Fabrication of SnS quantum dots for solar cell applications: issues of capping and doping

Citation for published version (APA):

DOI:
10.1002/pssb.201350377

Document status and date:
Published: 01/01/2014

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Fabrication of SnS quantum dots for solar-cell applications: Issues of capping and doping


1 Debye Institute for Nanomaterials Science – Physics of Devices, Utrecht University, Faculty of Science, High Tech Campus 21, 5656 AE Eindhoven, The Netherlands
2 Thin Film Factory, Foeke Sjoerdwei 3, 8914 BH Leeuwarden, The Netherlands
3 Energy research Center of the Netherlands (ECN), Solar Energy, High Tech Campus 21, 5656 AE Eindhoven, The Netherlands
4 Eindhoven University of Technology (TU/e), Department of Applied Physics, Plasma & Materials Processing, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
5 Laboratory of Nanostructures and Nanomaterials, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic

Received 4 December 2013, revised 21 April 2014, accepted 19 May 2014
Published online 4 July 2014

Keywords chalcogenides, chemical bath deposition, core–shell particles, quantum dots, solar cells, Tin sulfide

* Corresponding author: e-mail j.k.rath@uu.nl, Phone: +31-30-2532961, Fax: +31-30-2543165

We present our recent study of SnS particles in the backdrop of significant developments that have taken place so far for which a review of the present status of this material, its structural, optical, electronic characteristics, and device performance is described. To further improve the performance of low-cost chalcogenide-based solar cells, we propose to employ a third-generation solar cells fabrication scheme, where an intermediate bandgap layer can be incorporated in a CIS solar cell to increase its current generation and efficiency. For this purpose SnS quantum dots (QD) embedded indium sulfide (In2S3) layer is developed. We address how to cap the QD surface for defect passivation and protection from ambient and the doping nature of the particles.

1 Introduction Among thin-film PV devices, copper indium gallium diselinite (CIGS) has attained the highest efficiency, a CuInGaSe2 cell in the laboratory has reached 20.8% efficiency [1]. To develop low-cost chalcogenide-based solar cells, a nonvacuum technique may be an answer. The power-conversion efficiency of a photovoltaic device made with ink-deposited Cu(InGa1–x)Se2 nanocrystal layer has reached more than 7% [2]. On the other hand, copper indium sulfide (CIS)-based devices show good promise, as more than 11% efficiency has been reported in the literature [3]. The advantage of CIS is the possibility to use a low-temperature, chemical route, and nonvacuum deposition process that will decrease the capital expenditure of solar-cell production. Quantum dots (QD) are a possible solution to overcome the Shockley–Queisser efficiency limit of 31% for single-junction solar cells [4]. To further improve the performance of chalcogenide-based solar cells, we propose to employ a third-generation solar-cell fabrication scheme, where an intermediate bandgap layer can be incorporated in a CIS solar cell to increase its current generation and efficiency. For this purpose a tin sulfide (SnS) QD embedded indium sulfide (In2S3) layer is being developed. We address how to cap the QD surface for defect passivation and protection from ambient and the doping nature of the particles.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
discuss the synthesis of SnS nanoparticles (NPs) and study their properties with the aim of applying them in any of the above-mentioned solar cells.

SnS preferentially crystallizes in the orthorhombic herzenbergite structure. Orthorhombic SnS is amphoteric in nature (like CdTe and CIGS), has a near-optimum direct energy bandgap around 1.35 eV, a high hole mobility (~90 cm² V⁻¹ s⁻¹ reported), it is nontoxic, relatively inert to ambient and has an absorption coefficient of >10⁴ cm⁻¹ [7–9], however, an indirect bandgap at 1.07 eV has also been reported [10]. Simulation studies confirm that this material has an indirect bandgap $E = 1.11$ eV and a direct gap of $E = 1.39$ eV [10]. These materials are intrinsically p-type [11] due to the tin vacancies along with the defect formation following the reaction, Sn $\rightarrow$ V(Sn) $+$ 2h $\rightarrow$ Sn(s).

Zincblende (ZB) SnS in particles and thin films has also been reported [12] which would make a clean interface with ZB CdS in a solar cell. They have a direct bandgap and large optical absorption strength. Though ZB SnS is predicted by simulation to be thermodynamically and dynamically unstable, reports of ZB SnS microparticles being synthesized, and deposited as thin films infer that technically it is feasible to fabricate these materials. There are two more structures for SnS; rocksalt and the high-temperature orthorhombic (Fig. 1).

