

Press-patterned diffraction gratings on high refractive index polyimide films

Ramil Mercado, Rebecca Rich, Wu-Sheng Shih, Udayan Senapati, and Doug Holmes
Brewer Science, Inc., 2401 Brewer Dr., Rolla, MO 65401 USA

ABSTRACT

Press-patterning of polymers to yield optical structures is being pursued in optics and photonics to yield low-cost optical components. This is a promising technology for the low-cost and high-throughput fabrication of polymeric photonic components. The processing of such imprinted photonic components is usually done using a metallic shim where a pattern is generated on the shim by electroforming or electroplating. The shims are then used to replicate patterns on plastics and polymers under high temperatures and pressures. Under the correct conditions, the polymer flows and replicates a diffraction grating.

Polymeric diffraction gratings and holograms have applications in a multitude of photonic applications for diffractive optics. This requires materials that are transparent in the visible region, and preferably have relatively high refractive indices in order to achieve a high diffraction efficiency. In addition, in order to facilitate processing by the press-patterning method that will be further described in this paper, polymeric materials that are amenable to spin-coating and show good thermoplastic behavior are also desired.

Optically transparent, high-refractive index polyimides were tested for their ability to be processed and patterned using a press-patterning method. A process that allowed the materials to be patterned were developed, and measurements were taken to validate the results. Our initial results showed successful press-patterned polyimide films with grating structures having submicron line and trench widths and step heights of less than 0.5 microns.

Keywords: High refractive index, diffraction grating, polyimide, press-patterning

1. INTRODUCTION

In previous papers [1, 2], a series of soluble, fully aromatic polyetherimides (OptiINDEX) were prepared as candidate materials for optical coating applications. These polyetherimides are soluble in a variety of organic solvents and are suitable for optical applications due to their excellent optical clarity at wavelengths from 400 nm to 2000 nm. The polymers are true solutions of polyetherimides and require no further high temperature or chemical imidization. As a result, the refractive indices inherent in the chemical structures are consistent and are affected only by the degree of solvent removal from the films. The solutions are easily formed into films by spin-coating processes, yielding good quality coatings at thicknesses from 1-15 microns. We have also found that the mechanical characteristics of polymers allow them to be processed by mechanical patterning techniques such as molding, casting, stamping, embossing, etc., which lead to rapid low-cost shaping for waveguide formation and diffraction gratings. The high indexes of refraction, ranging from 1.65 to 1.78 in the visible region (400-700 nm), would enable the decrease in the optical thickness of the gratings, thus allowing for thinner grating structures.

In this paper, we focus on characterizing a set of three (3) polyetherimides and the fabrication of grating structures using materials, equipment and methods developed by Brewer Science, Inc.

2. EXPERIMENTAL

2.1 Equipment and Methods

Traditional spin-coating techniques were used to prepare films of varying thicknesses using a CEE[®] 100CB spinner/hotplate (Brewer Science, Inc.). The coating solutions were applied onto glass, quartz, or silicon substrates by spin coating at 500 to 5000 rpm for 80 seconds. A soft bake was performed on a 100°C hotplate for 2 minutes, followed by a final bake on a 205°C hotplate for 1 minute to ensure the complete removal of residual solvent. The thickness of each coating was then measured with a Gaertner ellipsometer or an Alpha-Step profilometer. Coating transparency, reported as percent transmission (%T) for a given film thickness, was measured with a Varian Cary 500 Scan UV-VIS NIR Dual Beam Spectrophotometer, with no corrections being made for scattering or reflective losses. The refractive index, and thickness, were measured on a Metricon 2010 Prism Coupler, operating at 401 nm, 632.8 nm, and 780 nm. Optical constant (n and k) data were obtained from thin films using a J. A. Woollam Variable Angle Spectroscopic Ellipsometer (VASE[®]). Differential scanning calorimetry (DSC) data were obtained using a TA Instruments DSC 2920 Modulated DSC. These were generated using the modulated mode, with a ramp rate of 3°C/min and a modulation of ±0.5°C/60 sec. For all sets of data reported, three heating and two cooling runs were performed, with a temperature range of 25°C to 350°C.

