Synthesis of Nickel complex of N,N-diethyl-N'-naphthoylacylchalcogoureatonickel(II) complexes as single source precursors from heteroleptic mixed ligands and nickel(II) salt for deposition of ternary thin films of nickel chalcogenide via AACVD

Tagbo Emmanuel Ezenwa[1]
Juliana Chineze Obi[1]
E. C. Obiano[2]

[1]Chukwuemeka Odumegwu Ojukwu University, Uli, Nigeria
[2] Taraba State University, Jalingo, Nigeria

Abstract. The mixed selenothioacylchalcogoureato with nickel (II) salt (N, N – diethyl-N'-naphthoylselenoureato) (N''N''-diethyl-N'''-naphthoylthioureato) nickel (II) using the mixed ligands and nickel(II) were prepared and characterized by elemental analysis, spectroscopic methods and single crystal X – ray method. Thermogravimetric analysis of the complex 2a showed single step decomposition with weight losses occurring between 244.12 °C and 595.04 °C. Compounds 2a was then used as a single - molecular precursor for the deposition of ternary materials NiSxSe1-x thin films through aerosol – assisted chemical vapor deposition. The phase and purity of the as-deposited thin films were confirmed by powdered X-ray diffraction, which showed that the as – grown films were aligned between two phases hexagonal NiSe (ICDD 04-010-3241 and hexagonal NiS (ICDD 04 – 004-4607) only. Morphological studies of the as-deposited films were performed by using field-emission scanning electron microscopy. The elemental composition of the thin films was determined by energy-dispersive X-ray spectroscopy.

Key words: nickel selenide, nickel sulfide, thin films, chemical vapor deposition, acyl thiourea.

Introduction

Nickel selenide and nickel sulfide semiconductors are potential materials for photoelectrochemical solar cells (Sharon et al., 1989: 303-312; Zainal et al., 2005: 111-117; Anuar et al., 2004: 19-25). They also exhibit interesting physical and chemical properties and have promising applications as catalysts (Oyama, 2003: 343-352) and in sensors (Mane and Lokhande, 2000: 1-31). Nickel selenide is an *p*-type semiconductor with a band gap of 2.0 eV and Nickel sulfide is also a *p*-type semiconductor with a band gap of 0.3 eV. Nickel selenide (Ni-Se) like Ni-S, has attracted a lot of attention because of their multiple phases bearing interesting physical and chemical properties (Masaki and Tsutomu, 1987: 73). The $NiSe_2$ phase is a Pauli paramagnetic metal that has a low magnetic susceptibility which increases at slow rate with increasing temperature (Inoue, 1980: 1180-1188). According to the literature, the solid- state reaction of elemental reaction of elemental Ni and Se and Ni salt and Se- containing compound at elevated temperature under inert atmosphere, was an early method of preparing nickel selenide (). A low- temperature method was devised, which bubbles toxic H_2Se gas into an aqueous solution of Ni^{2+}, thus precipitating phase-impure Ni-Se (Metcalf et al., 1982: 154). An alternative method to avoid the toxic route, was devised by Parkin and co-workers using liquid ammonia with the elements but the Ni-Se obtained at room temperature as amorphous. Annealing the amorphous Ni-Se at 250 – 300 °C, resulted in a crystalline mixture of $NiSe_2$ and NiSe (Henshaw, et al., 1997: 231-236). Crystalline films can also be obtained by MOCVD (Song and Bochmann, 1997: 231).

The preparation of micro-crystalline $NiSe_2$ by a hydrothermal method has been reported (Han et al., 1999: 2302-2304; Zhang et al., 2000: 213-216). The route has also been used previously to prepare nanocrystalline nickel selenide of different morphologies from different solvents (Han et al., 1999: 2302-2304; Zhang et al., 2000: 213-216). Thin films of NiSe have also been obtained by solution growth (Pramanik and Biswas, 1986: 145) electrodeposition and reactive diffusion (Nielsen and Ritsko, 1978: 632) and chemical bath methods (Hankare et al., 2010: 228-231).

Three types of single source precursors of different classes have been used to deposit thin films of nickel selenide by AACVD method and LPCVD has also been used to find the influence of the ligands on the deposited thin films by the two techniques (Panneerselvam et al., 2010: 6080-6091). The precursors were diseleno imidodiphosphinato $[Ni\{(SeP^iPr_2)_2N\}_2]$, diselenophosphinate $[Ni(Se_2P^iPr_2)_2]$, and diselenocarbamate $[Ni(Se_2CNEt_2)_2]$ which revealed that the morphology of the films deposited depended largely on the concentration, temperature flow rate and residence time of the precursor and the nature of substrate (Panneerselvam et al., 2010: 6080-6091).

There are very few literature reports that provide coverage of other Ni-S phases. Nickel sulfide is responsible for 'glass cancer'; an instant glass fracture (Panneerselvam et al., 2010: 6080-6091). The rhombohedra phase of Ni_3S_2 also called (heazle woodite) is yellow in colour and manifests metallic properties. The structure is a slightly distorted body – centred cubic form of S with Ni atoms in some of the pseudo-tetrahedral holes. The phase is changed to a face centred cubic (fcc)$Ni_{3+x}S_2$, at 550 ^oC. In this phase, there are sub-stoichiometric Ni atoms which are distributed randomly in the cubic closed packed structure of sulphur atoms, with vacancies. It has been reported that Ni_7S_6 exists in two polymorphic forms; a hexagonal phase at lower temperature of 400 °C while an orthorhombic phase forms at a higher temperature above 400 °C (Kullerud and Yund, 1962: 126-175; Swain, 1981: 151). The change from one form to the other is slow; it has been suggested that the crystal structure likely changes from hexagonal via monoclinic to orthorhombic as the stoichiometry changes from Ni_9S_8 (via Ni_7S_6) to Ni_6S_5 (Gronvold and Rost,1956: 1620-1634).

