

High refractive index photocurable resins

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ABSTRACT

The performance of optoelectronic devices can be increased by incorporating a high refractive index layer into the system. This paper describes several potential high refractive index resin candidates. Our materials include the added advantages over other systems because the new materials are cationically photocurable and free flowing, have low shrinkage upon cure, have no (or little) volatile organic components, are applicable by a variety of methods (dip coating, roller coating, injection molding, or film casting), can be applied in a variety of thicknesses (10-100 μ), are fast-curing, and possess robust physical properties. Particular attention focuses on the refractive index in the visible spectrum, light transmission, and formulation viscosity.

Keywords: UV curable, high refractive index, low shrinkage, transparent

1. INTRODUCTION

The performance of optoelectronic devices, such as cover layers for optical disks, diffraction gratings, molded microlenses, flat panel displays, imaging sensors, photonic circuits, and light-emitting diodes (LEDs), can be improved by the incorporation of a high refractive index material layer¹⁻³¹. With the improvement afforded by a high refractive index layer, many technologies will become more efficient and economical, which will lead to wide commercial distribution.

Few high refractive index materials are available today. In these systems, they typically have short pot lives and require long cure programs and/or high temperatures, which may degrade device performance. Utilizing an ultraviolet (UV) cure system would eliminate heating, mixing, and drying processes associated with a thermal cure. Most commercially available photocurable materials utilize a free-radical mechanism of cure and are dependent on oxygen concentration. Oxygen negatively affects free radical polymerizations by reacting with the radical and leads to undesirable side reactions. Consequently, there is a demand for materials that possess the aforementioned properties.

Our research focuses on the development of cationically photocurable high refractive index materials. By selecting the cationic mechanism of curing, we have eliminated the dependence of the cure on the presence of oxygen. Fortunately, numerous commercially available materials are curable by a cationic mechanism. Therefore, with the availability of these types of materials, we have developed materials that are easily tailored, according to customer-specific criteria. Here we report our development of cationic photocurable resins.

2. EXPERIMENTAL

The photocurable resin solutions were prepared by heating and mixing the appropriate resin(s), reactive diluent(s), and catalyst (photoacid generator, PAG) at 80°C. Resins and reactive diluents 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. All resin samples contained 2% by weight PAG. The higher viscosity resin solutions required preheating in a 100°C oven prior to deposition.

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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. During our work, we used 100-mm silicon wafers and 76-mm quartz wafers. After spinning, some films contained microcrystalline domains and required a short bake at 100°C prior to UV curing.

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 approximately 3.7 mW/cm², measured at 365 nm. Typical exposure doses were 1.5-4 J/cm² (6-18 minutes).

Percent transmission data for the films are 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 was employed.

The refractive indices, and where possible, thicknesses, were measured on a Metricon 2010 prism coupler, operating at 401 nm, 632.8 nm, and 780 nm. In thick samples (greater than 20 μ), the bulk sample mode was used. In thin samples (less than 20 μ), the prism coupling/single film mode was used.

Thicknesses not observable by the prism coupler, due to thicknesses outside the limits of the device, were measured via digital calipers (VWR International, catalog number 62379-531.) The calipers were zeroed on the bare wafer, and at least three measurements were taken around the wafer. The average of the measurements was taken as the thickness of the film. The accuracy of the calipers is 0.01 mm (10 μ.)

Optical constant (n and k) data were obtained from thin films using a J.A. Woollam variable angle spectroscopic ellipsometer (VASE®). The thin film was obtained by diluting the resin solution to 20% solids in cyclopentanone and spin-coating a film at 3000 rpm, with 4500 rpm/s ramp rate, for 60 seconds. The film was cured with 2 J/cm². Data are collected from 300 nm to 1700 nm.

Viscosity data are obtained on a TA Instruments AR2000 rheometer using the 25-mm aluminum disk geometry. Viscosity was measured as a function of temperature from 23°-75°C.

3. RESULTS

3.1 Viscosity

The resin solutions were prepared according to procedures defined in the experimental section. After preparation, the viscosities of the solutions were measured and compared (Figure 1.)

