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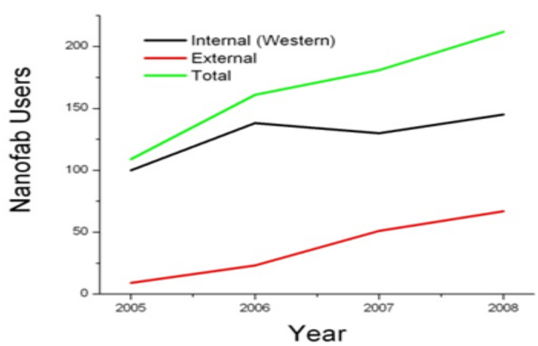
Dr. Bernie Kraatz, New Director of Nanofabrication Laboratory

The Dean of Science has appointed Bernie Kraatz, Associate Professor, to a three year term as director, starting August 1, 2008.

Dr. Kraatz joined the Department of Chemistry in 2007, moving to Western from the University of Saskatchewan. In 2006, he was awarded the Canadian Society for Chemistry's Award for Pure and Applied Chemistry. Dr. Kraatz's research interests are diverse, ranging from bioconjugate design to interfacial electron transfer, and complement those in Materials and Biomaterials in the Department of Chemistry and the Faculty of Science.

At the end of July, Dr. Silvia Mittler completes her three year term as Director of the Nanofabrication Laboratory. Prof. Mittler joined Western's Department of Physics and Astronomy in 2003 as a full Professor and its first Tier 1 Canada Research Chair (Photonics of Surfaces and Interfaces). Prior to her move to Western, Silvia was a group leader at the Max Planck Institute for Polymer Research in Mainz, Germany.

During Silvia's tenure as director, the total number of nanofab users has nearly doubled. The laboratory has experienced a dramatic increase in the number of external users, clearly establishing the reputation of Western's Nanofab as a regional facility.



- The Nanofabrication Laboratory is a state of the art "hands-on" facility in The Physics and Astronomy Building. It combines class 10,000 and class 100 cleanroom environments where users are trained in cleanroom protocol, the use of the tools and performing various processes.
- If you wish to become a NanoUser, visit the website www.uwo.ca/fab where you'll find forms and instructions.
- To discuss your processing, material and project requirements contact Rick Glew, the Laboratory Manager

This Issue

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Ontario Photonics Consortium Activities at Western: Looking back; looking forward

R. H. Lipson, Department of Chemistry, University of Western Ontario

The majority of the photonics and nano activities taking place at Western began because of the opportunities that arose when the CFI-funded Nanofabrication Laboratory (http://www.uwo.ca/fab/) opened in September 2004. This class 100 cleanroom facility houses a suite of instrumentation including SEM imaging, FIB lithography, silicon DRIE, ion beam implantation and analyses, and TEM specimen preparation. Many of the applications initiated through OPC funding involved lithographic patterning of novel materials for plasmonic, photonic band gap (PBG) materials, and biophotonics applications.

The Ontario Photonics Consortium (OPC) was funded by the older provincial Ontario Research and Development Fund in 2000. This initiative brought together chemists, physicists and engineers from the University of Western Ontario, McMaster University, the University of Waterloo, the University of Toronto, and the University of Ottawa. Historically, the consortium was established as a result of a $45M investment by the Ontario Government for a proposal synthesized from three earlier separate requests; the first dealing with fundamental science in the area of photonic band gap materials (UWO, lead PI Ian Mitchell); the second with photonic devices (McMaster, lead PI Peter Mascher) and the third also from McMaster (lead PI, Wei-Ping Huang) dealing with large systems. While the objectives of the three proposals were quite distinct, it was also recognized that innovations and breakthroughs in any one of the three areas would positively impact the others, and hence, the merger.

This article describes some of the exciting research in the photonics/nanomaterials field which has been realized at Western as a result of the collaborative opportunities made possible by the Ontario Photonics Consortium.