The NiS_2 (Vaesite) and NiS (Millerite) materials are popular due to their widespread applications. The former is a *p*–type semiconductor (narrow band gap of 0.3 eV) material with potential applications in photo–electrochemical solar cells (Sharon et al., 1989: 303-312). IR detectors (Licht et al., 1987: 863-864), catalysts (Oyama, 2003: 343-352) and drug delivery sensors (Oyama, 2003: 343-352). It has also been reported as a highly efficient catalyst in hydrodesulphurization reactions in improving octane number of naphta (Neurock and VanSanten, 1994: 4427-4439), as well as a cathode in lithium rechargeable batteries (Cheon et al., 1997: 1208-1212). The latter exists as two polymorphs bearing distinct properties (Sparks and Komoto, 1967: 398-399) with potential applications in IR detectors and PEC storage devices (Pramanik and Biswas, 1986: 145-147).

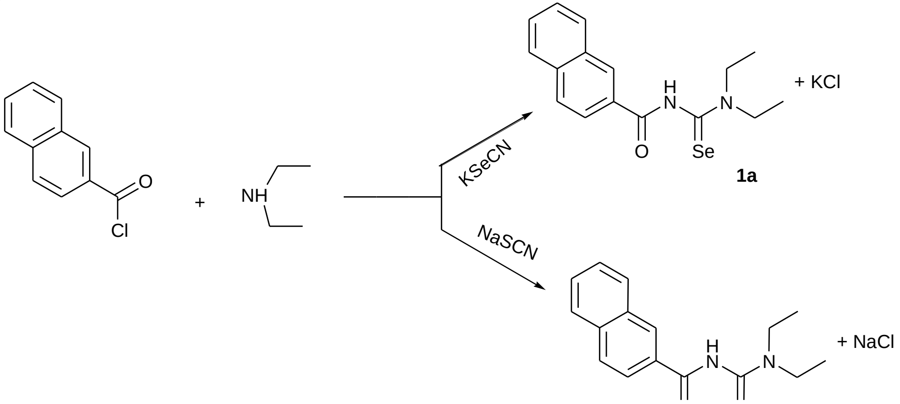
Although Ni-S nanomaterials have been reported for a couple of years to date, recent interest has however focused on their thin film materials for exploitation in solar cell applications. The NiS thin films have been grown on glass (Pramanik and Biswas, 1986: 145-147) and polymer substrates (Pramanik and Bhattacharya, 1987: 1105-1106) from a solution-based (chemical bath deposition) route. Other techniques such as electrodeposition (Zaina et al., 2005: 111-117) successive ionic layer adsorption and reaction (SILAR) (Sartale and Lokhande, 2001: 101-104) laser ablation (Lee et al., 1993:

2100-2104) hydrothermal route (mainly for nanoparticles) (Zhang et al., 2004: 8116-8117) of solution – processing method (Yu and Yoshimura, 2002: 9-15) and by CVD methods have been used to deposit thin films of NiS and other phases of the Ni-S series.

The use of multiple source precursors has been phased out by single source precursors, for obvious reasons pertaining to material and stoichiometric impurity issues, among many others (Sheldrich, Wachhold, 1997: 206-224). The single source route has attracted a lot of interest recently as not much has been reported on its use. The use of laser guided photo-chemical and thermal CVD to deposit thin films of NiS from *bis*(isopropylxanthat)nickel(II) precursor has also been reported (Cheon et al., 1997: 1208-1212).

The present study aims at synthesizing novel acylchalcogenourea complexes of Ni and their subsequent use as single source precursors towards deposition of the ternary Ni-chalcogenide thin films $NiS_{1-x}Se_x$ through AACVD technique. The single source precursors were prepared from mixed ligands, 1a and 1b which has been reported (Ezenwa and Obi, 2018: 1-13) in equal mole ratio and nickel (II) salt to form **2a.** The as-prepared ternary complex was used as single source precursors to deposit to deposit thin films of $NiS_x Se_{1-x}$.

In the pursuit of the synthesis of new precursors the symmetrical ligands (1a-b) were complexed with nickel (**2a)**. The complex was obtained at high yield by using less-toxic materials and can be scaled up to deposit ternary thin films of nickel sulfide selenide by AACVD (Fig. 1).

