structures, but also to arbitrary shapes. Currently, Zhang and colleagues are developing fully parallel arbitrary patterning plasmonic lithography.

Alfred A. Zinn

Defects in Solar-Cell Materials Enhance Efficiency

Scientists working to improve solar cells have traditionally sought to eliminate defects found in their materials. However, it has been known for some time that polycrystalline solar cells with grain-boundary defects can be more efficient than their single-crystal counterparts. I. Visoly-Fisher, D. Cahen, and S. Cohen of the Weizmann Institute in Israel and A. Ruzin of Tel Aviv University have recently used a number of scanning probe techniques to determine how grainboundary defects improve the performance of one type of polycrystalline solar cell. As reported in the June issue of Advanced Materials (p. 879), the researchers characterized the electrical properties of single grain boundaries and grain surfaces of ~1 µm CdTe grains in p-CdTe/n-CdS polycrystalline thin-film solar cells. The tools used included scanning capacitance microscopy, scanning Kelvin probe microscopy, atomic force microscopy (AFM), and conductive probe AFM.

Most commercial solar cells are made of single-crystal semiconductors such as silicon, but single crystals are expensive to manufacture. The more cost-effective solar cells made of polycrystalline films were found to outperform their single-crystal counterpart cells, which was an unexpected outcome. When light strikes the solar cell, the semiconductor within it serves as an antenna, absorbing the light energy and allowing the free flow of electrons



Figure 1. Grain boundaries within solarcell films can improve the light-toelectricity conversion because they provide a path along which free electrons are efficiently collected and channeled.

present in the semiconductor. These electrons are then harvested as an electric current for external use. The researchers at Weizmann Institute demonstrated that grain boundaries within CdTe/CdS polvcrystalline solar cells improve the light-toelectricity conversion because they provide a path along which the free electrons are efficiently collected and channeled on their way out (see Figure 1). The researchers indicated that the efficient collection of electrons is due to the beneficial effects of the CdCl₂ vapor treatment that occurs during processing of these cells. The treatment getters both defects and impurities along the grain boundaries and alters the doping profile to facilitate spatial separation of electrons and holes, thus reducing recombination.

Large-Scale Synthesis of Nearly Monodisperse Au and Ag Nanoparticles Achieved

Gold and silver nanoparticles are important in diverse areas ranging from fundamental research to applications in electronics (single-electron transistors), catalysis, chemical sensors, and biosensors. These applications require nanoparticles in the 2-100 nm range that are surfacederivatized with hydrophobic and hydrophilic surfactants. H. Hiramatsu and F.E. Osterloh of the University of California, Davis, have demonstrated an inexpensive, versatile, and reproducible method for the large-scale synthesis of organoamine-protected gold and silver nanoparticles in the 6-21 nm (Au) and 8-32 nm (Ag) range and with polydispersities as low as 6.9%.

Usually such nanoparticles have been fabricated by either the citrate method or the two-phase (Brust) method. The citrate method produces nearly monodispersed gold nanoparticles in the size range of 2-100 nm; however, the resulting solutions have a low nanoparticle content, and the solvent choice is restricted to water. Moreover, the resulting nanoparticles cannot be surface-derivatized with hydrophobic surfactants. The two-phase method, on the other hand, allows the introduction of hydrophobic thiols as surfactants, but it suffers from the limitation to small particle sizes (<10 nm), greater polydispersity, and higher costs for the phase transfer agents.

The synthesis described by Hiramatsu and Osterloh in the June 29 issue of *Chemistry of Materials* (p. 2509) requires only three reagents, namely, tetrachloroauric acid or silver acetate, oleylamine, and a solvent. The particles are stable in solid form and can be easily modified with hydrophobic and hydrophilic thiols to



Stran

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vield nanoparticles soluble in organic agents or water. The amine in the oleylamine provides the reducing equivalents both for tetrachloroauric acid and silver acetate. The carbon double bond does not play a significant role in the process, since other aliphatic amines work equally in the reaction. Oleylamine was chosen because it is commercially available and is inexpensive, said the researchers. The reaction typically proceeds over the course of ~2-24 h. The size of the metal nanoparticles can be controlled by varying the concentrations of the metal precursor and the amine and by adequately choosing the growth temperature.

The researchers also show that the resulting particles have oleylamine weakly adsorbed on the surface and that this surfactant can be easily exchanged with aliphatic and functional thiols, thus allowing the solution of gold and silver nanoparticles in both aqueous and nonaqueous media.

Rosalía Serna

General Approach for Fabricating Inorganically Coupled Colloidal Quantum Dots and Rods Developed

A.P. Alivisatos of the University of California, Berkeley, and colleagues there and at Lawrence Berkeley National Laboratory (LBNL) have fabricated coupled quantum dots and segmented nanorods into tunable, linear, and multiple-branching forms. The linear and branched topology can be created at any point during the growth of heterostructures, not just at nucleation. To calculate the electronic interactions of the branches in three dimensions, the researchers developed a method that draws on the technique of local density approximation (LDA), extended to the entire system.

As reported in the July 8 issue of Nature (p. 190), the Alivisatos group used suspensions of cadmium, selenium, tellurium, sulfur, and other constituents. When these are assembled from liquid solution, crystals of different cadmium compounds are formed. A given structure begins with a quantum dot. The dot is then made to sprout four arms made of the same or a different compound. The arms of such a tetrapod can be lengthened into nanorods containing segments of different compounds. Nanorods, whether or not they are the arms of tetrapods, can be induced to branch into separate rods of the same or a different compound (see Figure 1a).

"Linear heterojunctions were formed when precursors for a second material were added to a growth solution containing preformed nanorods or tetrapods," said the researchers. The research group synthesized linearly extended rods with CdS rods and CdSe extensions. They synthesized branched rods with CdS rods and CdTe branches.

"Nanoprobe x-ray energy dispersive spectrometry...confirm[ed] the presence of Te at either end of branched-rod heterostructures, Se in the central rod, and Cd throughout," the researchers said. These results were further corroborated by powder x-ray diffraction, transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). HRTEM revealed a continuation of anisotropic wurtzite growth in the second semiconductor, the researchers said.

They concluded that "a branched junction forms when the new material initially grows in the zinc-blende structure, followed by a reversion to anisotropic wurtzite growth, forming the branches. Zinc-blende formation is favored by a high supersaturation of the precursors immediately following injection, with wurtzite growth resuming as concentrations drop."

To calculate the electronic states of the nanostructures, L.-W. Wang of the Computational Research Division at LBNL said that LDA, which is sufficient for calculating electronic structures of small systems, would be impractical for a nanosystem. The memory needed for calculation increases as the square of the number of atoms in the system, while the needed processing power increases as the cube.

So, Wang and his colleagues developed a hybrid method. They drew on LDA to determine the charge density in one small region of a crystal, then by "charge patching," they extended the charge density to the entire system, in this case, a quantum dot or nanorod.

To accurately model a nanostructure, Wang began by "passivating" its surface with fractionally charged pseudohydro-



Figure 1. (a) Tetrapods of CdSe (left) extended with segments of CdTe (upper right), which can be made to branch in turn (lower right). (b) Calculations using local density approximation, the charge-patching method, and the folded spectrum method yield atom-by-atom electronic maps of a tetrapod with one leg of CdSe and three of CdTe. On the left, green marks the conduction band's lowest energy state, which is physically separated in the structure from the valence band's highest energy state, shown in green on the right. For the calculated tetrapod, each branch has a diameter of 2.2 nm and a length of 4.2 nm.