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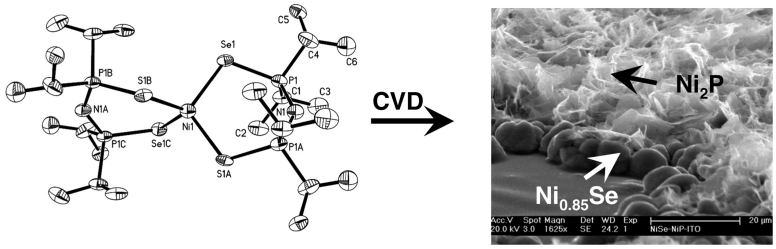

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The Chemical Vapor Deposition of Nickel Phosphide or Selenide Thin Films from a Single Precursor

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Nickel phosphide and nickel selenide semiconductors are potential materials for photoelectrochemical solar cells.[1,2] They also have interesting electrical and magnetic properties and have promising applications as catalysts[3] and in sensors.[4] Nickel phosphide is an n-type semiconductor with a band gap of 1.0 eV, whereas the selenide is a p-type with a band gap of 2.0 eV. There are only few reports on the deposition of nickel phosphide films which include by magnetron sputtering,[5] electrodeposition,[6] electroless deposition,[7] or the reaction of orthophosphoric acid on a nickel substrate.[1] Nickel selenide films were prepared by electrodeposition,[2] solution growth,[8] reactive diffusion,[9] or chemical vapor deposition (CVD) methods.[10] As far as we know there is no report on the deposition of a $Ni_{0.85}Se/Ni_2P$ heterostructure. Single source precursor (SSP) chemistry has attracted considerable interest for the growth of semiconductor thin films and nanoparticles.[11] Herein we report the synthesis and characterization of imido-bis-(diisopropylthioselenophosphinate) nickel(II), $Ni[^iPr_2P(S)NP(Se)^iPr_2]_2$, an interesting complex used as SSP for the growth of nickel phosphide (Ni_2P) or nickel selenide ($Ni_{0.85}Se$) and in sequence for $Ni_{0.85}Se/Ni_2P$ layers. There are reports for the formation of different phases of the same material from a SSP[12] but to best of our knowledge there are no reports for the deposition of phosphide and selenide materials from the same precursor.

The SSP was synthesized by the deprotonation of the ligand $[^iPr_2P(S)NHP(Se)^iPr_2]$[13] using sodium methoxide to form the anion which is subsequently reacted with nickel(II) nitrate hexahydrate in methanol to produce a dark-red precipitate. Recrystallization of the complex from toluene gave red crystals. X-ray crystallographic studies reveal that a nickel atom is tetrahedrally coordinated through the sulfur and selenium atoms (Figure 1). The crystal structure shows the presence of independent monomeric units which are separated by normal van der Waals distances. The sulfur and selenium atoms are disordered as observed for the $Pt[^iPr_2P(S)NHP(Se)^iPr_2]$[13] complex and are refined with equal occupancies for both atoms. The six-membered $NiSSeP_2N$ ring adopts puckered pseudo-boat conformation.

Decomposition was studied by thermogravimetric analysis (TGA) (N_2 atmosphere at 10 °C min^{-1}) which reveals a single-step decomposition between 300 and 368 °C. Low-pressure metal-organic (LP-MOCVD) experiments were carried out using a custom-built cold-walled low-pressure reactor tube which has been described elsewhere.[14] Deposition was carried out on a glass substrate for 60 min at temperatures between 475 and 375 °C, and the precursor temperature was kept constant at 300 °C. Nickel phosphide films were deposited at temperatures of 475, 450, and 425 °C, whereas nickel selenide films were deposited at temperatures of 400 or 375 °C. X-ray diffraction pattern (XRD) of the as-deposited films at 475 °C and 450 °C showed hexagonal Ni_2P (JCPDS 74-1385), with preferred orientation along the (111) plane (Figure 2a), whereas as-deposited films at 425 °C show a mixture of both Ni_2P and Ni_5P_4. The scanning electron microscopy (SEM) images of the films grown at 475 °C reveal the morphology composed of convoluted wires with granules randomly attached to them (Figure 2b). Energy dispersive X-ray analysis (EDX) of these films shows that they are composed of only nickel phosphide without any major contamination of sulfur or selenium (475 and 450 °C). The analyses on wires show 54% of nickel and 46% of phosphorus, whereas on granules show 45% of nickel and 55% phosphorus.