Tin sulphide can exist in different compositions; SnS, SnS₂, and SnS₃, etc. [13]. SnS₂ has an n-type character with an indirect bandgap of 2.36 eV. In unoptimized deposition conditions, the presence of other phases, such as SnS₂, SnS₃, etc. with SnS material shows a shift of bandgap to higher energies.

This paper will first provide the present status of SnS material and its device application to present the motivation behind our study and then results of the present study will be
described to draw the attention of the readers of the potential of the SnS/In2S3 core–shell NPs in solar-cell applications.

2 Status report of SnS
2.1 Synthesis of SnS Tin sulfide materials can be grown in single-crystal form, among others, by the Bridgman method [14, 15] and chemical vapor transport [16]. Ribbon crystalline SnS has been implemented in photodetectors. However, low-cost PV application demands fabrication of this material in thin-film form, as the following section will concentrate.

2.1.1 SnS thin film Thin-film SnS can be formed by both vacuum and nonvacuum deposition techniques. The fabrication techniques are spray pyrolysis [17], thermal evaporation [18–20], chemical vapor deposition (CVD) [21] chemical bath deposition (CBD) [22–25], pulsed CVD [26], hot-wall vacuum deposition (HWVD) [27], atomic-layer deposition (ALD) [28, 29], electrodeposition [30–32], sulfuroidation of tin films [33–35], solid-state multilayer synthesis [36], successive ionic layer adsorption and reaction (SILAR), i.e., multiple dipping of a substrate in cationic and anionic precursors [37, 38], plasma-enhanced chemical vapor deposition (PECVD) [39], RF sputtering [101], and a solvothermal route [40]. Using a two-step method, SnS layers can be formed by sputtering tin onto (Mo-coated) glass substrate and then annealing in 5% H2S in an argon gas environment for a temperature in the range 300–450 °C [41]. At present, it is not possible to conclude which method will deliver the best-quality SnS. The advantages of the methods that use liquid chemical routes (CBD [22–25], electrodeposition [30–32], SILAR [37, 38], and solvothermal route [40]) lie in the absence of expensive vacuum chambers and pumps and the low-temperature fabrication (<100 °C and even RT) that lead to low capital expenditure for fabrication. The chemical routes are also suitable for upscaling and industrial fabrication. On the other hand, for conformal growth on complicated nanostructures, such as nanorods, ALD, and pulsed CVD can be employed. However, nanostructures can also be made directly with self-assembled SnS of various dimensions (0D, 1D, or 2D), as described in the next section.

2.1.2 SnS of various morphologies Recently, many methods have been developed to fabricate SnS with various morphologies, including, SnS nanorods and nanosheets [42, 43], nanoﬂakes [44], dendritic-like structures [45], nanoporous SnS frameworks by templated synthesis, [46], nanodisks [47], nanoﬂowers [48], nanobelts [49], fullerene-like NPs by laser ablation [50], and nanowires [51]. By changing the reaction conditions the morphologies and shapes can be manipulated in the same deposition process [52, 53]. The mechanism of the growth in various directions to create these complex structures is not well understood and needs a thorough study. It is also not clear whether any of these structures will have any application in devices. What is certain is that QD type structures will be very desirable, as various schemes to employ them in solar-cell device structures have been proposed. Hence, synthesis and understanding of its growth mechanism is more in focus. The next section will give a review on the SnS QDs reported so far.

2.1.3 SnS QD One interesting SnS structure is the QD [54]. Several excellent reports on SnS, In2S3, and related compound nanomaterials can be found in the literature [55–57]. SnS QDs have been made by SILAR (1.4 nm, 1.32 eV) [38, 58] and solution growth of colloids [54, 59–62]. Strong absorption (>105 cm−1) in the visible region (400–800 nm) of sub-10-nm SnS nanocrystals has been reported and the particles do show quantum confinement [63]. Good monodispersity of QD-sized (~4 nm) orthorhombic SnS particles with ethanolamine (EA) ligands has been achieved [54]. These NPs were made by solution growth using precursors SnBr2 and Na2S in the presence of EA in ethylene glycol. All these studies show that for QDs, solution growth has been most successful and the simplicity of parameter variations allows the growth of desired QDs in a controlled manner. Hence, in this study we have chosen the colloidal route to produce SnS QDs.

Attention should be given to the fact that SnS2 nanocrystallites can also be formed in a favorable deposition process [64, 65], hence, suitable parameter optimization is necessary to obtain the desired type of SnS NPs. In the present study, we are interested in SnS QD and not SnS2 or any other chemical form.

