Novel Optical Materials in the Twenty-First Century

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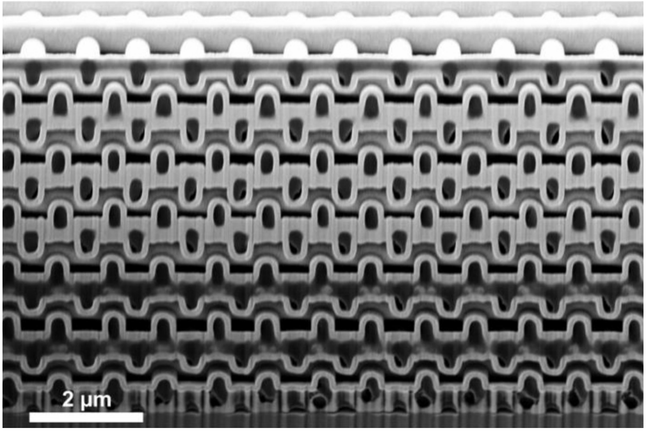
It is a somewhat daunting task to speculate on optical materials for the next century. Before proceeding, it is perhaps useful to imagine how someone may have tried to write such an essay 100 years ago. Looking back at volume 1 of the *Journal of The Optical Society of America*, discussion of materials was limited to photographic emulsions, metallic films, and color filters. Of course, an optical scientist of that time could have had no inkling of the revolutions that were to follow (lasers, semiconductor electronics, fiber optics, to name but a few) that would transform our concept of optics, give birth to the field of "photonics," and in many ways redefine what we mean by an "optical material." Although it is hard to imagine that the twenty-first century could be as revolutionary as the twentieth century was for the field of optics and photonics, it certain that things will change in ways that we cannot imagine. With that in mind, this essay focuses on some recent advances in materials that in our opinion are promising. Whether they will significantly impact our field well into the twenty-first century, time will tell.

Even in the last few decades, the face of photonic materials research has changed markedly. Thirty years ago, the field was dominated by the development of new bulk materials, such as new IR glasses, nonlinear crystals, or doped laser crystals, while today research in new photonic materials has more emphasis on advances at the nano or micro scale that can result in materials with new or enhanced properties. There is also a great deal of research in integration of different photonic materials for enhanced functionality, resulting in flexible photonic platforms, infrared photonics devices, semiconductor-core fibers and integration of III-Vs, organics, or carbon electronics into silicon electronic platforms. The tremendous growth in the breadth and depth of the field of optical materials resulted in The Optical Society's decision to launch a new journal devoted to the subject, *Optical Materials Express,* in 2011.

New Optical Materials

Some of the most interesting work in the development of new materials for optics and photonics is in cases where the "newness" is related to the physical structure of the material at the nanoscale, rather than to its chemical structure. One may categorize these into three main types. In the first types nanostructuring modifies the electronic structure directly producing new material properties that are quite unlike the bulk, as observed, for example, in plasmonic nanoparticles; semiconductor quantum dots; or two-dimensional monolayer structures such as graphene, silicene, germanene, molybdenum disulfide, or boron nitride. Graphene is one of six different basic forms of nanocarbon: graphene, graphite, fullerenes, nanodiamond, nanotubes, and nanocones. These forms of nanocarbon provide an attractive set of building blocks for future nanoelectronic and nano-optic devices [1]. Both graphene and carbon nanotubes are particularly interesting since their optical absorption extends smoothly across an extremely wide wavelength range, allowing for diverse applications such as infrared detectors and solar cells. Quantum-confined semiconductors, i.e., quantum wells, wires, and



▲ **Fig. 1.** Oblique-view electron micrograph of a woodpile photonic-crystal polymer template (black to dark gray) coated with Al:ZnO (bright gray.) (Frölich and Wegener, Opt. Mater. Express **1**(5), 883–889 [2011].)

dots, also fall into this category, although in this case the partial confinement results in relatively small modifications to the electronic properties. Nevertheless, quantum-well materials have already become the materials of choice for semiconductor lasers and are the basis of the important quantum-well infrared photodetector (QWIP) devices. Quantum wires and quantum dots offer the possibility of improved laser and detector materials, while quantum dots also offer significant efficiency improvements for solar cells and for displays. Improvements in mid-infrared detector materials based upon advances in strained-layer superlattice structures and nBn-type structures are also likely.

