FABRICATION OF PHASE OPTICAL ELEMENTS
BY ION-EXCHANGE IN GLASS

P. Senthilkumaran, P. J. Masalkar and R. S. Sirohi

Applied Optics Laboratory, Physics Department
Indian Institute of Technology, Madras 600 036, INDIA.

(Received May 19, 1993 and Revised Received December 21, 1993)

ABSTRACT

Phase optical elements have unit amplitude transmittance and have phase transmittance
values between $-\pi$ and $+\pi$. Normally fabrication of phase elements is done either by
recording intensity pattern on a photographic plate and bleaching it or by transferring the
intensity pattern on to photoresist coated plate to get corresponding phase variation. This
paper presents a way of making phase optical elements through ion-exchange in glass.
As examples phase gratings and phase zone plates were fabricated and their
performances were studied.

1. INTRODUCTION

There are wide varieties of optical elements working on the principles of reflection,
refraction, diffraction, interference, polarization and so on. Diffractive optical elements
have unique place in optics. Holographic optical elements work on the principle of diffraction.
In computer generated holography coding schemes rely on the principle of diffraction to
realize phase recording. So there is a need to find methods to fabricate efficient
diffractive optical elements. The phase optical elements are more efficient than
amplitude optical elements working on the principle of diffraction.

Many works have been reported on ion-exchange process for making optical
waveguides. Recently Yatagai et al. [1] reported on the fabrication of phase only
holograms using ion-exchange process and optimized the maximum phase difference
that must be introduced on the wavefront so as to have maximum first order diffraction
efficiency [2, 3].

Phase optical elements fabricated by ion-exchange in glass have certain advantages
over those fabricated on photoresist or by bleaching process. Elements fabricated by
bleaching process have problems like emulsion shrinkage, moisture sensitivity of gelatin
and so on. These problems persist even if dichromated gelatin is used as the recording
medium. In the case of phase elements fabricated on photoresist, cleaning these elements
poses difficulty, since photoresist is soluble in many of the organic liquids normally used
for cleaning. All these elements are more vulnerable to physical damage like scratches
compared with phase elements fabricated by ion-exchange process in glass. Phase
elements fabricated by ion-exchange process do not suffer from problems which are
associated with bleached optical elements and elements fabricated on photo-resist.
2. ION-EXCHANGE IN GLASS

In this process monovalent alkali ions from glass are exchanged with a different monovalent ions from a salt melt or metallic thin film at a high temperature. Fick's laws of diffusion govern the exchange of ions. The change in composition of glass due to ion-exchange causes a change in its refractive index which is proportional to the concentration of the ions that have diffused into glass. Electric field can be used to enhance the ion-exchange. The concentration of the index modifying ions embedded inside glass due to the field assisted ion-exchange is given by [4]

\[
\frac{\partial C}{\partial t} = \frac{D_a}{1 - \alpha C} \left[ \nabla^2 C + \frac{\alpha (\nabla C)^2}{1 - \alpha C} - \frac{e\vec{E} \cdot \nabla C}{kT} \right]
\]

(1)

where \(\alpha = 1 - \frac{D_a}{D_b}\); \(D_a\) and \(D_b\) are the coefficients of diffusion of the ions diffusing into and out of glass respectively, \(C\) is the concentration, \(e\) the electronic charge, \(k\) the Boltzmann's constant, \(T\) the temperature and \(\vec{E}\) the applied electric field. The boundary conditions for Eqn. (1) depend on the method of ion-exchange and the geometry.

When the concentration \(C\) is small, the change in refractive index of glass is linearly proportional to the concentration itself, and the stress induced in glass structure due to the difference in the size of the exchanging ions is negligible. The refractive index is then given by

\[
n(x, y) = \Delta n_{\text{max}} \cdot C(x, y) + n_0
\]

(2)

where \(C(x, y)\) is the normalized concentration distribution in glass, \(n_0\) is the refractive index of the base glass and \(\Delta n_{\text{max}}\) is the maximum change in refractive index.