3.2 Spin speed curves

Resin solutions were then deposited onto silicon and quartz wafers and spun. Different spin speeds were employed to achieve thickness variation. Figure 2 details the effects of this parameter on the thickness of the films.

3.3 Refractive indices obtained through VASE measurements

A portion of each resin solution was diluted with cyclopentanone and coated on silicon wafers and cured. Figure 3 shows the comparison of n values for the cured films. In all cases, k was less than 0.002 throughout the visible spectrum.

3.4 Refractive indices as a function of wavelength for different thickness films

The bulk films were also examined for their refractive indices through the use of a prism coupler. This measurement was used to determine any variation in refractive index for the different thicknesses of films. Figure 4 displays the variation in refractive index for the different thicknesses tested. The trend in this figure is representative of all materials tested.

3.5 Percent transmission

The films coated on quartz wafers were examined for their percent transmission. Figure 5 displays the percent transmission data for the studied materials.

3.6 Thermal stability of EXP04215

Composition EXP04215 was coated on a quartz wafer, cured, and stored in a 100°C oven. Its percent transmission was periodically obtained to determine its thermal stability. Figure 6 details the thermal stability of an EXP04215 film.

3.7 Light stability of EXP04215

Composition EXP04215 was coated on a quartz wafer, cured, and continually irradiated with broadband radiation. Its percent transmission was periodically obtained to determine its light stability. Figure 7 shows the stability of a film of EXP04215 to light.

Viscosity Data

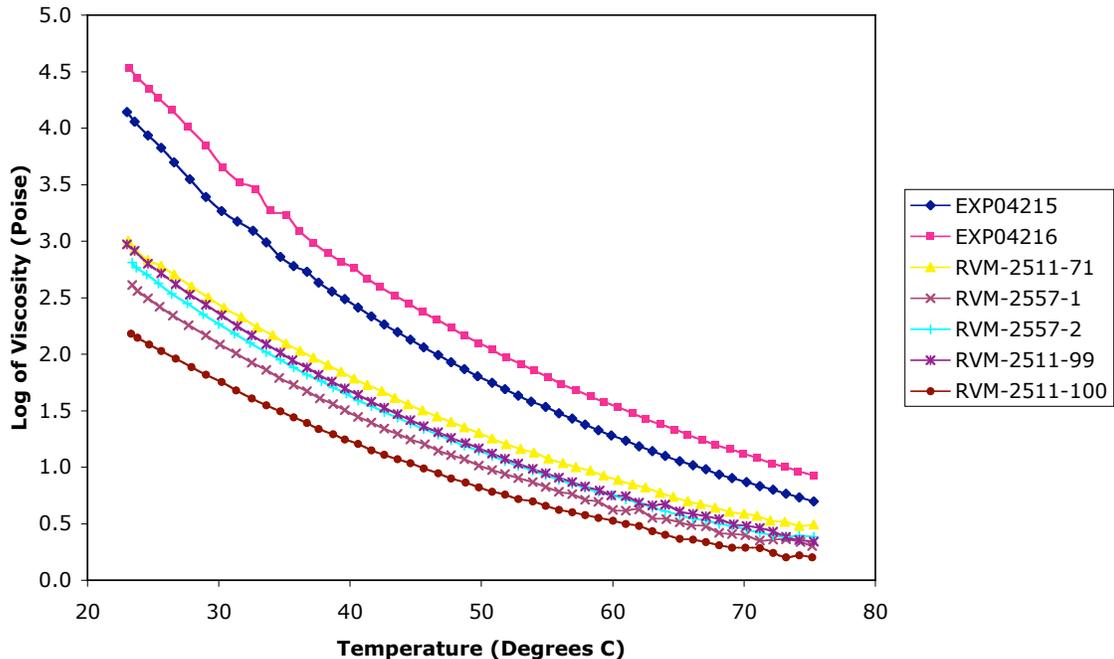


Figure 1. Viscosities of resin solutions studied.

