Press-patterned UV-curable high refractive index coatings

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ABSTRACT

The research and development of organic materials for use in optical components and devices aims to take advantage of several unique properties of these materials, including their stability, tailorability, and flexibility. In this study, by carefully controlling the components, we have developed a material that offers significant advantages over common optical materials. Specifically, the new material has a high refractive index and is curable with ultraviolet (UV) light, solvent free, and transparent over a wide wavelength range. We applied the material to a substrate via spin coating, although other application methods are possible.

The production of optical components through press-patterning has received a large amount of attention. The low cost of replication and high throughput of the process provide the potential for low-cost optical components. Typically a metallic plate is patterned via electroplating or electroforming to produce a negative image on the plate. This plate is then pressed into the patternable material and subsequently treated to form the desired pattern in the organic material. Here we report our initial attempts at press-patterning structures into a UV-curable high refractive index material.

Keywords: High refractive index, UV curable, press-patterning, optoelectronic

1. INTRODUCTION

Recently, great effort has been focused on developing novel and efficient optoelectronic devices [1-4]. These devices will provide the foundation for advanced technologies that will eventually be brought to the marketplace to improve our way of life. Brewer Science, Inc., applies its extensive expertise to developing materials, processes, and machines for the advancement of the microelectronics [5-8] and optoelectronics [9-14] industries by providing full-service solutions to our customers' needs.

Development efforts have focused on the use of organic materials in optoelectronic devices because of the flexibility, toughness, and tailorability of these materials [1-4]. Until recently [11], most organic materials have had reduced refractive indices and have been cured using thermal methods. Increasing the refractive index of the organic materials and utilizing a UV curing mechanism hold several advantages, including minimal shrinkage during curing, the ability to cure at room temperature, no emission of by-products, and more efficient devices.

To fully realize the materials' potential, Brewer Science has been developing processes and machines to provide enabling solutions for device manufacturing. CON-TACT® planarization technology has been introduced with thermal- and photo-processing capability [15-17] within a machine. The CON-TACT® machine has demonstrated the capability to planarize topographic surfaces using processes that include heat and UV light [15-16]. The versatility of this technology allows the sub-micron patterns to be generated by press-patterning using a thermal process [13] as well as a light process [17]. In contrast to a step-and-repeat process, CON-TACT® technology processes the entire substrate surface in one step. It is a wafer-level processing technology.

In the past, we have reported the development of enabling high refractive index materials, processes, and machines useful for the generation of structures in these materials [9-14]. Our efforts have involved three different chemistries, or series of chemistries, which have been briefly summarized elsewhere [14]. Previously, we have reported the generation of patterns in our "B-Series" of materials in another article [13]. Pattern generation in the "A-Series" will be described in a subsequent publication. Here we report the generation of patterns/structures in one of our "C-Series" materials, which are solvent-free, UV-curable, high refractive index materials.

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2. EXPERIMENTAL

The photocurable resin solution was prepared by mechanical agitation of the appropriate resin(s), crosslinker(s), and catalyst (photoacid generator, PAG) at room temperature. The resin and crosslinker were selected according to their viscosities, densities, refractive indices, and transmissions. The PAG utilized was selected based on its absorbance curve and corresponding acid strength.

Traditional spin-coating techniques were used to prepare films of varying thicknesses using a CEE® 100CB spinner/hotplate (Brewer Science, Inc.). The films were spun at speeds between 1000 and 5000 rpm, with an acceleration rate of 4500 rpm/s. Substrates used were 100-mm silicon wafers and 76-mm quartz wafers.

Curing was achieved through the exposure of the film on a substrate to broadband UV radiation using a Canon PLA-501F parallel light mask aligner with xenon lamp. The output of the UV source was ~3.7 mW/cm^2, measured at 365 nm. Typical exposure doses were 1-2 J/cm^2 (6-13 minutes).

Percent transmission data for the films were obtained by coating a film on quartz, curing the film, and analyzing the film on a Varian Cary 500 Scan UV-Vis-NIR dual beam spectrophotometer. The data are presented as percent transmission for wavelengths from 300-3300 nm. The average scan was 0.1 second, and the data interval was 1 nm. A baseline and zero correction were employed.

The refractive indices and thicknesses were measured on a Metricon 2010 prism coupler, which operated at 401 nm, 632.8 nm, and 780 nm using the prism coupling/single film mode.

Optical constant (n and k) data were obtained from thin films using a J.A. Woollam M2000 variable-angle spectroscopic ellipsometer (M2000 VASE®). The thin film was obtained by diluting the resin solution to 20% solids in cyclopentanone and spin coating a film at 2000 rpm, with 4500 rpm/s ramp rate, for 60 seconds. The film was cured with an exposure dose of 1 J/cm^2. Data were collected from 190 nm to 1000 nm.

