Ternary Precursors for Depositing I-III-VI$_2$ Thin Films for Solar Cells Via Spray CVD

K.K. Banger
Ohio Aerospace Institute, Brook Park, Ohio

J.A. Hollingsworth
Washington University, Saint Louis, Missouri

M. H.-C. Jin
Ohio Aerospace Institute, Brook Park, Ohio

J.D. Harris and S.A. Duraj
Cleveland State University, Cleveland, Ohio

M. Smith and D. Scheiman
Ohio Aerospace Institute, Brook Park, Ohio

E.W. Bohannan and J.A. Switzer
University of Missouri at Rolla, Rolla, Missouri

W.E. Buhro
Washington University, St. Louis, Missouri

A.F. Hepp
Glenn Research Center, Cleveland, Ohio

December 2002
Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at http://www.sti.nasa.gov

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA Access Help Desk at 301–621–0134

- Telephone the NASA Access Help Desk at 301–621–0390

- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076
Ternary Precursors for Depositing I-III-VI$_2$ Thin Films for Solar Cells Via Spray CVD

K.K. Banger
Ohio Aerospace Institute, Brook Park, Ohio

J.A. Hollingsworth
Washington University, Saint Louis, Missouri

M. H.-C. Jin
Ohio Aerospace Institute, Brook Park, Ohio

J.D. Harris and S.A. Duraj
Cleveland State University, Cleveland, Ohio

M. Smith and D. Scheiman
Ohio Aerospace Institute, Brook Park, Ohio

E.W. Bohannan and J.A. Switzer
University of Missouri at Rolla, Rolla, Missouri

W.E. Buhro
Washington University, St. Louis, Missouri

A.F. Hepp
Glenn Research Center, Cleveland, Ohio

National Aeronautics and Space Administration

Glenn Research Center

December 2002
Acknowledgments

We gratefully acknowledge the NASA Glenn Research Center for financial support cooperative agreement NCC3–947.

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov
Abstract

The development of thin-film solar cells on flexible, lightweight, space-qualified substrates provides an attractive cost solution to fabricating solar arrays with high specific power (W/kg). Thin-film fabrication studies demonstrate that ternary single source precursors (SSP’s) can be used in either a hot or cold-wall spray chemical vapour deposition (CVD) reactor, for depositing CuInS$_2$, CuGaS$_2$ and CuGaInS$_2$ at reduced temperatures (400 to 450 °C), which display good electrical and optical properties suitable for photovoltaic (PV) devices. X-ray diffraction studies, energy dispersive spectroscopy (EDS)
and scanning electron microscopy (SEM) confirmed the formation of the single phase CIS, CGS, CIGS thin-films on various substrates at reduced temperatures.

1. Introduction

Photovoltaic modules based on I-II-III-VI$_2$ ternary chalcopyrite absorber layers, have been the focus of intense investigation for over two decades. The use of chalcopyrite absorbers are highly appealing since their bandgaps correlate well to the maximum photon power density in the solar spectrum for both terrestrial (AM 1.5), and space applications (AM0), while displaying long term stability and excellent radiation tolerance [1–4]. Additionally, by adjusting the percent atomic composition of either Ga for In and/or S for Se, the bandgap can be tuned from 1.0 to 2.4 eV, thus permitting the fabrication of multi-junction solar cells [5]. One of the key technical issues outlined in the 2001 US Photovoltaic roadmap is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. Thus, an important step for device fabrication for high specific power (W/kg$^{-1}$) thin film solar cells, is deposition onto flexible lightweight substrates. A novel approach is the use of ternary I-II-III-VI$_2$ single source precursors (SSP’s) in a spray chemical vapour deposition (CVD) process. Although, a rich and diverse array of binary SSP’s [6–8] are reviewed and tested, the number of known ternary SSP’s is still limited, as is their use in deposition processes [7]. Hence, in this paper we highlight recent advances, summarizing a highly promising technique for thin film growth, via molecular design of ternary SSP’s for use in various spray CVD processes.

