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# Template-Directed Directionally Solidified Eutectic Metamaterials

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Final Report



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Since the last report in September 2017, the MURI team made a number of important capstone accomplishments. Braun and Thornton continued their investigation of eutectic solidification in two and three-dimensional templates. In the CsCl-AgCl eutectic system, they explored a transition in microstructure from rods to lamellae as solidification velocity was increased. This allows switching between one-dimensional and two-dimensional photonic crystals in the same material through adjustment of only processing parameters. This work was published in Advanced Optical Materials. Braun and Thornton also examined phenomenon in which the steady-state lamellar orientation of a eutectic...(see attached abstract).

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**Final Report**

As stated in the initial proposal project summary, this MURI team set out to "establish a major program of research on the template-directed directional solidification of eutectic metamaterials." Before the team started working on this subject, almost nothing was known about the effect of two and three dimensional templates on the microstructure of eutectics. To illustrate just one example of how far the team extended the understandings of template-directed eutectic solidification, here we provide the abstract and Figure 1 of a paper Braun and Thornton will submit shortly

"By controlling the confinement effects arising from the templates, complex architectures that resemble the Archimedean tessellations have been obtained in organic molecules, and polymer composites. However, these structures are limited in the range of feature sizes and synthesis routes' lack of compatibility with other classes of materials. Here, we show that sub-micron scale Archimedean-like lattices are obtained through directional solidification of eutectic materials into two-dimensional templates. We solidified a lamellar binary eutectic within pillar templates (prepared by interference lithography), and by merely varying the cooling rates, structures resembling the honeycomb lattice, kagome lattice, and square-hexagonal-dodecagonal lattice were achieved. Phase-field model simulations confirmed that these structures emerge due to the kinetic effects of template confinement on chemical transport during the solidification process. Given the wide range of feature sizes and the numerous possible combinations of eutectic materials and two-dimensional templates, this approach could be useful in the fabrication of functional architectures with features in the size range of tens of nanometers to microns, thus bridging the elusive gap of visible spectrum photonic quasicrystals."

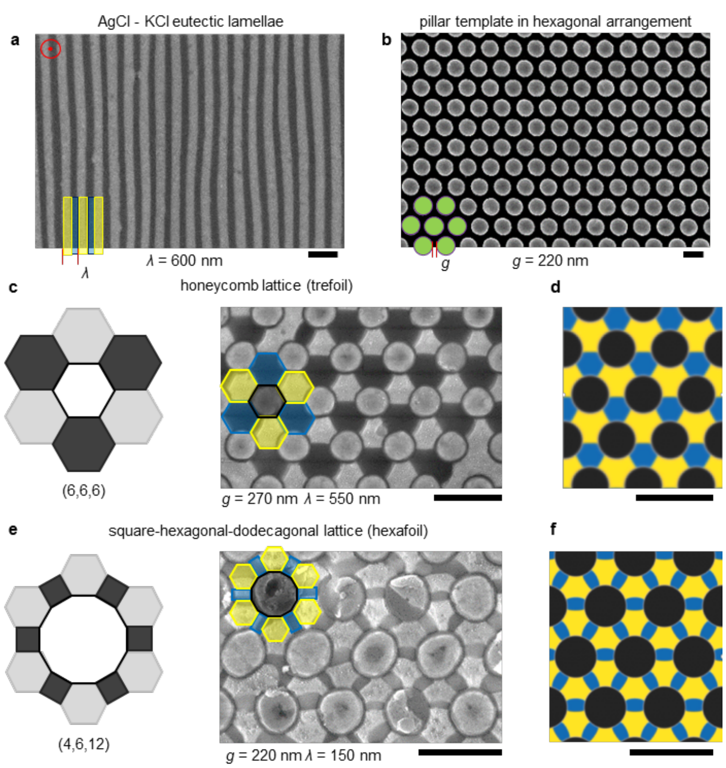

Figure 1: Solidification of molten eutectic within pillar template. a. SEM image of AgCl (in bright/ shaded yellow) – KCl (in dark/ shaded blue) eutectic solidified at a cooling rate of 25 °C/min forming a lamellar structure with the average lamellar spacing λ = 600 nm. b. SEM image of a pillar template sample showing the hexagonal arrangement of pillars, with an edge gap of g = 220 nm. c. Schematic and experimental observation of the honeycomb lattice (trefoil) in the pillar template when λ/g ~ 2. d. Phase-field simulations predict a similar pattern at the steady-state condition. e. Schematic and experimental observation of square-hexagonal-dodecagonal lattice (hexafoil) when λ/g ~ 0.67. f. Phase-field simulations predict a similar pattern at the steady-state condition. All scale bars are 1 μm.