2.2 Characterization methods for SnS In this section, we will describe possible characterization methods for SnS and the gathered optical, structural, and electrical characterization data. This information will be useful to explain the characteristics of the SnS QDs made in the present study. Structural studies have been made to identify the materials and to understand their growth process, whereas optical and electrical studies have been made to establish their device application potential. The bandgap Eg is calculated using the expression \((ahv)^n = B(hv - E_g)\), where \(B\) is a constant, \(n\), a value that depends on the type of electronic transition, is 2 for direct bandgap and 0.5 for indirect bandgap, respectively. For SnS films, the absorption coefficient values \(>10^4\ cm^{-1}\) for energy above the band edge and more than \(10^5\ cm^{-1}\) in the visible region have been observed, confirming excellent optical properties for solar-cell application. SnS phase can be identified in X-ray diffraction (XRD) spectra by a strong peak at \(2\theta = \sim 31.7^\circ\) ascribed to (111) plane (JCPDS data (39-0354)) [66], whereas the main characteristic XRD lines of other phases are: SnS2 phase \(2\theta = \sim 14.9^\circ\) (002) plane (JCPDS 89-3198) and Sn2S3 phase \(2\theta = \sim 39.7^\circ\) (160) plane (JCPDS 72-0031). According to some reports on the XRD pattern of SnS powder, the dominant peaks are at \(2\theta = \sim 31.55^\circ\) corresponding to the reflecting plane (101) and \(2\theta = \sim 31.9^\circ\) corresponding to the (040) plane [35]. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selective-area diffraction pattern
(SADP) have been very useful in microscopically characterizing the structure, crystalline or amorphous, crystal size and distribution, and core–shell structures.

Raman spectroscopy, just as XRD, is used to identify SnS and its other phases [51, 59, 61, 29, 34, 99], however, there is quite a spread in data of the peak positions, which may be attributed to various structures, sizes, and shapes. The Raman modes of SnS NPs show broadening and are shifted towards lower wave number side as compared to Raman modes of SnS single crystal. This is due to the phonon confinement effect. SnS single crystals show $A_g$ modes at 111, 238, 264 cm$^{-1}$ and $B_{2g}$ modes at 47, 78, 170, 194 cm$^{-1}$, whereas SnS particles show strong peaks roughly around 77, 109, 170, 182 (strongest), 229, and 260 cm$^{-1}$ [59]. The most intense Raman peak for SnS$_2$ material with a dominant (001) XRD peak is near 317 cm$^{-1}$ [34].

The doping nature of the SnS material is analyzed by Hall measurements, which according to most reports show around $10^{16}$ cm$^{-3}$ holes as free carriers, suggesting a p-type nature [67, 68, 22].

2.3 Reported solar cells SnS has a high absorption coefficient ($\alpha > 10^4$ cm$^{-1}$) [69]. An earlier theoretical optimum conversion efficiency of SnS solar cells was estimated to be 25% [70], whereas it can reach the Shockley–Queisser efficiency limit of 31%. Device simulation employing available data of the materials shows that a-Si/ SnS and ZnS/SnS heterojunctions can deliver high efficiencies of 14.30% and 16.26%, respectively [71]. SnS p-layer absorber (along with ZnS, ZnO, CdS, ITP, SnO$_2$ buffer (window) layers) has been implemented in solar-cell structures. The SnS/c-Si heterojunction, which acts as a heterojunction interface that hinders the current flow [71]. However, SnS as a window layer of around 50 nm can deliver >13% efficiency for a c-Si/SnS solar cell. The suitability of SnS material as an absorber layer for PV application is unquestionable, however, a solar-cell efficiency of only around 2% so far has been reached [72] and the possible causes for this low performance are being identified. The orthorhombic phase of SnS has a low ionization potential (4.7 eV) (in comparison to typical absorber materials (CdTe, CuInSe$_2$, and Cu$_2$ZnSnS$_4$)) due to which, band misalignment with commonly used buffer layers (CdS and ZnO) occurs [73]. A large barrier is therefore predicted with commonly used back contact and buffer layers. Using a proper n-type semiconductor, an efficiency of 2.1% for a SnS/zn$_{12}$Mg$_{o}$ heterojunction has been achieved [74] and a pulsed CVD grown SnS-based device employing an ALD Zn(O,S) buffer layer showed an NREL-certified total area (0.71 cm$^2$) solar-cell efficiency of 2.04% and an active-area (uncertified) efficiency of 2.46% [26]. Moreover, the defect formation due to Sn vacancies is speculated to be one of the reasons for the poor characteristics of SnS cells. It is not clear whether the same defect formation mechanism will also hold for the SnS QDs. It is energetically favorable to push the defects to the particle boundaries, keeping the bulk (interior of QD) defect free. The boundary can be passivated by appropriate ligands, shell or by embedding into a passivating matrix. SnS NPs are now explored extensively for both inorganic- and organic-based solar cells [56].

