



# Deposition of phase pure nickel sulfide thin films from bis(*O*-alkylxanthato)-nickel(II) complexes by the aerosol assisted chemical vapour deposition (AACVD) method

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## ABSTRACT

Bis(*O*-alkylxanthato)nickel(II) complexes (alkyl=hexyl and octyl) have been synthesised and their X-ray single crystal structures determined. Nickel sulfide thin films were deposited from both complexes at different deposition temperatures by the aerosol assisted chemical vapour deposition (AACVD) method. Phase pure rhombohedral NiS and mixture of rhombohedral NiS (millerites) and Ni<sub>17</sub>S<sub>18</sub> were deposited onto the glass and silicon substrates at temperatures between 250 and 400 °C. SEM images show that the films are based on irregular grains, nanodendrites and feather like morphologies.

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## 1. Introduction

Nickel sulfide has much more complicated phase diagram than iron or cobalt sulfides. The Ni–S system has many crystalline phases and stoichiometries, including NiS, NiS<sub>2</sub>, Ni<sub>3+x</sub>S<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>3</sub>S<sub>4</sub>, Ni<sub>4</sub>S<sub>3+x</sub>, Ni<sub>6</sub>S<sub>5</sub>, Ni<sub>7</sub>S<sub>6</sub>, and Ni<sub>9</sub>S<sub>8</sub> [1–3]. Nickel sulfide has two polymorphs with unique properties [4]. At high temperature NiS has a “NiAs-type” structure whereas at temperatures below 620 K, it has rhombohedral symmetry (millerite). In the NiAs type each Ni is octahedrally coordinated, and in the rhombohedral form the Ni atom is surrounded by five sulfur atoms in a tetragonal pyramidal coordination. The hexagonal NiS undergoes a first-order phase transition from a semiconducting antiferromagnetic phase to a metallic phase whereas the rhombohedral NiS is semi-metallic with temperature independent paramagnetism [5].

It is a *p*-type semiconductor with a narrow band gap (0.5 eV) finds applications in cathode materials for rechargeable lithium batteries [6], catalysts [7,8], IR detectors [9], and sensors [10] as well as photoelectrochemical and solar cells [11,12].

Nickel sulfide (NiS) thin films have been deposited by hydrothermal method (Ni<sub>3</sub>S<sub>2</sub>, NiS) [13], laser ablation (NiS) [14] by successive ionic layer adsorption reaction (SILAR) technique [15] and soft solution-processing (Ni<sub>3</sub>S<sub>2</sub>, NiS<sub>2</sub>, and Ni<sub>3</sub>S<sub>4</sub>) [16]. O'Brien et al. studied the growth of nickel sulfide thin films deposited by low pressure (LP) and aerosol-assisted chemical vapour deposition (AACVD) methods using single source dithiocarbamate Ni(S<sub>2</sub>–CNRR')<sub>2</sub> (RR') EtEt, MeEt, Me<sup>n</sup>Bu, or Me<sup>n</sup>Hex precursors [17,18]. The latter method was used to deposit nickel sulfide thin films using nickel complexes of thiobiuret and dithiobiuret as single source precursors [19]. The thioburet complexes were also used as single molecular precursors for the synthesis of nickel sulfide nanoparticles [20]. The thermolysis of the nickel thiobiuret precursor in oleylamine gave Ni<sub>3</sub>S<sub>4</sub> nanoparticles while NiS nanoparticles were obtained by injecting

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the precursor solution in oleylamine into hot octadecene. The  $\text{Ni}_3\text{S}_4$  particles had different morphologies (wires, rods, spheres, and triangles) depending upon the reaction conditions, whereas NiS was obtained as wires only [20].

Cheon et al. have reported laser-driven photochemical vapour deposition of nickel sulfide from nickel bis(isopropylxanthate) [8]. Pyridine adducts of nickel(II) xanthates Ni(II) thiourea and alkylthiourea complexes have also been used as single source precursors for the deposition of nickel sulfide thin films by the AACVD technique [21,22]. Garje et al. [23] used nickel furfuraldehyde thiosemicarbazone adduct as a precursor for the deposition of nickel sulfide thin films. Nickel sulfide nanocrystallites were also synthesized by the pyrolysis and solvothermal decomposition methods using the same precursors. Recently Saeed et al. [24] used nickel(II) complexes of N-(di-alkyl-carbamothioyl)-4-nitrobenzamide (alkyl=ethyl or n-propyl) to deposit nickel sulfide thin films by AACVD.

In this study we report the synthesis of bis(O-alkylxanthato)nickel(II) complexes (alkyl=hexyl and octyl) and their X-ray single crystal structures. The complexes were used as single source precursors to deposit nickel sulfide thin films at different temperatures by AACVD.

## 2. Experimental

All reagents were purchased from Sigma-Aldrich and used as received. Solvents were distilled prior to use.

