Low optical loss planar waveguides prepared in an organic–inorganic hybrid system

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HfO_2-(3-glycidoxipropil)trimethoxisilane (GPTS) planar waveguides were prepared by a sol–gel route. A stable sol of Hafnia nanocrystals was prepared and characterized by photon correlation spectroscopy and high resolution transmission electron microscopy. The suspension was incorporated in GPTS host and the resulting sol was deposited on borosilicate substrates by the spin coating technique. Optical properties such as refractive index, thickness, number of propagating modes, and attenuation coefficient were measured at 632.8, 543.5, and 1550 nm by the prism coupling technique as a function of the HfO_2 content.

Sol–gel materials have been widely used in the development of optical materials in the planar waveguide format for use in integrated optics (IO).[1–5] One of the important reasons for that relies on the particle size control of the precursor material. In general, it is possible to produce particle sizes sufficiently small to keep Rayleigh scattering losses to an acceptable low level even for important volume fraction of nanoparticles.[3,6] In fact, in multicomponent materials the mixing of the precursors on a molecular scale in order to avoid phase separation is one of the intrinsic characteristics of the sol–gel methodology. However, if the phase separation is controlled, solid state properties of the nanoparticulate phase could lead to special properties. In this way, loading silica based hosts with different nanosized materials, one can tailor refractive index, increase scratch resistance, or enhance optical properties.[3,7,8] In particular, the (3-glycidoxipropil)trimethoxisilane (GPTS)–HfO_2 binary system could be of significant technological importance because it offers the possibility of producing planar waveguides with a controlled refractive index depending on the HfO_2/GPTS molar ratio. Hafnium dioxide is transparent over the range from 300 nm to 10 μm and exhibits high refractive index, about 1.95 at 1000 nm.[9] Moreover, densification of GPTS based films can be achieved at low temperatures while keeping optical quality.[10]

This letter reports on the preparation of hafnia nanocrystals with controlled sizes and the optical characterization of the hybrid planar waveguides obtained by loading GPTS with the nanocrystals.

Hafnia nanocrystals were prepared from a suspension of hafnium oxichloride in ethanol. The mixture was kept under reflux for 2 h resulting in completely transparent colloidal suspensions. Hafnia nanocrystals could be identified by high resolution transmission electron microscopy (HRTEM) analysis. Figure 1 shows the HRTEM image where the arrows show typical nanocrystals that could be easily identified by the planes spaced by 3.17 Å (hkl = 111 for monoclinic HfO_2–PCPDF file 34-0104). Figure 2 shows the particles size distribution obtained from photon correlation spectroscopy analysis. An effective mean diameter of 4.0 nm is obtained for the hafnia sol with a narrow size distribution of about 3 nm.

GPTS was diluted in buthanol (volume ratio 1:0.5). A prehydrolysis treatment was performed by addition of HCl

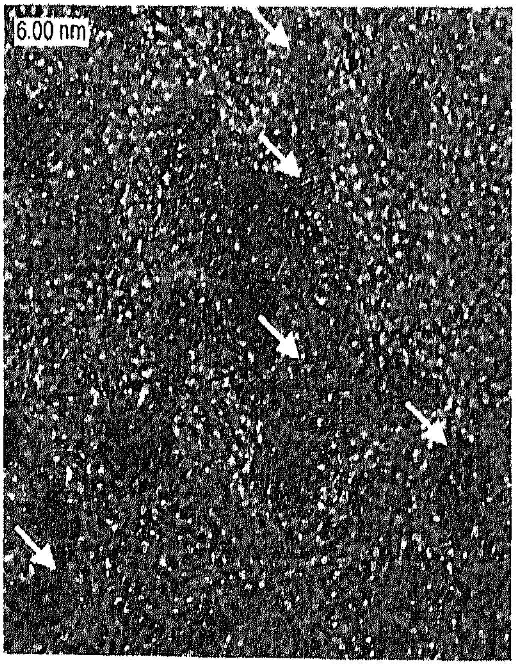

FIG. 1. HRTEM image obtained for the HfO_2 sol. The arrows indicate some typical hafnia nanocrystals.

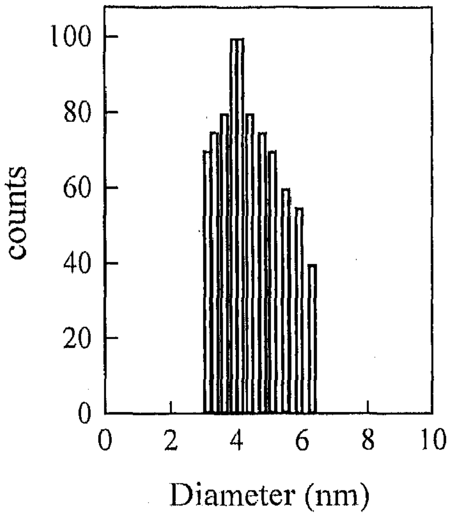

FIG. 2. Particle size distribution obtained for the HfO_2 sol by photon correlation spectroscopy.