2. Experimental

The SSP’s are synthesized based on a modification of the procedure reported by Kanatzidis [9,10]. Films were deposited on conventional soda-lime, corning 7059 slides, Si(100), and Si(111) substrates. Thin films of CuGaS$_2$ and CuGa$_x$In$_{1-x}$S$_2$ were deposited using $\{[PPh_3]_2Cu(SEt)_2In(SEt)_2]\ 1$ and the new Ga analogue 2, which was not fully characterized [11] in a custom-made horizontal hot-wall spray CVD reactor [9,12,14], whereas films of CuInS$_2$ were deposited using $\{[PBu_3]_2Cu(SEt)_2In(SEt)_2]\ 3$ in a custom-made vertical cold wall spray CVD reactor [13]. The CuGaS$_2$ deposition was conducted using a 0.011 M mixed toluene/methylene bromide solution (86 vol % toluene) (1.3 mmol; 1.10 g); substrate temperature of 450±5 °C with an Ar carrier-gas flow rate of 4.0 L/min [11]. The Cu(In,Ga)$_2$S$_2$ deposition was conducted with similar deposition parameter used for CuGaS$_2$ above except, a 0.01 M toluene solution of the In 1 and Ga 2 SSP’s in an attempt to achieve a ratio of In$_{0.75}$Ga$_{0.25}$. Films were characterized by optical transmission spectroscopy (Perkin Elmer, Lambda-19, Cary 5 UV-VIS-NIR spectrophotometer), scanning electron microscopy-EDS (Hitachi S-3000N), X-ray diffraction (Philips PW3710 : Cu Kα, 1.541 Å) and Van der Pauw four point probe system (Bio-Rad HL5500PC). Reported SEM-EDS measurements are accurate to ±3%

3. Results and Discussion

We have previously reported the preparation and utility of ternary SSP’s to the semiconductor CuInS$_2$ in a horizontal hot wall spray CVD process [9,12,14]. We now report, the preparation of ternary SSP for the fabrication of thin-film CuGaS$_2$, in addition, the versatility of ternary SSP’s in a spray CVD process is demonstrated by their use in either a hot and cold wall reactors of either horizontal or vertical configuration (Fig.1). Spray CVD studies utilizing the new Ga SSP in a toluene/CH$_2$Br$_2$ solution
afforded well-adhered, visually smooth and optically transparent dense thin film exhibiting a pink-green surface tint. X-ray diffraction (XRD) analysis confirmed the film to be 112 oriented, tetragonal single phase CuGaS2 (Fig. 2). The 220/204 reflections and the 312/116 reflections were split consistent with the tetragonal distortion of the crystal lattice [15]. Lattice parameters $a$ and $c$ were calculated from X-ray $d$ spacings, 
\[
\frac{1}{d^2} = \frac{1}{a^2} (h^2 + k^2) + \frac{l^2}{c^2},
\]
where $h$, $k$, and $l$ are the Miller indices of individual reflections [16]), Table 1. Comparison of the data collected from the CuGaS2 thin film shows they are in good agreement with the JCPDS reference values for single-crystal CuGaS2 and with those reported in literature [17].

SEM images reveal the films are dense with an average grain size of 410 nm, with a columnar grain structure (Fig. 3(c) to (d)). The surface microstructure consisted of faceted grains many of which exhibited a trigonal shape (Fig. 3(a) to (b)), which occurs as a result of close-packed intersecting (112) faces of the chalcopyrite lattice. These are the lowest surface-energy faces and typically control chalcopyrite morphology [8,18,19].

The resistivity for the CuGaS2 thin film samples deposited at 450 °C on fused silica were determined using the four-point probe method [20] and found to be 15.6(4) $\Omega \cdot$cm, which is comparable to those reported in literature [20,21]. The optical bandgap of the films were determined from the derivative of the optical transmittance data (Fig. 4), which correlates well with the reported direct band gap of CuGaS2, $E_g = 2.43$ eV [22].

Initial studies using a homogeneous toluene solution of the two ternary SSP’s 1 (0.0075 M) and 2 (0.0025 M) for fabrication of an alloy film Cu(In:Ga)S2 was also investigated [11]. Although a thin-film was deposited, composition and microstructure varied along the length of the thin film. XRD reflections representing the 112 planes were broad and complicated by the presence of an unidentified reflection in that region. The 220/204 planes was represented by a single unresolved reflection that yielded an average grain size of ~40 nm. The relative contribution of Ga and In to the multinary structure was determined by comparing the 2-theta values for this reflection in the multinary pattern to those in the patterns of the ternary end-members, CuInS2 and CuGaS2 (Fig. 5(f)). The composition of each metal was assumed to vary linearly with 2-theta from 100% In to 100% Ga based on Vegard’s Law. The tetragonal splitting was neglected in the CuGaS2 pattern by averaging the 2-theta values for the 220 and the 204 reflections. The atomic percent of Ga in the film was found to increase along the length of the film (front to rear), (Fig. 5). A uniform composition over large areas was not achieved and none of the compositions were close to the expected In$_{0.75}$Ga$_{0.25}$ ratio. The variation in film composition is understandable since the Ga derivative decomposed at higher temperatures then its In analogue. Therefore, using two SSP’s with matching thermal profiles can provide an effective means for depositing multi-ternary films.