2.2 Method for Fabricating Patterned Films

All materials were applied to substrates on a CON-TACT[®] tool and processed using either a standard CON-TACT[®] tool or a thermal CON-TACT[®] tool prototype, which is capable of using a conductive chuck to heat the wafer.

For the process of press patterning, a coating of about 5 microns was spin-applied to a 4-inch wafer before patterning. This was accomplished by diluting each material to about 15% solids using cyclopentanone and using the manual spin coating recipe. The standard manual spin coating recipe consists of a dynamic application of the polymer solution for 5 seconds at 100 rpm, followed by a 30-second spread spin at 2500 rpm. A 12-inch SKW 3-2 CMP test wafer (from SKW Associates, Inc.), with line widths ranging from 500 nm to 500 microns, with a step height of about 885 nm, was used to pattern the reference polymer film using a press patterning process. Under appropriate conditions, negative patterns of SKW 3-2 test wafer patterns are replicated on the polymer film surface. This process is shown on the left in Figure 1. This patterned polymer template was then used in the CON-TACT[®] tool to duplicate the SKW 3-2 test wafer patterns on an optical film coated wafer as shown on the right in Figure 1. The pattern transfer process is summarized by the following:

- A spin-coated wafer is placed on a heated chuck.
- The patterned polymer mask is brought into contact with the coated wafer, backed by an optically flat surface.
- The chuck presses upwards, transferring the pattern from the film to the coating.
- The coated and patterned wafer is separated from the film.

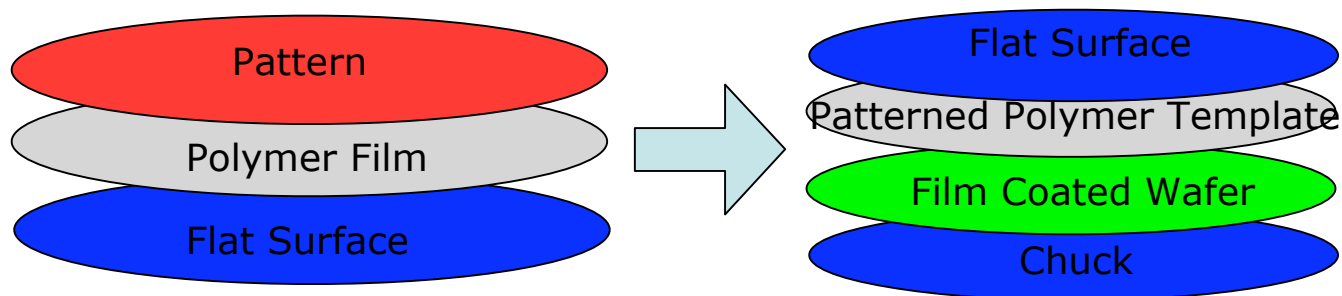


Figure 1. Schematic diagram of the pattern transfer process.

The patterns transferred onto the wafer and glass substrate were characterized. Interferograms were generated on a Veeco WYKO NT-3300 Optical Profiler. Scanning electron microscope (SEM) images were obtained from an LEO-1560 microscope.

3. RESULTS

3.1 Optical Data

Refractive indices of the three polymers were obtained by two different methods. Results from both ellipsometric and prism coupling methods are shown in Figure 2. There is good agreement in the refractive indices obtained between the two methods; however, there appears to be a systematic difference in the values of the refractive index obtained for OptiNDEX B44. Imaginary refractive index (k) data are shown in Figure 3. As shown by the graph, all three polyetherimide systems have k less than 0.005 in the visible region. This, in addition to the transmission data, indicates excellent optical clarity for the polymers. Figure 4 shows the transmission curves of the three polyetherimide systems, all at 5-micron thicknesses. As seen before [1], both OptiNDEX B38 and B44 show excellent transmission in the visible range, approximately 85% at 400 nm and more than 90% from 420 nm and beyond into the near-infrared region for 5-micron thick films. The EXP04062 polymer, utilizing *m*-BAPS (Chriskev) in place of BAPS (Chriskev) as a comonomer, shows a vast improvement in transparency over the structurally related OptiNDEX B38, achieving more than 99% transmission in the visible to near-IR range, and more than 90% transmission in the near ultraviolet (to 370 nm).