SnS$_2$ QD (5.7 nm) has been employed in organic/inorganic hybrid solar cells exploiting its n-type character [65]. The n-type character and relatively high bandgap of SnS$_2$ implies that during preparation of SnS material care has to be taken to ensure that it is free of SnS$_2$ (and other forms of SnS) that may also form during processing.

3 Present study The above-described literature amply suggests that SnS film is a very promising material for solar cells, however, much understanding is needed for a successful implementation in devices. Central to this development is the need to find a growth process of device-quality material and the choice of material, considering that SnS can exist in many forms. With this aim we choose to develop SnS QD by a solution method that allows many possibilities to manipulate the growth process. Being a nonvacuum technique and low-temperature process, it will have added advantages for low-cost industrial fabrication.

3.1 Synthesis SnS NPs were synthesized by a colloidal route [75]. A mixture of 0.02 M SnCl$_2$ (Sigma–Aldrich) mixed with triethanolamine (Acros) and 0.1 M sodium sulfide (Sigma–Aldrich) were used as precursors; both solutions are ethylene glycol (Sigma–Aldrich) based. The synthesis was carried out at room temperature under a nitrogen atmosphere. It was observed from TEM studies that the SnS particles are prone to clustering and use of surfactants to isolate the NPs was necessary. Triocylphosphine oxide (TOPO) was thus added to the first precursor with ratio of TOPO:Sn at 1:1 to avoid clustering, which resulted in particles of ~4 nm size, compared to 12-nm-sized features without TOPO, confirming the quantum-dot nature of TOPO-clad SnS particles (particles smaller than the Bohr radius necessary for quantization). Bohr’s radius of SnS is estimated to be 7.24 nm using the relation, $a = \frac{\hbar^2}{\mu_e \varepsilon^2}$, where $\varepsilon$ is the dielectric constant of SnS, $h$ is Planck’s constant, $\mu_e$ is the reduced mass of an exciton, $e$ is the charge of an electron [76]. Energy-dispersive X-ray spectroscopy (EDX) (Fig. 2) confirmed the chemical composition to be indeed SnS and not any other composition.

Other properties of the particles were also evaluated. For the optical absorption measurement particles spread on glass by drop casting were studied. As the thickness of the films cannot be accurately estimated in this case, a precise value of absorption coefficient ($\alpha$) is hard to obtain. Hence, estimating the bandgap from the Tauc plot was found to be erroneous, instead the method of estimating bandgap from the absorption edge in an absorption versus energy plot [77] was employed. Figure 3 shows the absorption (in arb. unit) on a log scale versus $E$ plot of SnS QDs drop casted on glass. A sharp drop in absorption occurs near 1.6 eV that can be
identified as the bandgap of the material. The estimated bandgap of the SnS QDs shows a blueshift from its bulk value, confirming quantum confinement, as expected for 4-nm particles [60]. We employed photothermal deflection spectroscopy (PDS), a direct method to get optical absorption. In a PDS experiment the sample is placed inside liquid (commercial name FC-40) in a cuvette. A laser light grazing the surface of a film (sample surface) illuminated by monochromatic light gets deflected due to the refractive-index gradient in the liquid adjacent to the film. The amount of deflection, recorded by a quadrant detector, is proportional to the absorption coefficient on an arbitrary scale, which is later calibrated against the absorption coefficient obtained from reflection transmission measurement at high absorption or by setting the saturated absorption coefficient, $\alpha$ to $1/d$ assuming $\alpha d = 1$, where $d$ is the thickness of the film. By PDS, absorption coefficient as low as $10^{-3}$ cm$^{-1}$ can be recorded. The optical absorption of the SnS films measured by PDS shows values over $10^4$ cm$^{-1}$ in the visible region, confirming high photocarrier generation potential.

After confirmation of the particle size and shape of the QD and the favorable optical property, the next step was to study how to dope and cap the particles.