Spin Speed Curves

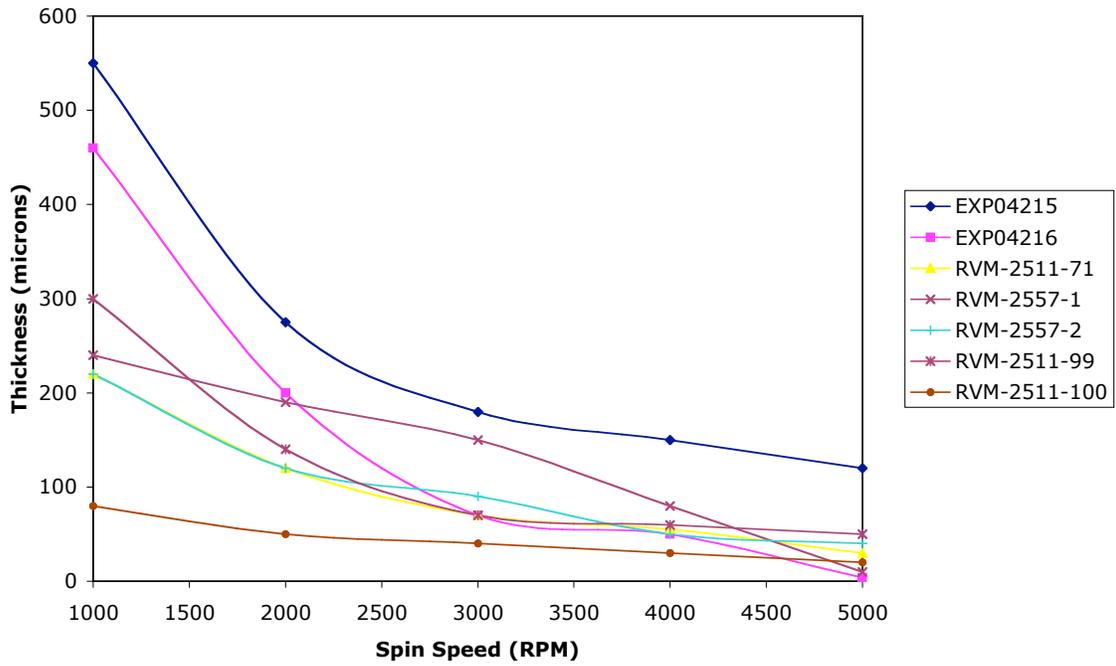


Figure 2. Spin speed curve for materials deposited on silicon wafers.