In order to fabricate the phase optical elements, we have used \(\text{Na}^+ \leftrightarrow \text{Ag}^+\) exchange in soda-lime glass from diluted \(\text{AgNO}_3\) melts. A metallic aluminium mask pattern was lithographically deposited on the glass surface and the ion-exchange was carried out through the openings in the mask at 300°C without electric field i.e., \(|\vec{E}| = 0\). The melt used was 1:1 : : \(\text{KNO}_3 : \text{NaNO}_3\) with 2% mole of \(\text{AgNO}_3\) melt. A diluted \(\text{AgNO}_3\) melt is used to avoid the formation of colloidal silver in glass which occurs in concentrated melts. The 1:1 : : \(\text{KNO}_3 : \text{NaNO}_3\) melt has the melting point at 220°C facilitating work at a lower temperature compared to melts diluted with \(\text{NaNO}_3\) alone which have a melting point near 310°C.

The ratio of self diffusion coefficients \(D_{\text{Ag}}/D_{\text{Na}}\) in sodium silicate glasses is 0.1 [5], thus \(\alpha = 0.9\). The maximum change in refractive index \(\Delta n_{\text{max}}\) depends on the glass composition and melt concentration and the coefficient of diffusion \(D_{\text{Ag}}\) which is a function of temperature. The values of \(\Delta n_{\text{max}}\) and \(D_{\text{Ag}}\) are obtained from the profiles of multimode planar waveguides reconstructed using IWK method [6]. We used the soda-lime glass for which the refractive index was 1.512, maximum change in refractive index \(\Delta n_{\text{max}}\) was 0.075 for the 2% mole \(\text{AgNO}_3\) melt and \(D_{\text{Ag}}\) was found to be \(1.2 \times 10^{-12}\) \(\text{m}^2/\text{s}\) at 300°C.

The values of \(\alpha, \Delta n_{\text{max}}\) and \(D_{\text{Ag}}\) thus obtained were used in the simulation of the fabrication process. This simulation is based on numerical solution of Eqn. (1) with
appropriate boundary conditions. We used the Alternating Direction Implicit Finite Difference Method for the numerical solution [7]. The boundary conditions for ion-exchange through a mask opening are shown in Fig. 1. The results of simulation are shown in Fig. 2. An opening of 23 μm is considered, and the contours show the refractive index profile; the refractive index values are also indicated.

\[
\frac{dC}{dy} = 0: \quad |x| \geq w/2
\]

\[
C = C_0: \quad |x| < w/2
\]

Fig. 1 Boundary conditions for ion-exchange process.

Fig. 2 Simulation of refractive index profile.

Using the above mentioned technique we have fabricated phase gratings and zone plates. This paper presents details of fabrication process and the performance of these optical elements.
3. OPTIMIZATION OF THE ION-EXCHANGE PROCESS

Binary linear gratings were used for obtaining optimum conditions of the ion-exchange process. The (s/d) ratio of these gratings is 0.575 and the pitch is 0.04 mm. The gratings were transferred on to the glass, and examined under the microscope for any defects etc. The concentration of silver nitrate, potassium nitrate and sodium nitrate were kept constant (AgNO₃ : KNO₃ : NaNO₃ = 2:49:49 mole %) during the trial runs. The temperature of the melt was kept at 300°C ± 5°C for all the experiments. Many runs were made by varying the diffusion time. The diffraction efficiency of ion-exchange produced gratings were measured, and Fresnel reflection corrections were applied. Fig. 3 shows the variation of diffraction efficiency as a function of diffusion time. Assuming a binary phase grating, the maximum diffraction efficiency for (s/d) = 0.575 should be 38.31% [8]. Maximum diffraction efficiency of 33.1% was obtained experimentally.

![Graph showing variation of diffraction efficiency Vs time](image)
Under the experimental conditions the maximum diffraction efficiency was obtained for the diffusion time of about 115 min. The lower efficiency is due to the ion-exchange gratings not being binary phase grating.