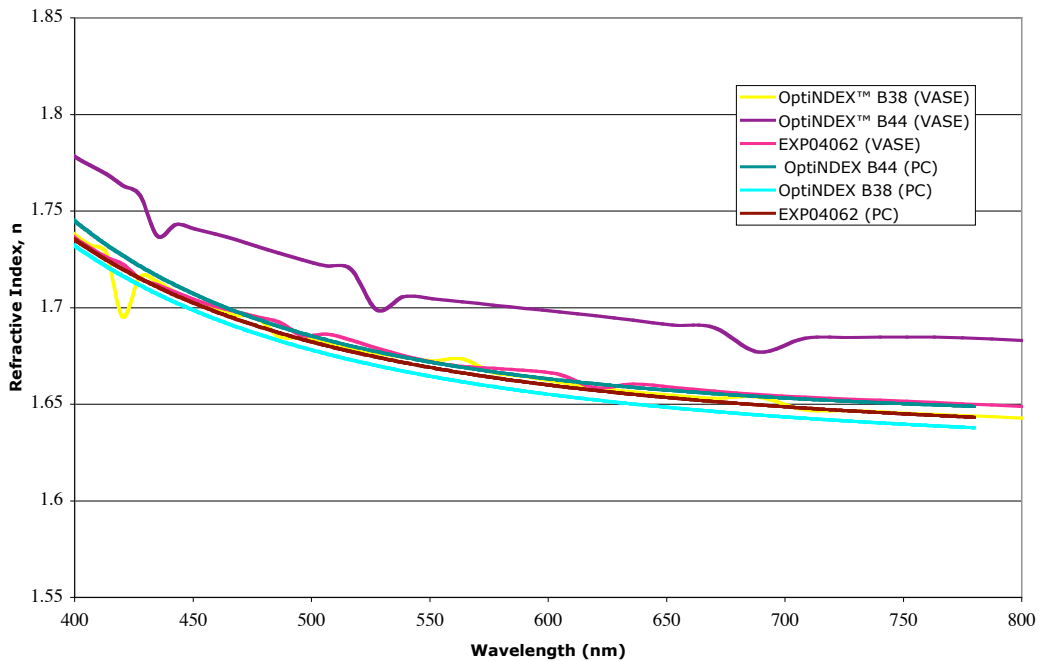


Figure 2. Polyetherimide refractive indices.