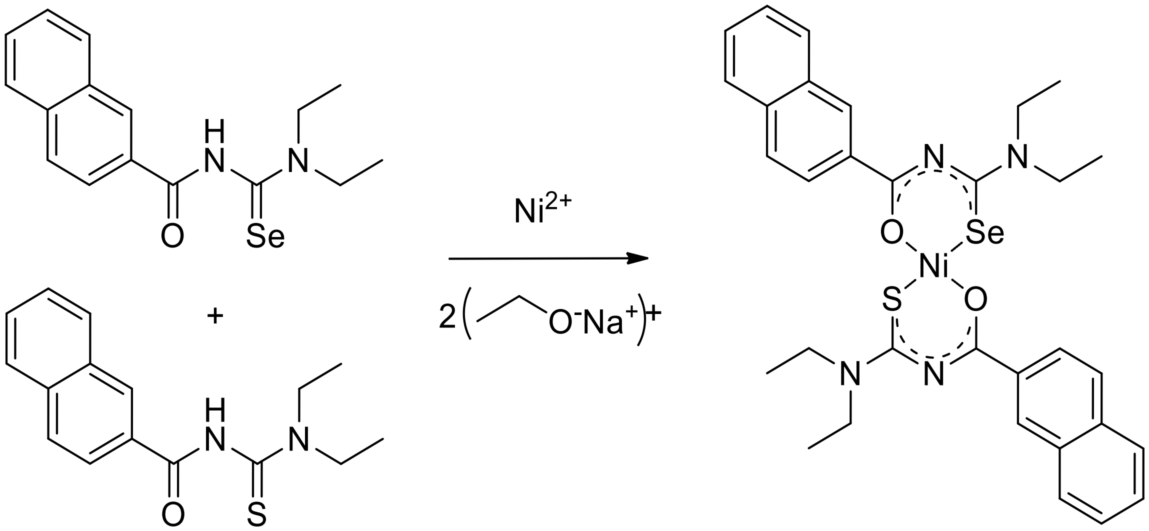


1a

1b

Fig 1. The process of complexing the symmetrical ligands (1a-b) with nickel (**2a)**

The **2a** exhibited very good adhesion to the glass substrates (confirmed by the scotch tape test). The complexes made were used to deposit the ternary thin films by AACVD. The structure of the complex was determined using single crystal X-ray crystallography, elemental analysis, NMR, melting point, GCMS, FTIR and TGA. Thin films were characterized using XRD, SEM, EDX to ascertain the phase and morphology of material obtained (Fig. 2).



2a

Fig 2. The morphology of the obtained material

Materials and Methods

Synthesis of Complex 2a

Ligand (**1a**) (2.00 g, 6.00 mmol), ligand (**1b**) (1.72 g, 6.00 mmol), were suspended in 50 mL of ethanol and warmed with stirring till a clear solution was obtained. This was followed by dropwise addition of sodium ethoxide (0.82 g, 12 mmol) in 20 mLof deionised water) and immediately by $Ni(CH_3COO)_2\cdot 4H_2O$ (1.993 g, 6.00 mmol) in 20 mLof deionized water. Slightly brown crystals were obtained in toluene/hexane mixture. Yield: [*N, N* –diethyl-*N'*-naphthoylthioureato) (*N"N"*-diethyl-*N'"*-naphthoylselenoureato) nickel (II**)** 1.5 g (37%). Melting point: 228-231 °C. (toluene/hexane mixture). Elemental analysis: [Found C, 56.8; H, 5.2; N, 8.3; S, 4.7; Ni, 8.6%;672.02$C_{32}H_{34}NiN_4O_2SSe$ requires C, 56.8; H, 5.0; N, 8.3; S, 4.70; Ni, 8.7].

^{1}HNMR (, 400MHz $CDCl_3$) δ / ppm: 1.32(ddt, *J* = 13.6,9.6,4.5 Hz, 12H), 3.74-3.95 (m,7H), 7.48 – 7.62 (m, 4H), 7.89(dt, *J* = 9.2, 5.3 Hz, 4H), 7.99(q, *J* = 8.00, 6.7 Hz, 2H), 8.26 – 8.36 (m, 2H), 8.26 – 8.36(m, 2H), 8.81(d, *J* = 3.8 Hz, 2H) ^{77}Se NMR (400 MHz) δ / ppm: 228.12, 194.57. IR absorptions ν_{max}/ cm^{-1} 1477.6 w (C-N); UV absorption λ max ($CHCl_3$)/nm 280, 288.6, 328.4, 395.6, 393.7, 414.3, (ε / dm^{3}mol^{-1}cm^{-1}, 1663.3, 1, 1663.3, 1,663.3, 218,184, 168). GCMS (ES$^+$) major fragments: (*m/z*) 677 [M+1], 333 [M-$C_{16}N_2H_{17}OSe$], 287 [M-$C_{16}N_2H_{17}OS$], 223 [M-$C_{14}H_{17}N_2O$].

Single-crystal X-ray Crystallography

1b: Data were collected at 173 K with a Stoe IPDS-II diffractometers by using Mo-Kα radiation.15 The structure was solved by direct methods and refined on F2 by full-matrix least-squares with 188 parameters and 2804 unique intensities. All non-hydrogen atoms were refined anisotropically. All H atom positions were clearly derived from difference Fourier maps and refined on idealized positions with Uiso = 1.2Ueq(C) or 1.5Ueq (Cmethyl), C–H distances of 0.95–0.98 Å. The H atom bonded to N was freely refined with the N–H distance restrained to 0.90(1) Å. The methyl H atoms were allowed to rotate but not to the tip. One ethyl group is disordered over two sites with a site occupation factor of 0.522(8) for the major occupied site. Bond lengths and angles involving the dis- ordered atoms were restrained to be equal.

2a: Data were collected at 130(2) K with a Bruker AXS SMART APEX CCD diffractometer by using Mo-Kα radiation. The structure was solved by direct methods and refined (Han et al., 1999: 2302) on F2 by full- matrix least-squares with 811 parameters and 16477 unique intensities. All non-hydrogen atoms were refined anisotropically. All H atom positions were clearly derived from difference Fourier maps and refined on idealized positions with Uiso = 1.2Ueq(C) or 1.5Ueq (Cmethyl), C–H distances of 0.95–0.99 Å. The methyl H atoms were allowed to rotate but not to the tip (Nielsen and Ritsko, 1978: 632).

