

Oxygen Implantation Allows Fabrication of Optical Channel Waveguides in Nd:YAG Transparent Ceramics

Transparent polycrystalline ceramics doped with rare-earth ions, among them Nd:YAG ceramics, have been revealed as excellent gain media for high-power continuous-wave or pulsed solid-state lasers. The combination of the excellent laser performance of Nd:YAG ceramics and waveguide technology may drive the realization of high-power integrated lasers with stable output. F. Chen and Y. Tan from Shandong University, China, and D. Jaque from the Autonomous University of Madrid, Spain, reported in the January 1 issue of *Optics Letters* (DOI: 10.1364/OL.34.000028; p. 28) the fabrication of channel waveguides in Nd:YAG ceramic by selective implantation of O^{3+} ions using a photoresist stripe template.

The researchers patterned on the surface of a 1 at.% Nd^{3+} -doped YAG transparent ceramic sample ($8 \times 10 \times 2 \text{ mm}^3$) with an average grain size of $15 \mu\text{m}$, a series of open stripes $10 \mu\text{m}$ in width and separated by $40 \mu\text{m}$. A $5\text{-}\mu\text{m}$ -thick photoresist layer was used as the implantation mask, through which O^{3+} ions were implanted at an energy of 6 MeV and a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$. After implantation, the researchers annealed the sample at 260°C for 1 h in air to reduce color centers and defects created during the implantation process.

The index profile of these channel waveguides, that the researchers reconstructed according to the index profile of the planar waveguide and calculated from the dark-mode spectrum, was formed by an enhanced index well ($\Delta n_w = +0.001$) in the waveguide region and an optical barrier wall with negative index changes ($\Delta n_b = -0.006$) at the boundary between the waveguide and the substrate. Experimental characterization of the near-field intensity distribution of the light carried in the quasi- TM_{00} mode matched well with simulations performed by the researchers using the finite-difference beam propagation method. The researchers also measured the waveguide's losses (which were $\sim 1.5 \text{ dB/cm}$) using the Fabry-Perot resonance method. The researchers said that this was approximately three times lower loss than similar waveguides produced by carbon implantation. The researchers performed spectroscopic characterization of Nd^{3+} in both the implanted and unimplanted regions, which showed that the spectrum of the ${}^4F_{3/2}$ metastable state was only slightly modified during the fabrication procedure, and its lifetime was reduced by less than 3% when compared with that of the bulk. The researchers

observed that ion implantation induced a slight broadening of the emission line at $\sim 936 \text{ nm}$ and a shift to shorter wavelengths. The researchers attributed this to a slight increment in the lattice disorder

and a slight change in the crystal field around the Nd^{3+} ions, due to slight changes in the unit cell volume. However, the researchers concluded that the luminescence properties of Nd^{3+} ions were

Dual Capsule Polymer Self-Healing Coating System Prevents Corrosion

Imagine tiny cracks in a patio table healing by themselves, or the first small scratch on a new car disappearing by itself. This and more may be possible with self-healing coatings being developed by S.H. Cho, S.R. White, and P.V. Braun of the University of Illinois at Urbana-Champaign. The coatings are designed to better protect materials from the effects of environmental exposure. Applications range from automotive paints and marine varnishes to the thick, rubbery coatings on patio furniture and park benches.

"Starting from our earlier work on self-healing materials at the U. of I., we have now created self-healing coatings that automatically repair themselves and prevent corrosion of the underlying substrate," said Braun, a University Scholar and professor of materials science and engineering. The researchers report their findings in a recent issue of *Advanced Materials* (DOI: 10.1002/adma.200802008).

To make self-repairing coatings, the researchers first encapsulate a tin-based organic catalyst into spheres less than $100 \mu\text{m}$ in diameter. They also encapsulate a mixture of hydroxyl and ethoxy functionalized siloxane oligomers (healing agent) into similarly sized microcapsules. The microcapsules are then dispersed within the epoxy-based coating material and this mixture is applied to the cold-rolled steel substrate.

"By encapsulating both the catalyst and the healing agent, we have created a dual capsule system that can be added to virtually any liquid coating material," said Braun, who also is affiliated with the university's Beckman Institute, Frederick Seitz Materials Research Laboratory, Department of Chemistry, and Micro and Nanotechnology Laboratory.

When the coating is scratched, some of the capsules break open, spilling their contents into the damaged region. The catalyst and healing agent react, repairing the damage within minutes or hours, depending upon environmental conditions.

The performance of the self-healing coating system was evaluated through corrosion testing of damaged and healed coated steel samples compared to control samples that contained no healing agents in the coating (see Figure 1). Reproducible damage was induced by scratching through the $100\text{-}\mu\text{m}$ -thick polymer coating and into the steel substrate using a razor blade. The samples were then immersed in a salt solution and compared over time.

