Stability of cubic tin sulfide nanocrystals: role of ammonium chloride surfactant headgroups

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Experimental

Materials

Tin(II) chloride ($SnCl_2$, reagent grade, 98%), oleylamine (OLA, >98%), thiourea (reagent grade, 98%) were purchased from Sigma-Aldrich and used without further purification. Hydrochloric acid (32%), sulfuric acid (95%), methanol (99.8%) and chloroform (99.9%) were purchased from Bio-Lab and used without further purification.

Oleyammonium chloride (OACl) synthesis

OACl was prepared by titrating hydrochloric acid over sulfuric acid while the evolved HCl gas was dried and bubbled into oleylamine. This process was stopped until bubbles started evolving from the oleylamine, indicating complete reaction with HCl.

SnS synthesis

56.8 mg of $SnCl_2$ and 5.5 ml of oleylamine were placed in a 3-necked flask in a glove-box and transferred to the Schleck-line. 22.83 mg of thiourea were dissolved in 3 ml of oleylamine and placed in a 1-necked flask in a glove-box and transferred to the Schleck-line. Glove-box was used in order to prevent moisture to react with the

precursors. The Sn-precursor was heated to 180^0C for 1 hr, until the $SnCl_2$ completely dissolved. Meanwhile the S precursor was heated to 170^0C for 1 hr and injected to the Sn precursor. Instantaneous color change to deep-brown indicated the occurrence of the reaction. OACl was added systematically to the synthesis by weighing specific amounts of OACl and subtracting the same number of moles of oleylamine. OACL was added to the Sn-precursor flask while handled in a glovebox. This ensured that the concentration of all other precursors remained the same while simultaneously increasing the ratio of OACl to oleylamine.

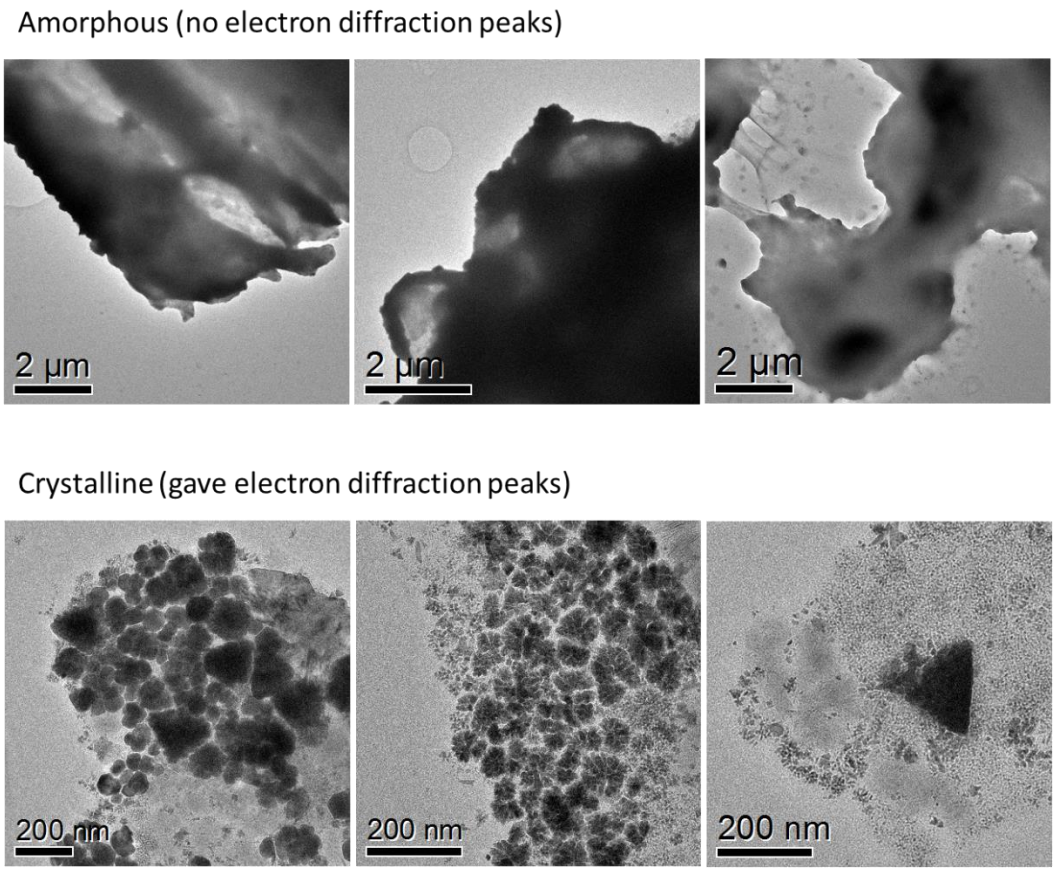

Figure S1. TEM micrographs taken from sample prepared with 100% OACl in the Sn precursor flask. Upper row: large amorphous substance. Lower row: nano-crystalline material.

