Prof. Yuval Golan

Area of interest:

thin films, semiconductor nanostructures, epitaxial electrodeposition.

Nanomaterials @ Interfaces Research Group

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<u>Aim of Research:</u>

The aim of our research is to identify and understand the chemical and physical interactions and interfacial processes that govern the formation of thin films and two- and three-dimensional assemblies of ordered nanoparticle systems. This includes the direct deposition of semiconductor thin films on single crystal substrates and on ultrathin (Langmuir) organic film templates, as well as surfactant controlled chemical deposition of nanoparticles of different shape and composition onto solid supports (from solution or from the air-water interface using the Langmuir Blodgett technique) for forming ordered super-crystalline films.

Characterization techniques include advanced electron microscopy, electron and x-ray diffraction techniques, plus a variety of optical techniques (photo- and cathodo- luminescence, optical absorbance, multiple beam interferometry). Surface force measurements (friction and adhesion) are performed in collaboration with Prof. J. Israelachvili at UCSB. We use various synchrotron radiation techniques for structural characterization, including grazing incidence x-ray diffraction (GIXD), grazing incidence small angle scattering (GI-SAXS), x-ray absorbance spectroscopy (EXAFS) and anomalous x-ray scattering.

<u>Short description of major research projects</u>

1. Ordered 2D and 3D arrays of surfactant coated nanowires and nanorods
[Students: (Dr.) Nataly Belman (graduated in 2009), Alexander Rabkin].

Currently funded by the Israel Science Foundation (ISF) and by the US-Israel Binational Science Foundation (BSF) Co-PI: Jacob Israelachvili, UCSB

Uniform nanoparticles of ZnS, ZnSe, PbS and CdS are synthesized by thermal decomposition of single precursor xanthate salts in molten alkylamine surfactant. The nanoparticles are studied under confinement in 2D (Langmuir trough) and in 3D using a surface forces apparatus (SFA). The conditions (and subsequent surfactant-semiconductor interactions) for shape (sphere, rod and wire), size and crystallographic phase -controlled nanoparticle formation are studied. In particular, we study the ordering of monodisperse nanoparticles into super-crystalline arrays with emphasis on the role of the structure of the surfactant (primary amines such as octadecylamine, ODA). The structure and orientation of the superstructures are studied and correlated with the polarization dependent optical properties. A large number of experimental techniques are used, including TEM, □-A isotherms, DSC, TGA, optical absorbance and emission (PL) measurements, in-house powder and thin film XRD (including temperature resolved XRD), synchrotron GIXD and GI-SAXS (ESRF), ^{67}Zn and ^{13}C SS-NMR and SFA. Figures 1(a,b) respectively show TEM and HRTEM images of arrays of ODA-coated ZnS nanorods. The nanoparticles self-assemble into a layered superstructure with a super-crystalline order which is directly templated by the surfactant: the *hierarchical structure* starts from the wurtzite structure of the ZnS mineral cores (Fig. 1c), follows to the 2D in-plane structure of the surfactant molecules adsorbed onto the ZnS facets, then to the resulting composite bilayer/nanorod structures (Fig. 1d) packed in sheets that are stacked in a smectic-like structure. A major breakthrough in this project was made last year, when we showed that spontaneous reaction of ODA with ambient CO_2 and reversible formation of octadecylammonium-octadecylcarbamate (OAOC) molecular pairs strongly affects the resulting nanoparticles and explains severe irreproducibility problems encountered by many groups working in this field. Furthermore, this allowed us to isolate the pure phases of ODA and OAOC and to determine their temperature-dependent phase behavior. For the first time, the structures of the alkylamines and their corresponding alkylammonium-alkylcarbamates were determined and reported in detail for chain lengths of C14, C16 and C18, as summarized in Table 1 below. The directional thermal expansion of alkylammonium-alkylcarbamates was determined from temperature resolved powder X-ray diffraction.