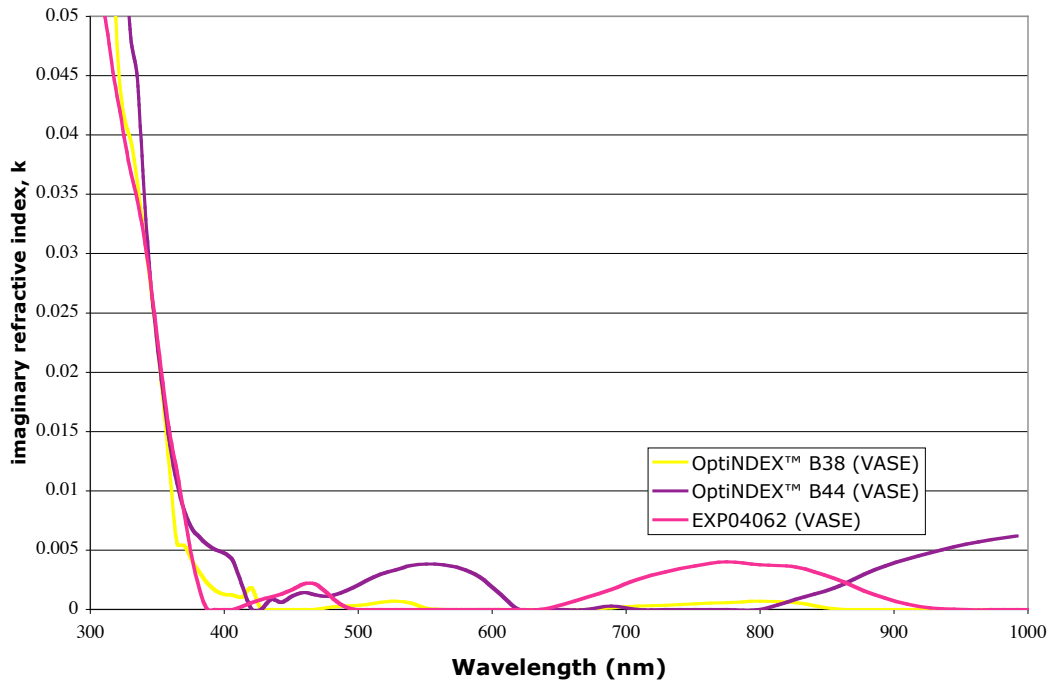


Figure 3. Polyetherimide imaginary refractive index (k) data.

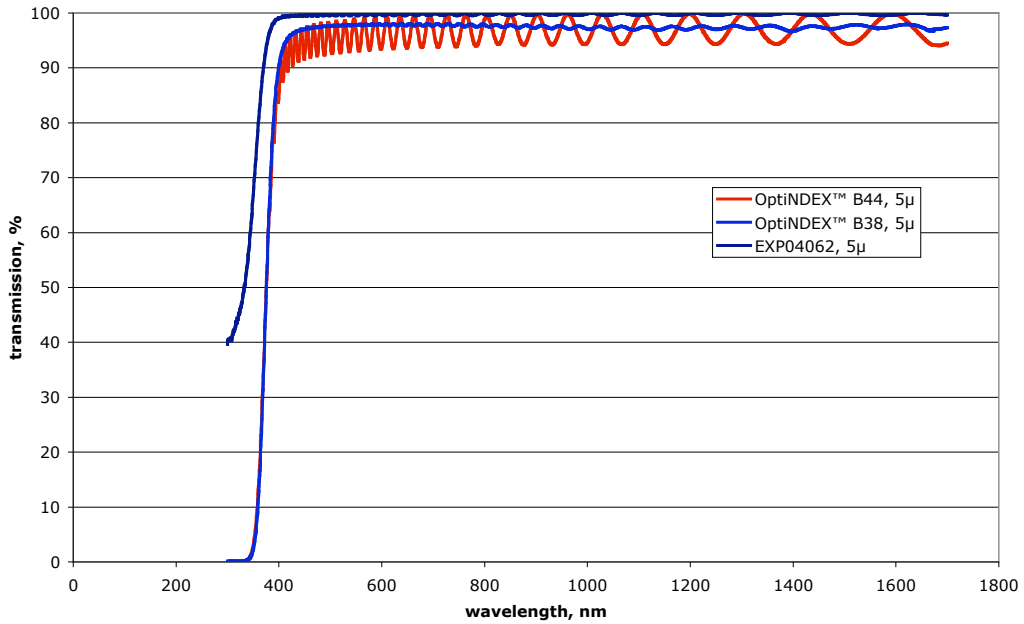


Figure 4. UV-visible transmission curves for selected polyetherimides.

3.1 Thermal Data

DSC data were generated for the polymers in OptiNDEX B38, OptiNDEX B44, and EXP04062 (Figures 5, 6, and 7, respectively). Sample sizes were not measured, thus the heat flow values are only relative to the empty reference pan, and exotherms are indicated by an upward curve. The first heating cycle was employed only to erase any previous thermal history and may also provide for residual imidization (the polymers are imidized in solution during synthesis). The second and third heating cycles, as well as the two cooling cycles, are used for the determination of the glass transition temperature (T_g) of the polymers. Using this method, the T_g of the polymers were determined to be 224°C (OptiNDEX B38), 283°C (OptiNDEX B44), and 193°C (EXP04062). The transitions are manifested in the corresponding cooling cycles as well, indicating good reversibility of the thermal transition.