4. FABRICATION OF PHASE ZONE PLATE

The binary amplitude zone plate (Axicon-Modulated Zone plate) was supplied by one of the authors of ref. [9]. It has wide openings at the centre which decrease as we go radially outwards. The diameter of the central ring (opening) is 90 μm and the pitch at the edge of the zone plate is 2.5 μm. Due to the lateral diffusion, the fine details get obliterated in the ion-exchange process as has been demonstrated by Yatagai et al. [2, 3]. Therefore zone plate makes an interesting object of study by ion-exchange process. The binary amplitude zone plate is transferred on to the glass plate and ion-exchange process is carried out to obtain the phase zone plate. To carry out the ion-exchange process the zone plate mask is deposited on the glass substrate by lithographic process. The lithographic process carried out using Shipley 1400-27 positive photoresist is shown in Fig. 4(a-g). The substrates were baked at 200°C for at least one hour, cooled and then the photoresist was spin coated on the surface at a speed of 4000 rpm to give a layer of about 1.0 μm thickness (Fig. 4a). After coating, the substrates were kept at 80°C for 30 minutes to remove any residual solvent present. Then the photoresist layer was exposed with Ultra-violet radiation through lithographic mask having opaque lines of width equal to that the windows to be made in the masking layer (Fig. 4b). After exposure the resist was developed using Shipley MF-319 Microposit developer. During development, the resist which had been exposed to Ultra-violet radiation gets etched at a higher rate than the unexposed resist and leaves behind a ridge structure as shown in Fig. 4c. The substrates are then baked at 120°C for an hour to remove the residual moisture. An aluminium film is then vacuum deposited on this surface (Fig. 4d). It was found that a thorough ionic cleaning of the substrate for at least ten minutes was necessary to ensure good adherence of the aluminium film to the substrate. The windows are then opened in the aluminium film (Fig. 4e) by removing the resist ridges by placing the substrate in boiling acetone for a few minutes. The ion-exchange is carried out for a specific time duration by placing the substrate in the melt : the ions diffuse through the openings (Fig. 4f). After the ion-exchange process is over the aluminium mask is etched out using NaOH solution to leave behind the phase optical element which has selected regions with different refractive index (Fig. 4g).

To check the uniformity of diffraction efficiency over the surface of the phase zone plate, it is scanned with a narrow beam (100 μm diameter) and variation of diffraction efficiency in first order is studied. It is found that the diffraction efficiency shows a variation of the type given in the Fig. 5 emphasizing the fact that the details at 2.5 μm have been significantly obliterated.

In order to study the refractive index variation in the phase zone plate, particularly in the central ring, a Mach-Zehnder interferometer is assembled, and adjusted for tilt fringes. The zone plate is inserted in one of the beams and imaged on the recording plane using a lens. The interferogram thus recorded is shown Fig. 6. The influence of
**Fig. 4a** Photoresist coated glass substrate.

**Fig. 4b** UV exposure through the lithographic mask.

**Fig. 4c** Photoresist pattern after etching.

**Fig. 4d** Aluminium thin film coating over the photoresist pattern.
Fig. 4e Lift-off process (etching) to make windows for ion-exchange process.

Fig. 4f Ion-exchange process.

Fig. 4g Phase optical element obtained in the ion-exchange process.

Fig. 4(a-g) Fabrication details for the ion-exchange process.

refractive index variation may be seen in the central ring. The maximum phase departure is estimated to be 138°.

5. PERFORMANCE ANALYSIS OF ZONE PLATE

The transmittance of a binary phase amplitude zone plate can be represented in the series form [10]

\[ t(r) = \frac{1}{2} + \frac{1}{\pi i} \sum_{n=-\infty}^{\infty} \frac{1}{n} \exp \left[ \frac{in\pi r^2}{r_1^2} \right] \]  (3)

where \( n \) is an integer; \( r_1 \) is the radius of the first zone and \( r \) is a variable representing the radial distance from the centre of the zone plate. The transmittance function for an axicon MZP is given by [9]
Fig. 5 Graph showing variation of diffraction efficiency vs distance from the centre of the zone plate.