Refractive Index Data - VASE

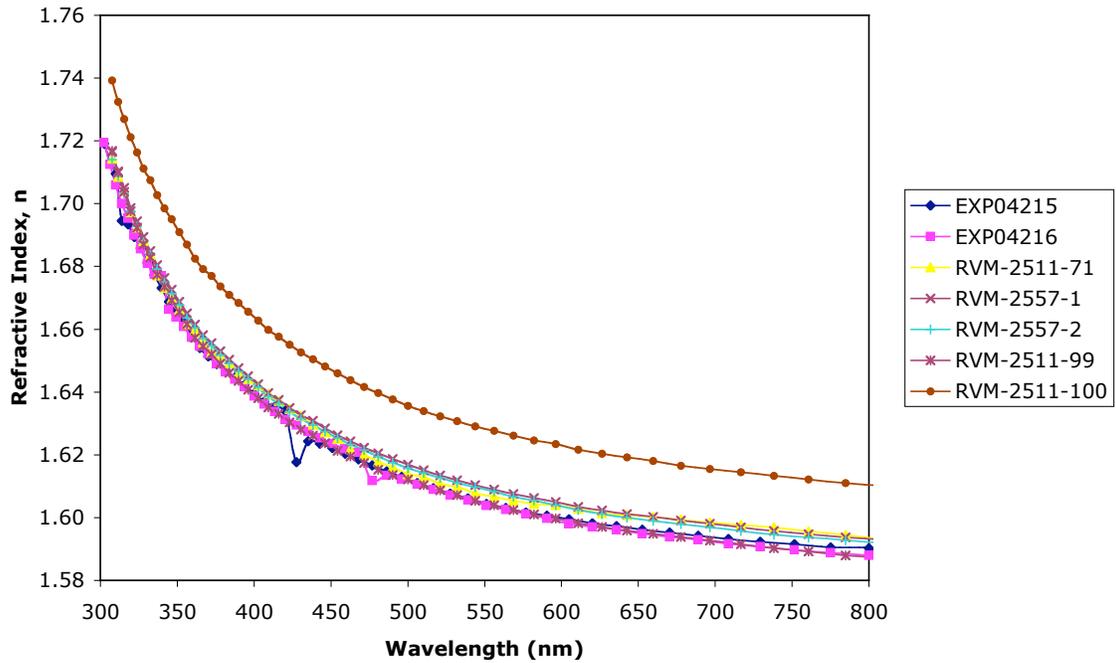


Figure 3. Refractive indices for materials coated as dilute solutions on silicon wafers.

Refractive Index vs. Wavelength For RVM-2511-99 Films

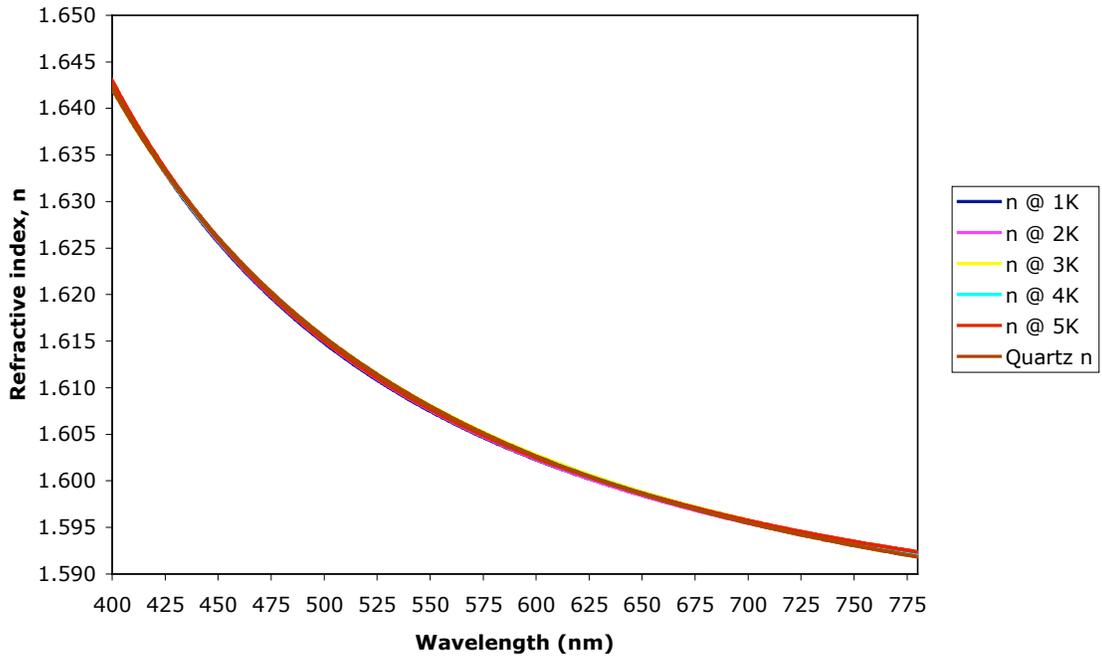


Figure 4. Refractive indices for bulk films of RVM-2511-99 deposited on silicon and quartz wafers.

