Sol-Gel Materials and Applications

Technology

Soreq NRC has developed the production process of an optical UV-cured adhesive, using sol-gel technology. The process involves fast preparation (minutes) of a viscous sol-gel resin followed by curing without shrinking or cracking. Curing can be performed by heating (few hours) or by UV light (few seconds). The substance is an excellent adhesive for glass, semiconductors, and metal. Recent development implements this method in a computer-controlled manufacturing device.

The process produces an optically clear adhesive (in the visible range) with desired refraction index and high thermal and irradiation stability. The mechanical properties of the sol-gel can also be controlled, ranging between silicone rubber and silica glass. The adhesive is manufactured as a resin, and then diluted with an appropriate diluent to increase its shelf life. Use of the adhesive is preceded by a brief process of diluent evaporation followed by curing. The product of the fast sol-gel process contains less than 30% organic residues, for making it resistant to high laser power, and it is therefore highly suited for optical applications. The adhesive has excellent transparency in the visible range, it is resistant to thermal cycling (-40°C to +120°C), and its adhesion strength is approximately 10 MPa.

High transparency (transmission over 90%) and the possibility to modify its refractive index by adding various components are clear advantages of this adhesive. It has been tested and found compatible for bonding components in solar energy systems, for example prisms (BK-7 glass) that concentrate light onto a sensor wafer (semiconductor). It can be used to construct solar concentrator modules with an energy conversion efficiency of 30%. This technology allows fabrication of optical elements at scales spanning the sub-micron to centimeter range. This enables mass-production of optical elements at low cost.

The hybrid organic-inorganic glass prepared by a Fast-Sol-Gel method allows integration of functional molecules (such as CNT and organic dyes) into a glassy sol-gel matrix for production of advanced optical elements (e.g., non-linear solid optical filters).

The benefits of SNRC’s fast sol-gel material production method are:

- Rapid manufacturing process
- Solidification without shrinkage and without formation of cracks
- Thermal- or UV-curable material with low organic content
- High optical transparency (optical loss < 0.01 dB/cm)
- High temperature stability > 300°C
- High laser damage threshold: 5 KW/cm² (CW), 2.5 GW/cm² (pulse)
- High adhesive strength > 10 MPa (to glass)
- Adaptable optomechanical properties (refractive index, dn/dT)
Applications

Optical filters based on carbon nanotubes (CNT)

Carbon nanotube molecules have sparked growing interest due to a number of unique physical properties: excellent electrical and thermal conductivities, high mechanical strength, and non-linear optical properties.

Carbon nanotubes are made of graphene, a graphite surface, which is rolled into a hollow tube. The ratio of length to diameter in these structures can reach several thousands, resulting in some of their unique properties.

Carbon nanotubes are fascinating compounds, exhibiting exceptional electrical and thermal conductivity, mechanical strength, and non-linear optical (NLO) properties. Their unique structures involve large $\pi$-$\pi^*$ electronic clouds. The energy level schemes thus created allow many electronic transitions between the ground and the excited states.

The glassy sol-gel matrix integrated with carbon nanotubes can be used as a non-linear filter, transmitting low-power laser radiation but absorbing the high-power radiation. Such filters can be used for eye and optical components protection.

The CNT composite glasses exhibit enhanced absorption at 532 nm, and saturable absorption at 1064 nm. The enhanced absorption at 532 nm was attributed to its 2-photon absorption; saturable absorption was attributed to depletion of the absorbing ground-state, and was analyzed using the modified Frantz-Nodvik equation. Absorption cross-sections were extracted for the saturable absorption phenomenon. Such CNT composite glasses may be used as "optical limiting" filters in lasers near 532 nm, or as saturable absorbing filters for passive laser Q-switching near 1064 nm.

