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Processing and optical properties of inorganic–organic hybrids (polycerams). I. MPEOU-based waveguides

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Abstract

Sol–gel techniques have been employed to synthesize a number of organic-modified hybrid materials (polycerams) using a functionalized organic polymer (N-triethoxysilylpropyl O-polyethylene oxide urethane) together with a range of metal alkoxides and acetates. Despite the disparate nature of the constituents, the chemistry and processing have been successfully controlled to achieve a high level of homogeneity down to the molecular level. The optical properties (index of refraction, loss, dispersion and transmittance) of the polycerams are reported as functions of various metal oxides. These properties are then correlated to the homogeneity of the network. Polycerams of differing compositions can be easily designed and synthesized to yield low-loss (< 1 dB/cm) optical waveguides with the desired refractive index and dispersion.

1. Introduction

Polycerams, also known as ormosils or ceramers, are polymer-modified ceramic materials, in which the organic and inorganic components can be combined on a molecular level. Wet chemical techniques offer a unique approach to the synthesis of such hybrid materials due to the low reaction temperatures [1]. Many organic groups, polymers or oligomers have been incorporated into silicon, titanium and aluminum oxide networks using sol–gel chemistry [2–7]. The properties of these organic–inorganic hybrids can be easily tailored with the choice of functionalized polymers and inorganic components (i.e., nmetal alkoxides).

Of particular interest are the optical properties of polycerams, for use in optics and optoelectronics. Most of the literature on the optical properties of polycerams has focused on the capability of tailoring the index of refraction [8–10]. Few claims have been made on the optical loss of these polyceram materials; an earlier publication by the present authors reported losses of 1.4 to 2.9 dB/cm in SiO_2–TiO_2–MPEOU (MPEOU stands for N-triethoxysilylpropyl O-polyethylene oxide urethane) polycerams [11], and Schmidt

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and co-workers reported losses below 0.1 dB/cm in Zr, Ti and Al–methacrylate acid waveguides with a thickness of > 20 μm and capped with a cover layer of smaller index [12,13].

The purpose of the present paper is to extend the boundaries of hybrid materials with low optical losses which can be synthesized via sol–gel techniques. In this study, a series of novel hybrid polyceram materials has been prepared in the form of dielectric waveguides which exhibit remarkable optical properties. The index of refraction of these systems can be varied with the incorporation of different metal oxides. The optical properties of the systems are reported as functions of different metal alkoxides. These optical properties include the index of refraction, Abbe number, absorption edge and most importantly optical loss.

2. Experimental procedures

Sol–gel derived polycerams were synthesized using the oxides of Si together with those of Ti, Ge, Pb, Zn, Zr or Ta as the inorganic species, and (N-triethoxysilylpropyl) O-polyethylene oxide urethane (designated MPEOU) with a formula of $(EtO)_3Si(CH_2)_3NHCO[CH_2CH_2O]_n$–H as the organic constituent. The precursors used were titanium iso-propoxide ($Ti(O^iC_3H_7)_4$), germanium n-butoxide ($Ge(O^nC_4H_9)_4$), lead n-butoxide ($Pb(O^nC_4H_9)_4$), zinc acetate ($Zn(OOCCH_3)_2$), zirconium n-propoxide ($Zr(O^nC_3H_7)_4$) and tantalum ethoxide ($Ta(OC_2H_5)_5$). MPEOU contains triethoxysilylpropyl modification at the urethane site, and hydroxyl at the terminal end of the polymer chain. It has a molecular weight of 300–400 g/mol and approximately 1 triethoxysilyl group per monomer unit.

As shown in Fig. 1, solutions were prepared by first refluxing tetraethoxysilane (TEOS) and water (acidified to 0.15M HCl) together with the polymer. The metal alkoxide, in an Si:metal mole ratio of 1:1, was then added after cooling the solution. After further mixing, the solutions were concentrated by rotary evaporation. The coated substrates were dried in a vacuum oven at 125°C for 72 h to yield dense MPEOU–SiO_2 based polyceram waveguides. The details of solution synthesis are included in an earlier publication [10].