### 3.2 Capping

The purpose of capping the QD surface is defect passivation and protection from ambient. To cap the QDs, normally organic ligands are widely used. As mentioned above, TOPO acts as an effective ligand around the SnS particles, not only to protect the particles from ambient, but also keep them separated. It has been reported that the charge-carrier mobility in quantum-dot solids is dependent on the ligand length and type of ligand [78]. In the case of TOPO, the ligand is nonconducting. This is proved from the poor conductivity mapping of the TOPO covered SnS QDs. The nonconductive nature of these ligands led us to apply a more conductive type of coating, In$_2$S$_3$. It has been reported that SnS/In$_2$S$_3$ has a type II structure, however, it is an interesting structure because of the fact that the conduction bands of SnS and In$_2$S$_3$ are aligned and the offset is entirely at the valence bands [79]. This will allow for easy transfer of electrons from the SnS. The thin In$_2$S$_3$ coating allows efficient charge transfer from and to the QDs and makes it possible to form a conductivity path between the shell-coated QDs. The In$_2$S$_3$ shell is coated using CBD at $60 ^\circ C$ for 24 min. The well-dispersed TOPO-clad SnS particles are immersed in the CBD bath for deposition of In$_2$S$_3$ layer. In this process, the dispersed particles are etched in HCl to remove TOPO and thereafter the particles were coated with In$_2$S$_3$. The core–shell NPs are separated by centrifugation. It is a single-layer deposition of the shell “around” the cores (or agglomerated cores). As will be seen from the XTEM image...
results a layer of In$_2$S$_3$ is formed during the CBD coating process. First, the influence of solvents was investigated.

The core–shell particles synthesized in the same batch have been dispersed in ethanol and toluene and particles have been studied by electron microscopy.

The size and shape of the core–shell NPs have been checked by a TECNAI12 TEM setup with a beam of 120 kV and by HRTEM imaging using a TECNAI20 with a beam of 200 kV. Particles dispersed in ethanol show a spherical shape, with size around 5 nm, whereas, NPs dispersed in toluene have shapes different from those in ethanol; in addition to a few spherical particles, a huge presence of nanorods (Fig. 4 left) and NPs in the form of square shapes (Fig. 4 right), with a size of 10–12 nm, was also observed. The TOPO-capped NPs are soluble in both ethanol and toluene, however SnS particles from the same synthesis batch dispersed in ethanol or toluene have shown different shapes. This could be due to the TOPO effect, i.e., some preferential orientation of the alkyl groups of the TOPO capping with respect to the solvent. The various shapes of SnS may be attributed to aggregation of NPs [40].

Henceforth, ethanol was used as the dispersing agent, because only with ethanol could dispersion spherical NPs be obtained. The effect of deposition time, temperature and pH of the solvent on the shell deposition during the CBD step for the synthesis of the core–shell SnS/In$_2$S$_3$ NPs was investigated. The CBD at 60–70°C was found to be appropriate, since this typically ensures formation of a dense coating without damaging particles (reaction is fast enough to get shell formation). Figure 5a shows the TEM image of the SnS/In$_2$S$_3$ NPs with the shell deposited for 24 min at 60°C. Spherical particles of sizes ranging from 2 to 8 nm were obtained, as shown in the histogram of the size distribution (Fig. 5b). The structure was first characterized by XRD (Fig. 6), which confirmed the presence of ZB SnS peaks, but In$_2$S$_3$ peaks are not clear. The TEM data indicate the presence of an amorphous (like) shell and the EDX indicates the presence of In and S, which we speculate to originate from In$_2$S$_3$. The amorphous-like or disordered In$_2$S$_3$ explains the absence of a clear In$_2$S$_3$ peak in XRD. We used scanning TEM to study single core–shell nanoparticle and afterward the EDX analysis has been carried out on that single particle. Figure 7 shows the top-view HRTEM of a SnS/In$_2$S$_3$ particles drop cast on a carbon grid. The image

![Figure 5](image1)

**Figure 5** (a) TEM image of SnS/In$_2$S$_3$ core–shell dispersed in ethanol, (b) size dispersion calculated on 100 particles.

![Figure 6](image2)

**Figure 6** XRD spectrum of SnS/In$_2$S$_3$ particles.

![Figure 7](image3)

**Figure 7** Planar HRTEM imaging of SnS/In$_2$S$_3$ particles drop cast onto a carbon grid. Inset: FFT of the image of the core particle.
shows a particle surrounded by an amorphous matrix, attributed to In$_2$S$_3$. The fast Fourier transform (FFT) (inset of Fig. 7) of the HRTEM of the core particle sufficiently infers its crystalline nature. The EDX spectrum revealed the presence of elements as expected (Fig. 8). However, it was not possible to separate In$_2$S$_3$ from the SnS material in the compositional analysis because of the proximity and overlap of Sn and In peaks. The EDX showed a mixture of all the constituents, due to lack of resolution and the presence of sulfur in both the layers.