The flexibility of the SSP’s in a spray CVD has been further demonstrated by their use in a cold wall vertical CVD reactor [13]. The XRD data obtained from the film grown using \[\{PBu$_3$\}$_2$Cu(SEt)$_2$In(SEt)$_2\] 3 in a cold-wall reactor revealed the typical tetragonal chalcopyrite CuInS2 phase with a 112 preferred orientation. The band-gap for the film grown form the liquid precursor, derived from a plot of $(\alpha E)^2$ versus E (Fig. 6), was found to be $\sim$1.46 eV. Although annealing the film showed a shift to a higher gradient band edge, it was found to have minimal effect on the observed
bandgap. SEM-EDS analysis showed the CuInS$_2$ thin-film to be near stoichiometric with atomic percents for Cu, In, and S as 26, 24, and 50 (±3%), respectively.

4. Summary

The versatility of the ternary SSP’s is clearly demonstrated by the preparation of various multi-ternary semiconductors. Spray CVD using SSP’s is a mild, simple, clean, and scalable technique for depositing CuME$_2$ (E= VI, M= III) thin-films at reduced temperatures. Although tests for the deposition of the wide bandgap alloy Cu(Ga:In)S$_2$, led to a non-homogenous film composition, it is evident the use of two SSP’s with similar thermal profiles, consistent film stoichiometry can be achieved. Spray CVD in conjunction with SSP design provides a proof-of-concept for a high manufacturability process. The work reported here on the molecular design of SSP’s for their use in a spray CVD process although still in its infancy, undoubtedly shows it as a mass producible, cost effective method for fabricating commercial thin film PV devices.

References


Fig. 1  Schematic of horizontal hot wall and vertical cold wall spray CVD reactors.

Fig. 2  XRD pattern XRD of spray-CVD grown CuGaS$_2$ film on Si(111). Reflections correspond to those reported for Gallite in JCPDS reference # 25-0279
Fig. 3  SEM of CuGaS₂ films deposited by spray CVD. a) surface view. b) Surface view; 30° tilt showing triangular shape characteristic of 112-oriented crystals. c) and d) edge views showing roughly columnar crystal-growth pattern.

Fig. 4  a) Transmittance vs. wavelength for CuGaS₂ thin film; (I = transmitted, Io= incident power; b) Plot of the derivative of the transmission data vs. energy.
Fig. 5  SEM images of the alloy film showing the variation in microstructure with composition. a–c) Film deposited in the first centimeter: CuIn_{0.43}Ga_{0.57}S_{2}.  d and e) Film deposited in the last centimeter: CuIn_{0.27}Ga_{0.73}S_{2}.  f) XRD spectra highlighting the 220/204 reflections of a CuGaS_{2} film (bottom; T_s = 450 °C), a CuInS_{2} film (top; T_s = 400 °C) and alloy films having In_xGa_y contents in the range: In_{0.43}Ga_{0.57} – In_{0.27}Ga_{0.73} (on fused silica).

Fig. 6  A plot of (\alpha E)^2 vs. E for the film grown in the cold-wall reactor, (\alpha is an absorption coefficient estimated from the optical transmittance data and E is a photon energy).
Table 1. Comparison of thin-film and single-crystal CuGaS2 lattice parameters, a and c, c/a, and the distortion parameter x. The d spacing of the 220 reflection was used to calculate a, and the d spacing of the 112 reflection was used with the calculated lattice parameter a to determine c. (x = 2 - c/a, given that a hypothetical c/a ratio of 2 would result in the absence of any tetragonal distortion)

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>c (Å)</th>
<th>a/c</th>
<th>x</th>
<th>Thin film fabrication method</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.353</td>
<td>10.495</td>
<td>1.9606</td>
<td>0.0394</td>
<td>Spray-CVD</td>
</tr>
<tr>
<td>5.35</td>
<td>10.48</td>
<td>1.959</td>
<td>0.0410</td>
<td>Evaporated film [14]</td>
</tr>
<tr>
<td>5.351</td>
<td>10.484</td>
<td>1.9593</td>
<td>0.0407</td>
<td>JCPDS card 25-0297:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Single-crystal from the elements</td>
</tr>
</tbody>
</table>
### ABSTRACT (Maximum 200 words)

The development of thin-film solar cells on flexible, lightweight, space-qualified substrates provides an attractive cost solution to fabricating solar arrays with high specific power (W/kg). Thin-film fabrication studies demonstrate that ternary single source precursors (SSP’s) can be used in either a hot or cold-wall spray chemical vapour deposition (CVD) reactor, for depositing CuInS₂, CuGaS₂, and CuGaInS₂ at reduced temperatures (400 to 450 °C), which display good electrical and optical properties suitable for photovoltaic (PV) devices. X-ray diffraction studies, energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) confirmed the formation of the single phase CIS, CGS, CIGS thin-films on various substrates at reduced temperatures.