Methods

Experimental

Conventional TEM was carried out using a Tecnai G2 TEM operating at 120 kV. TEM and SEM samples were prepared by solvent evaporation from chloroform suspensions onto Cu lacey TEM grids. Topography images were taken using an FEI Verios 460L high resolution SEM. Accelerating voltages ranged from 3kV to 10kV and currents of 25pA to 50pA were used. Powder X-ray diffraction was performed on a Panalytical Empyrean powder diffractometer equipped with a position sensitive X'Celerator detector using Cu Kα radiation (1.5418Å).

Computational

To calculate the effect of adsorption of ligand molecules on the surface energies in the π phase, we have considered the commonly observed (100) surface (see Experimental Results below and Ref.1). Our calculations consisted of structural relaxation of a supercell containing a thin film with a defined surface. For the (100) surface of the π-phase, a 128-atom unit-cell, was constructed from two 64 atom primitive π phase unit-cells, contiguous in the (100) direction of the crystal lattice and followed by a vacuum layer with a thickness equivalent to 6 atomic layers exposing two (100) surfaces. For comparison we considered the dominant, lowest energy surface of the orthorhombic phase of SnS: (010) (where b lattice parameter is larger than a and c parameters) the most common plane presented in experimentally grown nanocrystalline platelets. The (010) surface of the orthorhombic phase was represented by a supercell consisting of 16 (2x2×4) orthorhombic unit-cells, superposed along the long unit-cell axis b which add up to 8 atomic layers (4 layers in each unit-cell) and an additional vacuum layer with a width of 6 atomic layers. These

unit-cells were previously employed to calculate the pristine surface energies.[1] See Figures S3 and S4 that illustrate the cubic and orthorhombic SnS supercells (128 atoms) with one ligand of ammonium chloride (NH_4Cl, 6 atoms) adsorbed on the surface.

Density functional theory calculations were performed with Quantum Espresso[2] and employed k-point sampling meshes of up to 3x3x1 for the cubic (100) surfaces supercell and for the orthorhombic phase surfaces. Ultrasoft pseudopotentials, including the d-electrons for Sn, were obtained from the GBRV pseudopotential database.[3] A 40 Ry energy cutoff was employed in the planewave expansion of the wave functions, and a 200 Ry cutoff, for the density. Atomic structure was determined by allowing relaxation of the system until forces were less than 10^{-3} Ry $Bohr^{-1}$. Exchange-correlation was represented in the generalized gradient approximation (GGA) by the PBE functional[4], following our earlier studies [1, 5-7] a choice motivated by the study of IV-VI semiconductors by Albanesi *et al.*[8], indicating a good description for this family of semiconducting materials even compared to more computationally demanding hybrid functionals such as HSE. [7, 9]

The surface energy $\sigma_{Pristine}$ is calculated as in our former study[1] as an average between the two exposed surfaces (top and bottom), thus the energy difference is divided by twice the surface area:

$$(1) \quad \sigma_{Pristine} = \frac{E_{Slab}^{N} - N \cdot \varepsilon_{bulk}}{2 \cdot A}$$

The surface energy with the adsorbed ligands was calculated from the relation:

$$(2) \quad \sigma_{surface}^{Lig} = \frac{E_{Slab}^{N+Lig} - N \cdot \varepsilon_{bulk} - E_{Lig}^{Form}}{A} - \sigma_{Pristine}$$

where E_{Slab}^{N+Lig} is the total energy of the N atom supercell with the adsorbed ligand(s), E_{Slab}^{N} is the total energy of the supercell without ligands, ε_{bulk} is the total

energy per atom of the bulk, and A is the area of one surface in the supercell, E_{Lig}^{Form} is the ligand molecule formation energy which is calculated as the total energy of the molecule in a large supercell.. As all of the configurations of surfaces adsorbed with ligands includes only one surface adsorbed with ligands and the other pristine, in equation 2 we subtract the pristine surface energy from twice the size of the average surface energy as it is calculated in equation 1. Thus, we remain with the surface energy of only the surface adsorbed with ligands.