Plasmonics

Plasmons are electron density waves created when optical light hits the surface of a metal. Plasmonics can be considered the study and application of the transfer of energy between the light and electrons. Ian Mitchell (Physics) and Kim Baines (Chemistry) with an undergraduate student Michelle Watroba initiated a collaboration to test optical scattering theory by examining the light scattering properties of 2-D lattices formed by metallodielectric nanoparticles arranged into an array on a lithographically-defined PMMA substrate. This work takes advantage of Baines' expertise in organometallic chemistry to make the nanoparticles (Fig. 1a) and Mitchell's extensive background in ion-beam physics. The light scattering particles consisted of spherical silica cores of submicron diameter (nanospheres) coated with a gold shell to a selected thickness ranging from tens through hundreds of nanometers. Experiments were also carried out with Senior Research Scientists Todd Simpson in the Nanofab to test the sensitivity of scattering to alteration of the shape of the array by driving the nanosphere into an ellipsoidal shape by ion-beam exposure (Fig. 1b). An array of spheres is shown in Fig. 2.

a) b)

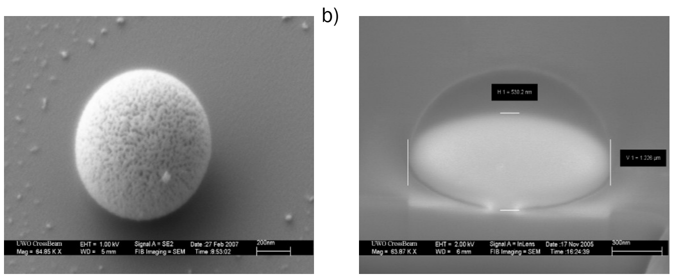

Figure 1: a) Scanning electron micrograph of a single gold-coated silica nanoparticle; b) Controlled deformation of a nano-sphere by ion-beam exposure.

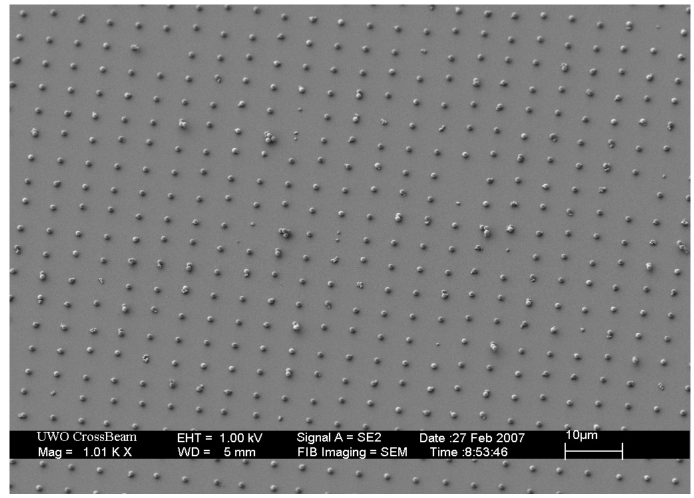

Figure 2: Scanning electron micrograph of a 2-D array of gold-coated silica nanoparticles.

In related work, physicist Silvia Mittler working with chemist Zhifeng Ding have characterized the electrochemistry of self-assembled monolayers (SAMs) of monomeric calix[4]arenes and heterodimeric calyx[4]arenes capsules filled with ferrocenium (shown schematically in Figure 3) on Au surfaces for data storage purposes [1].

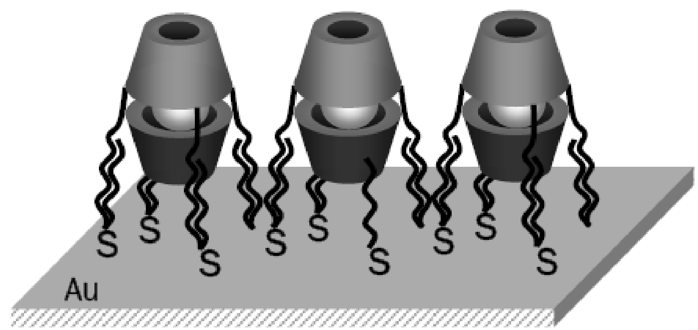

Figure 3: Structure of calix[4]arene heterodimers on gold.

This molecular guest host systems can be filled with a variety of guest molecules. OMCVD (organo- metallic chemical vapour deposition) grown gold nanoparticles coated with these calix[4]arene heterodimer capsules leads to distinct surface plamon resonances whose spectral position depends on the dielectric constant of the guest molecule. Mittler and her group in cooperation with Patrick Ronney and Chitra Rangan from the Department of Physics at the University of Windsor could show experimentally and theoretically how the surface plasmon resonance shifts by systematically varying the dielectric function of a monolayer on a gold nanoparticle with fixed thickness.