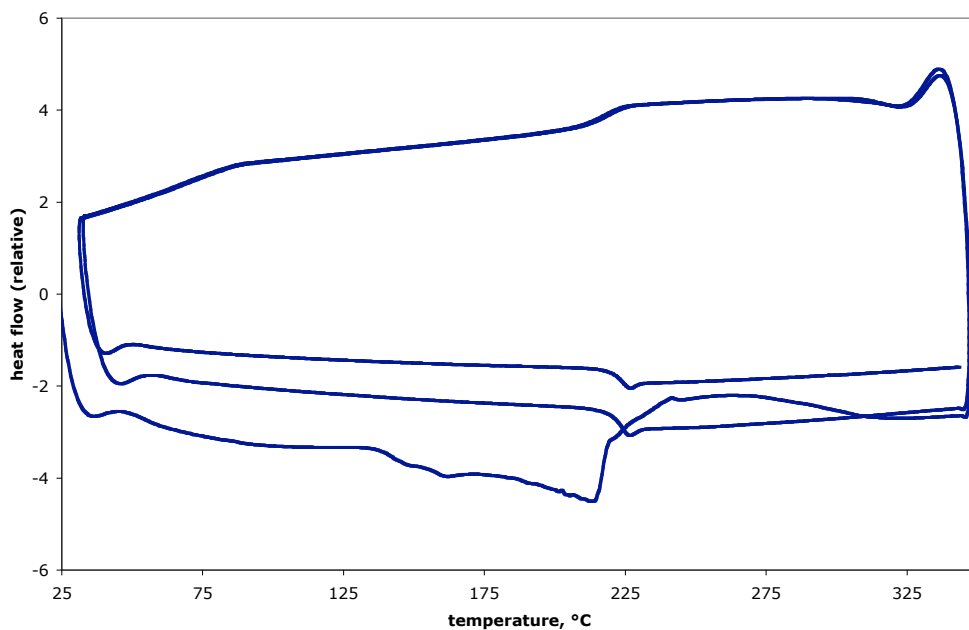


Figure 5. DSC plot of OptiNDEX B38.

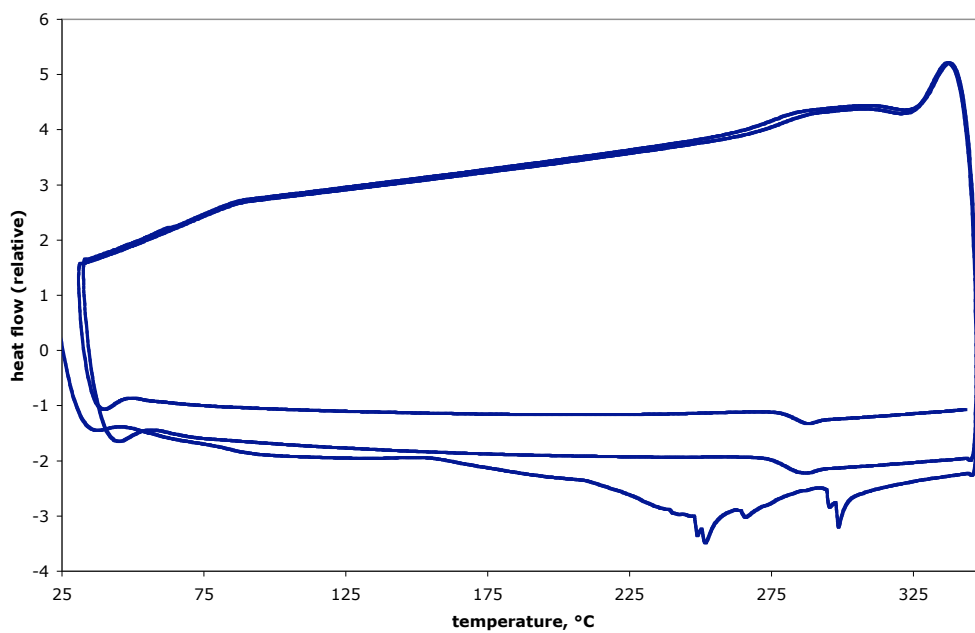


Figure 6. DSC plot of OptiNDEX B44.