Results and Discussion

The crystal structure of 1a and 1b has been reported, and that of 2a was prepared with aqueous solution of nickel(II)acetate tetra hydrate as shown in the scheme absorptions v max/ cm-1 1600 of carbonyl group w (C=O) and that of N-H, the band of C-N was observed 1350.1 cm-1 in the ligands 1a and 1b and not found in the nickel complex 2a.The formed metal complex was stable under ambient conditions and showed good solubility in most organic solvents, including toluene and THF. The crystal structure 2a was determined by single crystal X-ray crystallography with thermal ellipsoid probability of 50 % (Fig. 3), (Table 1).

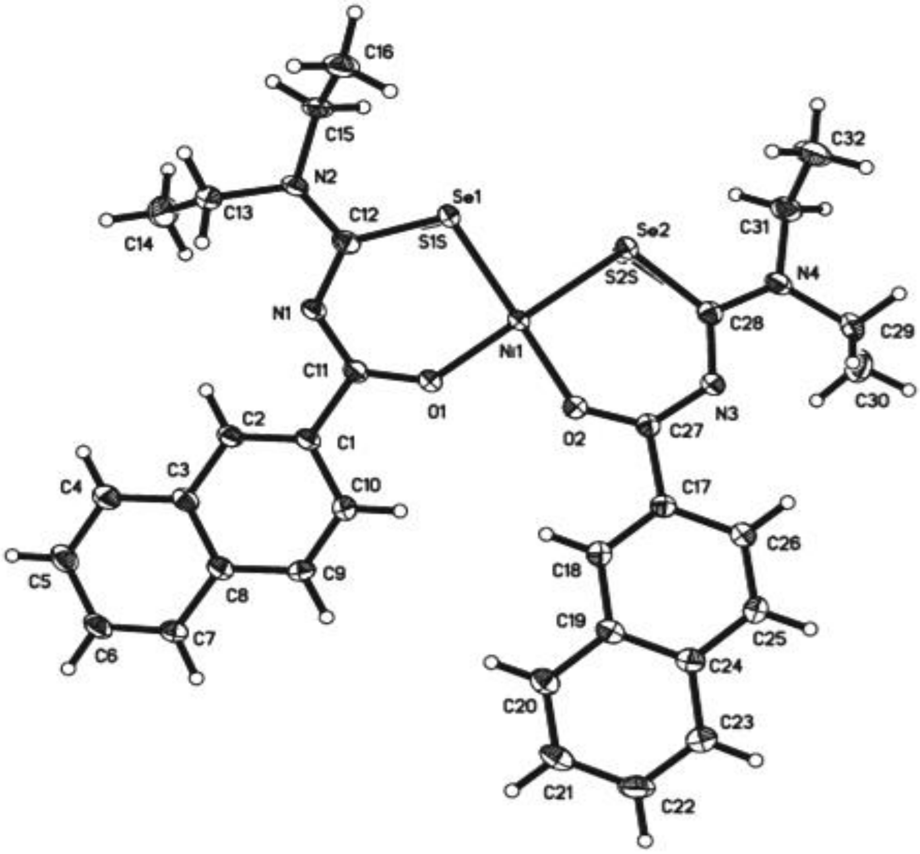


Fig. 3. X-ray single crystal structure [N, N – diethyl –N’-naphthoylselenoureato][N’’,N’’- diethyl–N’’’-naphthoyl thioureato]nickel(II) with thermal ellipsoid probability 50 %. 2a

Table 1. Structural refinement data of mixed ligand complex of Nickel 2a

Compound	**$C_{32}H_{34}N_4O_2NiS_{1.09}Se_{.91}$**
Formula weight	672.02
Crystal system, space group	Monoclinic, P2 (1)/ C
a (Å)	10.8470(2)
b (Å)	10.0831 (2)
c (Å)	27.3991 (5)
α (°)	90
β (°)	98.5460 (10)
γ (°)	90
Volume ($Å^3$)	2963.40 (10)
Z	4
D_{calc} (Mgm^{-3})	1.506
Absorption coeff. (mm^{-1})	3.228
Crystal size (mm)	0.21 x 0.13 x 0.03
Theta range for data collection (°)	4.12–72.28
Data/ restraints / parameters	5291 / 0 / 374
Goodness-of-fit on F^2	0.993
Final R indices [I>2σ(I)]	R1 = 0.0345, wR2 = 0.0761
R indices (all data)	R1 =0.0491, wR2 =0.0813
Largest diff. peak and hole ($e.Å^{-3}$)	0.367 and -0 .374
Reflections collected / unique	14547 / 5605 [R(int) = 0.0429]
Limiting indices	-13<=h<=9, -12<=k<=12, -32<=l<=33

The single crystal X–ray structure of complex (2a) (Figure.2) shows nickel in a square planar environment with a S2 Se2O2 and S1 Se 1O1donor sets. Both ligands of each unit chelate to form heteroleptic bidentate nickel in a square planar d8 complex (NC2 OS Se– Ni). The ligand bites angles (1)–Ni (1)–Se (1) = 95.39 (12) ° and O (1) – Ni (1)–S (1) = 94.59(17) ° are higher than the expected perfect square planar of 90°.

Both sulphur/selenium oxygen ligands form a six membered ring when coordinated and are arranged in a near perfect square planar orientation which deviates due to twisting observed about the central N atom. The angles between the nitrogen atoms of the two rings C (11)–N (1)–C (12) = 123.2(3) °; C (27)–N (3)–C(28) = 123.0(3) ° behave in the same manner as crystal structures bis [N,N,-diethyl–N'naphthoylthioureato] nickel (II) and the seleno analogue bis [N,N,-diethyl– N'- naphthoylselenoureato] nickel (II).