The Mittler-Rangan team have also examined how the surface plasmon spectrum depends on the proximity of the nanoparticles with respect to each other, in both air and water environments. The wavelengths of the spectral features are strong functions of the distance dependences of the electromagnetic dipolar and quadrupolar interactions between the particles. As shown in Figure 4 the experimental spectra are in excellent agreement with the simulations. These results are expected to valuable for optimizing sensor applications.

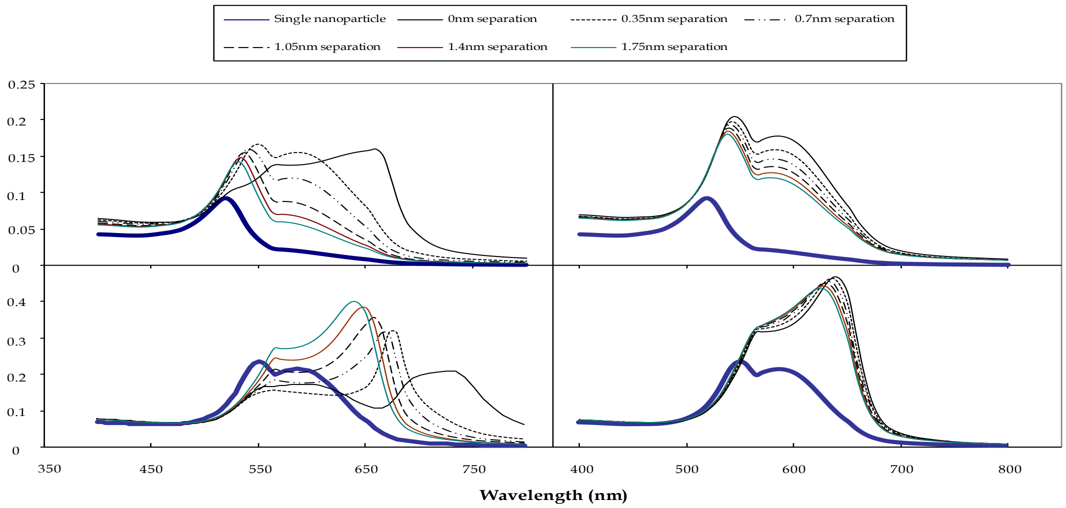

Figure 4: Calculated extinction spectra for nanoparticle pairs with varying separations. Particles are (top left) uncoated in air, (top right) coated in air, (bottom left) uncoated in water and (bottom right) coated in water. Coatings have a refractive index of 1.45 and a thickness of 1.75 nm. The particle radius is 7 nm. The separation is measured as the distance between surfaces, which for coated particles corresponds to the coating surface, not the nanoparticle surface.

More recently, François Lagugné-Labarthet (Chemistry) was recruited to Western to develop novel surface spectroscopies. One technique that has already begun to show great promise is Tip-Enhanced and Surface–Enhanced Raman spectroscopy (TERS and SERS, respectively) for the detection of biomolecules on surfaces [2]. Part of his overall strategy involves using the Nanofab to fabricate SERS substrates with reproducible behaviours. Lagugné-Labarthet and graduate student Betty Galarreta have made well-controlled lithographic patterns of noble metals (Au) on glass as shown in Fig. 5a-b. The inter-structure gap between the features (between 30 and 50 nm) is a key parameter for optimizing the SERS enhancement via the surface plasmon resonance of the metal. Depending on the sizes and gaps of the structure, the plasmon frequency can be finely tuned as shown in figure 5 c. Figure 5d shows an example of a SERS spectrum of a monolayer of guanosine triphosphate (GTP) measured under a confocal microscope. The spectra are significantly enhanced when deposited on their platform while it appears very weak on a flat gold surface. The vibrational information contained in the SERS spectrum can provide invaluable information about their insertion into the biological membranes, their structural conformations, or their interactions with surrounding molecules, and are important for understanding many fundamental bioprocesses.