In the calculation of the adsorption energy for each of the ligands we employed the formula in equation 3.

$$(3) \quad E_{Adsorption}^{Lig} = E_{Slab}^{N+Lig} - E_{Slab}^{N} - E_{Lig}^{Form}$$

where E_{Slab}^{N+Lig} is defined as in equation 2, E_{Slab}^{N} is the total energy of the pristine surface slab of the N atoms supercell and E_{Lig}^{Form} is defined as in equation 2.

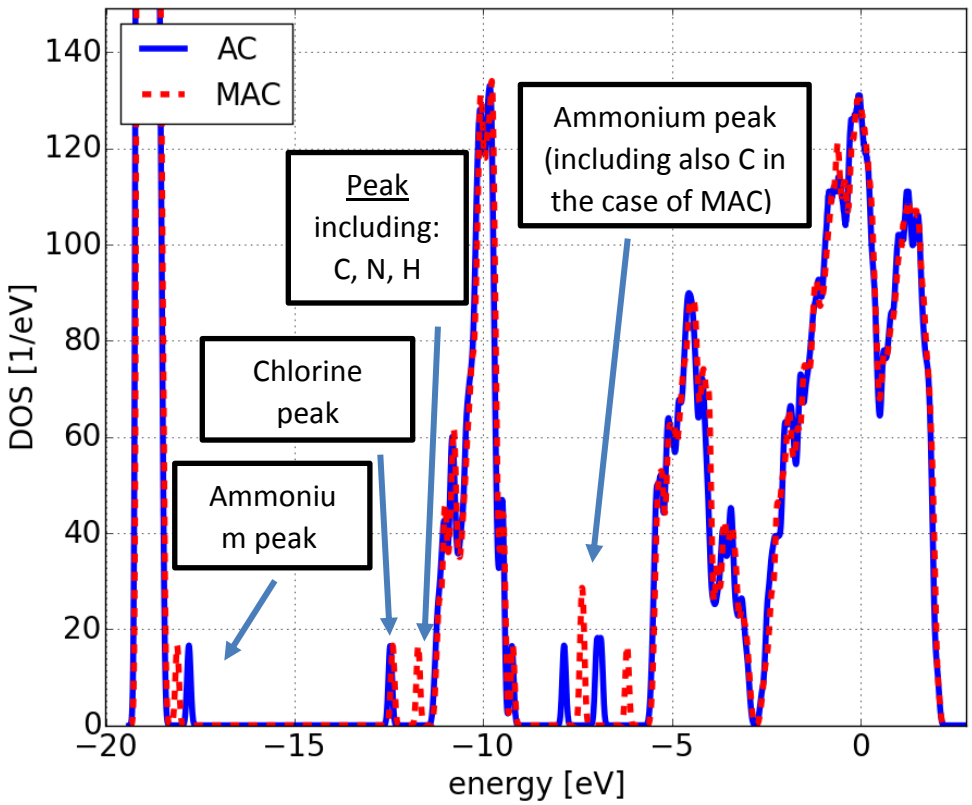

Figure S2: Total DOS per unit-cell of the 100 surface of π SnS with adsorbed ammonium chloride (AC) and methyl ammonium chloride (MAC).

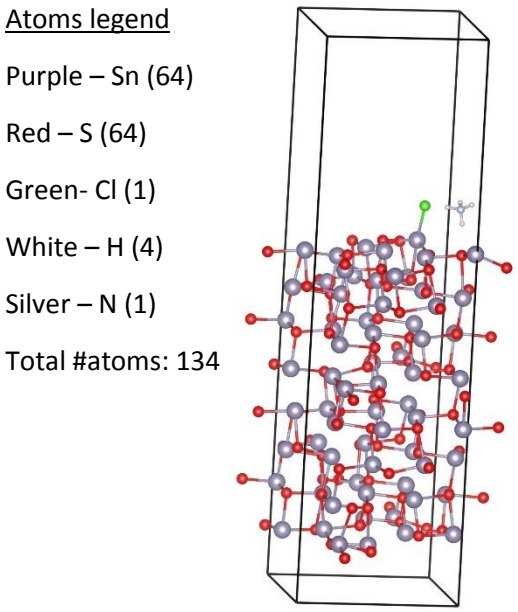

Figure S3: Supercell of the (100) surface of π SnS with an ammonium chloride ligand adsorbed on the surface. The atomic positions were optimized after a relaxation calculation (DFT-PBE) allowing all atoms to move inside the fixed supercell.