In order to get a more clear view of the core–shell structure cross-sectional TEM images of the particles were made. The HRTEM image of these particles (Fig. 9) confirms a homogeneous shell coating of a few nanometers around the crystalline SnS core particles.

The optical absorption of the SnS/In$_2$S$_3$ core–shell particles dispersed in ethanol was measured by dual beam UV-VIS spectroscopy. The bandgap of the particles was estimated from the absorption edge. The core SnS QD has a bandgap of 1.6 eV, as expected for the quantum size of ~4 nm. The In$_2$S$_3$ material showed a high bandgap of 2.6 eV, as expected. The effect of CBD time on the absorption spectra measured for colloidal dispersions of synthesized core–shell NPs is illustrated in Fig. 10. The red line is the absorption of the ethanol, and it has been used as a reference. The absorption spectra of the various films showed an increased effective bandgap from 1.6 eV for the bare SnS QDs to higher values with increasing thickness of In$_2$S$_3$ coating. This can be explained by the effective-medium approximation of the optical properties of two types of materials, SnS and In$_2$S$_3$. It is noted that the bandgap can be tuned by changing the thickness of the shell in addition to changing the SnS QD diameter.
and the ligand does not facilitate conductivity between the TOPO acts as a barrier to the tip reaching the QD surface/C223

periods of In$_2$S$_3$ shell (indicated in minutes). As-grown SnS

Optical absorption of SnS core with different coating

Figure 10

Figure 10 Optical absorption of SnS core with different coating periods of In$_2$S$_3$ shell (indicated in minutes). As-grown SnS particles and pure In$_2$S$_3$ (left most curve) are also given for comparison.

3.2.1 Conductivity mapping of capped layers

Normally a contact-mode atomic force microscopy (C-AFM)

is used to obtain the current characteristics of nanostructures

in a thin film [80]. However, the contact mode has the

inherent drawback that the lateral force exerted on the sample

can be quite high. This can lead to movement and damage of

soft or loosely sticking samples. A noncontact mode, like the
tapping mode, is safe to use for such materials, but it is only

good for topography and not current mapping. The idea is to

have a modified noncontact mode. We tried two such tmodes:
torsional resonance tunneling AFM (TR-TUNA) and peak-force
resonance tunneling AFM (PF-TUNA), compared their

results to obtain accurate information on topography and

current mapping.

In the torsional resonance mode, a pair of piezoelectric

actuators vibrates the base of a rectangular cantilever. When

the two piezo-elements are driven by out-of-phase sinusoidal
signal, torsional resonance mode can be excited, in which the
cantilever undergoes twisting oscillations about the long axis
of the cantilever. The cantilever tip vibrates in the lateral
direction (unlike in the tapping-mode AFM). The normal

force between the tip and the sample has no direct effect on

the torsional resonance; oscillation is affected by the lateral
force gradient only. In this mode, lateral forces that act on the
tip cause a change in the torsional resonant frequency,
amplitude, and/or phase of the cantilever. Though the TR-

AFM is a contactless mode, it is believed that the tip comes
close to the sample surface and a tunnel current is set up
between the tip and the sample even with a small applied
voltage. TR-TUNA has the ability to achieve low-force scanning, while maintaining the tip in the near-field. However, an experimental difficulty was encountered. TOPO acts as a barrier to the tip reaching the QD surface and the ligand does not facilitate conductivity between the tip and the QD. The conductivity mapping was not possible

for SnS/TOPO. Hence, we replaced TOPO with In$_2$S$_3$. This
allows a conducting path between the tip and the particle in a
conductivity-mapping measurement using TR-TUNA. The
first experiments with TR-TUNA on our SnS/In$_2$S$_3$ samples
showed encouraging results, both clusters and individual
particles could be detected simultaneously by TR-TUNA
[81]. Figure 11d shows the current mapping of SnS/In$_2$S$_3$
particles by TR-TUNA. However, it was apparent that
current images were rather noisy and showed a slight amount
of blurring. This may be attributed to the signal collected
from the substrate and any neighboring particles. As
mentioned by Bruker Co. stable operation at low torsional
resonance amplitude, that is desirable for a TR-TUNA
operation, can be extremely challenging. Moreover, we
observed that the current mapping of an individual particle
showed a double peak, which we speculated to be an artifact
of this measurement [81]. To resolve these issues, another
technique, namely PeakForce AFM (PF-AFM), was
employed. This is a modified tapping mode; the only
difference is that while the oscillation amplitude is kept
constant when approaching the sample in a tapping mode, the
force distance dependence is followed during every
approach and withdrawal cycle and the scanner feedback is
used to control the maximum force in a PF-AFM. The
frequency of oscillation in PF-AFM is much smaller than the
resonance frequency of the cantilever and although the tip
comes into contact with the sample for only a short period,
the contact is better defined and longer compared to that in
the tapping mode. A tunnel current is recorded in PF-TUNA
between the tip and the sample, just as with TR-TUNA,
however, even with a smaller voltage.