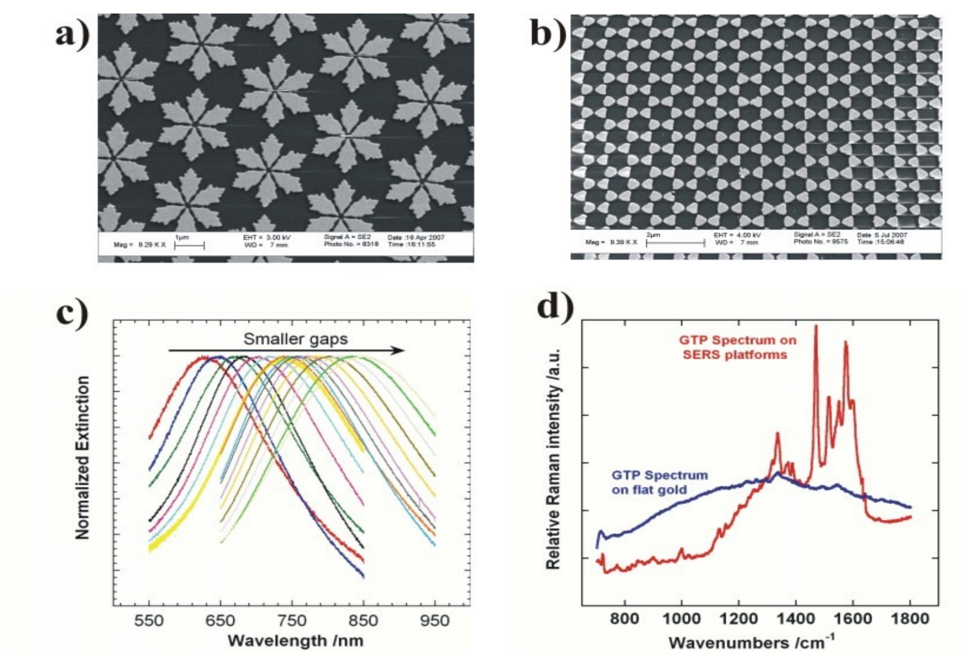

Figure 5: Examples of plasmonic devices made using the e-beam lithography technique. a) The sharp structures of the nano-snowflakes have gaps in the 50-100 nm range. b) The triangles have a side of 400 nm and a 20 nm gold thickness. c) The Plasmon frequency can be tuned very accurately depending on the size of the triangles and associated gaps. d) Raman spectra of a monolayer of GTP deposited on flat gold and on SERS platforms. The laser power is similar in both experiments.

Biophotonics

Peter Norton (Chemistry), Nils Petersen (NINT) and graduate students Jessica McLachlan, Natasha Patrito, and post-doc Claire McCague have developed a method for the modification of the surface of poly(dimethylsiloxane), PDMS, to enhance its ability to serve as a platform for cell adhesion in microfluidic devices [3]. The process involves depositing a thin layer of aluminum onto the polymer in the presence of an Ar plasma. The PDMS surface can then be patterned by depositing metal through a stencil mask thereby allowing cells to adhere to specific locations on the surface (Figure 6). Such arrays allow the study of cell-cell interactions, cell motility, and cellular responses to various spatial and geometric perturbations.

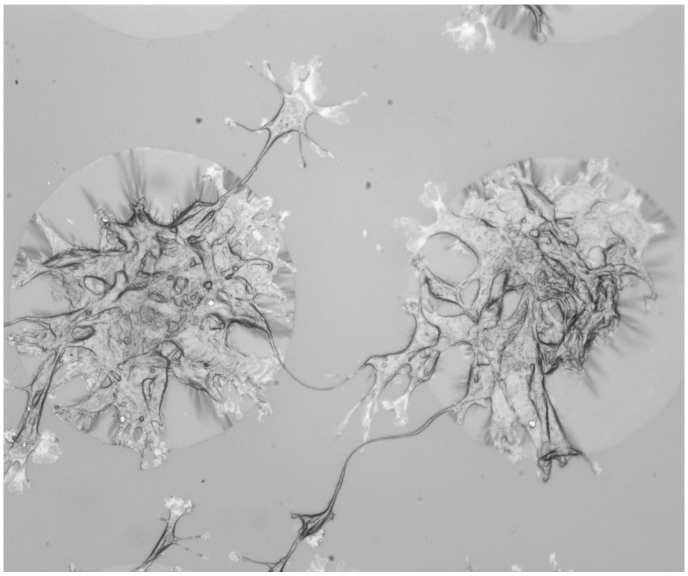

Figure 6: Optical micrograph of patterned C2C12 cells on modified PDMS

Zhifeng Ding is developing improved and integrated tools to investigate single live cells and semiconductor nanostructures to provide insight into the relationships between structure and property and or function [4,5,6,7]. One important approach is the use of Scanning Electrochemical Microscopy (SCEM) which involves measuring the current of species contained in the solution gap between a tip and the substrate. SECM is useful in a wide range of applications, including imaging of biological molecules. For example, Figure 7 shows an SECM image of two COS 7 live cells from which information about their metabolism can be derived.

