process reproducibility is not very good. Lately, an excellent exposure system was reported(1), where positive feedback elements were utilized for keeping the interference pattern against the perturbations caused by vibration, air currents, and others. In this paper, we describe formation of high contrast corrugations which have large aspect ratio and high process tolerance with conventional exposure optical system. It was achieved by optimizing optical parameters of photoresists in a 325nm He-Cd laser holographic exposure system thoretically and experimentally.

2. Positive acting photoresists and optical parameters

Positive acting photoresists (posi-resists) are composed of a photoactive agent (dissolution inhibitor), an alkali soluble base resin, and an organic solvent system. Although they have weak points that they are harder and more brittle than negative acting photoresists, they are superior in their resolution, dry-etching resistance and process simplification. Hence, in this study we used this kind of resists. For posi-resists the absorption of light by the photoactive inhibitor can be used as a tag for this agent. This absorption decreases as the compound is destroyed. The decrease is localized in the immediate region where the destruction occurs. In general, these resists are described by next three optical parameters(2) : A, an exposure absorption dependent term ; B, an exposure independent absorption term ; C, an optical sensitivity term. Furthermore, concerning to development which is one of the distinct parts in the photoresist process, the etching or dissolution rate (R), as a function of relative inhibitor concentration (M), is quite important. This function R(M) describes the development process for a resist and developer chemistry(3). First of all, "A-" and "B-" optical parameters of several different posi-resists were extracted from UV spectra analysis. Figure 1 shows the values of " A+B " as functions of exposure wavelength. Obviously, g-line (436nm) photoresists have high values at 325nm and might not be suitable for high contrast corrugations, because they might result in low sensitivity and degradation of the shape. For i-line (365nm) resists, however, both parameters were suppressed and almost constant in the range of 325 to 436nm. This suggests these resists might be fairly suitable for this laser holographic exposure. The examination in detail will be set forth later. First, we simulated corrugation-shapes of well-established three typical g-line posi-resists. Also, we calculated both s- and p-polarized plane-wave interference effect. Furthermore, difference of the substrate (GaAs or Si) was examined.

3. Intensity in the photoresist

In calculation of corrugation-shapes, we can apply the optical exposure system using the phase-shift (PS) mask. When the incident beam enters PS-mask, several odd-mode diffraction lights are generated. By setting up an optimum projection lens to remove the high-order diffraction lights, we could obtain only fundamental $\pm$1st-order lights. On the surface of the resist, two plane-wave beams interfere and form the peridic corrugations. This condition is identical

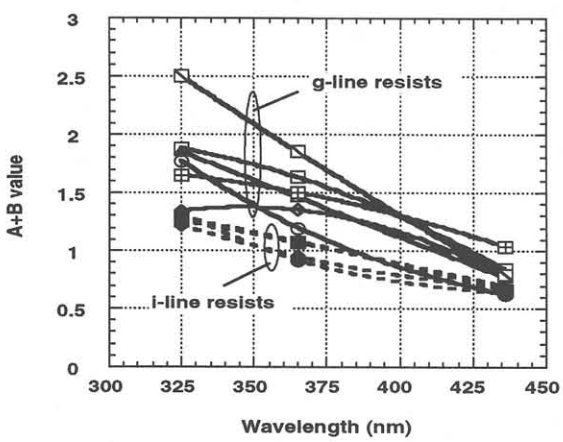

Fig.1 Optical parameters of posi-resists as functions of wavelength

with the experimental holographic exposure optical system. In order to obtain the intensity distribution in the planar layer of photoresist, the scalar model is quite versatile. In this case, however, some calculation error was induced by the physical phenomena such as imaging by reflected waves in the resist, vectorial interference and the like. Hence, we applied the Yeung's vectorial model[4] based on the theory of thin-film optics. The intensity distribution G(x,y) in the image plane is given by Debye integral[5]. In the laser holographic exposure, we should only treat the part of coherent image formation which is based on the Abbe's principle. Hence, the equation which we solve is shown below:

$$G(x,y) = \left| \iint_{-\infty}^{\infty} \tilde{a}(f,g)\ \tilde{P}(f,g) \bullet \exp\left[2\pi i\left(fx+gy\ \right)\right] df dg \right|^2, \tag{1}$$