It is worth contrasting this with Figure 2 of the team's first publication on this subject, Adv. Mater., 2015:

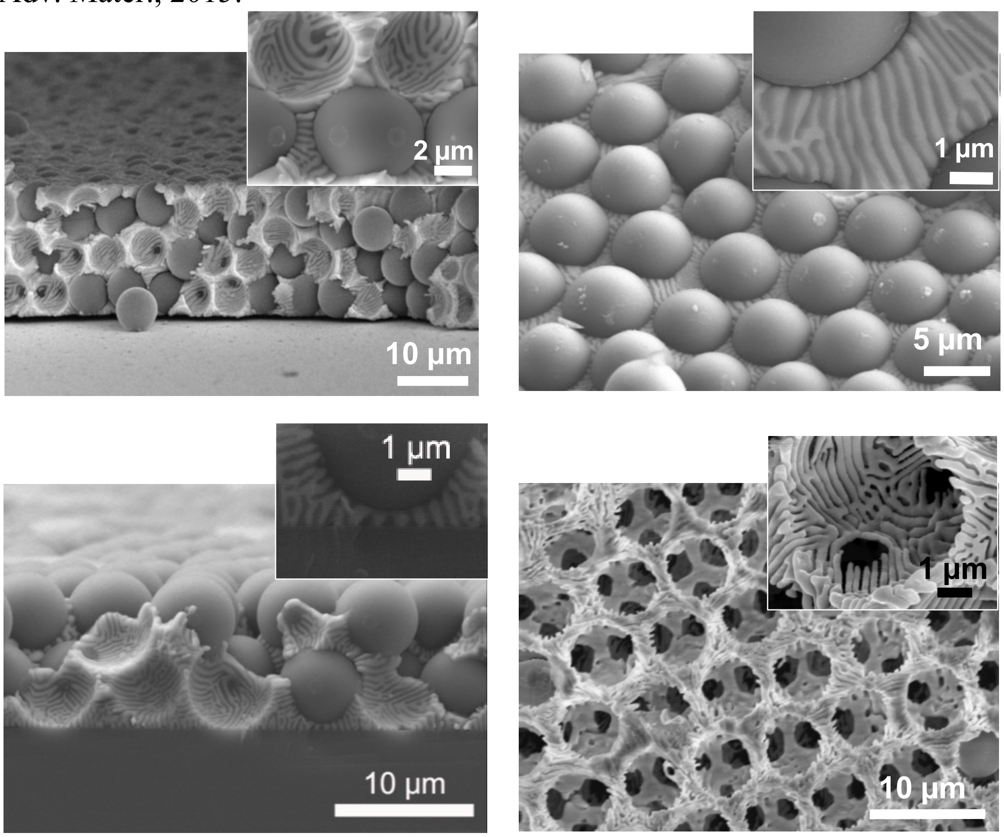


Figure 2. SEM images of the air cooled AgCl-KCl eutectic templated by the 6 μm diameter colloid template. Representative (a) cross-sectional and (b) plan view SEM images. Inset of (a) shows complex self-organized 'wavy' structures inside the template and the inset of (b) exhibits the lamellar structure formed between silica particles on top of the template. (c) A partially infilled template. The inset shows the eutectic first initiating at the substrate with the expected lamellar structure, and then the lamellae change direction. (d) The mesostructured AgCl inverse opal formed by HF and DI water etching of the silica and KCl. Inset, higher magnification view.

In 2015, the team only knew that the interaction of a solidifying eutectic with a template would alter the microstructure. Today, the team has the ability to simulate, in advance, the effect of a template with a solidifying microstructure, has collected high quality optical data from the microstructure formed by a solidified eutectic, and has learned how to combine eutectic solidification with highly functional templates to make materials with potential for non-reciprocal optical properties.