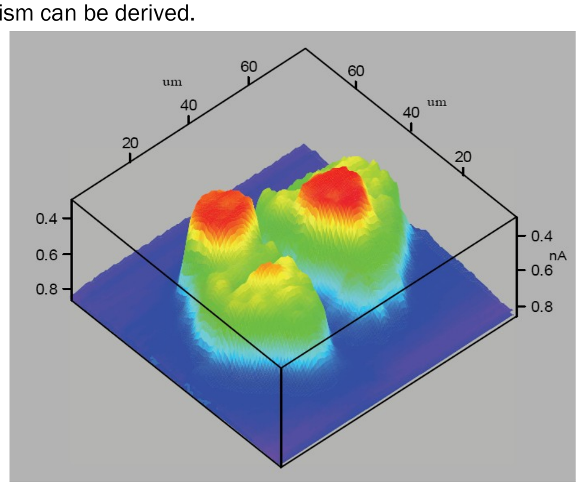

Figure 7: SECM images of two COS 7 live cells

Novel materials

Novel materials, fabrication techniques, and applications of photonic crystals (PCs) are core areas of research at Western. Rob Lipson and Kim Baines joined forces with co-supervised student Yun Yang to examine the possibility of fabricating PCs by optical lithography in photoresists made from Si- or Ge-containing polymers [8]. PCs have periodic structures which localize light and prohibit a certain range of wavelengths from propagating within the material. The PBG structures are made from two substances with significantly different refraction indices, n. In a similar manner to semiconductors which exhibit electronic band structure due to their periodic atomic spatial arrangement, the periodic variation of the index of refraction in a PC produces a band structure for photons, with well-defined energy-momentum levels. One condition that is required to open a band gap is that the periodic index contrast of the crystal must be large ($\Delta n \sim 2$). This can not usually be achieved using commercially available carbon-based photoresists. Instead patterned carbon-based resists are usually used as masks for subsequent etching into high index substrates such as Si. The Baines group was able to synthesize a series of photosensitive polymers having Si and Ge backbones. As shown in Fig. 8, these polymers could be patterned by optical lithography. The indices of refraction of Si- and Ge-based films are sufficiently large that their use photoresists can in principle lead to photonic band gap structures in a single fabrication step.

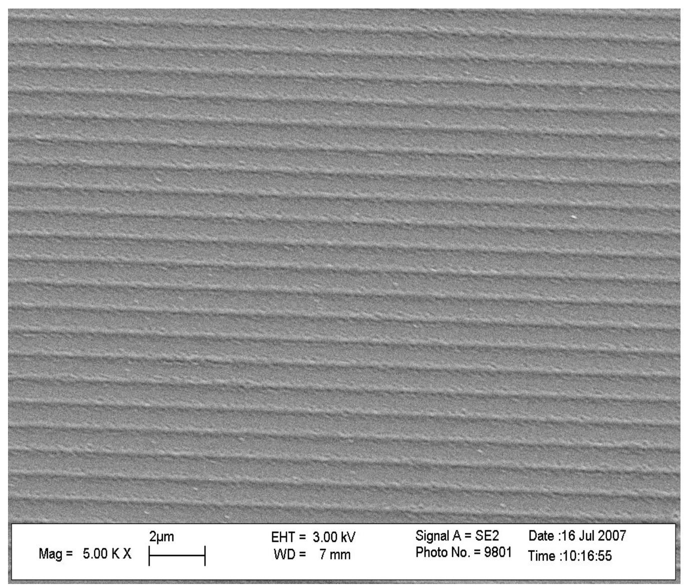

Figure 8: SEM image of a germanium thin film (poly(p-methoxyphenylmethylgermane) patterned by 2-beam interference lithography.