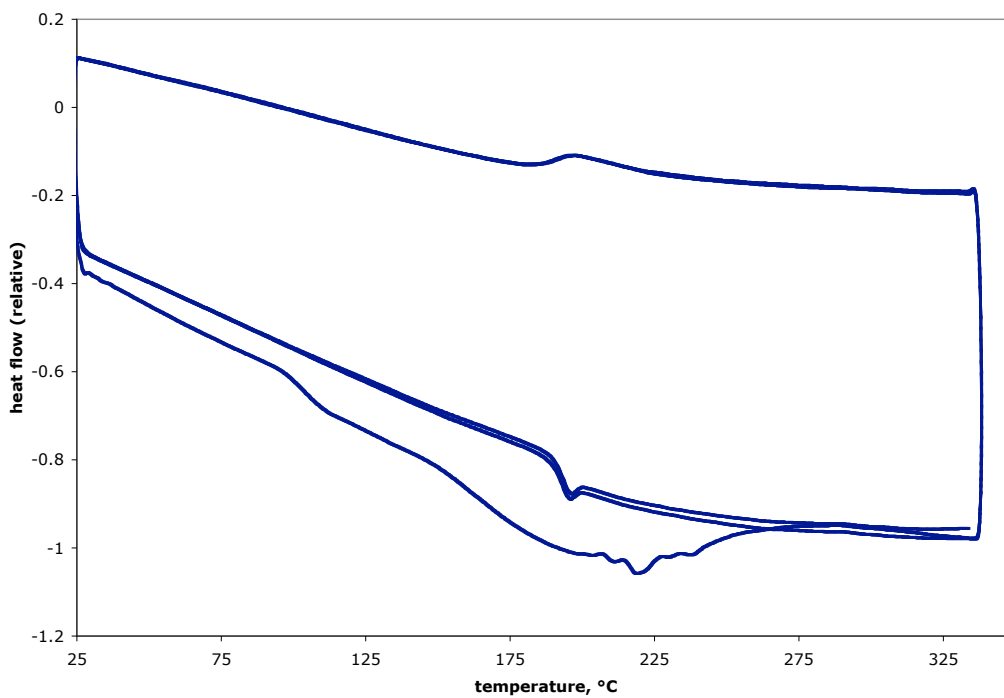


Figure 7. DSC plot of EXP04062.

3.3 Press-Patterning

A series of pattern transfer experiments was carried out with the chuck temperature ranging from 100°C to 175°C, patterning time ranging from 60 seconds to 300 seconds, and patterning pressure of 100 psi. The interferogram of the original test wafer is shown in Figure 8. The structures shown in the figure are 5.0-micron line and trench widths.

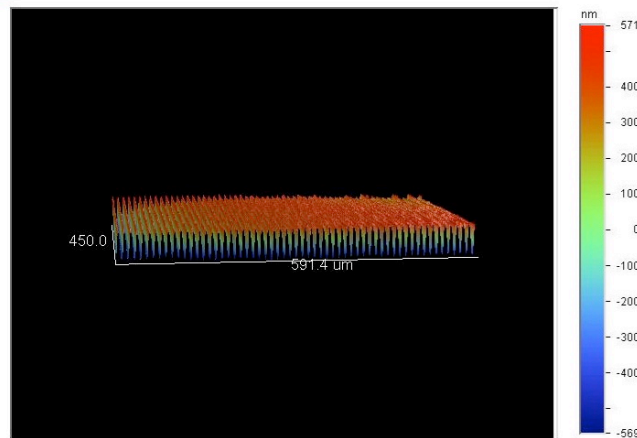


Figure 8. Interferogram of the original (SKW 3-2 CMP) test wafer pattern.

The following table shows the results of the pattern replication trials. Step heights from 0.05 to 0.90 microns were obtained using OptiNDEX B38, while step heights ranging from 0.02 to 0.60 microns were obtained using OptiNDEX B44.

Material	Spin Speed (rpm)	Coat Thickness (μm)	Temperature ($^{\circ}\text{C}$)	Pressure (psi)	Time (sec)	Step Height (μm)
B38	2500	5.5	175	100	60	0.21
B38	2500	5.5	175	100	300	0.62
B38	2500	5.5	175	100	120	0.90
B38	2500	5.5	175	100	180	0.6
B38	3500	4.5	175	100	120	0.3
B38	2500	5.5	100	100	120	0.05
B38	2500	5.5	130	100	120	0.35
B38	2500	5.5	155	100	120	0.60
B38	2500	5.5	175	100	120	0.70
B44	2500	5	120	100	120	0.50
B44	2500	5	IR	60	120	0.60
B44	2500	5	155	100	120	0.02