The thermal processes for creating a pattern-bearing template and press-patterning high refractive index materials on substrates have been disclosed in a previous paper [13]. Instead of using a thermal process, the CON-TACT® machine equipped with UV capability was used for this work to press-pattern the UV-curable materials. UV radiation was illuminated through the optically transparent plate that bears an optically flat surface as illustrated in earlier publications [13, 15].

A 300-mm SKW 7-2 test wafer (from SKW Associates, Inc.), with various line width and pitch sizes and with a step height of about 900 nm, was used to prepare the pattern-bearing template. The template was installed in the CON TACT® machine for press-patterning processing. This template was used to process all the wafers reported in this work. The material was spin-coated on 100-mm silicon wafers at 5000 rpm for 60 seconds with an acceleration of 4500 rpm/s using a CEE® CB100 spin coater. The wafer was placed into the CON-TACT® machine with pre-determined parameters. Three press-patterning times, 30, 60, and 120 seconds, were used. The press-patterned wafer surface was then cured using UV light. Once the process was completed, the wafer was removed from the machine and characterized.

The SKW 7-2 wafer and the patterned wafer surfaces were characterized using a Dektak 8 stylus profilometer (from Veeco Instruments) for step height measurement. Cross-section scanning electron microscopy (SEM) using a Leo 1560 microscope was performed on the wafer pressed for 120 seconds to verify the step height and film thickness.

3. RESULTS

3.1 Material characterization

3.1.1 Spin speed curves

Once the resin solution was prepared according to the procedure in the experimental section, the material was applied on various substrates using spin coating to create the films. Through variation of the spin speeds and identical curing parameters, different thicknesses of films were obtained as shown in Figure 1.

3.1.2 Refractive index measurements obtained through use of a prism coupler

The films of the material generated by varying the spin speeds during spin coating were measured on a prism coupler to determine the refractive index of each film. Through these measurements, extrapolated refractive index curves were generated, as detailed in Figure 2.

3.1.3 Optical constant data generated through VASE measurements

A portion of the material was diluted as indicated in the experimental section to accommodate VASE measurements. The optical constants for the thinner film are shown in Figure 3.

3.1.4 Transmission data for a film on quartz

A film of the material was generated on a quartz wafer so that the transmission spectrum could be determined. The results from this measurement are shown in Figure 4.

3.1.5 Refractive index data for different irradiation doses

Three films of identical thickness were generated using the same spin speed parameters. The films were subjected to different doses of UV radiation and analyzed on the prism coupler. The extrapolated refractive index curves for the three films are shown in Figure 5.

3.2 Pattern characterization

3.2.1 Step height measurements of the SKW 7-2 and press-patterned wafers

The wafers coated with the "C-Series" material were successfully press-patterned. Step heights at various pitch sizes (20 µm, 30 µm, 50 µm, and 100 µm) and feature density areas (10% and 90%) on the SKW 7-2 test wafer were measured. The different pitch sizes also represent different feature density areas as well. The measured step heights ranged form 940 nm to 960 nm, which is within the vendor's step height variation specification. The step heights measured from press-patterned wafers ranged from 900 nm to 940 nm. The scanned step height profiles for a 100-µm pitch area of the SKW 7-2 test wafer and the wafer press-patterned for 120 seconds are shown in Figures 6 and 7. Table I summarizes the step heights measured from the SKW 7-2 and pressed wafers.

3.2.2 Cross-section SEM characterization

Cross-section SEM study revealed the film thicknesses in three areas with different pitch sizes, 50 µm (Figure 8), 10 µm (Figure 9), and 6 µm (Figure 10), were very comparable. Based on the SEM measurements, these three pitch areas also represented three different feature density areas, 55%, 75%, and 93%, respectively. The feature density is defined as the ratio of line width to pitch. Film thicknesses measured from these three pitch areas, within the lines and trenches, are summarized in Table II.