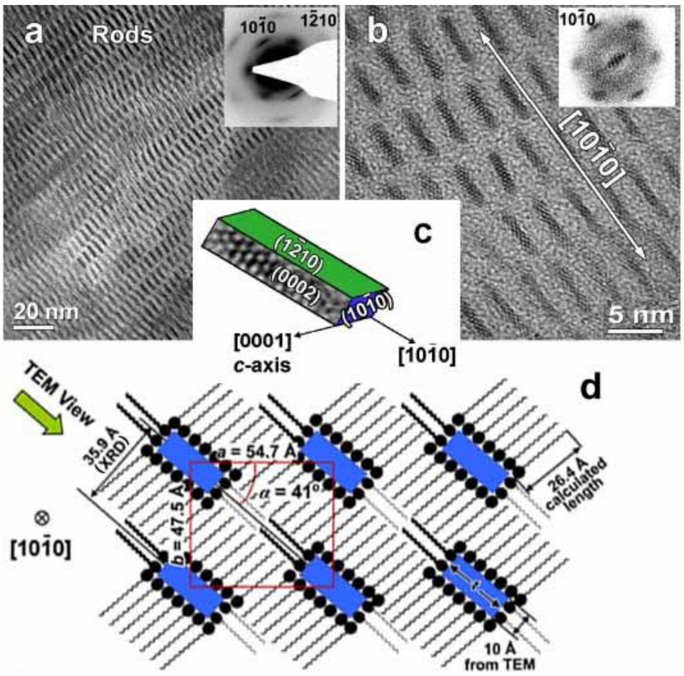

Figure 1: (a) TEM image showing an array of ultranarrow ZnS nanorods coated with octadecylamine surfactant molecules (Inset: corresponding electron diffraction pattern). (b) HRTEM lattice image and corresponding FFT pattern. (c) Results of crystallographic analysis showing the planes and directions of the wurtzite structure of the rods. (d) Packing model based on powder XRD, TEM, GIXD and GISAXS analyses. The rods are viewed edge-on from the [10.0] direction, while the green arrow denotes the top view direction as viewed by TEM.

Table 1. Orthorhombic unit cell dimensions for the pure alkylamines and for the room temperature and high temperature phases of alkylammonium - alkylcarbamates derived from temperature-resolved powder XRD measurements.

	alkylamine (AA)			alkylammonium-alkylcarbamate (AAAC) room temperature (RT)			AAAC high temperature (HT)		
	a [Å]	*b* [Å]	*c* [Å]	*a* [Å]	*b* [Å]	*c* [Å]	*a* [Å]	*b* [Å]	*c* [Å]
C14	5.60	7.35	36.03	7.75	9.66	42.06	6.46	8.85	39.38
C16	5.60	7.35	40.53	7.75	9.66	47.17	6.46	8.85	44.23
C18	5.60	7.35	45.16	7.75	9.66	52.31	6.46	8.85	48.75

2. Chemical solution deposition of thin films of metal chalcogenides with controlled morphologies – fundamental studies and applications [Students: (Dr.) Michael Shandalov (graduated in 2007), Tsofnat Ganigar, Anna Osherov, Moshiel Biton]. *Currently funded by Vatat (Israeli Defense Grant)*

Chemical solution deposition is employed for obtaining high quality nanocrystalline PbSe thin films on GaAs and Si with a wide range of microstructures *from nanocrystalline to monocrystalline films*. The optical, electrical and interfacial properties of these films are studied in detail. More recently, this technique has been extended for growth of PbS films. Notably, monocrystalline films of PbSe and PbS with a well-defined orientation relationship with the substrate were successfully deposited using this technique, as demonstrated in Fig. 2.

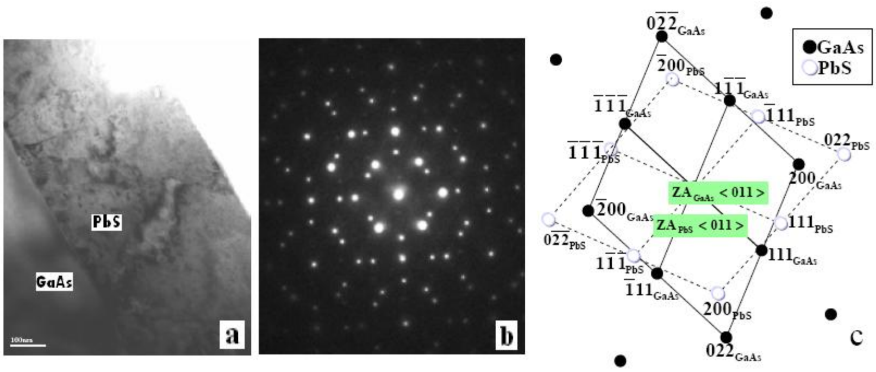

Figure 2. 'Chemical epitaxy' of PbS on GaAs. (a,b) Cross-sectional TEM and electron diffraction of a chemically deposited monocrystalline film. (c) Indexing of the diffraction pattern, indicating a well-defined (100)GaAsII(011)PbS ; [011]GaAsII [0-11]PbS orientation relationship.