Here we will now highlight some of the more recent developments of the team. We refer the reader to our previous annual reports for a more in-depth report of annual activities. Braun and Thornton have investigated several aspects of template-directed eutectic solidification in the past year. In the CsCl-AgCl eutectic system we explored a transition in microstructure from rods to lamellae as solidification velocity was increased. This allows switching between one-dimensional and two-dimensional photonic crystals in the same material through adjustment of only processing parameters. A manuscript for this study was published in Advanced Optical Materials. We also examined a phenomenon in which the steady-state lamellar orientation could be changed inside a pillar template. When confined by a template, solid-solid phase boundaries orient themselves perpendicular to the surface of the template and thus an otherwise vertically aligned lamellar eutectic becomes horizontally aligned in a pillar template. The model's predicted structures closely matched those observed in experiment and the undercooling values obtained from the model revealed that horizontally aligned lamellae are favorable. We further investigated template-directed eutectic solidification through pillar array templates by changing the solidification direction to be parallel to the axis of the pillars. The phase-field model predicts well-ordered spoke-like structures for hexagonal, square, and other lattices of pillar arrangement in which the minority phase connects the pillars to their neighbors with spokes. The number of spokes can be tuned with the volume fraction of the template and the solidification velocity. Additional morphologies were realized when changing the cross section shape of the pillars, including arrays of C-shapes, X-shapes, and corkscrews. The model's predictions show good agreement with experimental results. Also, the model was modified to include contact angle boundary conditions to account for differing interfacial energies at the template surface. A study was performed using the Pb-Sn system as a basis while varying the equilibrium contact angles between the template and the multiple eutectic phases. The effects of solid-wetting and solid-dewetting conditions and also unequal $\alpha$-template and $\beta$-template interfacial energies were determined. Additionally, a thorough review of template-directed eutectic solidification for optical materials was conducted and a review paper was published in Advanced Optical Materials. Finally, numerous heat transfer calculations were conducted to determine temperature profiles, solidification directions and rates, and thermal gradients.

Thornton and Martin continued their investigation of spinodal decomposition in the $VO_2$-$TiO_2$ system. Specifically, we studied the effect of varying surface mobility and deposition rate on the length scale and morphology of the phase-separated structures of a thin film. In related work, Martin leveraged competition between energetically degenerate states to achieve large field□driven responses. Here, a new route to such effects involving domain□structure competition is demonstrated, which arises from strain-induced spontaneous partitioning of $PbTiO_3$ thin films into nearly energetically degenerate, hierarchical domain architectures of coexisting c/a and $a_1/a_2$ domain structures. Using band-excitation piezoresponse force microscopy, Martin manipulated and acoustically detected a facile interconversion of different ferroelastic variants via a two-step, three-state ferroelastic switching process (out-of-plane polarized $c^+$ → in-plane polarized a → out-of-plane polarized $c^-$ state), which is concomitant with large nonvolatile electromechanical strains (≈1.25%) and tunability of the local piezoresponse and elastic modulus (>23%). It is further demonstrated that deterministic, nonvolatile writing/erasure of large-area patterns of this electromechanical response is possible, thus showing a new pathway to improved function and properties.

Rogers, Thornton, and Braun used in 3D structures as frameworks for templated growth of organized lamellae from AgCl–KCl eutectics. The 3D structures were formed through processes of stress release in 2D structures formed on prestrained elastomeric substrates, followed by transfer of these 3D structures to highly thermally stable substrates. Following transfer to the thermally stable substrate, a AgCl-KCl eutectic was introduced onto the structure above the meting point of the eutectic. The unique thermal gradients generated by the structure then lead to the formation of a lamellar eutectic with lamellae following the complex geometry of the initial 3D structure. Lewis and Braun continued their collaborative work in the direct ink writing of 3D eutectic compositions, including efforts on the direct ink writing of new compositions.

Terrones has focused over the past year on the interactions of adsorbates with graphene, including the study of the adsorption of noble gases on pristine and nitrogen-doped graphene. Single-layer graphene samples were synthesized by chemical vapor deposition and transferred to transmission electron microscopy grids. Several noble gases were allowed to adsorb on the suspended graphene substrate at very low temperatures. Raman spectra show distinct frequency blue shifts in both the 2D and G bands, which are induced by gas adsorption onto high quality single layer graphene. These shifts, which we associate with compressive biaxial strain in the graphene layers induced by the noble gases, are negligible for nitrogen-doped graphene. Additionally, a thermal depinning transition, which is related to desorption of a noble gas layer from the graphene surface at low temperatures (ranging from 20 to 35 K), was also observed at different transition temperatures for different noble gases. These transition temperatures were found to be 25 K for argon and 35 K for xenon. Moreover, we were able to obtain values for the compressive biaxial strain in graphene induced by the adsorbed layer of noble gases, using Raman spectroscopy. Ab initio calculations confirmed the correlation between the noble gas-induced strain and the changes in the Raman features observed. In related work, Terrones demonstrated the direct solution synthesis of colloidal few-layer TMD alloys, $Mo_xW_{1-x}Se_2$ and $WS_{2y}Se_{2(1-y)}$, exhibiting fully tunable metal and chalcogen compositions that span the $MoSe_2-WSe_2$ and $WS_2-WSe_2$ solid solutions, respectively. Chemical guidelines for achieving the targeted compounds were identified, along with comprehensive structural characterizations. The excitonic transition of the TMD alloy nanostructures can be readily adjusted between 1.51 and 1.93 eV through metal and chalcogen alloying, correlating the compositional modulation to the realization of tunable optical properties.