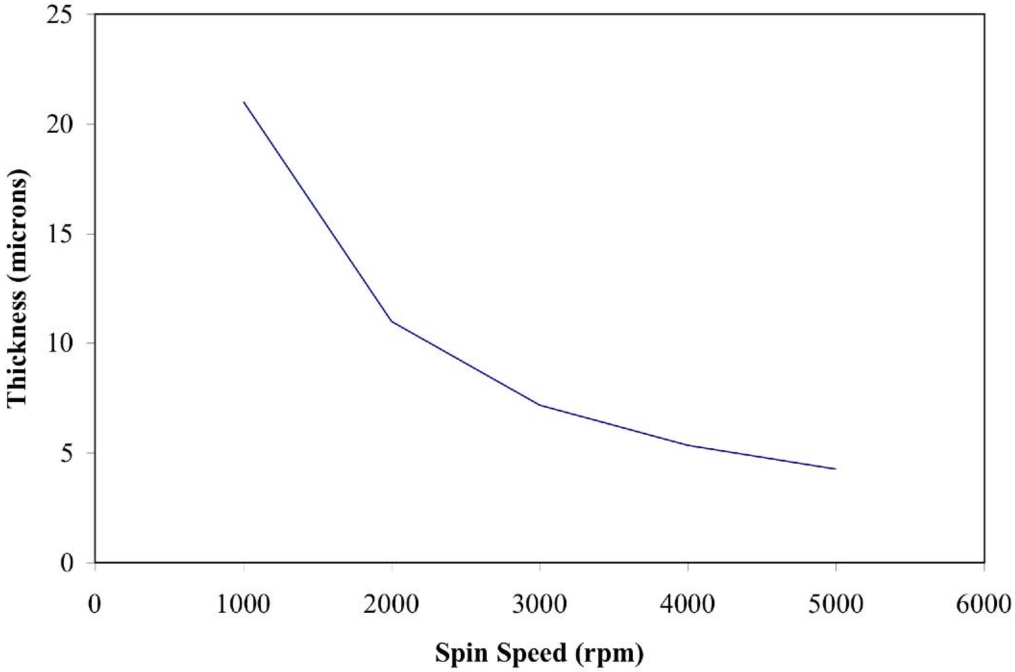

Figure 1. Spin-speed curve for material deposited on silicon wafers.

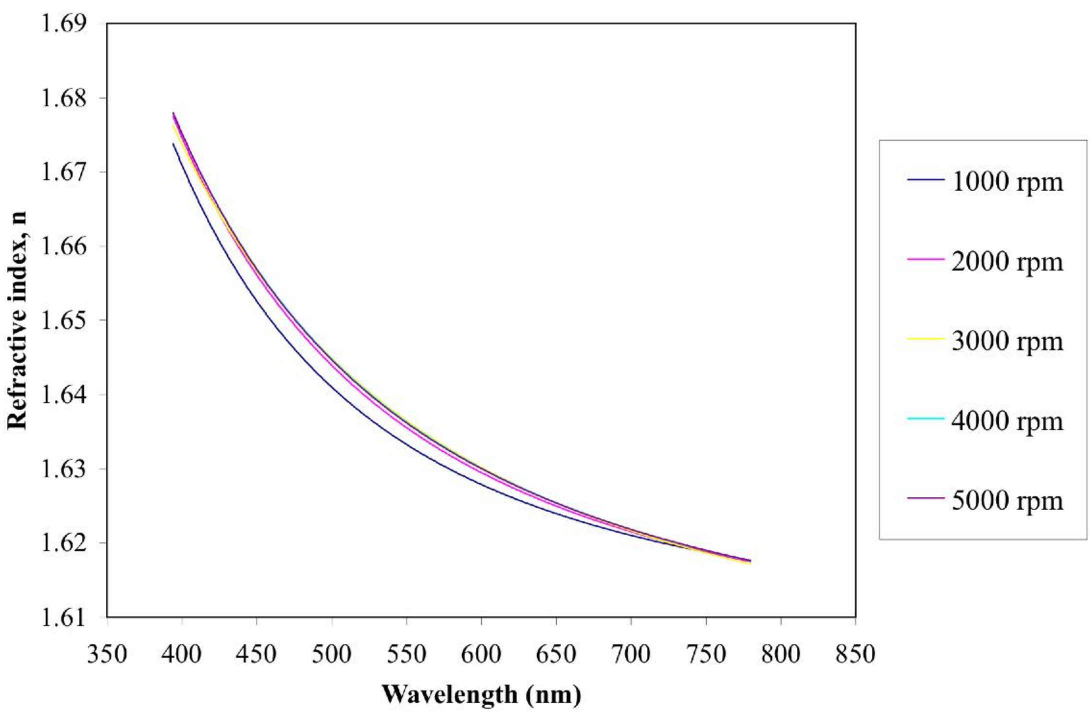

Figure 2. Extrapolated refractive index curves for the cured material coated on silicon wafers at various spin speeds.