With this background we performed both PF-TUNA and

TR-TUNA on the same SnS sample coated with TOPO.

Though the topography gives the same images in both

TR-TUNA and PF-TUNA, in the conductivity mapping in

Fig. 11 we see a marked difference in what we observe by
these two techniques. TR-TUNA (Fig. 11a) does not show
current at these nanostructures, confirming our understand-
ing of the limitation of this technique. The PF-TUNA,
however, correctly detects current mapping at the nano-
structures (Fig. 11b). The PF-TUNA experiments were done
in a cleanroom chamber. First, the base substrate (n type
crystalline Si wafer) was scanned and a smooth and clean
area of the substrate was identified. Then the substrate was
translated to a measured distance controlled by the X–Y

table and the SnS dispersed in solvent was drop cast on the
substrate. The substrate was translated back to the original

position to scan over the dropped SnS particles. The particles
are characterized to be SnS by a separate experiment, as
confirmed by EDX and TEM of the same particles drop cast
on a carbon grid. PF-TUNA thus clearly confirms the

cative nature of the SnS NPs. Moreover, the current scan
across a nanoparticle by PF-TUNA does not show the
dip (Fig. 11c), which confirms our analysis of the artifacts
of TR-TUNA [81]. Needless to say, current mapping of

SnS/In$_2$S$_3$ core–shell particles is possible by PF-TUNA just
as is obtained by TR-TUNA (Fig. 11d).
Putting together the conductivity mapping data of SnS/In$_2$S$_3$ core–shell by TR-TUNA and the SnS/TOPO by PF-TUNA, we can say both the core and the shell show conductivity and the charge transport across the core/shell interface takes place without hindrance.

This SnS/In$_2$S$_3$ structure is interesting for solar cell unlike a typical Type II heterojunction such as SnS/CdS in which electrons from the core see a barrier to transport at the core/shell interface. We assume that this type of band alignment of SnS/In$_2$S$_3$ holds for the amorphous (like) In$_2$S$_3$ shell that is obtained in our case. Amorphous In$_2$S$_3$ (made by CBD) is semiconducting in nature and photoactive [82, 83].

### 3.3 Doping

The use of nanocrystals and QD in the semiconductor device application is hindered by poor conductivity that arises from the difficulty in doping these structures. The efficient doping in QDs has to confront the existing knowledge on the impurity incorporation mechanism in nanostructures, which says that nanostructures will prefer to push impurities out of the bulk towards the grain boundaries, known as “self-purification effect” [84, 85], due to a purely thermodynamic effect [86]. However, doping in QDs has been claimed by many groups [87–91], though the exact mechanism of doping in these materials has not been explained. Most of the published reports indicate that SnS films are p-type in nature, attributed to the Sn$^{2+}$

