



Making Ternary Quantum Dots From Single-Source Precursors

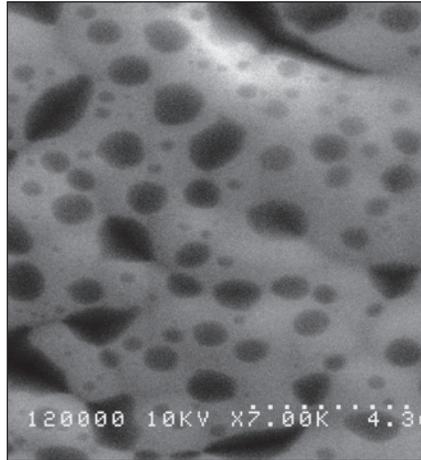
Relative to a prior process, this process is simpler and safer.

John H. Glenn Research Center, Cleveland, Ohio

A process has been devised for making ternary (specifically, CuInS₂) nanocrystals for use as quantum dots (QDs) in a contemplated next generation of high-efficiency solar photovoltaic cells. The process parameters can be chosen to tailor the sizes (and, thus, the absorption and emission spectra) of the QDs.

The process used heretofore to synthesize quantum dots in general involves *in situ* pyrolysis of reagents in the presence of a passivating solvent/ligand that not only serves as a medium for the formation of the QDs via pyrolysis, but also readily coordinates to the surfaces of the QDs, thereby preventing further nucleation. The prevention of further nucleation, also known as capping, serves to regulate the size of the QDs.

The present process is simpler and involves less handling of toxic reagents. Instead of the reagents of the prior process, one uses a compound of the type described in the first of the two immediately preceding articles, "Improved Single-Source Precursors for Solar-Cell Absorbers."



CuInS₂ Nanocrystals and Agglomerates on a polished silicon surface are shown in this scanning electron micrograph. The average diameter of the nanocrystals in this batch is 13.4 nm.

The single-source precursor is dissolved in trioctylphosphine under an inert atmosphere. The resulting solution is subsequently injected into a hot stirred so-

lution of trioctylphosphine oxide (TOPO) in order to facilitate controlled decomposition of the precursor to obtain the desired capped ternary quantum dots.

Aliquots of the solution are removed during the formation of the nanocrystals and are monitored via ultraviolet/visible-light spectroscopy to obtain information on the sizes of the nanocrystals. When the desired size range is reached, the reaction solution is cooled and methanol is added to remove excess precursor, leaving the TOPO-capped ternary nanocrystals to be harvested. The figure shows the product of one of several experiments performed to test this process.

This work was done by Sheila Bailey, Kulbinder Banger, Stephanie Castro, and Aloysius Hepp of Glenn Research Center. Further information is contained in a TSP (see page 1).

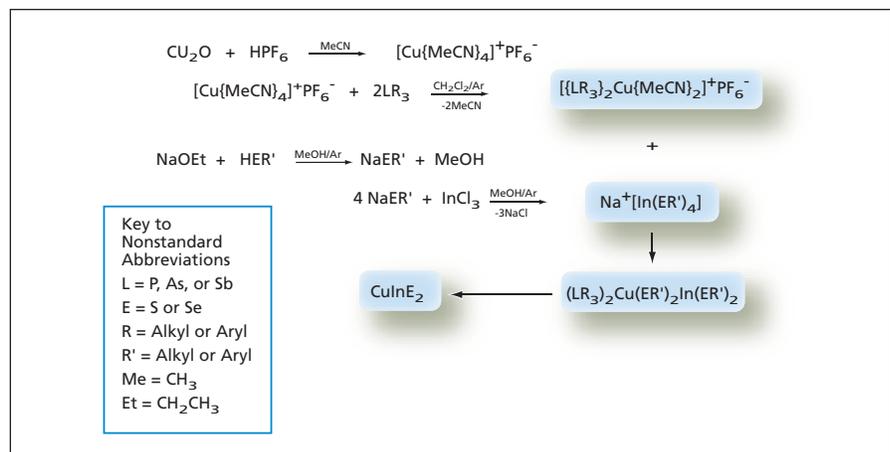
Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17446-1.

Improved Single-Source Precursors for Solar-Cell Absorbers

Deposition properties and final compositions can be tailored.

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Improved single-source precursor compounds have been invented for use in spray chemical vapor deposition (spray CVD) of chalcopyrite semiconductor absorber layers of thin-film solar photovoltaic cells. The semiconductors in question are denoted by the general formula CuIn_xGa_{1-x}S_ySe_{2-y}, where x ≤ 1 and y ≤ 2. These semiconductors have been investigated intensively for use in solar cells because they exhibit long-term stability and a high degree of tolerance of radiation, and their bandgaps correlate well with the maximum photon power density in the solar spectrum. In addition, through selection of the proportions of Ga versus In and S versus Se, the bandgap of CuIn_xGa_{1-x}S_ySe_{2-y} can be tailored to a



These Sequences of Chemical Reactions are representative of the synthesis of a single-source precursor, in this case, [(LR₃)₂Cu(ER')₂M(ER')₂] followed by formation of the chalcopyrite semiconductor (in this case, CuInE₂) from the precursor.

value between 1.0 and 2.4 eV, thus making it possible to fabricate cells containing high and/or graded bandgaps.