where $\tilde{a}(f,g)$ is the amplitude of the Fourier transform of the object labeled with (f,g), $\tilde{P}(f,g)$ is the exit-pupil function of the projecton lens whose (x,y)-component of the direction cosine is ($-\lambda f$, $-\lambda g$). Next, we calcluated the intensity profiles in typical three resists. Every parameter is shown in Tabel I. A-, B- and C-parameters are the values at 325nm. Also the γ -values for i-line and g-line are inclusive of post exposure bake (PEB) procedure. Figure 2 shows the constant-intensity contours in the resists on GaAs in the case of incident beams of equal intensity. They are normalized by the exposure energy of unit area which entered the PS-mask. Every resist thckness is 0.1 μ m and 0.3 μ m. Bulges are produced in the resist between the grooves at standing wave minima 0.1 μ m and 0.2 μ m from the substrate, and constrictions appear at standing wave maxima 0.05 μ m and 0.15 μ m from the substrate. Obviously, type-gC resist has a distict standing wave which is caused by the low imaginary part of refractive index. In the experimental film thickness 0.1 μ m, however, we do not have so much difference in the intensity distributions of the three resists.

4. Calculation of corrugation-shape and comparison with experimental results

In order to obtain the cross-sectional corrugation-shape, we used the most accurate and simple "string model"[6] for development process. Also photoactive agent concentration (M) is obtained from the Dill's formula[2].

Polarization dependence For the high contrast of corrugations, s-polarized light (s-light) is more profitable in spite of low exposure energy compared to p-polarized light (p-light). Hence, in this experiment we used s-light. This effect is caused by the difference of interference mode, which means that s-light and p-light is the interference scalarly and vectorially. A corrugation aspect ratio for the case with s-light is about 10%-higher than the case with p-light.

Substrate dependence The difference of both substrates of GaAs and Si could be mainly caused by the reflectivity distinction. In 325nm wavelength, GaAs has about 15%-higher reflectivity than that of Si extracted from the refractive index[7]. Hence, concerning to exposure energy, GaAs is more advantageous.

Developing-time dependence Here, we simulated the shape of corrugations about three g-line resists. Calculation conditions are shown next ; s-light, GaAs substrate, 0.1 μ m-resist thickness and a period of 255 nm which corresponds to a 2nd-order diffraction grating in GaAs DFB lasers. Figure 3 shows the cross-sectional transitions of periodic corrugations for every resist. The exposure condition and developing times are also shown in Fig.3. Apparently, type-gA resist has well-known sinusoidal shapes which is just affected by the incident beam interference profiles. In this case, however, the allowance of process is quite narrow, in other words, the corrugations vanished only 30 seconds after beginning to develop. In the case of using type-gB or gC resist, the allowance could be extremely improved. Furthermore, in these cases, the shapes are oblong and the aspect ratios are very high.

Experimental In fabricating periodic corrugations, first, substrates were spin-coated with diluted photoresists of several kinds. The thickness was about 100nm after baking for 30min. at 90℃. Two spherical s-polarized beams from a 10mW He-Cd laser at 325nm via 5μm ϕ pinholes were merged on the photoresists to form an interference pattern. Figure 4 shows cross-sectional SEM photographs of type-gA and gB resists. Comparison with Fig.3 shows that agreement between the theoretical and experimental results are excellent. It is obvious that high-quality periodic corrugations are obtained when the optimum photoresist is

Table I Optical parameters of posi-resists

Resist	A (μ m^{-1})	B (μ m^{-1})	C(cm^2/mJ)	γ (i-line)	γ (g-line)	comment
Type-gA	0.82	0.95	0.016	1.27	1.69	conventional
Type-gB	1.26	0.62	0.015	1.44	2.27	new
Type-gC	1.04	0.30	0.016	1.86	3.44	the newest