Nanoscopic metal particles exhibit properties markedly different from those of bulk metals. These nanoplasmonic materials [2] have gained a great deal of attention since the discovery of surface-enhanced Raman scattering (SERS) in the 1970s. Benefiting from recent advances in nanofabrication techniques, research in nanoplasmonics has recently been very successful in using noble metal (especially silver and gold) nanostructures to control light fields well beyond the limit of diffraction. Such control has already contributed to enhancing light interaction with tiny amounts of matter down to the single-molecular level. This enhancement, where the plasmonic particles effectively act as nanoscopic antennas that collect and redirect electromagnetic fields may find applications in diverse fields, including infrared detection, solar cells, and nonlinear optics. Recent work has focused on materials for plasmonics other than silver and gold, including oxides and nitrides, particularly TiN. Other compounds, alloys, and nanostructured materials are likely to prove useful for plasmonic applications.

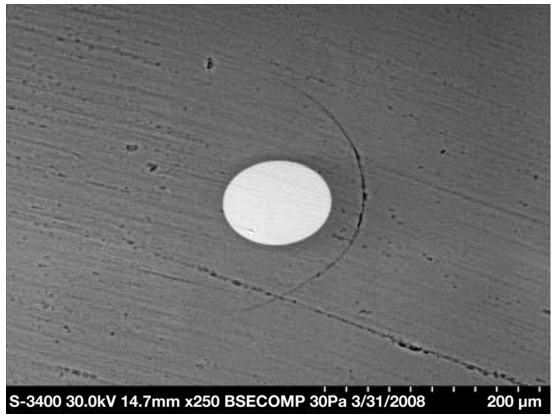
A second category encompasses cases where micro or nano structure provides enhanced functionality of known photonic materials, for example, ceramics and advanced polymer composites. Ceramic fabrication processes provide the properties of crystals with the functionality of amorphous materials, enabling large parts to be formed that are relatively strain free and have homogenous doping relative to single crystals in applications where high thermo-mechanical performance and large apertures are needed. This is leading to improved laser gain media with superior optical quality, with engineered index and doping profiles that make possible diode-pumped solid-state lasers in the 100-kW range. Similarly, optical ceramics are now offering advantages in applications such as efficient lighting, solar-energy harvesting, and radiological and nuclear detection. Optical polymer nanocomposites (OPNs), composites of nanoscopic inorganic particles in a polymer host, have emerged as a promising field thanks to advances in optical polymer materials, nanoparticle synthesis, and nanoparticle functionalization and dispersion techniques. OPNs have the potential to fulfill a broad range of photonic functions including highly scattering materials for backlighting of liquid crystal displays, narrowband filters, integrated magneto-optic and electro-optic devices, and optical amplification and lasing.

Third, metamaterials [2] are periodic composite materials of the type shown in Fig. 1 that may have bulk properties that are very different from the component materials, for example, negative-index metamaterials. The origins of this field can be traced back to research in the 1950s on microwave engineering for antenna beam shaping; artificial materials have recently regained a huge interest triggered by attractive theoretical concepts such as superlensing and invisibility at optical frequencies. Metamaterials often employ plasmonic nanostructures, providing a close connection between the two fields. The strong local fields that occur in these materials can be used to strongly modify the nonlinear properties of the component materials. For example, second and third harmonic generation (SHG and THG) may be strongly enhanced and nonlinear optical refraction and absorption may be strongly modified in these metamaterials, since the nonlinearity scales with the electric-field enhancement to a higher power.

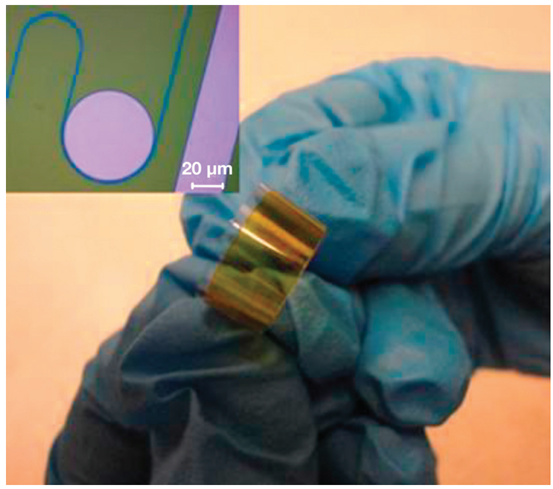
Advances in Optical Materials Integration and Processing

Just as interesting and groundbreaking as the advances in new materials is the research in integration of different photonic materials for enhanced functionality, resulting in flexible photonic platforms; infrared photonics systems; semiconductor-core fibers; and integration of SiGe, SiC, SiGeC, and III-Vs and of organics or nanocarbons into silicon electronic platforms. Additionally, new processing methods such as direct laser writing are resulting in new photonic platforms that were not previously possible.