The control samples corroded within 24 h and exhibited extensive rust formation, most prevalently within the groove of the scratched regions, but also extending across the substrate surface, the researchers report. In contrast, the self-healing samples showed no visual evidence of corrosion even after 120 h of exposure.

"Our dual capsule healing system offers a general approach to self-healing coatings that operates across a broad spectrum of coating chemistries," Braun said. "The microcapsule motif also provides a delivery mechanism for corrosion inhibitors, antimicrobial agents, and other functional chemicals."

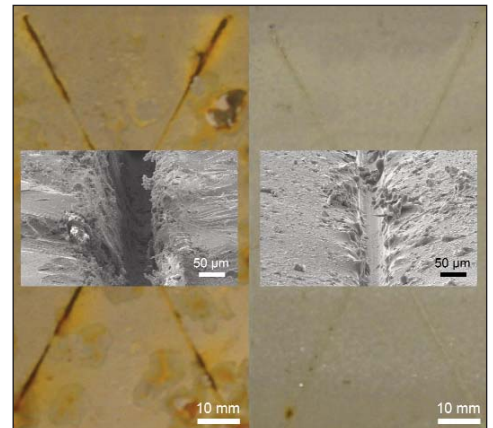


Figure 1. The background images show the dramatic reduction in corrosion of steel plates coated with a self-healing coating (right) as compared to a conventional coating (left) after they were both scratched and subsequently immersed in 5% salt (NaCl) water for five days. The foreground pictures are scanning electron microscope images of the control (left) and healed (right) scratch showing the repair of the scratch in the self-healing coating.

well-preserved in the channel waveguides they fabricated, and believe that O^{3+} ion implanted channel waveguides in Nd:YAG ceramic are suitable as active integrated devices.

JOAN J. CARVAJAL

Ab Initio Calculations Demonstrate Impermeability of Graphene with Defects to Helium Atoms

Applications for graphene as ultrathin barrier membranes were envisaged after recent experiments showed that graphene sheets are impenetrable to standard gases, including He. It was also recently suggested that graphene needs to be free of defects—even single-atom vacancies—in order to maintain its impermeability. Recently, however, O. Leenaerts, B. Partoens, and F.M. Peeters from the University of Antwerp in Belgium used *ab initio* calculations to show that graphene with common defects is still impermeable, and that large defects are required to make graphene permeable.

As reported in the November 10, 2008 issue of *Applied Physics Letters* (DOI: 10.1063/1.3021413; #193107), Leenaerts, Partoens, and Peeters used density functional theory (DFT) to simulate defects in a $4 \times 4 \times 4$ graphene supercell (one defect requires a larger supercell) with a distance of 16 Å between adjacent layers. The researchers selected six defects that preserve the sp^2 hybridization of the 6–12 C atoms that form the periphery of the defect. The researchers first examined the approach of a He atom toward the center of a carbon hexagon in a graphene monolayer, keeping, as a first approximation, the C atoms fixed, and calculated the potential energy barrier to be so large that penetration at any temperature is impossible. The barrier to He penetration was barely decreased when the graphene was allowed to relax, as shown with molecular dynamics simulations performed within DFT formalism. The researchers showed that, at the turning point of the He atom, graphene relaxation is very small because it occurs on a much larger time scale than that for the motion of the much lighter He; almost all graphene relaxation occurs after deflection of the He atom. Graphene relaxation was therefore ignored to a very good approximation when calculating potential energy barriers to He penetration for graphene with defects, although the researchers said that this approximation may not hold for heavier penetrants.

For the six defects studied, the lowest penetration barrier was always found in the center of the defect, as expected intuitively. The researchers also found that the penetration barrier decreases exponentially

with the size of the defect, as measured by the number of C atoms that form the defect; extrapolation shows that large defects are required for He penetration at room temperature. The researchers concluded that “even defective graphene is a suitable candidate for making impermeable nanomembranes for future applications and therefore can be considered the thinnest possible material for constructing a micro- or nanoballoon.”

STEVEN TROHALAKI

Ho³⁺-Doped Nanophase Glass Ceramics Enhance Efficiency of Si Solar Cells

In the December 15, 2008, issue of *Optics Letters* (DOI: 10.1364/OL.33.002982; p. 2982), F. Lahoz from the University of La Laguna in Tenerife, Spain reports how Ho^{3+} -doped oxyfluoride glass ceramics are suitable to up-convert photons from the ~1170 nm sub-bandgap region of silicon into higher energy photons that can be absorbed by the silicon in solar cells. Since the proposed material is transparent at 1540 nm, it can be used complementarily to the Er^{3+} phosphors that have also been proposed to increase the efficiency of solar cells.

