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Author(s)	Zakhidov, A. Anvar; Baughman, H. Ray; Vardeny, Z. Valy et al.
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Photonic Crystals from Inverted Opals: Tunability, Solvatochromizm and Optics of Metallicity Gaps

Anvar A.Zakhidov[1,2], Ray H.Baughman[1], Valy Z.Vardeny[3], Nayer Eradat[3],
Katsumi Yoshino[4], Sergey B. Lee[4], Masanori Ozaki[4], Satoshi Tatsuhara[4],
Hirotake Kajii[4], Ilyas Khayrullin[5] and Mike Kozlov[5]

[1]*Honeywell International, Morristown, NJ 07960, USA*
Phone: (973) 455-3935, Fax: (973) 455-5991, e-mail: Anvar.Zakhidov@AlliedSignal.com
[2]*Uzbekistan Academy of Sciences, Tashkent 700135, Uzbekistan*
[3]*University of Utah, Salt Lake City, USA*
[4]*Osaka University, Suita, Osaka 565-0871, Japan,*
[5]*New Jersey Institute of Technology, Newark, USA*

Periodic three-dimensional nano-structures at the scale of 100-1000 nm attracts increasing interest, since such structures would be photonic crystals (PC) with potential photonic band gaps (PBG) in visible or infrared spectral range, where a number of exciting phenomena is expected. Particularly the low threshold lasing, omnidirectional mirrors and superprisms and other new effects have been predicted in PBG-systems. Some of this phenomena have been already demonstrated in microwave region, where the cm and mm scale of periodicity allows easy fabrication of 3-D PCs. However realization of PBG systems in optical spectral range has not been achieved till recently. We suggested a concept of tunable PBG, in which a width, position or the type of PBG can be modulated or switched by having electrically tunable material (e.g. conducting polymer or liquid crystal) as one of PC components. One needs then highly porous periodic matrices of a material A PC component, which can be filled with a material B to make a two-component PC structure. In the present talk we describe self-assembly methods to create such tunable PCs both for optical spectral bands. Moreover we show that tunability can be preferably achieved in inverted opals, which have small filling factor and mesh-type geometry. We also demonstrate that a change of topology from a continuous network type to a discontinuous or so called cermet topology changes a PBG in a certain class of metallic PCs.

In a first part of the presentation we describe optical photonic crystals with cubic superlattice symmetry and lattice parameters at optical wavelengths by a synthetic method, which is based on multi-step templating processes that start with self-assembled opals. Novel electronic and optical materials obtained include diamond inverse opals, a new form of carbon called "cubic graphite", and truncated and untruncated inverse and direct opals of various insulators, semiconductors, and metals. In this presentation we show that carbon inverted opals created both by CVD route and via annealing of polymeric epoxy materials, and inverted opals made of semimetals, like Bi or Bi-Te have not only interesting PC optical properties but also show in transport the change of temperature dependence of conductivity from a metallic one to an activation, semiconducting behavior. We discuss the origin of this transformation as due to weak localization effects at the narroe necks, connecting tetrahedral and octahedral clusters

We also have developed a new technology to create from metals structures which are most desirable for optical metallic photonic crystals. It will be shown both experimentally and by modeling that so called metallic photonic band gaps or metallicity-PBG can be created in inverted opals and indeed are found in IR region. This m-PBG is not related with Bragg scattering, but is derived from plasmon bands, with strongly reduced plasmon frequency due to lower effective electron concentration in mesh type structures. At the same time metallic inverse opals may serve as matrices for even more sophisticated photonic crystals. The two-step templating process obtains the nanostructures when the precursor porous opal silica matrix is infiltrated with corresponding molten metal under pressure followed by chemical removal of silica spheres. At the next step we demonstrated filling of such matrices with a ternary material, making even more sophisticated nano-composite structures.

The SEM and TEM images of the silica-free material show the array of hollow spheres (filled with air or vacuum) arranged so that the resulted structure mimics the predecessor fcc lattice of SiO_2 spheres. This hollow cages having diameter 200-400 nm (depending upon the diameter of silica spheres in the precursor opal) should be ideally interconnected by small circle openings having diameter of 40 nm or smaller. In case of metals and semiconductors this small circular windows evolve into large openings, due to low wetting.

Optical properties, including reflectivity of various inverted opals infiltrated with polymer or dye, are described for selected elastomeric, insulating, semiconducting, and metallic photonic crystals. First the wide tunability of Bragg diffraction bands upon filling inverted opals by liquids with different refractive index is demonstrated. This color change effect is demonstrated for several types of inverted opals, and we call it as the physical or structural solvatochromism, originating only from a superstructure, contrary to a chemical solvatochromism, which is associated with a color change due to change of the chemical composition.

Finally we demonstrate that metallic photonic crystals show unusual optical and electronic properties, which strongly depend on their topology: which is created either of continual network mesh or separated balls in a matrix (cermet) structure. In a visible range the bright and sharp colors of Bragg scattering are observed originating from enhanced light penetration deep into the metallic mesh through semi-transparent barriers and diffracting from many layers, like in gem opals. However the presence of metallic mesh makes this Bragg reflections much more lustrous, than in dielectric opals, making them effective colored mirrors. In infrared range the reflectivity of network type nanofoams shows the structure, reminescent of plasmon edge of metals but significantly shifted by order of magnitude towards longer wavelengths of about 7000-8000 cm^{-1}.