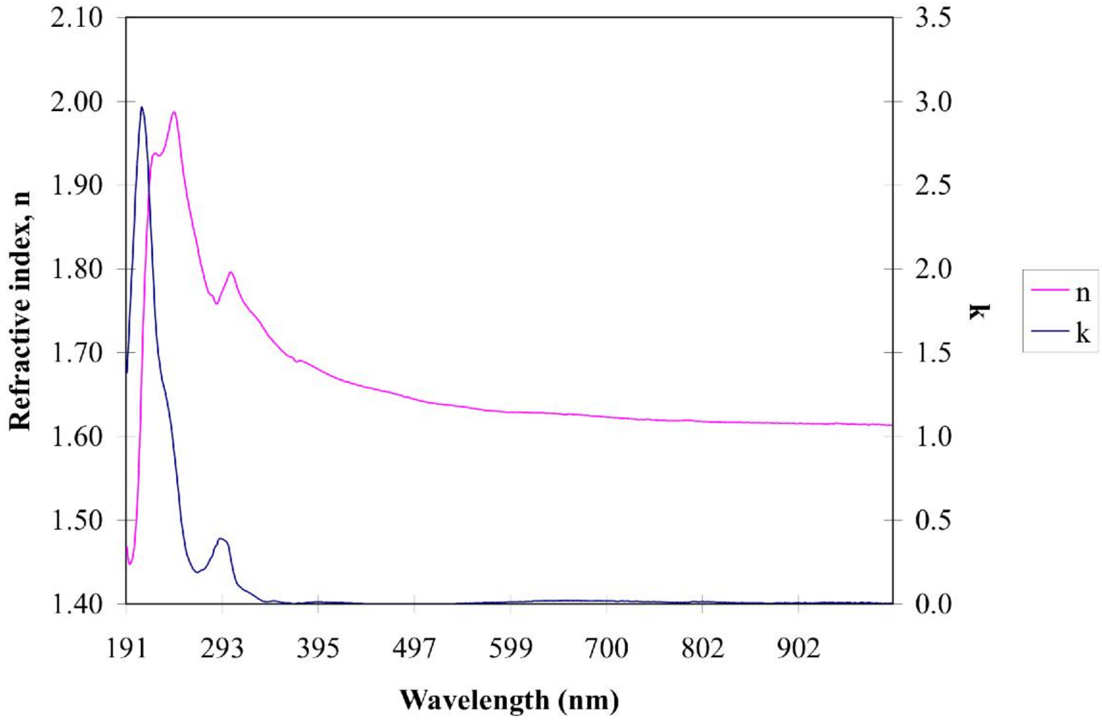

Figure 3. Refractive index and extinction coefficient data for a cured thin film.

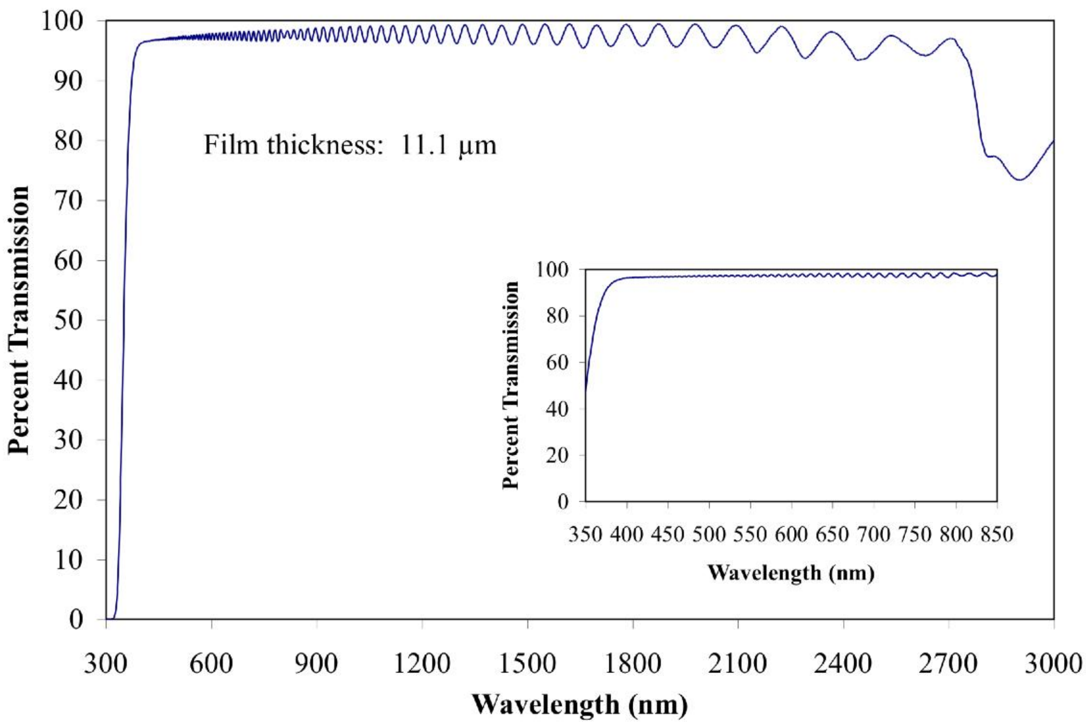

Figure 4. Percent transmission data for a film coated on a quartz wafer.