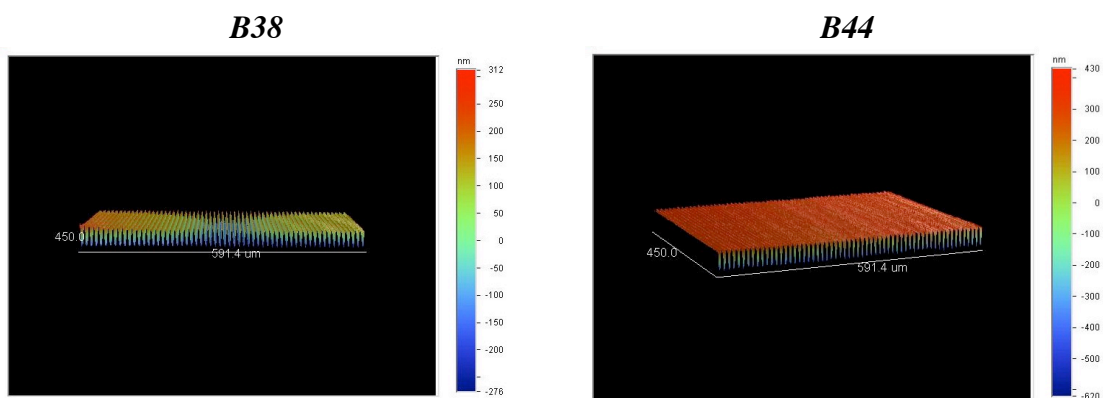


Figure 9. Interferograms of patterns replicated on OptiNDEX B38 and B44 films.

The method was then extended by using a metallic mask. The metal mask was used to create a secondary master using the polymer film as described previously (Figure 1). The patterned polymer template was then used to pattern another 4-inch glass wafer with the film of OptiNDEX B44 at the same temperature and pressure as was used previously (125°C, 100 psi). This yielded patterns of submicron features (approx. 250 nm), as shown in Figure 10.

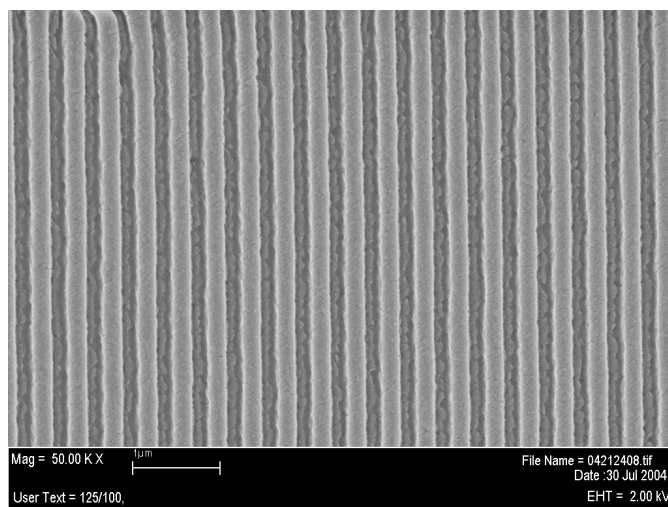


Figure 10. SEM micrograph of press-patterned OptiNDEX B44 film showing features of approximately 250 nm.

4. DISCUSSION

Many aromatic polyimides are generally intractable [3]. We have addressed these issues by synthesizing and imidizing soluble polyetherimides and directly applying them from solution instead of applying solutions of the poly(amic acid) precursors. This approach helps improve the optical film properties [4], as the elimination of water, such as that which occurs from bulk imidization, is avoided. Also, having the polyetherimide already in solution precludes the necessity of having to process the polymer films at high temperatures (greater than 230°C) in order to generate the high refractive indices. This minimizes the requisite processing to what is necessary to eliminate solvent.