The longer C (12)-Se (1) bond=1.847(4) Å; and shorter C (12) – S (1) bond = 1.790(6) Å as a result of the larger size of selenium compared to sulphur. The pattern of the bonds in the two ligands indicates that the formal negative charge is localized predominantly on the S and Se atoms.

Table 2. Selected bond angles and bond lengths (Å) of Single X-ray crystal structure of complex 2a

Bond	Bond length	Bond	**Angle**
Ni (1) – O (1)	1.790 (6)	S (2) – Ni (1) – O (2)	**95.35 (16)**
Ni (1) – O (2)	1.8589 (17)	Se (2) – Ni (1) – O (2)	**95.32 (9)**

Ni (1) – Se (1)	2.194 (3)	Se (1) – Ni (1) – O (1)	**95.39 (12)**
Ni (1) – Se (2)	2.201 (2)	S (1) – Ni (1) – O (1)	**94.59 (13)**
Ni (1) – S (1)	2.249 (5)	Se (2) – Ni (1) – S (1)	**86.42 (12)**
Ni (1) – S (2)	2.287 (5)	Se (1) – Ni (1) – Se (2)	**85.52(17)**
C (12)-Se (1)	1.847(4)	Se (1) – Ni (1) – S (2)	**85.42(13)**
C (28)-Se (2)	1.842(4)	S (1) – Ni (1) – S (2)	**86.3(3)**
C (12)-S (1)	1.790(6)	C (11)–N (1)–C (12)	**123.2(3)**
C (28)-S (2)	1.826(2)	C (27)–N (3)–C (28)	**123.0(3)**

Ni – Se bond lengths range from 2.194 (3) – 2.201(2) Å and Ni – S bond lengths range from 2.249 (5) to 2.875 (5) Å, from the selected bond lengths and angles in Table 2. This indicates that the Ni – S length is longer than Ni – Se even though the size of selenium is larger than sulphur. This may be explained by the higher reactivity of selenium than sulphur towards the metal, which is reflected in the situation outside the metal environment. C (28)-Se (2) = 1.842(4) Å is longer than C (28)-S (2) = 1.826(2) Å which is controlled by the atomic size of the chalcogenides and less affected by the influence of metal environment.

The bite angles S (2) – Ni (1) – O (2) = 95.35(16)°; Se (2) – Ni (1) – S (1) = 86.42(12)°; Se (2) – Ni (1) – O(2) = 95.32(9)°; Se (1) – Ni (1) – O (1) = 95.39(12)°; deviate from perfect square planar may be as a result of bond interactions. The observations follow same trend observed in binary precursors obtained from **1a** and **1b**.[38]

The occupancies of the metal and chalcogenides as obtained from the single crystal structure data were Ni = 1, S = 1.09 and Se = 0.91 and from inductively coupled plasma ICP Ni = 1.0, S = 1.14, and Se =1.28 showing disorder in the complex. Comparing the data from the two sources showed the closeness to the theoretical data of the crystal Ni = 1, S =1, and Se = 1.0 an indication of the purity of the crystal formed.

Thermal Studies of Precursor 2a

The precursor **2a** showed single step decomposition with weight losses occurring between 244.12°C and 595.04°C. The residue amounts to 30.0% for the precursor. The residue was not quite close to the calculated value of 25.0 % $NiS_{1.09}Se_{0.91}$ obtained in the crystal structure, but close to the calculated value of 25 % of NiSSe based on the occupancy 1: 1: 1 of inductively coupled plasma optical emission spectroscopy ICPOES.

AACVD studies of $NiS_{1-x}Se_x$ from (N,N-diethyl-N' –naphthoylthioureato)[N''N''-diethyl-N'''-naphthoylselenoureato) nickel(II) (2a)

The deposition studies were carried out at between 360 °C and 480 °C, but the films obtained at 480°C was less crystalline than observed at lower deposition temperatures. All films could be indexed closer to NiSe (ICDD 04 – 010 – 3241) in green stick than NiS (ICDD 04 – 004 – 4607) in dark gray, at all deposition temperatures (Fig. 4). The volume of cell are quite closer at temperatures of 360 °C, 400 °C and 440 °C with a range of 59.55 – 60.01 (10^6pm^3), to the volume cell of NiSe phase than with NiS Phase and significant difference at 480 °C with values of 53.71 × 10^6 pm^3 with NiS and 60.09 × 10^6 pm^3 with NiSe indicating closeness to NiSe phase.