Elemental analysis was performed in the University of Manchester micro-analytical laboratory. TGA measurements were carried out by a Seiko SSC/S200 model at a heating rate of  $10^\circ\text{C min}^{-1}$  in nitrogen. Infrared spectra were recorded on a Specac single reflectance ATR instrument ( $4000\text{--}400\text{ cm}^{-1}$ , resolution  $4\text{ cm}^{-1}$ ). Melting points were recorded on a Barloworld SMP10 melting point apparatus. XRD studies were performed on a Bruker AXSD 8 diffractometer using  $\text{CuK}\alpha$  radiation. The samples were mounted flat and scanned between  $20^\circ$  and  $70^\circ$  in a step size of 0.05 with a varying count rate depending upon the sample. TEM images were collected on a Philips CM200 transmission electron microscope using an accelerating voltage of 200 kV. TEM samples were prepared by

evaporating a drop of a dilute suspension of the sample in toluene or hexane on carbon coated copper grid. The excess solvent was allowed to dry completely at room temperature. Some images were also collected on a Teccnai microscope using accelerating voltage of 300 kV.

### 2.1. Synthesis of $\text{K}(\text{S}_2\text{COHex})$

KOH (19.0 g, 338 mmol) was dissolved in 1-hexanol (175 ml) at room temperature by stirring. The solution was cooled to  $5^\circ\text{C}$  by placing the flask in an ice bath.  $\text{CS}_2$  (29 ml) was then added drop-wise to the ice cold solution while stirring vigorously. The reaction mixture was allowed to stir for another 30 min after the addition of  $\text{CS}_2$  and then allowed to settle while in ice. After 2 h, the solid product was removed by filtration and recrystallized from EtOH.

### 2.2. Synthesis of $\text{K}(\text{S}_2\text{COOct})$

Prepared by the same method as described in Section 2.1 by using 1-octanol instead of 1-hexanol.

### 2.3. Synthesis of bis(O-hexylxanthato)nickel(II) $[\text{Ni}(\text{S}_2\text{COHex})_2]$ (1)

A solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.62 g, 9 mmol) in  $\text{H}_2\text{O}$  was slowly added to the solution of  $\text{K}(\text{S}_2\text{COHex})$  (3.90 g, 18 mmol) in  $\text{H}_2\text{O}$  while stirring. The white precipitate was filtered and washed by  $\text{H}_2\text{O}$ . The precipitate was finally dried in air. Yield 3.5 g (68.7%). Elemental analysis: found: C, 46.030%; H, 7.44%; S, 30.55%; Ni, 14.19%; calc. C, 40.68%; H, 6.34%; S, 31.03%; Ni, 14.20%. IR ( $\nu_{\text{max}} / (\text{cm}^{-1})$ ): 0(w), 1435(s), 1229(s), 1162(s), 1027(s), 939(s).

### 2.4. Synthesis of bis(O-octylxanthato)nickel(II) $[\text{Ni}(\text{S}_2\text{COOct})_2]$ (2)

Prepared by the same method as described in Section 2.3 using  $\text{K}(\text{S}_2\text{COOct})$ . Yield 5.2 (72.5%). Elemental analysis: found: C, 46.030%; H, 7.63%; S, 27.21%; Ni, 12.24%; calc. C,

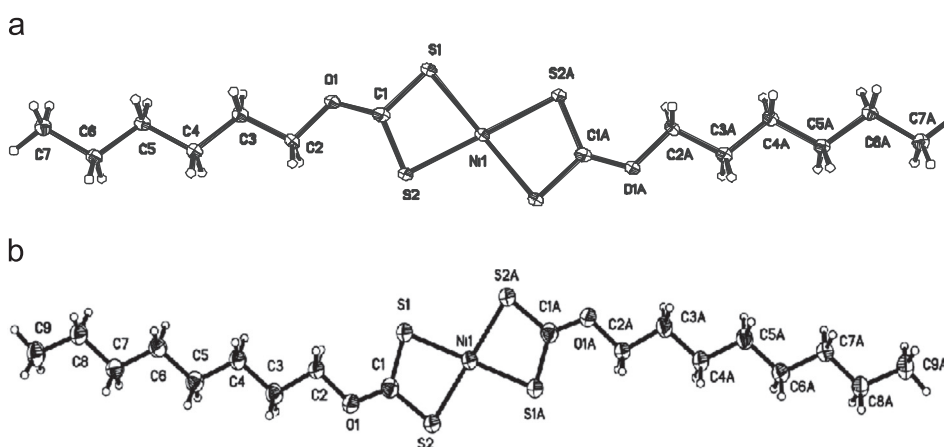


Fig. 1. The X-ray single crystal structures for bis(O-hexylxanthato)nickel(II) (1)  $[\text{Ni}(\text{S}_2\text{COHex})_2]$  and bis(O-octylxanthato)nickel(II) (2)  $[\text{Ni}(\text{S}_2\text{COOct})_2]$ .

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