0.1 M. The molar ratio GPTS:H_2O was 1:0.5. The resulting solution was submitted to vigorous stirring overnight at room temperature before loading with the HfO_2 nanocrystals. Three waveguide samples, hereafter identified by the acronyms W1, W2, and W3, were prepared with molar ratio HfO_2:GPTS = 10:90, 30:70, and 50:50, respectively.

Thin films were deposited on 50×50×2 mm borosilicate glass substrates by spin coating at 2000 rpm for 30 s. The films were treated by ultraviolet (UV) exposition with a Beltron UV lamp emitting in the range 280–320 nm and then heated at 130 °C for 1 h in order to achieve densification.

The refractive index and the thickness of the waveguides were measured for both transverse electric (TE) and transverse magnetic (TM) polarization by an *m*-line apparatus (Metricon mod. 2010) based on the prism coupling technique. We used a gadolinium gallium garnet prism with a refractive index of 1.9644 at 632.8 nm. The apparatus was equipped with Si and Ge detectors to collect the visible and near infrared (NIR), respectively. Two He–Ne lasers, operating at 632.8 and 543.5 nm and one diode laser operating at 1550 nm were employed. The resolution in the determination of the angles synchronous to the propagation modes was 0.0075°. In order to measure propagation losses the light intensity scattered out of the waveguide plane, which is proportional to the guided intensity, was recorded by a fiber probe scanning down the length of the propagating streak. The losses were evaluated by fitting the intensity to an exponential decay function, assuming a homogeneous distribution of the scattering centers in the waveguide. The measurements were performed by exciting the transverse electric TE_0 mode of the waveguide with the three lasers cited hereabove.

The refractive index of the borosilicate substrate was 1.4732, 1.4703, and 1.4560 at 543.5, 632.8, and 1550 nm, respectively for both TE and TM polarization. The optical parameters of the HfO_2–GPTS planar waveguides so obtained by modal measurements, are reported in Table I. The waveguides support many propagating modes depending on their thickness, refractive index, and exciting wavelength. As expected, the refractive index of the film increases with the nominal HfO_2 content. The observed variation is of the same magnitude from that observed in related organic–inorganic hosts containing modified zirconia nanoparticles.[11]

TABLE I. Optical parameters measured at 543.5, 632.8, and 1550 nm (TE polarization) for the HfO_2–GPTS planar waveguides. Attenuation coefficient is measured by exciting the TE_0 mode.

Sample	W1	W2	W3
HfO_2/GPTS (molar ratio)	10:90	30:70	50:50
Thickness (±0.1 μm)	3.3	3.4	4.5
Refractive index at 543.5 nm (±0.0005)	1.5007	1.5150	1.5302
Refractive index at 632.8 nm (±0.0005)	1.4960	1.5111	1.5252
Refractive index at 1550 nm (±0.001)	1.481	1.498	1.516
Number of modes at 543.5 nm	4	5	7
Number of modes at 632.8 nm	3	4	6
Number of modes at 1550 nm	1	2	3
Attenuation coefficient at 632.8 nm (±0.1 dB/cm)	1.7	2.6	2.6
Attenuation coefficient at 1550 nm (±0.1 dB/cm)	0.4	1.2	1.2

The total loss of a planar waveguide consists of absorption and scattering contributions, with the latter being usually predominant at the wavelengths of interest in integrated optics. The scattering optical loss measured for an amorphous waveguide is the sum of two contributions: volume scattering, due to local fluctuation in the refractive index resulting from density and compositional variation, and surface scattering due to surface roughness. The HfO_2–GPTS planar waveguides exhibit reasonably low loss for the wavelenght of interest in IO. In particular, the W1 waveguide exhibits a single propagation mode in the third telecom window with an attenuation coefficient of 0.4 dB/cm. Figure 3 shows the absorption spectrum, after baseline subtraction, obtained for a bulk sample with the same composition of the W1 waveguide. Some absorption bands assigned to combination and

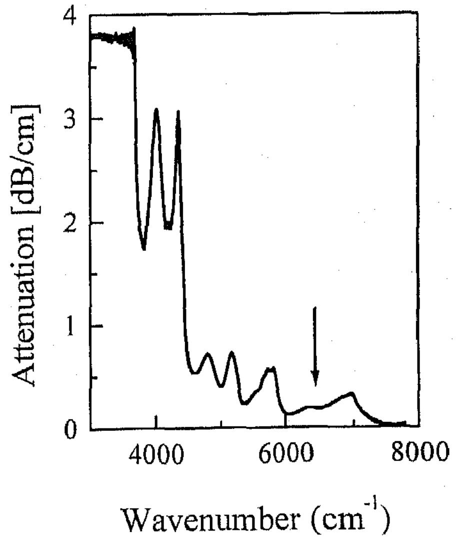

FIG. 3. Absorption spectrum of the HfO_2–GPTS system (HfO_2:GPTS = 10:90).

