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, CuInS₃) 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.” The single-source precursor is dissolved in trioctylphosphine oxide under an inert atmosphere. The resulting solution is subsequently injected into a hot stirred solution 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, Kulvinder Banga, 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.

John H. Glenn Research Center, Cleveland, Ohio

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 CuInₓGa₁₋ₓSₓSe₂₋ₙ, 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 CuInₓGa₁₋ₓSₓSe₂₋ₙ can be tailored to a lution of trioctylphosphine oxide (TOPO) in order to facilitate controlled decomposition of the precursor to obtain the desired capped ternary quantum dots.

These Sequences of Chemical Reactions are representative of the synthesis of a single-source precursor, in this case, [(LR₃)₂Cu(ER')₄] followed by formation of the chalcopyrite semiconductor (in this case, CuInS₃) 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 CuInGa1–xS1–ySe2–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 [(LRx)2Cu(ER′)2M(ER′)2]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 CuInGa1–xS1–ySe2–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 conjugate acid of the thiol or senenol with NaOEt (where Et signifies an ethyl group) in CH3OH, 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 NaSCH3 with InCl3 and add CuCl and PR3.

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).

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Spray CVD for Making Solar-Cell Absorber Layers

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

John H. Glenn Research Center, Cleveland, Ohio

Spray chemical vapor deposition (spray CVD) processes of a special type have been investigated for use in making CuInS2 absorber layers of thin-film solar photovoltaic cells from either of two subclasses of precursor compounds: [(PBu3)2Cu(SEt)2In(SEt)2] or [(PPh3)2Cu(SEt)2In(SEt)2] or [(PPh3)2Cu(SEt)2In(SEt)2]. 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.

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