Martin Zinke-Allmang working with student Kenneth Kar Ho Wong, and Engineering Professor W.K. Wan are examining the elastic properties of non-woven fibres with nanometer diameters using high resolution scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) [9]. These polymers are becoming the biomedical materials of choice in many restorative and regenerative medical procedures because their physical properties, such as porosity and mechanical strength, can be tailored to suit specific applications. In recent experiments, an electro-spinning process was used to produce non-woven polymer mats composed of fibres with diameters between 50 nm and 500 nm. Figure 9 shows a mat of poly(vinyl alcohol) (PVA) formed in this way. Elastic moduli were found using the clamped beam model to fit the deflection values along the suspended fibre after some accurate measurements of the geometry and diameter of the fibre were established.

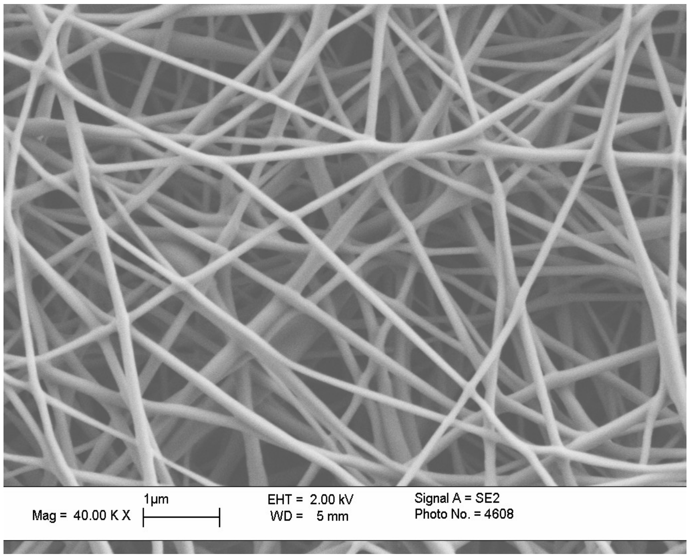

Figure 9: A SEM image of a PVA fibres mat

Lipson and Cheng Lu have studied the synthesis and optical properties of thin films of β-barium borate (β-BaB_2O_4; β-BBO). They have made high quality thin films of β-BBO which are amenable to contact lithography (Figure 10) [10]. The films are produced by spin coating metallo-organic solutions with a poly(vinyl pyrrolidone) (PVP) additive, followed by O_2 plasma treatment and thermal baking. In addition, the BBO thin films could be reoriented by seeding the precursor gels with an organic molecule prior to thermal treatment. Using either approach, the films exhibit more efficient second harmonic generation than those made by literature methods.

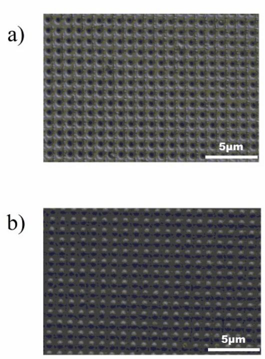

Figure 10: SEM images of a) the Si mask used for contact lithography and b) the patterned β-BBO film

In different experiments, new routes to thin films of solid state VO_2 have also been developed using sol-gel methods. By precisely controlling the processing conditions, (baking temperature, ambient gas in the oven, baking time, solvent etc.), VO_2 films can be synthesized that are highly resistant to oxidation for long periods of time. Furthermore, by varying the processing conditions, the morphology of the resultant VO_2 films can be controlled to produce of nano-belts, nano-ribbons or nano-wires made of V_2O_5. These materials have in part been characterized using Raman imaging in collaboration with the Ding group (Figure 11). VO_2 undergoes a phase change from semiconductor to metal near 70°C on the picosecond time scale. The films produced at Western are being examined by OPC member Dwayne Miller at the University of Toronto using femtosecond electron diffraction [11] to better understand this remarkable transition.