%Transmission

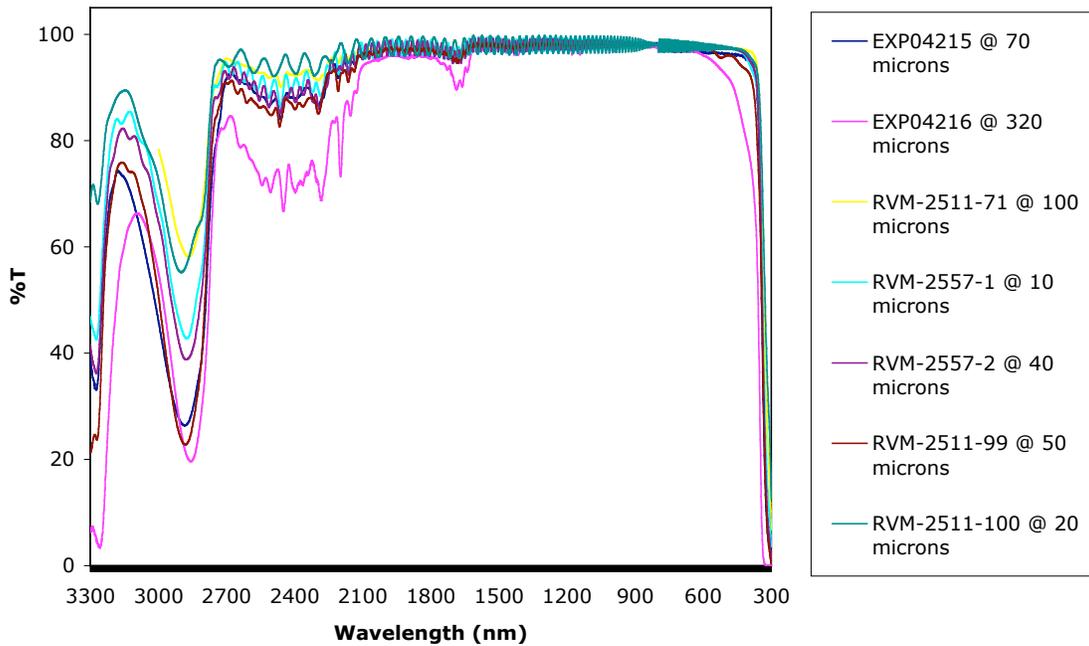


Figure 5. Percent transmission curves for films coated on quartz wafers.

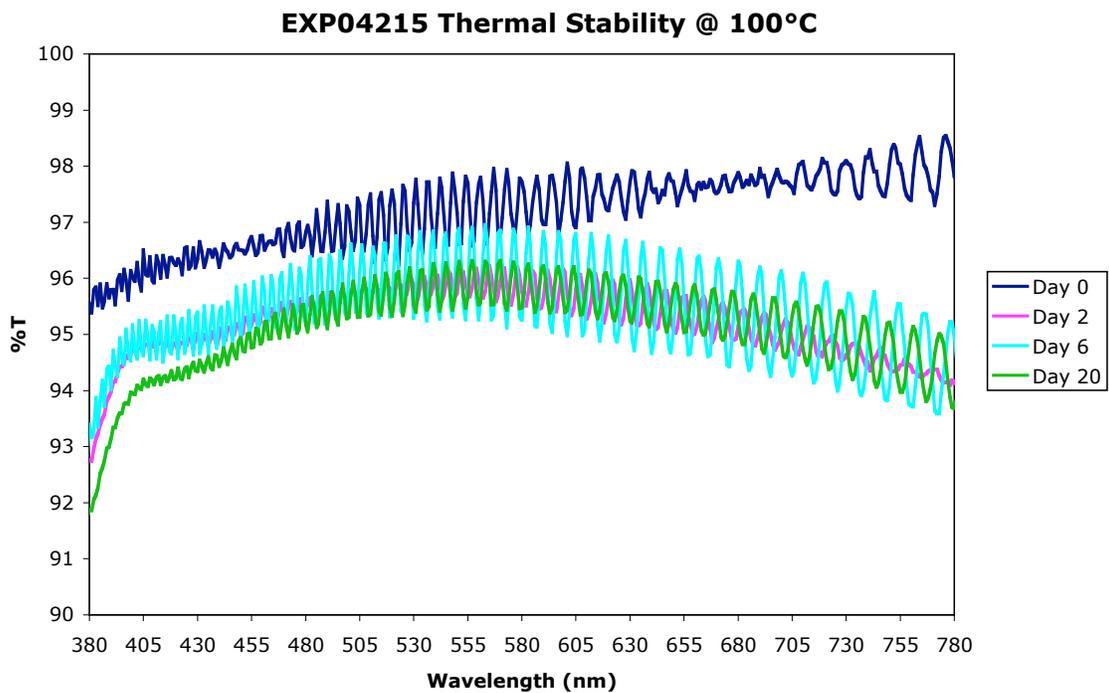


Figure 6. Stability of EXP04215 film on quartz over time at 100°C.