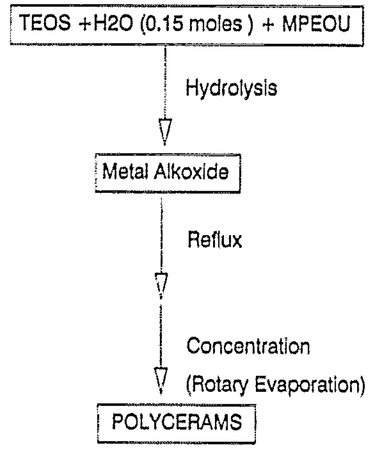

Fig. 1. Schematic illustration of the synthesis of MPEOU-based polycerams.

Each polyceram composition was composed of 80% by volume MPEOU, assuming full conversion of TEOS and metal alkoxide to SiO_2 and metal oxide. The calculations were based on complete burn-out of solvents and lack of residual –OR and –OH bonds. In the case of ZnO–SiO_2–MPEOU, the acetate remained in the network.

A profilometer (Dektak IIA) was used to measure the film thickness. The index of refraction was obtained using a multi-angle ellipsometer equiped with a He–Ne laser (Gaertner). Small-angle X-ray scattering (SAXS) experiments were conducted with a Kratky camera on clear, free-standing films cast from solution. Transmittance spectra were obtained using a UV–VIS Spectrometer (Perkin–Elmer). SAXS and UV experiments were conducted twice on each composition to ensure reproducibility.

The dispersion was obtained using a prism-coupling technique to launch laser light into the TE_0 and TM_0 modes of the waveguide. Measurements were conducted at wavelengths of 632.8, 514.5, 488 and 457.9 nm using helium–neon and argon lasers.

The optical loss of the polyceram films was measured using a prism-coupling technique to obtain a streak in the waveguide. These measurements were made using a helium–neon laser ($\lambda = 632.8$ nm), and losses were obtained in dB/cm. Fig. 2 depicts the loss measurement system set-up.

3. Results

The homogeneity of bulk polycerams was investigated with SAXS. Fig. 3 shows the SAXS profiles of ZrO_2–, ZnO_2–, TiO_2–, Ta_2O_5–, GeO_2– and PbO–SiO_2–MPEOU polycerams in the form of Guinier plots. The horizontal intensity versus M^2 plots in all cases reflects the asymptotic scattering from compositional fluctuations. In the higher angular region where the smeared intensity is essentially independent of angle, the true intensity is likewise angular independent. The intensity in this region is determined by the beam length. The SAXS data in this region show a high degree of chemical homogeneity.

Table 1 summarizes the optical properties of the above polycerams. The index of refraction of the polycerams ranges between 1.495 ± 0.011 (MPEOU–SiO_2–ZnO) and 1.631 ± 0.001 (MPEOU–SiO_2–Ta_2O_5) and the films have an average thickness of > 2 μm. The thickness of the film together with the difference between the index of refraction of the film and that of the substrate determine the number of modes which a waveguide can support. Here, the index of refraction

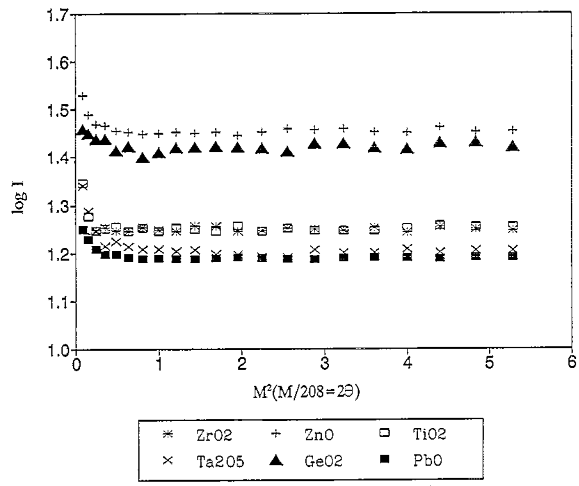

Fig. 3. SAXS profiles of ZrO_2–, ZnO_2–, TiO_2–, Ta_2O_5–, GeO_2– and PbO–SiO_2–MPEOU bulk polycerams.