Infrared materials are notoriously difficult to process, causing integrated mid-infrared devices to be extremely challenging to fabricate. Progress in development of materials for such applications has slowly evolved to the point where interesting integrated devices based on chalcogenides are now being produced [5]. Chalcogenides, being composed of weakly covalently bonded heavy elements, have bandgaps that are in the visible or near-infrared region of the spectrum, and low vibrational energies make them transparent in the mid-infrared. They can also act as hosts for rare-earth dopants. Advances in processing using CHF_3 gas chemistry etching have now resulted in As_2S_3 rib waveguides with losses as small as 0.35 dB cm^{-1}. Chalcogenide fibers, although studied since the 1980s, still have not shown improvement over heavy-metal oxides for mid-infrared transmission, but as fiber draw capabilities improve, many other materials are becoming possibilities for fibers in this wavelength range, for example, the demonstration of a fiber with a crystalline silicon core, shown in Fig. 2. Additionally, developments in photonic-crystal fibers, where in some cases most of the optical mode does not overlap with the material, provides yet more avenues for optical fibers for new wavelength ranges using materials for which implementation in traditional fibers would be impossible. As photonics becomes more pervasive in practical systems, researchers are finding materials platforms for devices and interconnects to meet industry needs. For example, patterning of photonic devices on mechanically flexible polymer substrates has produced high-quality flexible photonic structures, an example of which is shown in Fig. 3.



▲ **Fig. 2.** Crystalline-silicon-core optical fiber with silica cladding. (Ballato *et al*., Opt. Express **16**(23), 18675–18683 [2008].)



▲ **Fig. 3.** A flexible microdisc resonator on polymer substrate. (Copyright © 2012, Rights Managed by Nature Publishing Group.)

Laser processing of traditional materials provides yet another avenue for new platforms for devices and interconnects, even though the materials themselves are not new. For example, femtosecond direct laser writing [7] relies on nonequilibrium synthesis and processing of transparent dielectrics with short-pulse lasers, which open up new ways to create materials and devices that are not currently possible with established techniques. The main advantage remains in the potential to realize three-dimensional (3D) multifunctional photonic devices, fabricated in a wide range of transparent materials. This technique offers enormous potential in the development of a new generation of 3D components for micro-optics, telecommunications, optical data storage, imaging, astrophotonics, microfluidics, and biophotonics at the micro and nano scale. Another related advance in laser-written photonics components is photo-thermo-refractive (PTR) glass, which requires heat treatment to develop laser-written index changes, usually in the form of gratings. This produces very-high-quality Bragg diffractive gratings with absolute diffraction efficiency in excess of 95%, allowing highly stable volume holographic elements to be fabricated.

In this century, full 3D design at the nanoscale will play an important role in the architectural design of optoelectronic components. At present, fabrication processing is mostly limited to stacks of two-dimensional (2D) layers with some coarse modifications in the plane. Laser direct writing, hierarchical self-assembly, and other advances in lithography will allow placement of structures of pre-determined size and topology at will anywhere within a 3D solid architecture. This will involve manipulation of single atoms for applications such as quantum computing (e.g., N-V complex in diamond, P in silicon, SiC, and other materials with defects) as well as structures involving anywhere from a few atoms to a few dozen atoms for other applications, such as optical modulators, laser diodes (quantum cascade lasers, QCLs), and nonlinear optical materials [improved SHG, THG, optical parametric oscillators, and optical parametric amplifiers (OPOs and OPAs)].

Summary

Advances in optical materials over the last thirty years have resulted in both evolutionary and revolutionary advancements of optics, optoelectronics, and photonics. However, this short article cannot begin to cover the areas that we expect to be impacted by optical materials. Advances in optical materials have begun to impact biophotonics and biomedicine with promise for improvements in human health and the treatment of disease [8]. The impact of advanced optical materials on solar cells is briefly discussed above but is not discussed in detail. Advances in manufacturing for inexpensive solar cell materials including amorphous silicon, materials containing organic dyes, and nanopatterning may speed their integration into power infrastructure. Work on developing quarternary and quinternary materials including dilute nitride materials may enhance efficiencies in high-efficiency multi-junction solar cells. Advances in optical materials will have a broader impact on energy consumption and sustainability through development of new, more efficient devices and applications such as photochromic and electrochromic materials for climate control in buildings and vehicles. Optical materials, including LCDs and organic light-emitting diodes (OLEDs) have led to a revolution in display technology. This will likely continue, resulting in even better displays, monitors, and TVs with brighter colors, blacker blacks, better contrast, better resolution, and wider field of view using new OLEDs or organic/inorganic composite LEDs incorporating rare earth and other materials. Polymer and organic/inorganic systems that enable wearable electronics and optoelectronics, including materials for neuroprosthetics incuding retinal imaging, are likely to become important. In short, we expect advances in optical materials to pervade almost every aspect of human life. The future of optical materials is bright.

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