

well-preserved in the channel waveguides they fabricated, and believe that  $\text{O}^{3+}$  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

### **Ho<sup>3+</sup>-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  $\text{Ho}^{3+}$ -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  $\text{Er}^{3+}$  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  $\text{Ho}^{3+}$  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  $\text{Ho}^{3+}$  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  $\text{Ho}^{3+}$  ions in the glass ceramic are located in a favorable fluoride environment, which increases the probability of radiative transitions. Second, the distances between  $\text{Ho}^{3+}$  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  $\text{Ho}^{3+}$  as a potential upconverter could be more efficient than that using the 1530–1560 nm absorption range ( $\text{Er}^{3+}$  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  $\text{Ho}^{3+}$ -doped glass ceramic is placed at the rear of a bifacial solar cell, followed by a second  $\text{Er}^{3+}$  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