A "single-source precursor compound" is a single molecular compound that contains all the required elements, which when used under the spray CVD conditions, thermally decomposes to form $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$. Relative to the use of multiple precursor reagents, the use of single-source precursors offers the advantage of better regulation of the chemical composition of the deposit, less susceptibility to contamination, and, most importantly, a simplified fabrication process.

The improved single-source precursor compounds of the invention are denoted by the general formula

$[(\text{LR}_3)_2\text{Cu}(\text{ER}')_2\text{M}(\text{ER}')_2]$, where L signifies P, As, or Sb; R or R' signifies an alkyl or aryl group; and E signifies S or Se. The general formula and molecular structure afford flexibility for tailoring the precursor to suit a specific CVD spray process and to tailor the chemical composition (more specifically, the proportions x and y) of $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$ formed in the process. In addition, by choosing L, R, R', and E according to their steric and electronic properties, one can tailor decomposition temperatures and the phases in the deposit.

A single-source precursor of the invention can be synthesized by the reaction of a stabilized Cu(I) cation with an In(III) or Ga(III) chalcogenide anion prepared *in situ* by reaction of the conju-

gate acid of the thiol or selenol with NaOEt (where Et signifies an ethyl group) in CH_3OH , as in the example of the figure. Alternatively, one could synthesize a single-source precursor by use of commercially available reagents in a new facile one-pot process: For example one could react NaSCH_3 with InCl_3 and add CuCl and PR_3 .

This work was done by Kulbinder K. Banger, Jerry Harris, and Aloysius Hepp of Glenn Research Center. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17445-1.

Spray CVD for Making Solar-Cell Absorber Layers

Spray CVD combines the advantages of metalorganic CVD and spray pyrolysis.

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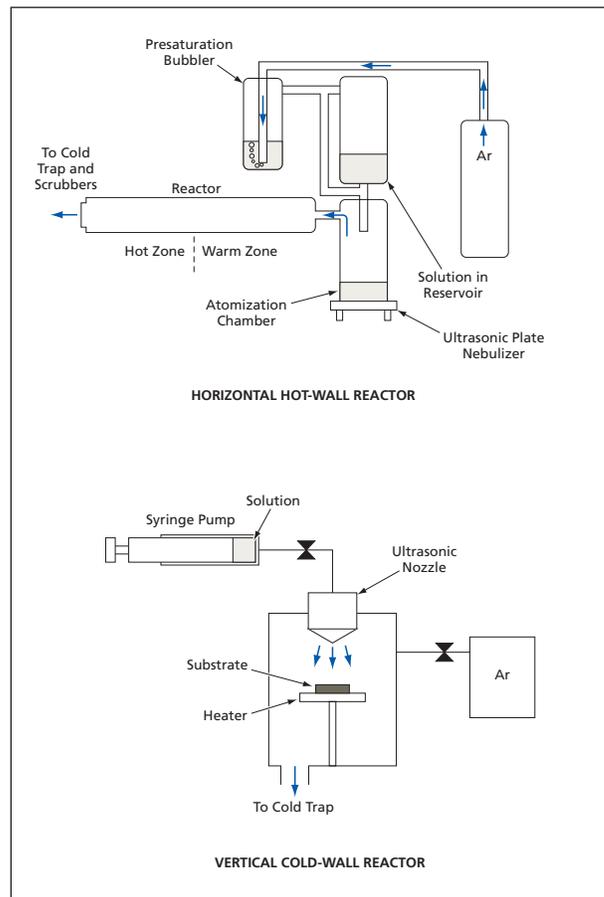
Spray chemical vapor deposition (spray CVD) processes of a special type have been investigated for use in making CuInS_2 absorber layers of thin-film solar photovoltaic cells from either of two subclasses of precursor compounds: $[(\text{PBU}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ or $[(\text{PPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ {where Bu, Et, and Ph signify butyl, ethyl, and phenyl groups, respectively}. CuInS_2 is a member of the class of chalcopyrite semiconductors described in the immediately preceding article. $[(\text{PBU}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ and $[(\text{PPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ are members of the class of single-source precursors also described in the preceding article.

In a spray CVD process of this type, a room-temperature solution containing the precursor compound is first ultrasonically nebulized. The resulting aerosol is swept into a two-zone reactor by a flow of argon, which serves as a nonreactive carrier gas. In the reactor, the aerosol first encounters the evaporation zone, which is a warm zone wherein the solvent and precursor evaporate. The resulting mixture of gases then enters the deposition zone, which is a hot zone wherein the precursor decomposes and the semiconductor film grows on a substrate as in conventional CVD.

Spray CVD affords a combination of the most desirable features (but without

the major difficulties) of metalorganic CVD and spray pyrolysis. These desirable features include growth of the film in an inert atmosphere, capability for deposition on a large area, laminar flow over the substrate, and storage and delivery of the precursor from a cool solution reservoir. The last-mentioned feature is especially advantageous in that it can prevent premature decomposition of a thermally labile precursor.

Two different spray CVD processes of this type have been tested in experiments thus far. In one process, a horizontal hot-wall reactor was used; in the other process, a vertical cold-wall reactor was used (see figure). In each process, the flow rate of argon was typically about 4 L/min. For the horizontal hot-wall re-



A Horizontal Hot-Wall and a Vertical Cold-Wall Reactor have been used in experiments on spray CVD for deposition of thin CuInS_2 films.