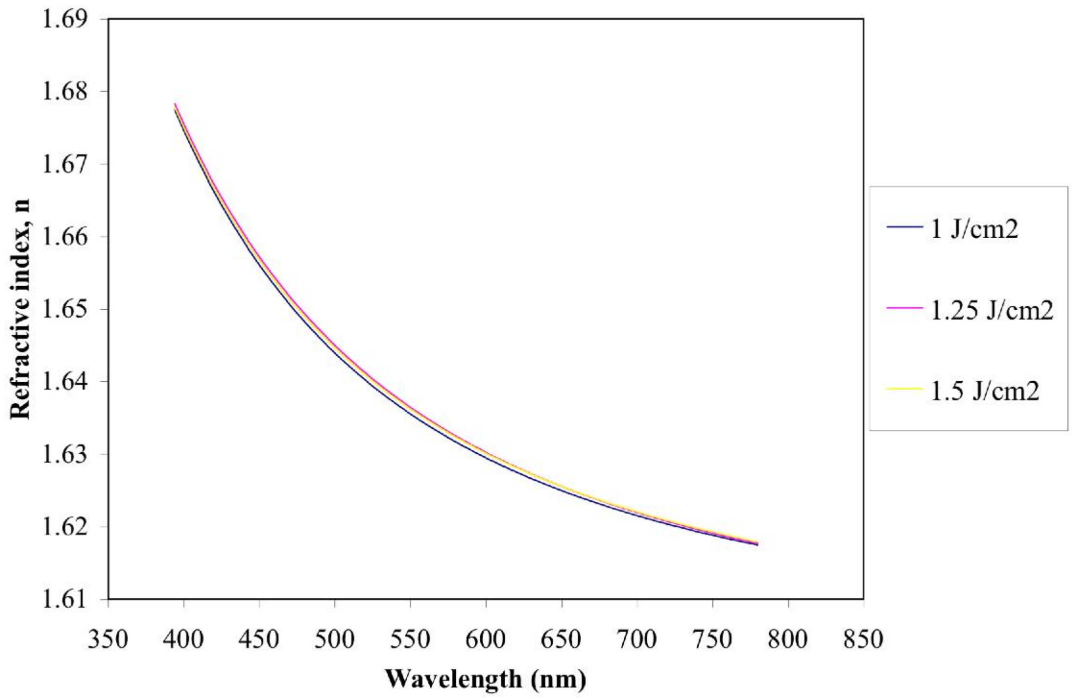

Figure 5. Extrapolated refractive index curves for films coated on silicon wafers cured with different amounts of UV radiation and analyzed on the prism coupler.

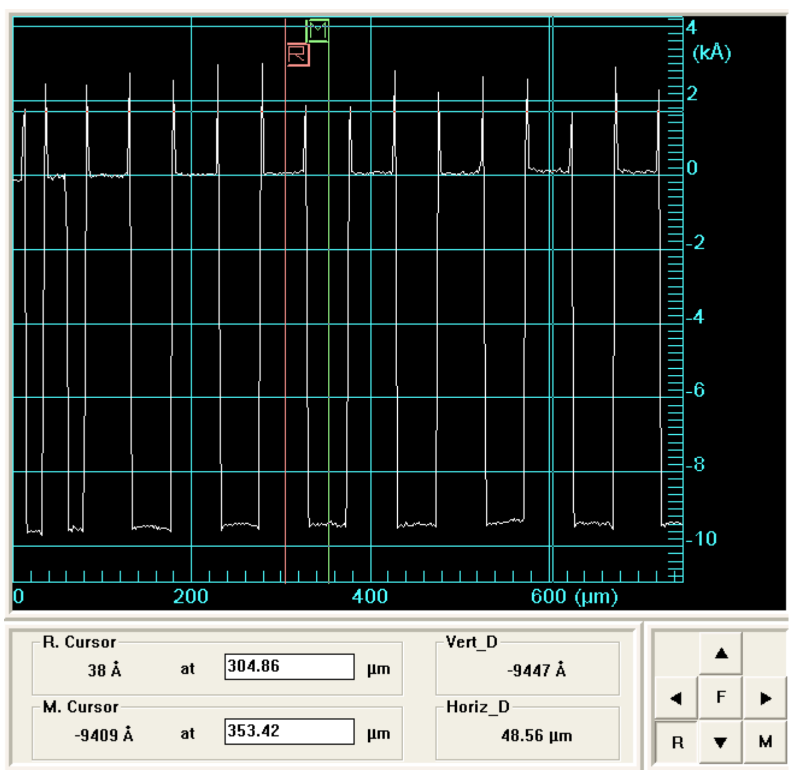

Figure 6. Step height profile of the SKW 7-2 test wafer in a 100-µm pitch size area.