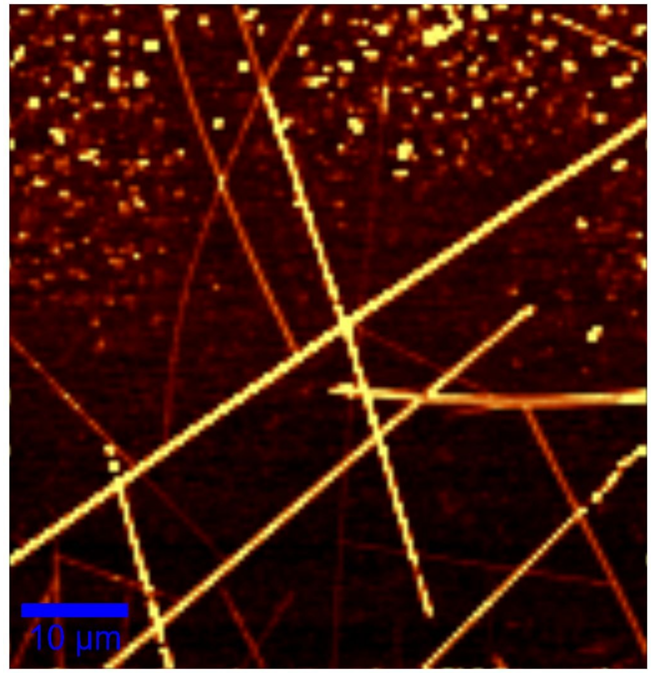

Figure 11: Raman image of nanowires of vanadium oxide obtained by detecting specific Raman modes of the material

Zhifeng Ding's group, in collaboration with T.-K. Sham (Chemistry) and Xueliang Sun (Materials Engineering) has found an electrochemical avenue to prepare strong blue luminescent nanocrystals (NCs) from multiwalled carbon nanotubes (MWCNTs) (Fig. 12) [12]. The search for a good carbon emitter is a challenging enterprise because neither of the two bulk carbon allotropes, graphite and diamond, give strong luminescence. The new carbon NCs prepared at Western are very attractive due to their promised applications in optoelectronic devices, biology labelling, and biomedicine.

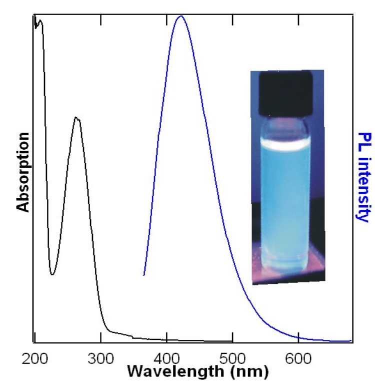

Figure 12: UV-visible absorption and photoluminescence spectra of carbon NCs in aqueous solution. Inset is the solution illuminated by an UV lamp.

Photonic Crystals

Lipson, Mitchell and graduate student Cheng Lu have developed novel optical lithography techniques that are expected to ultimately be used for fabricating PCs. In one approach near-field Diffraction Element Assisted Lithography or DEAL was devised to fabricate two-dimensional lattice patterns in a photoresist [13]. Specifically, a diffraction element was used to pre-pattern the coherent output of a laser prior to its capture in a photoresist. The pattern symmetry and spacing can be readily modified with the same experimental arrangement since the near-field diffraction pattern strongly depends on the nature of the diffractive element and the distance between the element and the photoresist. The patterns that are formed can serve as masks for patterning high index materials to create photonic band gap materials. Alternatively, they have the potential to behave as two-dimensional photonic band gap arrays provided the polymer used exhibits a large enough index contrast.

In a second approach, a Babinet-Soleil compensator was inserted into the path of one of the three beams used for noncoplanar beam interference lithography [14]. This birefringent element could change the phase of the beam so that either a positive two-dimensional pattern or an inverse-like structure is generated in a photoresist without disturbing the mechanical geometry of the setup. As shown in Figure 13 large defect free sample areas (>1cm^2) with sub-micron periodic patterns with different morphologies could obtained by simply "dialing" up a specific phase difference for one of interfering beams.

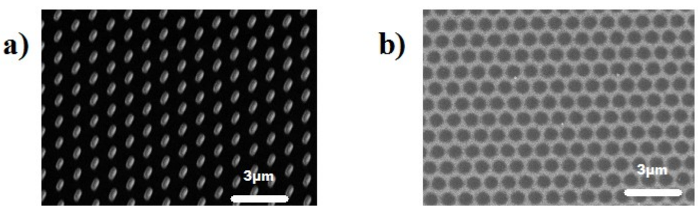

Figure 13: a) SEM image of a pattern formed in a SU-8 photoresist when all three beams used for IL had the same phase, (N_1, N_2, N_3) = (0, 0, 0). The marker indicates a 3 um scale; b) SEM image of a pattern formed in a SU-8 photoresist when the phase of the third beam was B/2 different from the other two, (N_1, N_2, N_3) = (0, 0, π/2). The bar marker indicates a 3 um scale.