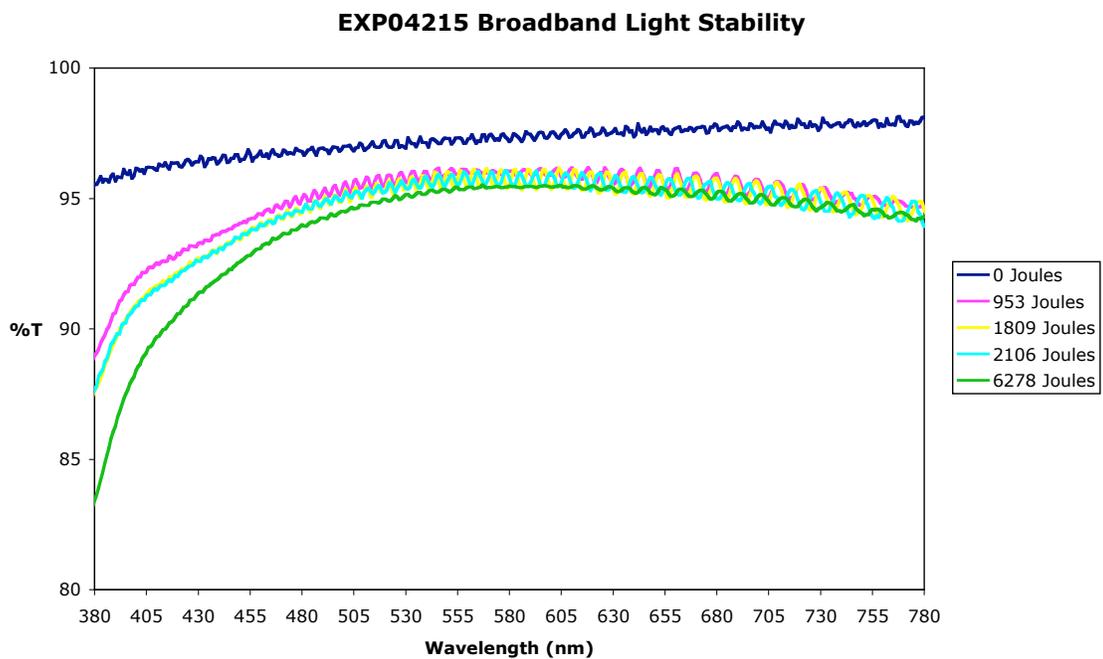


Figure 7. Stability of EXP04215 film on quartz wafer exposed to broadband irradiation.

4. DISCUSSION

The advancement of optoelectronic devices is creating a demand for high refractive index materials. Consequently, we are developing solutions to this problem. Specifically, we are developing high refractive index materials that are UV curable, are flowable, have low shrinkage upon cure, have no (or little) volatile organic components, are applicable by a variety of methods, can vary in thickness from 10-100 microns, are fast-curing, and possess robust physical properties.

As indicated in the experimental section, our materials are based on epoxy and vinyl ether compounds. We chose these materials because of several useful attributes. First, they are well known and well-studied materials^[4-6]. Also, they are both able to polymerize and crosslink through a cationic mechanism, which unlike free-radical chemistry (vinyl/acrylate/methacrylate-based materials), are not sensitive to the presence of oxygen^[4-6]. And finally, they are mechanically, thermally, and chemically robust materials and are used in a variety of applications^[4-6].

Because we are developing solvent free (or minimal solvent containing) resin solutions, an important factor is the viscosity of the resin solution. In Figure 1, the viscosities of the resin solutions are plotted as the log of the viscosity (Poise) versus temperature. EXP04215 and EXP04216 have the highest viscosities due an absence of additives. On the other hand, the RVM-2511-99 (a novolac epoxy resin) formulation does not contain any additives and it has a low viscosity. The viscosity of the novolac epoxy resin is lower than that of the epoxy resin in EXP04215 and EXP04216. As expected, the solution that contains the greatest amount of additive (RVM-2511-100) has the lowest viscosity.