Hybrid photonic crystals composed of chemically deposited semiconductor nanocrystals within micropatterned Si matrices are being fabricated in collaboration with Prof. Amir Sa'ar of the Hebrew University in Jerusalem. We have recently demonstrated resonative emission in these hybrid materials, in which the emission wavelength of the chemically deposited nanoparticles is tuned to match the periodic structure of the photonic crystal (Figure 3). Tuning of the emission wavelength of the nanoparticles is achieved in various ways, including control over particle size (quantum size effects), the composition of the nanoparticles (notably solid solutions), surface treatments and temperature-dependent emission experiments at cryostatic conditions. Quite recently, multiple exciton generation (MEG) was demonstrated in our PbSe and PbS monocrystalline films, challenging the common notion and indicating that

MEG might not be restricted to nanomaterials. These findings are summarized in an article that was published in *Nature Physics* (2009). Further research efforts are currently focused on chemical deposition of thin films of copper sulfides and selenides.

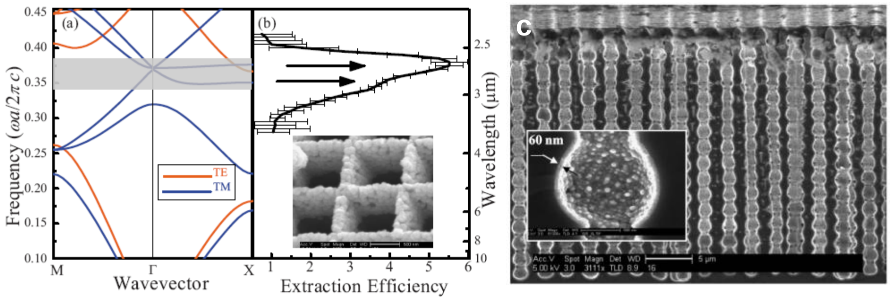

Figure 3: (a) The calculated photonic band structure and (b) the measured extraction efficiency for the 2D composite PC (top view SEM image of the composite PC is shown in the inset). Blue lines are related to TM modes while red lines are related to TE modes. The shaded area in (a) indicates the frequency range of slow-light modes and their correlation with the extraction peaks, marked by arrows in (b). (c) SEM cross-section view of a 3D macroporous silicon composite PC. The inset shows a magnified image of a PC unit cell with a thin film of chemically deposited spherical PbS nanocrystals, about 60 nm in thickness and covering the pore walls.

3.Semiconductor nanocrystals on polydiacetylene Langmuir film templates [Students: (Dr.) Yevgeniy Lifshitz (graduated in 2009), Alexander Upcher; project in collaboration with Dr. Amir Berman, BGU Biotech. Eng.]. *Currently funded by Mafat (Israeli Defense Grant)*

We have elucidated the structure of the different phases (crystalline monomer phase, blue phase, red phase) of polydiacetylene Langmuir films using *in-situ* synchrotron grazing angle x-ray diffraction (GIXD) and *ex-situ* TEM. We have also detected and reported, for the first time, 2-photon polymerization in polydiacetylene films. More recently, the phase transition kinetics were monitored using optical absorbance spectroscopy. Current research is underway in order to take advantage of the progress gained in the above-mentioned studies in order to fabricate organic devices (notably, transistors) and hybrid organic-inorganic devices by using *well-defined* Langmuir film templates of a specified crystallographic phase (blue, red, etc.) for oriented nucleation of semiconductor nanocrystals such as CdS, ZnS, PbS and evaluation of their optical and electrical characteristics. Recent progress includes combinatorial chemical sensors with high specificity based on chemically modified PDA films (funded by *Mafat*).

Impact:

There are several areas in which our research has made considerable impact in recent years:

1. Studies of surfactant-coated nanoparticle arrays. There are very few groups studying the *structure* of the molecularly thick surfactant films responsible for the passivation of nanomaterials. We have clearly shown that the mutual chemical and structural relations between the surfactant and the mineral core are responsible not only for the ordering in 2D and in 3D, but also for the size, size uniformity, shape and growth direction of the nanoparticles. Our recent studies on these issues were published in *JACS* and in *Nano Lett.* and have gained considerable interest in the nanomaterials community.
2. The study of Langmuir films as templates for growth of nanocrystalline semiconductors has attracted considerable attention in the nanomaterials community. In particular, the use of synchrotron surface diffraction for determination of the ultrathin film structure directly at the air-water interface has drawn significant attention.
3. Advances in chemical bath deposition (CBD) of grain size and orientation controlled semiconductor thin films. Our demonstrations of high quality material grown by CBD on GaAs including single crystal films and nanocrystalline films with controlled particle size and subsequently controlled bandgap are proving to be not only of fundamental interest, but also of significant technological importance.