Among the diverse photonic crystal (PC) applications, PC sensors have drawn much attention because of their high sensitivity and compact structure [15]. Jayshri Sabarinathan (Engineering) has developed a PC waveguide based pressure sensor which has many applications in MEMS and microfluidic applications. Sensing is performed by measuring the transmission variation through the PC waveguide due to the changes in the refractive index of the region surrounding the PC. When pressure is exerted on the waveguide it mechanically deforms the waveguide and alters the transmission characteristics of the waveguide. The changes in light intensity due to the relative displacement of the PC waveguide with respect to substrate can be correlated to the fluid pressure. The device shown in Fig. 14 consists of an air bridge PC waveguide with a triangular air hole lattice coupled with conventional dielectric waveguides on input and output side, designed on a silicon-on-insulator (SOI) wafer. Simulations show nearly 72% and 0% transmission when the distance between the PC waveguide and the substrate was 600 nm and 0 nm respectively. The maximum sensitivities, that is, the large intensity variations with small displacements were achieved when the PC waveguide was between 300 nm to 200 nm.

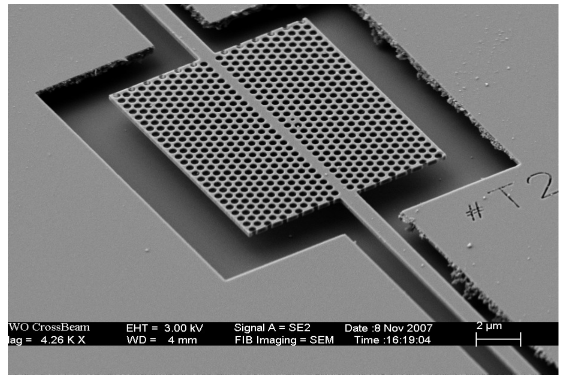

Figure 14: SEM micrograph of a Photonic Crystal air-bridge wave guide for pressure sensor applications

Conclusions

The examples above constitute only a very small subset of those that continue to develop even though the formal activities of the OPC have concluded. They show that photonics studies are a platform for strong collaborations between researchers in chemistry, physics and engineering. The work has strong fundamental and applied relevance, and therefore, it is expected that the resultant collaborations and the future of photonics research at Western have a bright future.

References

1. S. Xu, G. Podoprygorina, V. Boehmer, Z. Ding, P. Rooney, C. Rangan, S. Mittler, Organic & Biomolecular Chemistry 5 558-568, 2007.
2. V. Guieu, F. LagugnépLabrathet, L. Servant, D. Tulaga, and N. Sojic, *Small*, 4, 96-99 2008.
3. Natasha Patrito, Claire McCague, Peter R. Norton, Nils O. Petersen, *Langmuir* 23, 715-719, 2007.
4. R. Zhu, Z. Ding, *Can. J. Chem.* 83 1779-1791, 2005.
5. X. Zhao, N.O. Petersen, Z. Ding, *Can. J. Chem.* 85 175-183, 2007.
6. P.M. Diakowski, Z. Ding, *Phys. Chem. Chem. Phys.* 9 5966 – 5974. 2007
7. R. Zhu, Z. Qin, J. J. Noel, D. W. Shoesmith, Z. Ding, *Anal. Chem.* 80 1437-1447, 2008.
8. Y. Yang, M.Sc. Thesis, The University of Western Ontario, 2008
9. Wong, K. H.; Zinke-Allmang, M.; Wan, W. K.; Zhang, J. Z.; Hu, P. Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 243, 63-74, 2006.
10. C. Lu, S. S. Dimov, and R. H. Lipson, *Chem. Mater.* 19, 5018-5022, 2007
11. B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. D. Miller, *Science*, 302, 1382-1385.
12. J. Zhou, C. Booker, R. Li, X. Zhou, T.-K. Sham, X. Sun, Z. Ding, *J. Am. Chem. Soc.* 129 744-745, 2007.
13. C. Lu, X. K. Hu, I. V. Mitchell and R. H. Lipson *Appl. Phys. Lett.* 86, 193110-1 – 193110- 3, 2005.
14. C. Lu, X. K. Hu, S. S. Dimov and R. H. Lipson, *App. Opt.* 46, 7202-7207, 2007.
15. S. Mittal and J. Sabarinathan, *Proceedings of the SPIE*, 5971, 59711J, 2005.

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