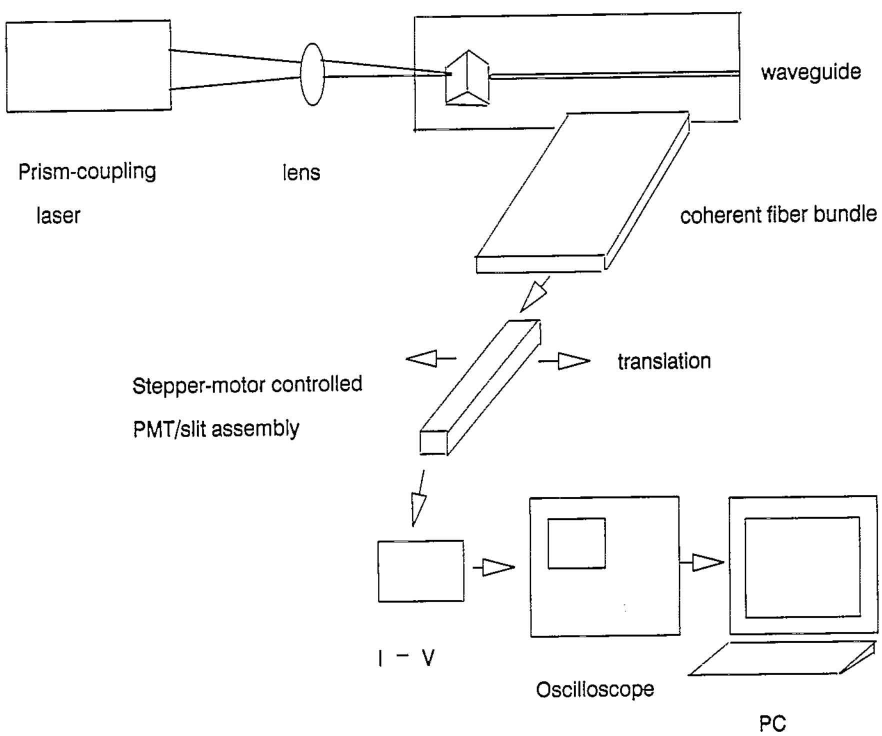

Fig. 2. Schematic of the waveguide loss measurement apparatus.

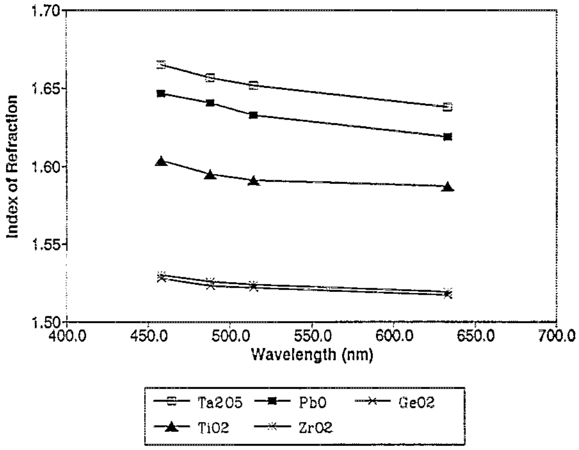

Fig. 4. Index of refraction of polycerams versus wavelength.

of the quartz substrate is 1.46, thus all waveguides support more than one mode. The optical loss of the films ranges between < 0.25 dB/cm and 3.27 ± 0.20 dB/cm.

Fig. 4 shows the indices of polycerams measured at four wavelengths ($\lambda = 632.8$, 514.5, 488 and 457.9 nm). A line connects the indices of each composition to show the behavior of the index of refraction versus wavelength. As mentioned in the Experimental section, the dispersion was measured using a prism-coupling technique where laser light is launched in the TE_0 and TM_0 modes of the waveguide, and the coupling angles of the two modes is used to determine the film's index of refraction. Often, in thin waveguides or waveguides with a small Δn between film and substrate, the coupling angles of the TE and TM modes nearly overlap and can hardly be resolved by eye. $ZnO–SiO_2$–MPEOU with an index of 1.495 ± 0.011 and a thickness of 2.11 ± 0.22 μm was one such waveguide where dispersion measurements could not be conducted with the naked eye.

4. Discussion

4.1. Homogeneity

Molecular homogeneity of polycerams is the a priori requirement for obtaining waveguides with high optical quality. The structures of polycerams depend on both the precursors and synthesis conditions. The molecular weight also directly affects the level of homogeneity which can be obtained. The number of reactive groups on the polymer determines the ability of the polymer to bond in more than one site with the inorganic phase. In addition, the polyceram constituents should have compatible polarity to exhibit molecular homogeneity. In this case, inorganic oxides are polar and MPEOU is relatively polar and is readily soluble in alcohol [7]. Finally, the pH of the solution can have a remarkable effect on the network structure since it directly affects the rates of hydrolysis and condensation [7]. Based on the SAXS data, the polycerams are consistent with materials having a high degree of chemical and physical homogeneity. A detailed comparison of SAXS data of all polyceram compositions based on desmeared and absolute intensity will be discussed in light of the densities of the constituents in a future publication [14].