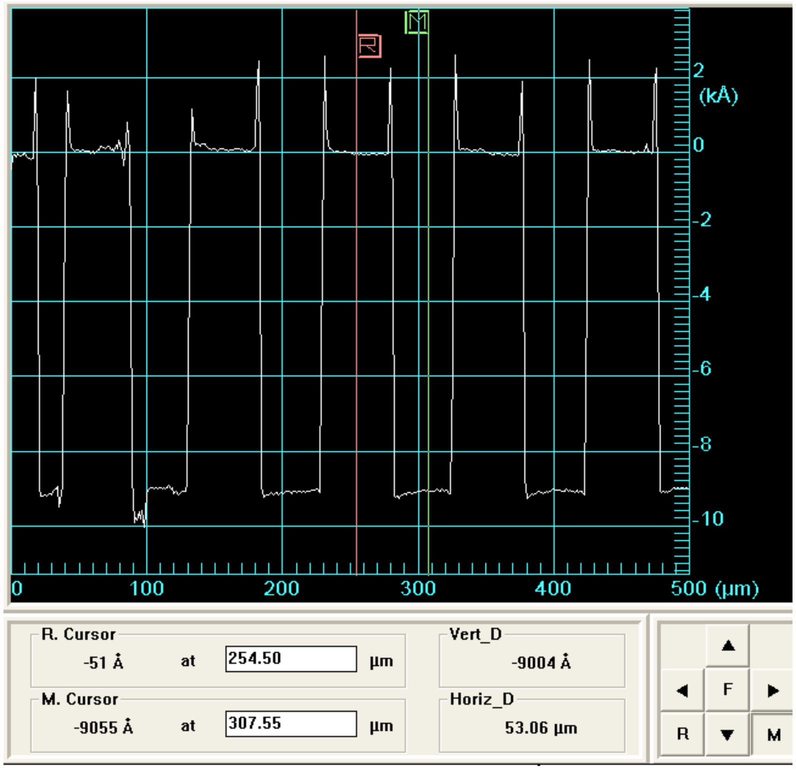

Figure 7. Step height profile of the press-patterned wafer (120 seconds press-patterning time) in a 100-µm pitch size area.

Table I. Step heights of the SKW 7-2 and press-patterned wafers at various pitches and feature density areas.

Pitch/Feature Density Area	SKW 7-2 Wafer Step Height (nm)	Press-Patterned Wafers	
		Press Time (Seconds)	Step Height (nm)
20 µm	956	30	919
		60	928
		120	937
30 µm	950	30	908
		60	910
		120	920
50 µm	947	30	900
		60	897
		120	916
100 µm	945	30	905
		60	902
		120	900
10%	939	30	900
		60	910
		120	926
90%	956	30	924
		60	925
		120	915

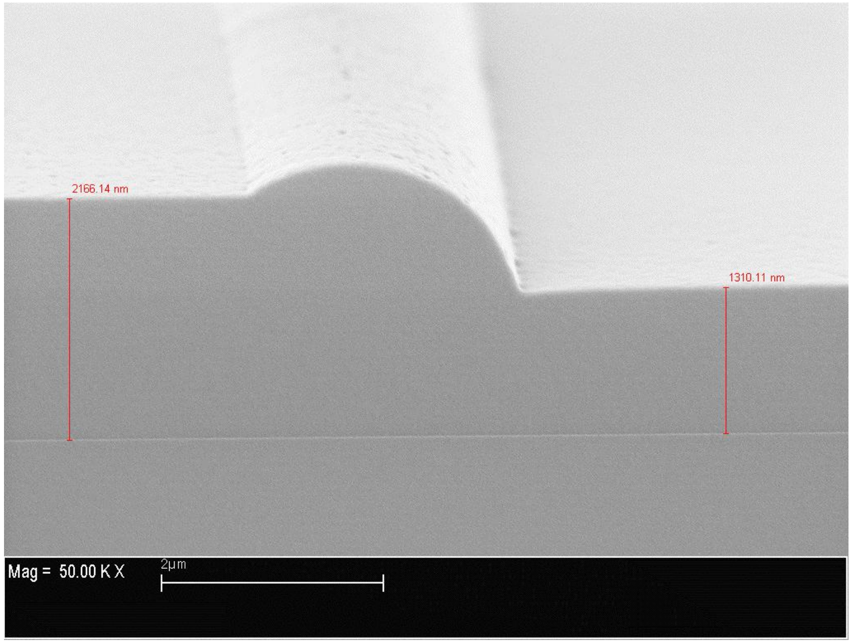

Figure 8. Cross-section SEM micrograph at 50-μm pitch (~55% feature density) on the wafer press-patterned for 120 seconds.