In order to adapt the incident solar spectrum to the properties of commercially available solar cells fabricated with Si, the use of photon upconversion materials is currently being investigated. Si is transparent to photons with wavelengths longer than its bandgap (~1.1 μm), and therefore the energy of these incident photons is lost. In an upconversion process, two or more low energy photons are transformed into one photon of higher energy. Therefore the upconversion material is able to absorb part of the sub-bandgap radiation and transform it into photons above the bandgap that can be absorbed by the solar cell and consequently create additional electron-hole pairs.

In Lahoz's work, efficient upconversion emission of Ho^{3+} ions in the visible (~650 nm) and near-infrared (~910 nm) regions is demonstrated when the sample is pumped at ~1170 nm. An oxyfluoride glass ceramic was selected as the host matrix. This material has a glassy structure with an oxyfluoride composition in which there are embedded fluoride nanocrystals. In order to produce the glass ceramic, the precursor glass underwent a thermal treatment (470°C for 36 h). As a result, the fluoride nanocrystals ($\beta\text{-PbF}_2$) were precipitated and the Ho^{3+} ions partitioned into them. After processing, the photoluminescence intensity of the glass ceramic was two orders of magnitude larger than in the precursor glass.

Two main factors explain this increase. First, the Ho^{3+} ions in the glass ceramic are located in a favorable fluoride environment, which increases the probability of radiative transitions. Second, the distances between Ho^{3+} ions are reduced and this increases the probability of energy transfer among them and thus the probability of upconversion processes.

The researcher also discusses that the use of Ho^{3+} as a potential upconverter could be more efficient than that using the 1530–1560 nm absorption range (Er^{3+} phosphors) since the solar irradiance at wavelengths near ~1170 nm is about a factor of two more intense than in the former range. The researcher also said that both upconversion materials can be used simultaneously and proposes a double layer structure where first a Ho^{3+} -doped glass ceramic is placed at the rear of a bifacial solar cell, followed by a second Er^{3+} phosphor with a mirror. This proposed structure offers the potential for an improvement of the efficiency of current Si solar cells.

ROSALÍA SERNA

EXAFS Offers Evaluation of Intrinsic Template Binding Site of Molecularly Imprinted Polymers

Molecular imprinting is a rapidly growing application which involves the design of molecularly imprinted polymers (MIPs) that possess recognition sites for molecules whose selectivity rivals that of natural antibodies. The binding cavities are fashioned through the extraction of the template molecule from the polymer, leaving behind a well-defined imprint cavity of specific structure and memory containing functional groups that enable specific, high-affinity molecular capture. Understanding these phenomena requires an efficient method to characterize the binding phenomena in a stable template cavity. To address this issue, C.J. Allender of Cardiff University, UK; S. Fiddy of CCLRC Daresbury, UK; M. Stockenhuber of the University of Newcastle, UK; and their colleagues have developed the first known direct experimental probe of a molecularly imprinted polymer active imprinting site using extended x-ray absorption fine structure (EXAFS), as reported in the January 8 issue of *Chemical Communications* (DOI: 10.1039/b811578h; p. 165).

MIP's potential for enhanced stability, lower cost, and selectivity at lower concentrations in comparison to their natural derivatives make them very attractive materials. However, their widespread applicability is often hindered by issues such as slow and inefficient template binding kinetics. Using EXAFS, researchers have been able to define template-polymer

interactions for a 4-vinyl pyridine–styrene–divinylbenzene copolymer imprinted with a dibenzoylmethane (DBM) and cobalt (Co^{2+}) system. EXAFS was successfully employed to determine the binding of the DBM in the polymer through identifying changes in the coordination shell of the cobalt.

Binding and template re-uptake studies with cobalt complexes using imprinted

and non-imprinted polymer (NIP) controls provided variations in data fit to models with fixed coordination numbers. These models suggest structural differences in the cobalt species that is sequestered in the MIP in comparison to the NIP, as well as substantiate the type of cobalt complex bound to each polymer. These results were supported by UV-Vis and IR spectroscopic data.

The use of EXAFS by these researchers to probe the template binding site in a MIP provided insight into the binding site features. The success of this technique lends itself to application in many more MIP systems, with the possibility of eliciting an improved understanding of the scientific theories involved in creating and evaluating stable imprinted polymeric materials.