4.2. Refractive index, optical loss and dispersion

For applications in integrated circuits, the total optical attenuation of a waveguide should be

Table 1
Index of refraction, thickness and optical loss of polyceram waveguides

Polyceram composition	Index of refraction at $\lambda = 632.8$ nm ± std. dev.	Thickness ± std. dev. (μm)	Loss ± std. dev. (dB/cm)
MPEOU–SiO_2–GeO_2	1.507 ± 0.006	1.73 ± 0.10	0.72 ± 0.13
MPEOU–SiO_2–ZrO_2	1.562 ± 0.009	1.97 ± 0.19	3.27 ± 0.20
MPEOU–SiO_2–TiO_2	1.571 ± 0.005	2.89 ± 0.15	< 0.25
MPEOU–SiO_2–PbO	1.622 ± 0.010	2.30 ± 0.23	1.54 ± 0.42
MPEOU–SiO_2–Ta_2O_5	1.631 ± 0.001	2.06 ± 0.26	0.91 ± 0.25
MPEOU–SiO_2–ZnO	1.495 ± 0.011	2.11 ± 0.22	1.08 ± 0.32

< 1 dB/cm. As seen in Table 1, these polyceram waveguides exhibit remarkably low attenuations. These low losses are also indicative of a high level of chemical homogeneity in the polyceram waveguides. The higher the number of constituents of a film, the higher the probability of obtaining high optical loss as attenuation is directly related to index of refraction fluctuations within the network. In addition to volume inhomogeneities, losses can also originate from surface scattering. The degree of surface roughness is a direct consequence of the relaxation ability of the polyceram constituents during spin-coating or upon subsequent densification. The presently observed low losses are indicative of high volume homogeneity as well as low surface roughness.

The higher attenuation of MPEOU–SiO_2–ZrO_2(3.27 ± 0.20 dB/cm), however, stems from a different source – the absorbing nature of Zr metal (dark yellow color). Fig. 5 shows the transmittance spectra of the polycerams, depicting an absorption band for MPEOU–SiO_2–ZrO_2 centered around 310 nm. The streak in the MPEOU–SiO_2–ZrO_2 waveguide was slightly lighter in color than the other waveguides, and faded out gradually across the waveguide, reflecting the higher loss. In general, however, all the polycerams exhibit full transmittance to low UV ranges, a necessary requirement for optical waveguiding.

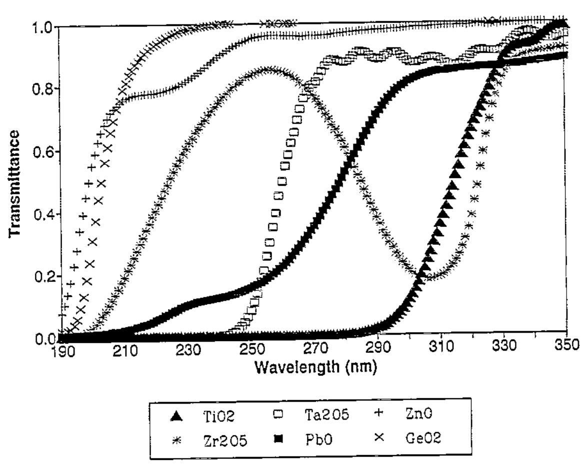

Fig. 5. UV transmittance plots of polyceram waveguides.

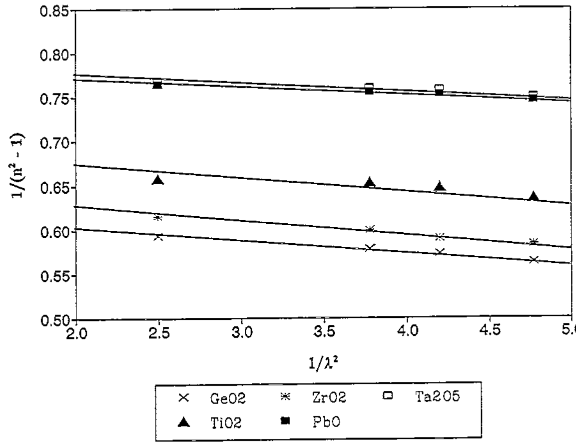

Fig. 6. Sellmeier plots for polycerams.