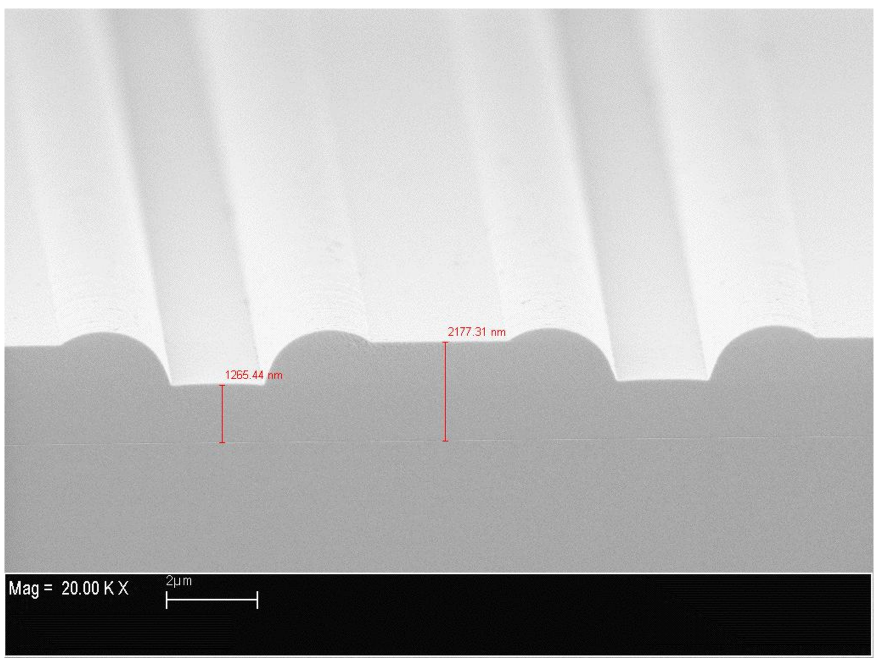

Figure 9. Cross-section SEM micrograph at 10-μm pitch (~75% feature density) on the wafer press-patterned for 120 seconds.

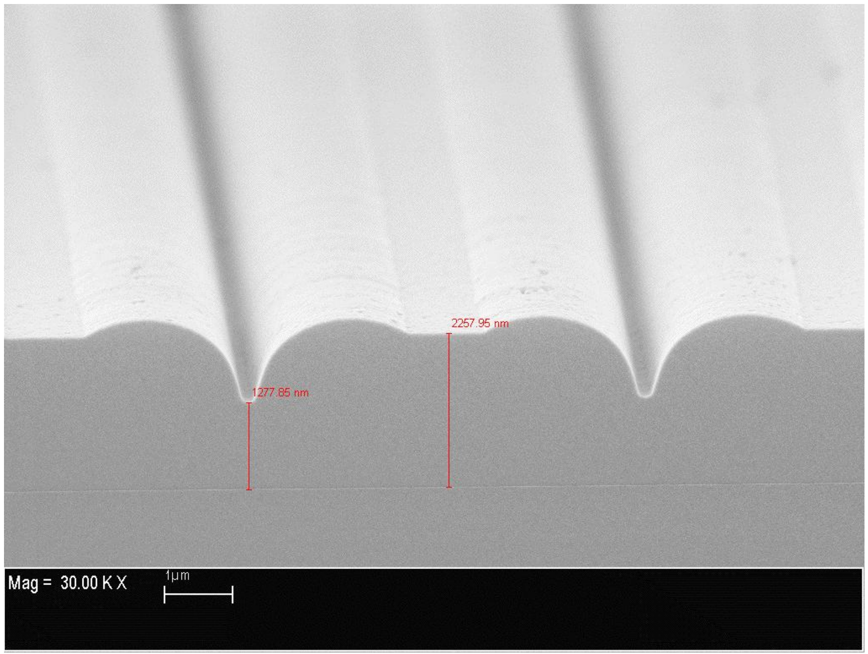

Figure 10. Cross-section SEM micrograph at 6-µm pitch (~93% feature density) on the wafer press-patterned for 120 seconds.

Table II. Film thickness, within the lines and trenches, at various pitch areas on the wafer press-patterned for 120 seconds.