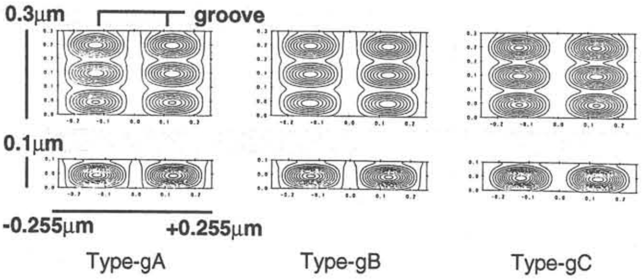

Fig.2 Constant-intensity contours in resists

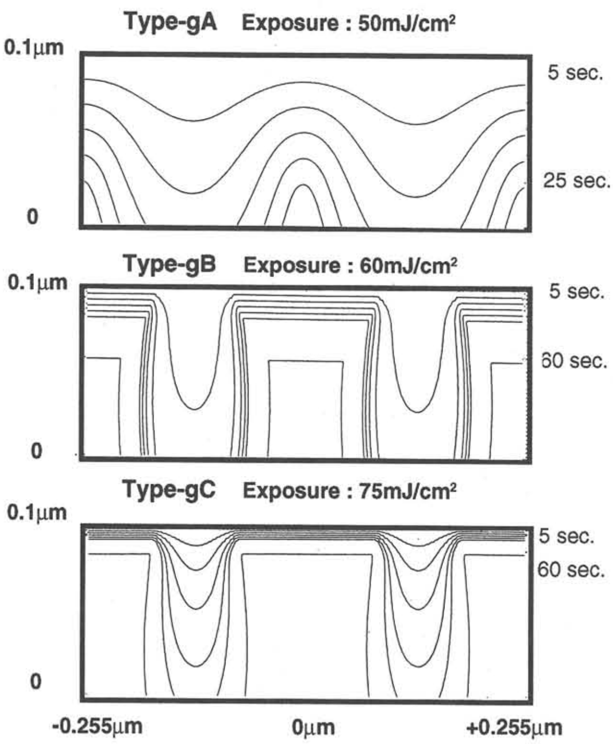

Fig.3 Cross-section shape of corrugations
development time
Type-gA : 5,10,15,20,25sec.
Type-gB and gC : 5,10,15,20,25,60sec.

used. As a result, the corrugation-shape mainly depended on γ value of the photoresists in addition to low values of "A" and "B". Hence, in the case of using type-gC which has an extermely high γ -value, the corrugation-patterning is quite difficult because of requiring so much exposure energy. High contrast corrugations and highly reproducible process are expected if optimum photoresist is selected.

5. Application of i-line photoresists

As mentioned before in Section 2, i-line resist could be feasible for this purpose, because of their low "A-" and "B-" parameters and high γ values. This suggests that it could form high contrast corrugations in low exposure energy. Here, we shall try a typical i-line resist "Type-iD" experimentally. The exposure system is the same as before. SEM photograph is shown in Fig.5. The result obtained agreed approximately with those expected. Obviously, we

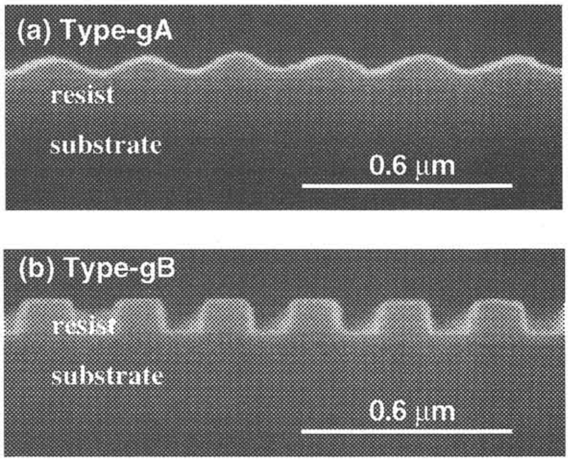

Fig.4 SEM photographs of cross-section shape using two g-line resists
Exposure : (a) 45mJ / cm² (b) 55mJ / cm²

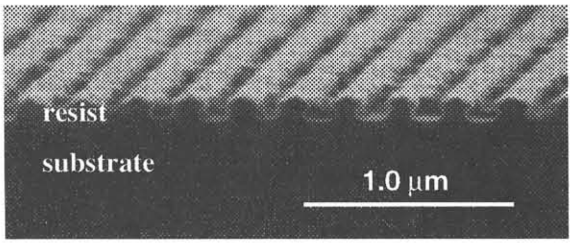

Fig.5 SEM photograph of cross-section shape using i-line resist **Exposure: 40mJ / cm²**

could obtain the oblong and high-contrast shape despite low energy.

6. Conclusions

Formation technique for periodic corrugations has been investigated theoretically and experimentally, by placing emphasis on optical parameters of photoresists. Consequently, high contrast corrugations were obtained along with high reproducibility by using posi-resists having optimum optical parameters. This result is very useful for fabrication of diffraction gratings in various kinds of opto-electronic devices.

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