Fig. 6 Interference pattern obtained from Mach-Zehnder interferometer configuration showing the refractive index variations.
\[ t(r) = \frac{1}{2} + \frac{1}{\pi i} \int H(x, y) \sum_{n=-\infty}^{\infty} \frac{1}{n} \exp \left( \frac{\pm ik r^2}{2f} \right) \]  

(5)

The amplitude of the spherical wave components are governed by another variable \( H(x, y) \). For the sake of simplicity in our discussion we take \( H(x, y) = 1 \). In the Axicon-MZP due to the variable \( H(x, y) \) the zone plate will not focus plane wave on to a point [10]. Because of that the imaging quality of such a zone plate cannot be as good as that of a binary zone plate. Since we have fabricated axicon MZP, we compare the \( t(r) \) in Eqn. (4) with the transmittance function \( t'(r) \) of a lens which is given by

\[ t'(r) = \exp(i\phi) \exp \left( \frac{\pm ik \ r^2}{2f} \right) \]  

(5)

where \( \phi \) is the constant phase factor; \( f \) the focal length of the lens and \( k \) is the propagation constant which is equal to \( (2\pi/\lambda) \). Therefore a zone plate may be considered as multiple lenses with the \( n \)-th focal length \( f_n \) given by

\[ f_n = \frac{r_n^2}{n\lambda} \]  

(6)

The plane wave incident on a zone plate is decomposed into a plane wave and large number of converging and diverging spherical waves of different radii of curvature.

6. SPHERICAL ABERRATION

It has been shown that a zone plate suffers from spherical aberration according to [9].

\[ |S| = \frac{1}{8} r_n^4 \left[ \frac{1}{a^3} + \frac{1}{b^3} \right] \]  

(7)

where \( a \) and \( b \) are respectively the positions of the point source and its image on the optical axis and \( r_n \) is the radius of the \( n \)-th zone. In order to study if ion-exchange process alters the magnitude of spherical aberration, the binary (master) and phase zone plate fabricated by ion-exchange process were examined in a lateral shear interferometer both in and out of focus conditions. The plane wave incident on the zone plate is focused at a distance \( r_n^2/\lambda \), besides have many other wavefronts. This focused wave is isolated from the rest by inserting a pin-hole of 100 \( \mu \)m diameter at the focal plane. See Fig. 7. The emergent wave is collimated again by an achromatic L. The collimated beam is incident on a plane parallel plate interferometer and the shear interferogram is observed in the reflected light for various defocusings introduced by axially displacing the lens L. Fig. 8, 9, 10 are the interferograms for the binary (master) amplitude zone plate while the corresponding interferograms for identical defocusings are shown in Fig. 11, 12, 13. Similarity between these interferograms suggests that the ion-exchange process does not introduce any additional spherical aberration.

The phase zone plate is also used for imaging. It is expected that since axicon-MZP is used as master zone plate in the ion-exchange process for the fabrication of phase zone plate the imaging quality will not be good. To filter out the undesirable waves, a stop is
Fig. 7 Experimental setup to study the aberration characteristics of the zone plate.

Fig. 8 Shearogram obtained inside the focus with binary amplitude zone plate used as an imaging element.

Fig. 9 Shearogram obtained at the focus with binary amplitude zone plate used as an imaging element.

Fig. 10 Shearogram obtained outside the focus with binary amplitude zone plate used as an imaging element.

Fig. 11 Shearogram obtained inside the focus with phase zone plate fabricated by ion exchange in glass used as an imaging element.
Fig. 12 Shearogram obtained at the focus with phase zone plate fabricated by ion-exchange in glass used as an imaging element.

Fig. 13 Shearogram obtained outside the focus with phase zone plate fabricated by ion-exchange in glass used as an imaging element.

Fig. 14 Experimental setup for imaging through a zone plate.

Fig. 15 (a) Image of a wire mesh with stop used; (b) Image of the wire mesh without the stop used; (c) Image of a Binary object.
inserted in the imaging setup (Fig. 14). A mesh is then imaged by the zone plate; a photograph of the image is shown in the Fig. 15a. A pin-cushion distortion may be seen; it is evident even when imaging is done without inserting the stop (Fig. 15b).

7. CONCLUSION

The method of fabricating diffractive phase optical elements using ion-exchange process in glass is described. The procedure for optimizing the diffraction efficiency has been presented and the performance of these phase elements studied.

The phase optical elements fabricated through ion-exchange process are less vulnerable to the environmental changes and physical damages. The performance of these diffractive phase elements are as good as those fabricated through conventional methods. However, the resolution attainable in ion-exchange optical elements is restricted by side-wise diffusion during the ion-exchange process.

REFERENCES