Pitch	Film Thickness	
	Line	Trench
50 µm	2.17 µm	1.31 µm
10 µm	2.18 µm	1.27 µm
6 µm	2.26 µm	1.28 µm

4. DISCUSSION

4.1 Material characterization

To develop new optoelectronic devices and make current technologies more efficient, high refractive index materials are required. One area that Brewer Science is focusing on is the development of UV-curable, high refractive index materials that have low shrinkage upon curing, can vary in thickness by several orders of magnitude, and are solvent free (or virtually solvent free), free flowing, transparent over a wide wavelength range, fast curing, and physically robust. Through careful selection of the components and their concentrations in the formulations, we can control the viscosity, refractive indices, cure speeds, and thermal properties of the resultant films. Here we detail the properties of a high refractive index, low-viscosity material.

The low-viscosity material used in this study gives significantly thinner films than we reported previously [11]. The spin-speed curve for the current formulation, as shown in Figure 1, displays typical thicknesses in the range of 5-22 µm.

An issue with UV-curing systems is that too little radiation can cause insufficient curing. This effect can be exacerbated through variation in film thickness. As seen in Figure 2, the extrapolated refractive index curves for the different spin speeds (and thicknesses) are nearly the same, which indicates that the films are sufficiently cured and display similar optical characteristics.

To obtain detailed information about the optical properties of the material, the film was studied using variable-angle spectroscopic ellipsometry. Due to limitations of the VASE measurements, a thin film of material was generated through dilution of the formulation. As seen in Figure 3, the extinction coefficient, k, is very low (near zero) until well below the visible spectrum (around 290 nm). This indicates that the material will not absorb light in the visible spectrum. As for the refractive index, typical dispersion is seen as the wavelength decreases and has values of approximately 1.62 at 800 nm and 1.68 at 400 nm. From this data, the Abbe number of the material was calculated to be 30.

In optical devices, the transmission of light is an essential feature of the device and materials that comprise the device. Accordingly, the transmission spectrum of the film on quartz was measured. As seen in Figure 4, the film is nearly transparent from 400 nm to 2700 nm, which indicates that the material is useful in applications where the visible spectrum is used, as well as the telecommunications spectrum (near infrared, 800-1600 nm).

In UV-cured systems, thorough curing is essential for environmental and physical stability. As detailed in Figure 5, films having the same thickness and exposed to different doses of UV radiation exhibit remarkably similar extrapolated refractive index curves. These results indicate that the material has received sufficient radiation at the lowest dosage to be considered fully cured.

4.2 Pattern characterization

Figures 6 and 7 indicate that the structures of the SKW 7-2 wafer were successfully duplicated on the press-patterned wafers coated with “C-Series” material. Nearly identical results were observed from wafers processed with different press-patterning times. Step height measurements, from different pitch size and feature density areas on all the processed wafers, indicated little ($\leq$6%) step height reduction on the pressed-patterned wafer when compared to that of the original step height measured from the SKW 7-2 wafer (Table I). The step height scanned profiles from Figure 6 further indicated that the original SKW 7-2 structures possessed overhang on the line edge, about 0.2 μm in height. This overhang was duplicated onto the press-patterned wafers (Figure 7). Further study using a microscope verified this finding.

It is suspected that the slightly decreased step height, compared to that of the SKW 7-2 wafer, could be due to number of factors, including variation introduced during the pattern generation process in the template and press-patterning and curing the of the “C-Series” material. These factors are influenced by the template material strength and wetting property of the ‘C-Series” material while it makes contact with the template surface. In addition, material shrinkage during template production and photocuring of the “C-Series” material could also contribute to the variation as well. A more in-depth study is required to verify the causes of step height decrease.

Cross-section SEM characterization shows an important fact that the film thickness stays nearly identical among the pitch size areas characterized (Figures 8 through 10). Film thickness measurements are summarized in Table II. This finding is critical to press-patterning. To press-pattern a low feature density area (fewer and/or thinner line structures), a large amount of material needs to be displaced to higher feature density areas in order to maintain good thickness uniformity. These three pitch areas also represent three feature density areas. A line thickness difference of less than 0.1 μm and a trench thickness difference of less than 0.05 μm were observed among the areas characterized. According to these measurements, a step height of about 900 nm, comparable to those obtained from the Dektak 8 stylus profilometer, was verified using SEM.

Different feature density structures surround these three SEM-characterized pitch areas [18]. The insignificant film thickness variation (Table II) indicates that CON-TACT® technology is capable of press-patterning structures with uniform film thickness. More thorough film thickness studies across the die and wafer, and from wafer to wafer, are warranted to better characterize the performance of press-patterning the “C-series” materials using CON-TACT® technology.

5. CONCLUSIONS

We have developed a novel transparent, UV-curable, solvent-free composition with a high refractive index. This material may be applied to substrates using spin coating, although other methods are possible. Pattern generation in the film was demonstrated by using a press-patterning technique that indicated reliable, regular structures could be easily replicated from a master film.

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