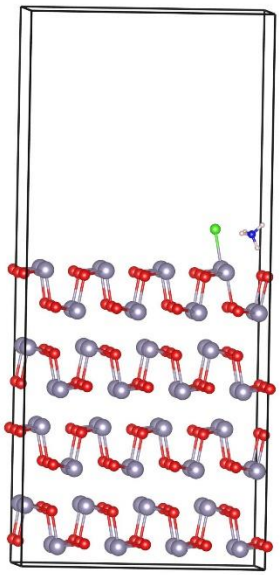

Figure S4: Supercell of the (010) surface of orthorhombic SnS with an ammonium chloride ligand adsorbed on the surface. The atomic positions were optimized after a relaxation calculation (DFT-PBE) allowing all atoms to move inside the fixed supercell.

Atomic position CUB SnS (100) surface (128 atoms):

a_lat= 22.439178 a.u.

b_lat= 22.439178 a.u.

c_lat= 78.537123 a.u.

ATOMIC_POSITIONS (a_lat)

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S	0.703546465	0.446453305	0.243663974
S	0.300067403	-0.043274661	0.257468957
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S	0.733516314	0.805187978	0.545858959

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Atomic positions ORT SnS (010) surface (128 atoms):

a_lat=76.17296 a.u.

b_lat=15.32945 a.u.

c_lat=33.56162 a.u.

ATOMIC_POSITIONS (crystal)

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S	0.328658687	0.87499963	0.495245538
S	0.328658687	0.87499963	0.745245538
S	0.328658687	0.87499963	0.995245481
S	0.470739363	0.374999384	0.130119224
S	0.470739363	0.374999384	0.380119224
S	0.470739363	0.374999384	0.630119167
S	0.470739363	0.374999384	0.880119281
S	0.470739363	0.874999384	0.130119224
S	0.470739363	0.874999384	0.380119224
S	0.470739363	0.874999384	0.630119167
S	0.470739363	0.874999384	0.880119281
S	0.527547446	0.125000247	0.00490815
S	0.527547446	0.125000247	0.25490815
S	0.527547446	0.125000247	0.50490815
S	0.527547446	0.125000247	0.754908207
S	0.527547446	0.625000247	0.00490815
S	0.527547446	0.625000247	0.25490815
S	0.527547446	0.625000247	0.50490815
S	0.527547446	0.625000247	0.754908207

Bond-valence analysis

The bond valence is defined as[10]

(4) $$BV = \sum v_i$$

Where

(5) $$v_i = exp\left(\frac{R_0 - R_i}{b}\right)$$

The parameters for Sn-S bonds is [10]

(6) R_0 =2.399 Å

(7) b =0.37 Å

The distance of first nearest neighbors:

(8) $R_i^{first\ NN}$ =2.65 Å

and the distance of second nearest neighbors:

(9) $R_i^{second\ NN}$ =3.3 Å

Thus

(10) $$v_i^{first\ NN} = exp\left(\frac{2.4-2.65}{0.37}\right) = 0.51$$

(11) $$v_i^{second\ NN} = exp\left(\frac{2.4-3.3}{0.37}\right) = 0.09$$

(12) $$BV = 3 \cdot exp\left(\frac{2.4-2.65}{0.37}\right) + 3 \cdot exp\left(\frac{2.4-3.3}{0.37}\right) = 1.8$$

The parameters for Sn-Cl bonds are

(13) R_0 =2.276 Å

(14) b =0.37 Å

The bond length for Sn-Cl bonds with ammonium chloride ligands on π:

(15) R =2.78 Å

(16) $$v_i = exp\left(\frac{R_0 - R_i}{b}\right) = exp\left(\frac{2.276-2.78}{0.37}\right) = 0.256$$

The bond length for Sn-Cl bonds with ethyl and methyl ammonium chloride ligands on π:

(17) R =2.56 Å

(18) $$v_i = exp\left(\frac{R_0 - R_i}{b}\right) = exp\left(\frac{2.276-2.56}{0.37}\right) = 0.464$$

The bond length for ammonium chloride on the orthorhombic phase is:

(19) R =2.92 Å

(20) $$v_i = exp\left(\frac{R_0 - R_i}{b}\right) = exp\left(\frac{2.276-2.92}{0.37}\right) = 0.175$$

From this analysis we conclude that the Cl atom is strongly bonded to the surface in the case of ethyl and methyl ammonium chloride ligands on the π phase and weakly bonded in the case of ammonium chloride on the orthorhombic phase.

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