ANIKA A. ODUKALE

Tough Ceramic Mimics Mother of Pearl

Mother of pearl, or nacre, the inner lining of the shells of abalone, mussels, and certain other mollusks, is renowned for both its iridescent beauty and its amazing toughness. Nacre is 95% aragonite, a hard but brittle calcium carbonate mineral, with the rest of it made up of soft organic molecules. Yet nacre can be 3000 times (in energy terms) more resistant to fracture than aragonite. No human-synthesized composite outperforms its constituent materials by such a wide margin. Now R. Ritchie and colleagues from Lawrence Berkeley National Laboratory have mimicked the structure of mother of pearl to create what may well be the toughest ceramic synthesized.

Through the controlled freezing of suspensions in water of an aluminum oxide (alumina) and the addition of polymethylmethacrylate (PMMA), the research team has produced ceramics that are 300 times tougher than their constituent components, as reported in the December 5, 2008 issue of *Science* (DOI: 10.1126/science.1164865; p. 1516).

Nacre's remarkable strength is derived from a structural architecture that varies over lengths of scale ranging from nanometers to micrometers. Human engineering has not been able to replicate these length scale variances. Two years ago, however, Berkeley Lab researchers A. Tomsia and E. Saiz found a way to improve the strength of bone substitutes through a processing technique that involved the freezing of seawater. This process yielded a ceramic that was four times stronger than artificial bone. When seawater freezes, ice crystals form a scaffolding of thin layers. These layers are pure ice because during their formation impurities, such as salt and microorganisms, are expelled and entrapped in the space between the layers. The resulting architecture roughly resembles that of nacre.

"Since seawater can freeze like a layered material, we allowed nature to guide the process by which we were able to freeze-cast ceramics that mimicked nacre," said Tomsia when this research was reported.

In this latest research, Ritchie, working with Tomsia and Saiz, refined the freeze-casting technique and applied it to alumina/PMMA hybrid materials to create large porous ceramic scaffolds that much more closely mirrored the complex hierarchical microstructure of nacre. To do this, they first employed directional freezing to promote the formation of thin layers (lamellae) of ice that served as templates for the creation of the layered alumina scaffolds. After the ice was removed, spaces between the alumina lamellae were filled with polymer.

"The key to material toughness is the ability to dissipate strain energy," said Ritchie. "Infiltrating the spaces between the alumina layers with polymer allows the hard alumina layers to slide (by a small amount) over one another when load is applied, thereby dissipating strain energy. The polymer acts as a lubricant, like the oil in an automobile engine."

In addition to making the lamellar scaffolds, the team was

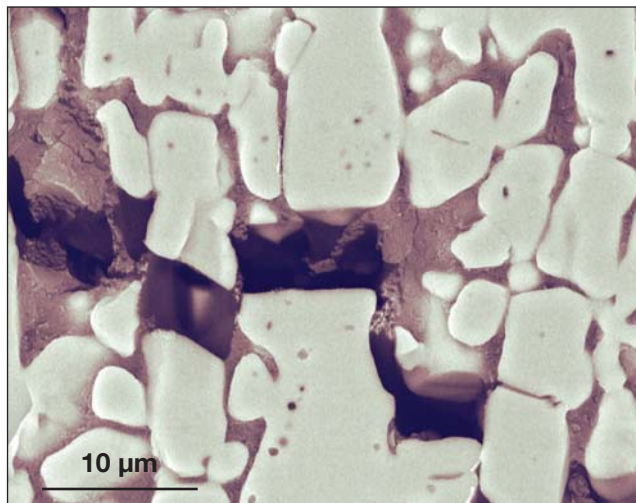


Figure 1. In the "brick-and-mortar" phase of the alumina/PMMA hybrid, aragonite "bricks" slide past each other to dissipate strain energy while the polymer "mortar" acts as a lubricant.

also able to fabricate nacre-like "brick-and-mortar" structures with very high alumina content (see Figure 1). They did this by collapsing the scaffolds in a perpendicular direction to the layers, then sintering the resulting alumina "bricks" to promote brick densification and the formation of ceramic bridges between individual bricks.

Saiz said, "Using such techniques, we have made complex hierarchical architectures where we can refine the lamellae thickness, control their macroscopic orientation, manipulate the chemistry and roughness of the inter-lamellae interfaces, and generate a given density of inorganic bridges, all over a range of size-scales."

For ceramic materials that are even tougher in the future, Ritchie said he and his colleagues need to improve the proportion of ceramic to polymer in their composites. The alumina/PMMA hybrid was only 85% alumina. They want to boost ceramic content and thin the layers even further. They also want to replace the PMMA with a better polymer and eventually replace the polymer content altogether with metal.

Ritchie said, "The polymer is only capable of allowing things to slide past one another, not bear any load. Infiltrating the ceramic layers with metals would give us a lubricant that can also bear some of the load. This would improve strength as well as toughness of the composite."

Such future composite materials would be lightweight and strong as well as tough, he said, and could find important applications in energy and transportation. □