![Current mapping image of TOPO clad SnS particles by TR-TUNA (a) and PF-TUNA (b). The scan of current mapping and the topography by PF-TUNA is given in (c) for the two particles indicated by an arrow in (b). (d) Current mapping of SnS/In$_2$S$_3$ particles by TR-TUNA.](image-url)
vacancies [67, 92, 29, 93], whereas an excess of tin can turn the material to n-type. However, there are no reports on the doping nature of SnS QDs. The current study looks at the electrical characteristic of our SnS QDs. Figure 12 shows the temperature dependence of current of SnS QD film that reveals Arrhenius characteristics. Here, we plotted log current instead of log conductivity because of the uncertainty of the thickness of the spread QD layer. The activation energy obtained from the slope of the curve for SnS QD film was 0.44 eV, indicating that the materials are not intrinsic in nature. Supported by the optical experiments, we will give a plausible explanation for the apparent doping characteristics. The doping nature of the SnS QD particles were probed by optical techniques, as Hall measurement was not sensitive enough to obtain the free-carrier concentration of these layers. The optical absorption measured by reflection transmission spectra showed an absorption edge ~1.6 eV, the expected bandgap of a material with the corresponding QD size of around 4 nm. Figure 13 shows the optical absorption of SnS QDs in solution measured by dual-beam spectroscopy for particles dispersed in solution. A striking observation is that no excitonic absorption peaks [94] are observed, only a monotonic rise of absorption at high energies. Moreover, there is a series of absorption peaks in the infrared region: 0.62 and 0.84 eV. Detailed optical absorption in the visible to infrared region was done by PDS that directly gives information on optical absorption coefficient. To ascertain the optical data in the infrared region where the absorption strength is very low, PDS, which is by several orders more sensitive technique (compared to standard reflection/transmission measurement) shows very distinct peaks. Figure 14 again confirms the presence of 0.62 and 0.84 eV peaks, moreover, another strong 0.4 eV peak is observed. We tentatively assign the 0.62 and 0.84 eV peaks to transitions involving deep levels in the bandgap of SnS [95, 96]. We hypothesize the absorption peak at 0.4 eV to be due to transfer of dopant electrons from sodium impurities to the lowest unoccupied quantum-confined orbital (LUQCO) of SnS QD. According to this hypothesis the partial filling up of the 1s orbital causes the bleaching of the excitonic transition peaks; the absence of excitonic peaks in our experiments (Fig. 13) confirms this. Moreover, the occupied electron makes 1s to 1p transition that is manifested as 0.4 eV peak, the expected value between these energy levels. Sodium is an excellent donor and transfer of electrons from sodium to unoccupied orbitals of organic molecules [97] and QDs [98] has been observed. In our experiments an excess of Na is present due to remnant Na from the precursor sodium sulfide in the synthesis process. We propose that sodium is attached to SnS and it transfers one electron to the LUQCO of SnS QD if LUQCO for SnS QD lies below the reduction potential of sodium to accept the electrons. Further work is in progress to identify the impurity and its electronic state in the density of states of SnS.

3.4 Towards solar-cell application In order to make these particles suitable for solar-cell application, their photosensitive properties and the technique to embed in a...
A semiconductor matrix was evaluated. The electrical properties of these SnS QD and SnS/In2S3 core–shell-coated layers on glass showed excellent photosensitivities (photoconductivity/dark conductivity) (Table 1); the value around $10^2$ for core–shell structures suggests low defective material, which may be speculated to be due to excellent surface passivation by the shell. The HRTEM shows that the SnS core is crystalline, however, the In2S3 shell is amorphous. As mentioned in Section 3.2, Type II band offset is considered for this core–shell structure, however, with an aligned conduction band. TR-TUNA current mapping of our SnS/In2S3 NPs demonstrates that the charge transfer does take place in such a geometry. Based on the finding of the n-type doping nature of our SnS NPs, we propose the following solar-cell structure; glass/Mo/p-type CIS/n-type SnS QDs embedded In2S3/ZnO buffer/grid. The advantage of this structure is to generate more current in the emitter layer due to the presence of SnS QDs. This can happen in two ways, (i) SnS QDs forming an intermediate band in the In2S3 host to form the so-called intermediate bandgap cell (IBG) [102], (ii) the total cell behaves as a multibandgap cell covering a wider solar spectrum. To achieve such a cell, the first challenge is to embed the SnS NPs in an In2S3 matrix.

Figure 15 shows the planar TEM image of the SnS particles distributed in an In2S3 matrix, whereas Fig. 16 shows the SEM image of SnS QD layers sandwiched between In2S3 layers. These results clearly show that a multijunction cell or an IBC cell applying an embedded SnS layer as an improved CIS cell can be fabricated, as we had proposed in the introduction. The device results, which are not in the scope of this paper, are in progress and will be published later.

**4 Conclusion** We have shown that SnS NPs and SnS/In2S3 core–shell structures can be fabricated by a wet chemical growth technique. Electron microscopy and atomic force microscopy techniques confirmed the QD sized SnS particles and the conformally grown In2S3 shell around them. These core–shell materials show high optical absorption that can be tailored with the amount of shell thickness by varying the shell-deposition time. Electron transport from the SnS core through the In2S3 shell is demonstrated by TR-TUNA and PF-TUNA measurement of conductivity resolved down to the level of individual nanoparticles. This is an important result for device application. This result, together with the excellent photosensitivity of the SnS/In2S3, materials suggests high potential in solar-cell applications. Through various experiments we tentatively assign n-type doping of the SnS particles. From this result we propose a novel cell structure that consists of a CIS p-type absorber and SnS embedded In2S3 n-type emitter that will provide extra absorption and current to the cell compared to a standard CIS cell.

**Acknowledgements** This research is carried out with a subsidy from the Netherlands Agency for Energy and the Environment (Agentschap NL) of the Ministry of Economic Affairs of The Netherlands: program EOS (Energie Onderzoek Subsidie)_LT. Partial support of Czech Science Foundation project 13-25747S is acknowledged.

**References**