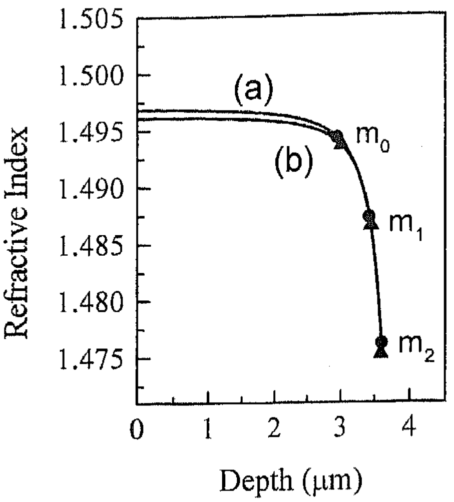

FIG. 4. Refractive index profiles of the W1 planar waveguide reconstructed from modal measurements at 633 nm for: (a) the TE and (b) TM polarization. The effective indices of the TE (●) and TM (♦) modes are reported.

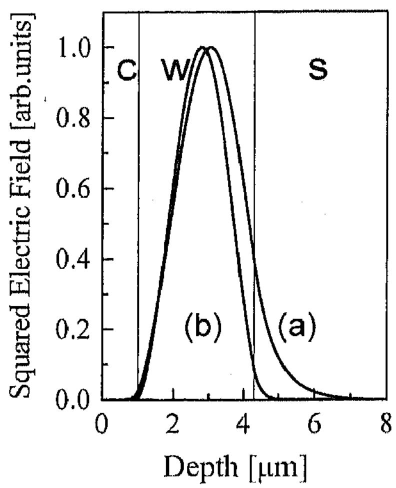

FIG. 5. Calculated squared electric field profiles of the TE$_0$ mode at 1550 nm (a) and 632.8 nm (b) across the layered structure–cladding of air C, waveguide W, and the borosilicate substrate S of the W1 planar waveguide.

overtones of the fundamental vibrational modes of the organic–inorganic system can be observed.[8] The attenuation coefficient at the wave number corresponding to 1550 nm, indicated by the arrow in the figure, is about 0.18 dB/cm. The scattering losses contribution could then be estimated to be about the 50% of the total losses for the W1 waveguide. The increase of the losses with the hafnia content could be assigned to the increase in both volume fraction and size of the nanocrystals. In fact, the scattering loss due to the presence of particles is proportional to the number of nanocrystals and to the sixth power of the particle size, neglecting multiple scattering.[6,12]

Figure 4 shows the refractive index profile of the W1 waveguide reconstructed from the effective indices at 632.8 nm by an inverse Wentzel–Kramers–Brillouin method.[13] The very small difference of the refractive index profiles obtained for TE and TM modes indicates that the birefringence in this waveguide is negligible. The other waveguides exhibit a similar behavior.

The hafnia loaded hybrid host gives satisfying results in the preparation of the waveguides. In fact, as shown in Fig. 4 and Table I, the planar waveguides support many propagation modes in the visible region and one propagation mode in the NIR region. Furthermore, they exhibit a single step profile with an uniform refractive index throughout the thickness. Figure 5 shows the squared electric field profiles of the TE$_0$ mode of the W1 waveguide, calculated at 632.8 and 1550 nm by using the parameters obtained by the m-line measurements. The modeling indicates that the optical parameters of the W1 waveguide, i.e., refractive index and thickness, appear appropriate for application in the third telecommunication window. In fact, the ratio of integrated intensity, i.e., the square of the electric field, in the waveguide to the total intensity, which includes also the squared evanescent fields, is 0.99 and 0.90 at 632.8 and 1550 nm, respectively. This means that an efficient injection at 1550 nm is possible for the produced waveguide.

In conclusion, stable sols of hafnia nanocrystals with mean size of 4 nm have been prepared and loaded in GPTS in order to prepare good optical quality planar waveguides. The optical parameters measured at 1550 nm, indicates that the monomode waveguide W1 produced by a HfO$_2$/GPTS = 1:9 molar ratio is the more suitable for passive IO application.

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