To create films of these materials, spin-coating was the application method employed (Figure 2,) however, numerous other methods could be used as well. These materials could be spin-coated on a variety of substrates with minimal modifications. EXP04215 and EXP04216, as the higher viscosity materials, required pre-heating at 100°C prior to deposition on the wafer in order to facilitate the complete coating. In some cases, particularly with EXP04215 and EXP04215, microcrystalline domains would form during spinning. The microcrystalline domains were eliminated with a short bake prior to UV curing. Consequently, additives will most likely be required for formulations that will be applied via spin coating.

In order to determine the optical constants of the materials via spectroscopic ellipsometry, the resin solutions were diluted with cyclopentanone; films were then spin coated and cured. As seen in Figure 3, the refractive indices of the materials are higher than most other commercially available materials, which are typically less than 1.60 in the visible spectrum. In addition, the resin solution RVM-2511-100 displays a slight improvement over the other systems in refractive index, which is a consequence of the higher loading of bromine. Moreover, due to the higher loading of additive in this formulation, the viscosity of this material is the lowest of the materials tested. Consequently, formulating a high refractive index material with low viscosity can be achieved through this method.

The refractive index of the bulk films was also measured using a prism coupler. As seen in Figure 4, there is little variation in the refractive index for the varying thicknesses for the RVM-2511-99 films. This is indicative of complete cure for all thicknesses. This trend was seen for all materials studied. In most cases, the refractive indices obtained through VASE measurements were similar to those obtained through prism coupler measurements.

The materials were examined for their percent transmission, as shown in Figure 5. All films were very transparent in the visible spectrum. In addition, the films were transparent in the 1300-1500 nm range, which

would allow their use in telecommunication applications. The film of EXP04216 did start to absorb near 400 nm, which is most likely due to its thickness. Studies are currently underway to examine the transparency of these materials at thicknesses of greater than 100 microns, to determine if alternative materials will be required at very large thicknesses.

The thermal stability of a 70 μ thick film of EXP04215 was examined. The film was coated on quartz, cured, and then stored in a 100°C oven. The transparency of the material was measured. As seen in Figure 6, there was very little decay in the transparency of the film, indicating good thermal stability of the material. In addition, there was no evidence of the film peeling away from the wafer (a sign of embrittlement.)

The light stability of a 70 μ thick film of EXP04215 was also examined. The film was prepared in an identical manner to the thermal stability sample. The film was then continuously exposed to broadband irradiation as indicated in Figure 7. The film does appear to lose some transmission in the UVA region, however, only after a substantial dose of irradiation. Further testing of this effect is underway, and this may necessitate the introduction of additives to quench this phenomenon.

5. CONCLUSIONS

We have demonstrated the preparation and characterization of several novel photocurable high refractive index compositions. These materials are free flowing yet contain minimal solvent (≤ 1 wt%), have high refractive indices (up to 1.62-1.66 in the visible spectrum), are easily cured, are applicable by a variety of methods, and are highly transparent, thermally stable, and light resistant.

REFERENCES

1. T. Flaim, Y. Wang, and R. Mercado, "High Refractive Index Polymer Coatings for Optoelectronics Applications," *Proceedings of SPIE: Optical Systems Design 2003*, vol. 5250, 2003, pp. 423-434.
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. L. Beecroft and C. Ober, "High Refractive Index Polymers For Optical Applications," *Journal of Material Science, Pure and Applied Chemistry*, A34(4), 1997, pp. 573-586.
4. E. W. Flick, "Epoxy Resins, Curing Agents, Compounds, and Modifiers, Second Edition: An Industrial Guide," Noyes Publications, 2nd edition, 1993.
5. B. Ellis, Ed., "Chemistry and Technology of Epoxy Resins," Kluwer Academic Publishing, 1st Ed., 1993.
6. S. K. Rajaraman, W. A. Mowers, and J. V. Crivello, "Interaction of Epoxy and Vinyl Ethers During Photoinitiated Cationic Polymerization," *Journal of Polymer Science: Part A: Polymer Chemistry*, vol. 37, 1999, 4007-4018.

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