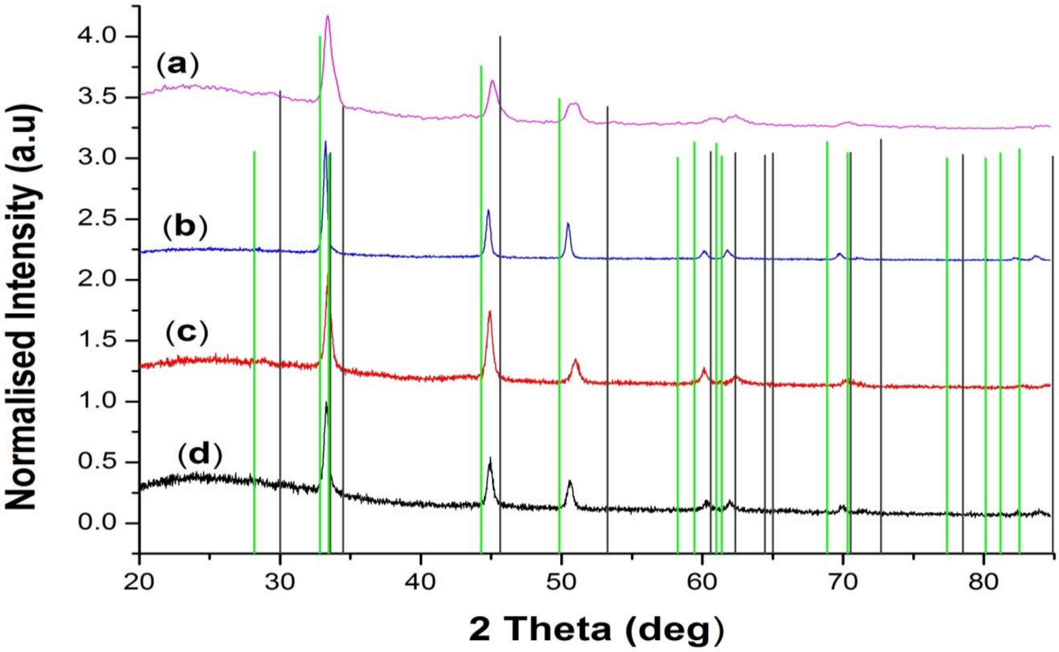


Fig. 4. XRD thin films of complex (2a) at temps (a) 480 °C (b) 440 °C (c) 400 °C and (d) 360 °C matched closely between the two phases hexagonal NiSe (green) (ICDD 04 – 010 – 3241) and hexagonal NiS (dark gray) ICDD 04 – 004 – 4607

The SEM images showed irregular-shaped, monodispersed sub-nanoparticles, in all deposited films (Fig. 5). The film deposited at 480 °C shows a ‘smooth’ layer underlying a ‘rough’ layer which shows similar characteristics observed in NiSe films grown at the same temperature and revealed by XRD.38 Films deposited at other temperatures exhibit fibrous-like; materials whose morphology is in between to those of NiSe and NiS films, and are more crystalline than at 480 °C, however, more to the former.

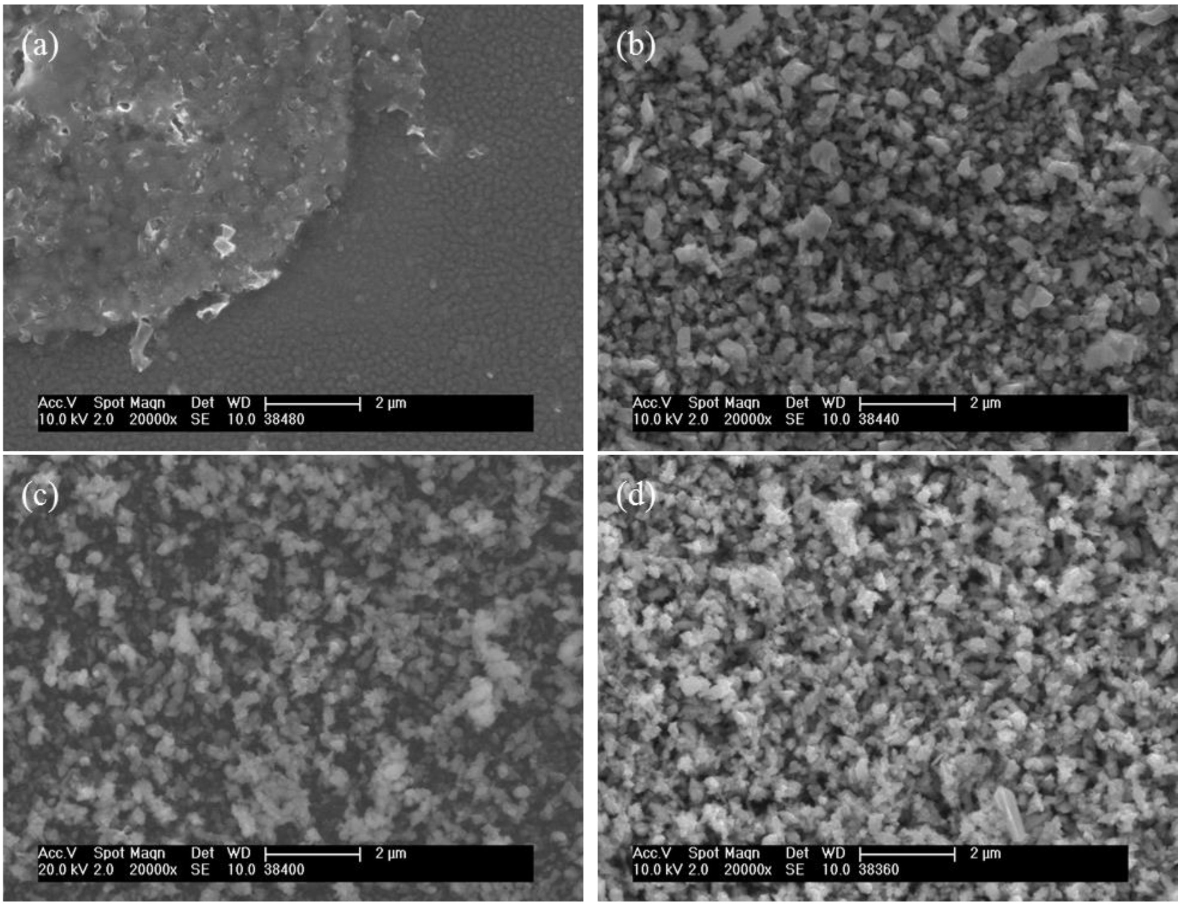


Fig. 5: SEM images of NiSxSe1-x obtained at 480 °C, 440 °C, 400 °C and 360 °C from thin films of complex (2a)

The EDX data reveal that the films obtained were Ni and Se dominated with an exception of the film grown at 480°C The data corroborates the observation made from the powder XRD analysis. A typical EDX spectrum is provided in Fig. 6.