4.1 Thermal Analyses

The DSC curves show that the T_g 's for the polyetherimide systems are consistent and reproducible. In addition, it is common to the three DSC curves that the first ramp to 350°C shows a variety of thermal transitions well below the glass transition temperatures. The curves for OptiINDEX B38 and B44 show a change in slope in the range from 150°C to about 200°C; in the case of EXP04062, this change in slope is between 100°C and 125°C. It appears that these quasi-glass transitions are useful in the press-patterning process. In the press-patterning process, the temperatures utilized are well below the glass transition temperatures, as indicated in the DSC graphs. It is quite probable that these non-reproducible transitions arise from the presence of minute quantities of residual solvent in the film. The residual solvent can serve as a plasticizer during the press patterning process and allow the film to flow even below the glass transition temperature. The results indicating better success at patterning for thicker films (5 μm versus 2 μm) bears this out as it is very likely to have more solvent trapped in the thicker film as opposed to the thinner one.

Thermal transitions that occur above 200°C are likely the result of the polymer fully imidizing. The transitions are non-reversible and are not unexpected, since the solution imidization process does not achieve 100% imidization. The reversibility of the thermal transitions over two full heating and cooling cycles to almost 350°C indicates the excellent thermal stability of the polyetherimides as well.

4.2 Press-Patterning

It was found that thicker coats were preferred to achieve the flow necessary for patterning. By using spin-coating to a thickness range of 5.0 to 5.5 microns, it was determined that patterning was possible at room temperature, as long as the solvent was removed by heating at the end of the press. Higher temperatures during the press resulted in better patterning for the B38 material, but the opposite was true for the B44. Feature sizes obtainable using this press-patterning method ranged from 250 nm to 5 microns. Research is ongoing on the press patterning of EXP04062. The lower glass transition temperature (193°C) for this material may allow for better patterning results at lower temperatures.

5. CONCLUSIONS

Mechanical pattern transfer in the optics and photonics industry involves generating a master substrate with the desired pattern on silicon wafers. Such patterns are generated on silicon wafers by photolithography. The pattern on the silicon wafer is then transferred on to nickel shims by electroforming (electroplating) process. The shims are used to emboss the optical structures on to the polymer films by the use of high temperatures and pressures. The subtleties of the electroforming process limit the quality of pattern transfer on to nickel shims resulting in poor quality optical components on occasions. This makes the entire process of replicating patterns from the silicon wafer to optical films and substrates fairly uneconomical and unreliable for the manufacture of high-quality optical components.

The press-patterning process described provides a means to generate imprinted optical structures on planar high refractive index polymeric films. The films are applied by spin-coating and baking processes and may be press-patterned at temperatures above or below the polymer glass transition temperatures. If a polymer solution is made using solvents that have high boiling points, the imprinting of diffraction gratings at temperatures below the glass transition temperature can be made feasible at certain thicknesses. This provides an added advantage over the normal hot embossing process where polymers or materials are typically processed above their flow temperatures. In addition the polymers with thicknesses down to a few microns can be press-patterned by raising the imprinting temperature and pressure towards the glass transition temperature of the polymers. Optical patterns ranging from 50 to 100 microns down to submicron feature sizes can be imprinted onto high refractive index polymer films.

The press patterning method described in this paper based on patternable polymer films as the replicating medium is more economical compared to the standard hot embossing processes that currently exist in the industry.

6. REFERENCES

1. Flaim, T.D., Y. Wang, and R. Mercado, "High Refractive Index Polymer Coatings for Optoelectronics Applications," *Proceedings of SPIE: Optical Systems Design 2003*, vol. 5250, Saint-Etienne, France, Sept. 29-Oct. 3, 2003.
2. R. Mercado, Y. Wang, T. Flaim, W. DiMenna, and U. Senapati, "Thin-film polyetherimides with controlled refractive indices," *Proceedings of SPIE: Organic Photonic Materials and Devices VI*, vol. 5351, 2004, pp. 276-283.
3. Hasegawa, M., and K. Horie, "Photophysics, photochemistry, and optical properties of polyimides," *Progress in Polymer Science*, 26, 2001, pp. 259-335.
4. Farr, I.V., *Synthesis and Characterization of Novel Polyimide Gas Separation Membrane Material Systems*, Ph.D. Dissertation, 1999, Virginia Polytechnic Institute and State University, Blacksburg, VA.

7. ACKNOWLEDGMENT

This work was partially supported by an award from the United States Department of Defense Missile Defense Agency under contract number DASG60-01-C-0047.