The electrical conductivity of CNT composites was studied as a function of the CNT concentration and modeled by percolation theory. The maximal measured conductivity was $\sigma \approx 10^{-3} (\Omega \text{cm})^{-1}$ for the CNT composites, representing a conductivity increase of at least 12 orders of magnitude compared to that of pure silica. A quite low percolation threshold was obtained, $\phi_c = 0.22 \text{ wt\% CNT.}$

Electrostatic Force Microscopy (EFM) and Conductive mode Atomic Force Microscopy (C-AFM) studies revealed that the conductivity occurs at the micro-level among the CNTs dispersed in the matrix.
Optical filters based on organic dyes

Nonlinear solid-state filters are highly useful devices that may be used to protect optical sensors in advanced optical systems by controlling the light exposure intensity. Soreq has developed a novel filter based on a bifunctional-chromophore doped in sol-gel matrix. The bifunctional-chromophore is composed of a 2-photon absorber (2PA) and photo-chromic (PC) moieties. The 2PA functionality acts as donor, and transfers the energy via Förster resonance energy transfer (FRET) to the PC material, which acts as the acceptor. The result is an enhanced absorption of long wavelength light.

We synthesized a new bifunctional-chromophore that incorporates a carbazole-derived 2PA fluorescent donor and a chromene-derived photochromic acceptor, covalently linked together in a single molecule by a ~6 Å carboxyl group or oxygen bridge. The bifunctional-chromophore was doped in an inorganic-organic hybrid matrix prepared by the fast-sol-gel process. These materials solidify without shrinkage or formation of cracks and present promising properties as optical matrices for smart filters. The dye-doped sol-gel disc presents high transparency in the visible region ("colorless"), which under UV-irradiation (one-photon absorption in the photochromic part of the molecule) transforms into a strongly absorbing filter ("dark colored"), due to conversion of the photochromic moiety to its "open" absorbing form. This ring-opening can also be induced by visible-light (620 nm) using the 2PA carbazole-derived moiety of the molecule. The 2PA mechanism of the carbazole derivative, FRET efficiency of the combined-molecule, and reversible dynamics of the photochromic moiety determine the nonlinear filter efficiency of these systems.
Sol-gel for Solar Power Systems

An ultra violet (UV) cured glassy material with less than 30% organic residues was fabricated by the fast sol-gel method. The material presents high thermal stability, good optical quality and high adhesive strength. It is suitable for optical bonding of devices in solar power systems. This technology enables mass-production of optical elements at low cost, while its curing can be thermal (few hours) or UV (few seconds), e.g., bonding of a prism concentrator to a semiconductor wafer. An example of such a device is a solar module with conversion efficiency of 30% comprising a prism concentrator bonded with a sol-gel to semiconductor wafer.
(A) BK-7 prism bonded to a semiconductor wafer. (B) Modules of a light concentrator (prism) bonded to a photovoltaic cell used to construct solar-cell modules.

Testing adhesive strength: (A) Two bonded fused silica cubes were measured in a tilt configuration. (B) A BK-7 prism bonded to a semiconductor wafer, measured in a peel configuration. (C) Stress-displacement chart for tensile strength up to breaking point at 14 MPa.

**Sol-gel micro-nano structures**

Soreq recently demonstrated the ability to create macroscopic (a few centimeters) fast sol-gel structures as well as microscopic (approximately 2 microns) and nano-scale (approximately 100 nanometers) structures. The fast sol-gel can be also used as the photoresist in direct laser writing (DLW) or nano-imprint lithography (NIL), resulting in optical elements with better optomechanical properties than those of organic photoresists.

A technology for fabrication of a hybrid glassy coating and bulks was demonstrated. Short curing time and glass-like properties of these technologies enable low cost mass production of photonic devices. Examples of such devices and applications are UV-curable adhesive materials with accurately matched refractive indices for high power optics, mass-production of bulk optics or nano-structured devices such as anti-reflective (AR) coating (moth-eye structures), anti-fog coating, passive waveguides, photonic circuits, Fresnel lenses and nano-sensors.
Macro scale components: (A) miniature fused-silica lens (B) sol-gel replica of miniature lens (C) coins, original and sol-gel replica.

Micro-scale components: (A) array of sol-gel grating lines (B) array of sol-gel waveguides.

Nano scale components: (A) scanning electron microscope image of holes in a gold master template, 300 nm in diameter and 600 nm deep, dimensions 10 µm × 10 µm (B) sol-gel replica of the array of holes; (C) magnification of the holes in the sol-gel element; (D) sol-gel replica of array of pillars.

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