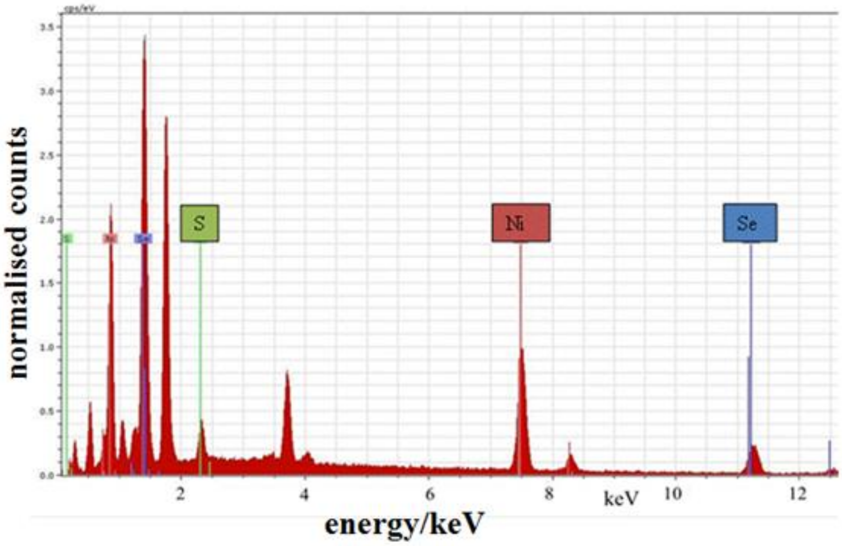


Fig. 6. EDX spectra of film obtained from complex (2a) mixed ligands and nickel salt as a representative as they are similar at 360 °C

Conclusion

In this work, we reported the synthesis of [*N,N* – diethyl – *N'*-naphthoylselenoureato][*N'',N''*diethyl – *N'''*-naphthoyl thioureato]nickel(II) $C_{32}H_{34}O_2NiS_{1.09}$ $Se_{0.91}$) (**2a**) from mixed ligands and Nickel(II) which was achieved by mixing their binary precursors of type *bis*(*N,N*–diethyl-*N*'-naphthoylselenoureato)metal(II) and *bis*(*N,N*-diethyl-*N*'-naphthoylthioureato)metal(II). The as-prepared complex 2a were characterized by elemental analysis and FTIR, mass spectrometer, UV and NMR (1H) spectroscopy. The single-crystal molecular structures of 2a, were also determined. Complexes 2a were used as SMPs to deposit ternary thin films of type, $NiS_{1-X}Se_x$ on glass substrates by AACVD at 360- 480 °C. The as-deposited thin films were characterized by PXRD, FE-SEM, and EDX.

Acknowledgements

T.E and J.C.O thanks the Chukwuemeka Odumegwu Ojukwu University for their nomination to TETF for PhD sponsorship and TETF for the funding and also acknowledge their Supervisors Paul O'Brien, Roger Whitehead and the University of Manchester for support and encouragement. The authors are also thankful to all sections of the University of Manchester that supported the work like Elemental and TGA analysis.

References

Anuar, K., Zainal, Z., Saravanan, N., Kartini, A.R. (2004). Cathodic Electrodeposition and Characterization of ni3se2 thin Films. AJSTD, 21(1), 19-25.

Cheon, J., Talaga, D.S., Zink, J.I. (1997). Laser and Thermal Vapor Deposition of Metal Sulfide (NiS, PdS) Films and in Situ Gas-Phase Luminescence of Photofragments from $M(S_2COCHMe_2)_2$. Chem. Mater., 9, 1208-1212.

Ezenwa, T. E, Obi, J.C. (2018). Phase-Controlled Deposition of Nickel Selenide, Nickel Sulfide Thin Films by Using Single-Molecular Precursors. Scientific Research Journal(SCIRJ), 6 (5), 1-13.

Gronvold, F., Rost, E. (1956). On the Sulfides, Selenides, and Tellurides of Palladium. E. Acta. Chem. Scand., 10, 1620-1634.

Han, Z. H., Yu, S.H., Li, Y. P., Zhao, H.Q., Li, F. Q., Xie, Y., Qian, Y.T. (1999). Convenient Solvothermal Synthesis and Phase Control of Nickel Selenides with Different Morphologies. Chem. Mater., 11, 2302-2304.

Hankare, P. P., Jadhav, B.V., Garadkar, K. M., Chate, P. A., Mulla, I.S., Delekar, S.D. (2010). Synthesis and characterization of nickel selenide thin films deposited by chemical method. Journal of Alloys and compounds, 490, 228-231.

Henshaw, G., Parkin, I. P., Shaw, G.A. 1997. Convenient, room-temperature liquid ammonia routes to metalchalcogenides. J. Chem. Soc., Dalton Trans, 2, 231-236.

Inoue, N., Yasuoka, H., Ogawa, S. (1980). Microscopic Magnetic Properties of Co $(S_xSe_{1-x})_2$ –^{59}Co NMR–. J. Phys. Soc.Soc. Jpn, 48, 1180-1188.