As expected, the index of refraction of the polycerams decreases with wavelength (see Fig. 4). This type of behavior is entitled 'normal' dispersion. In addition, the change in index of refraction, Δn between wavelengths $\lambda = 632.8$ nm and $\lambda = 457.9$ nm increases following the sequence $GeO_2 < ZrO_2 < TiO_2 < PbO < Ta_2O_5$–$SiO_2$–MPEOU. Note that the index of refraction of Ta_2O_5–SiO_2–MPEOU is the highest and the index of GeO_2–SiO_2–MPEOU is the lowest. This indicates that polycerams with higher indices of refraction exhibit higher dispersions, Δn, at least for the systems investigated here.

The refractive indices were fitted in an oscillator (Sellmeier)-type dispersion equation,

$$\{[n(\lambda)]^2-1\}^{-1} = A/\lambda^2 + B, \qquad (1)$$

where the constants A (slope) and B (y intercept) were determined in a least-squares fit with a goodness of fit (R^2) of > 0.84. Fig. 6 shows these plots. The above calculations were then utilized to determine the Abbe number of each composition. The Abbe number, ν_d, is defined as

$$\nu_d = (nd-1)/(nF - nC), \qquad (2)$$

where n_d, n_F and n_C are the refractive indices for the helium d line (587.6 nm), the hydrogen F line (486.1 nm) and the hydrogen C line (656.3 nm). These Abbe numbers are shown in a n_d–ν_d map in Fig. 7, where the present contour of

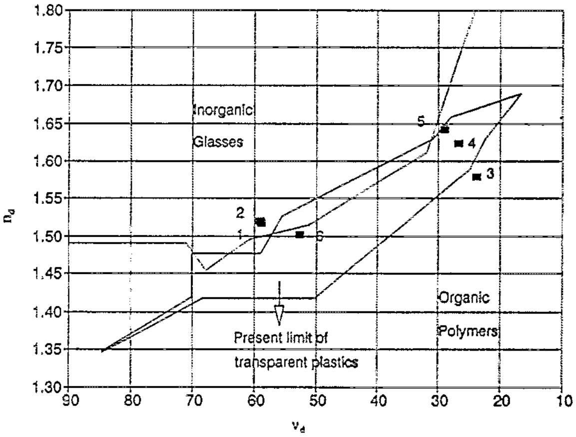

Fig. 7. Plot of n_d–ν_d of polycerams: 1, MPEOU–SiO_2–GeO_2; 2, MPEOU–SiO_2–ZrO_2; 3, MPEOU–SiO_2–TiO_2; 4, MPEOU–SiO_2–PbO; 5, MPEOU–SiO_2–Ta_2O_5; 6, MPEOU–SiO_2–ZnO.

transparent plastics as well as the separation between glasses and polymers are indicated. The Abbe number of ZnO–SiO_2–MPEOU was obtained using an Abbe monochromator. As expected, the Abbe numbers of the polycerams fall between those of glasses and polymers, covering a wide range of values. A high Abbe number corresponds to a low dispersion and vice versa. Here, polycerams labelled 1, 2 and 6 corresponding to MPEOU–SiO_2–GeO_2, MPEOU–SiO_2–ZrO_2 and MPEOU–SiO_2–ZnO compositions have the highest Abbe numbers but lowest indices of refraction. By contrast, polycerams 3, 4 and 5 corresponding to MPEOU–SiO_2–TiO_2, MPEOU–SiO_2–PbO and MPEOU–SiO_2–Ta_2O_5 compositions have the lowest Abbe numbers but highest indices of refraction. The significant range of values indicates a high level of flexibility in tailoring polycerams with desired material dispersion.

5. Conclusions

Various compositions of polycerams were synthesized to yield planar dielectric waveguides with remarkable optical qualities. Most waveguides had losses < 1 dB/cm, and covered a wide range of optical dispersion comparable with those of optical glasses. The underlying property which enabled the achievement of these waveguides was the chemical homogeneity of the networks, as observed by small-angle X-ray scattering (SAXS) studies.

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