Kullerud, G., Yund, R.A. (1962). The Ni-S System and Related Minerals. J. Petrology, 3, 126-175.

Lee, H., Kanai, M., Kawai, T., Kawai, Sh. Kawai. (1993). Growth of Oriented NiS Films on Si(111) and Al2O3(012) Substrate by Pulsed Laser Ablation. J. App. Phys., 32 (1), 2100-2104.

Licht, S., Hodes, G., Tenne, R., Manassen, J. (1987). A light-variation insensitive high efficiency solar cell. Nature, 326, 863-864.

Mane, R.S., Lokhande, C.D. (2000). Chemical deposition method for metal chalcogenide thin films. Mater,Chem, Phys, 65, 1-31.

Masaki, I., Tsutomu, F. (1987). Kβ2/Kβ1,3 X-ray intensity ratios of arsenic, selenium and bromine in various chemical states (chemical state analyses of As, Se and Br by X-ray method. 4). X-ray Spectrum, 16, 73-76.

Metcalf, H., Williams, J. E., Caskta, J.F. (1982). Modern Chemistry. New York: Holt, Reinhart, Winstone, pp. 154.

Neurock, M., VanSanten, R.A. (1994). Theory of Carbon–Sulfur Bond Activation by Small Metal Sulfide Particles. J.Chem.Soc, 116, 4427-4439.

Nielsen, P., Ritsko, J. J. (1978). Reactive diffusion and electronic structure at the nickel/selenium interface. J. Appl. Phys., 49, 632.

Oyama, S.T. (2003). Novel catalysts for advanced hydroprocessing: transition metal phosphides. J. Catal., 216, 343-352.

Oyama, S.T. (2003). Novel catalysts for advanced hydroprocessing: transition metal phosphides. J. Catal., 216, 343-352.

Oyama, S.T. (2003). Novel catalysts for advanced hydroprocessing: transition metal phosphides. J. Catal., 216, 343-352.

Panneerselvam, A., Periyasamy, G., Ramasamy, K., Afzaal, M., Malik, M. A., O'Brien, P., Burton, N.A., Waters, J., van Dongen, B.E. (2010). Factors controlling material deposition in the CVD of nickel sulfides, selenides or phosphides from dichalcogenoimidodiphosphinato complexes: deposition, spectroscopic and computational studies. Dalton Trans, 39, 6080-6091.

Pramanik, P., Bhattacharya, S. (1987). Deposition of chalcogenide thin films by solution growth technique on polymer surfaces. Mater. Sci. Lett., 6 (9), 1105-1106.

Pramanik, P., Biswas, S. (1986). Deposition of nickel chalcogenide thin films by solution growth techniques. J.Solid State Chem., 65, 145.

Pramanik, P., Biswas, S. (1986). Deposition of nickel chalcogenide thin films by solution growth techniques. J.Solid State Chem., 65, 145-147.

Sartale, S.D., Lokhande, C.D. (2001). Preparation and characterization of nickel sulphide thin films using successive ionic layer adsorption and reaction (SILAR) method. Mater. Chem. Phys., 72, 101-104.

Sharon, M., Tamizhmani, G., Levy-Clemen, C., Rioux, J. (1989). Study of electrochemical and photoelectrochemical properties of nickel phosphide semiconductors. J. Sol. Cells, 26, 303-312.

Sharon, M., Tamizhmani, G., Levy-Clemen, C., Rioux, J. (1989). Study of electrochemical and photoelectrochemical properties of nickel phosphide semiconductors. J. Sol. Cells, 26, 303-312.

Sheldrich, W. S., Wachhold, M. (1997). Solventothermal Synthesis of Solid-State Chalcogenidometalates. Int. Ed. Engl., 36 (3), 206-224.

Song, X. J., Bochmann, M. (1997). Synthesis of phosphinochalcogenoic amidato complexes of divalenttransition metals and their thermolysis to metal selenide and telluridephases. J.Chem. Soc., Dalton Trans, 231.

Sparks, T., Komoto, T. (1967). Metal-to-semiconductor transition at the magnetic ordering temperature of NiS. Phys. Lett. A., 25 (5), 398-399.

Swain, M.V. (1981). Nickel sulphide inclusions in glass: an example of microcracking induced by a volumetric expanding phase change. J. Mater.Sci.,16, 151.

Yu, S.H., Yoshimura, M. (2002). Ferrite/Metal Composites Fabricated by Soft Solution Processing. Adv. Funct. Mater., 12 (1), 9-15.

Zainal, Z., Saravanan, N., Mien, H. L. (2005). Electrodeposition of nickel selenide thin films in the presence of triethanolamine as a complexing agent. J.Mater Sci Mater Electron., 16, 111-117.

Zainal, Z., Saravanan, N., Mien, H. L. (2005). Electrodeposition of nickel selenide thin films in the presence of triethanolamine as a complexing agent. J.Mater Sci Mater Electron., 16, 111-117.

Zhang, L., Yu, J.C., Mo, M., Wu, L., Li, Q., Kwong, K. W. (2004). A General Solution-Phase Approach to Oriented Nanostructured Films of Metal Chalcogenides on Metal Foils: The Case of Nickel Sulfide. J. Am. Chem. Soc., 126, 8116-8117.

Zhang, W. X., Hui, Z. H., Cheng, Y. W., Zhang, L., Xie, Y., Qian, Y. T. (2000). A hydrothermal method for low-temperature growth of nanocrystalline pyrite nickel diselenide. J. Cryst. Growth, 209 (1), 213-216.