The same precursor can deposit nickel selenide films instead of nickel phosphide at temperatures 400 or 375 °C. XRD pattern of the as-deposited films show hexagonal $Ni_{0.85}Se$ (JCPDS 18-0888), with preferred orientation along (101) plane (Figure 2c) with traces of $NiSe_2$ (JCPDS-18-0886) at 2θ values 28.58 and 33.72. Traces

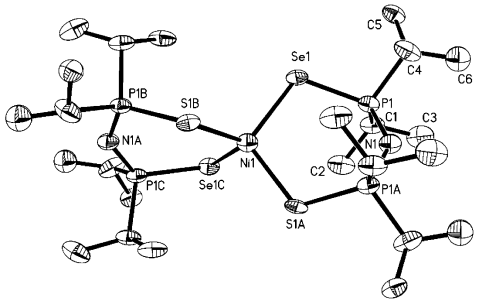

Figure 1. X-ray single-crystal structure showing one component of the disordered $Ni[^iPr_2P(S)NP(Se)^iPr_2]_2$ complex with 50% probability level ellipsoids and H atoms on the isopropyl rings omitted for clarity.

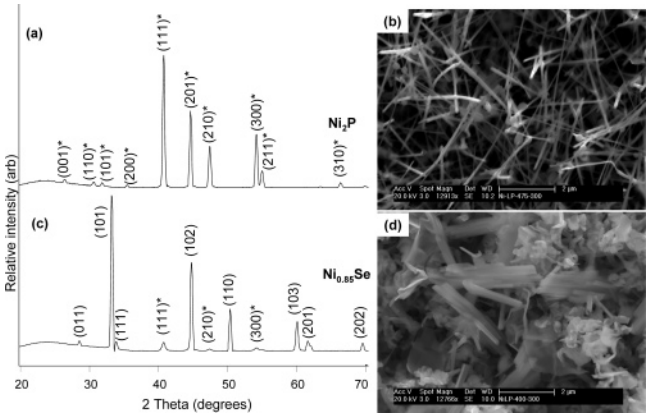

Figure 2. XRD pattern (a) and SEM image (b) of nickel phosphide films deposited at 475 °C; XRD pattern (c) and SEM image (d) of nickel selenide films deposited at 400 °C; ∗= Ni_2P peaks.

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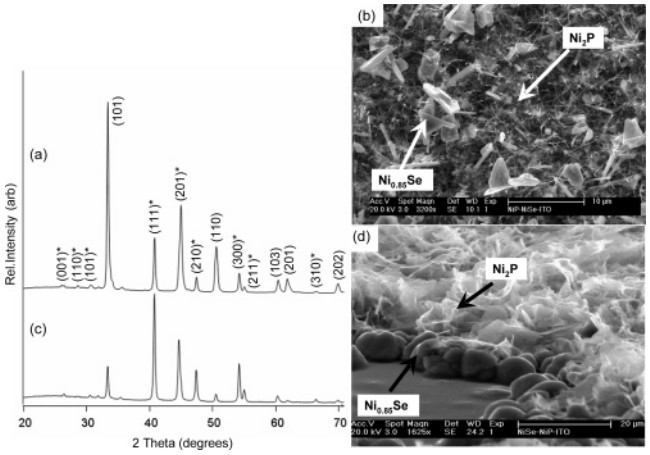

Figure 3. XRD pattern (a) and SEM image (b) of a thin film showing a mixture of nickel phosphide (∗) deposited at 475 °C and nickel selenide deposited at 400 °C; XRD pattern (c) and SEM image (d) showing a layered growth of nickel phosphide (∗) deposited at 475 °C on top of nickel selenide deposited at 400 °C.

of Ni_2P were observed at 2θ values 40.97, 47.65, and 54.21°. SEM images of films deposited at 400 °C show irregular clusters with stack of wires (Figure 2d). EDX results show nickel (46%), selenium (43%), and phosphorus (11%). The films were rich in nickel which may be due to the presence of the traces of nickel phosphide (Ni_2P) which also accounts for the phosphorus contamination in the films. The resistivity values for Ni_2P films was 8.6×10^{-4} Ω-cm (NiP_3, 1.6×10^{-3} Ω-cm)[15] which increases as the phosphorus content increases[5a] and for $Ni_{0.85}Se$ films was 1.7×10^{-3} Ω-cm ($NiSe_{2.03}$, 3.0×10^{-4} Ω-cm; $NiSe_{1.93}$, 7.0×10^{-5} Ω-cm)[16] at room temperature.

The X-ray photoelectron spectra (XPS) of the as-deposited nickel phosphide film revealed Ni $2p_{3/2}$ peak at 853.52 eV and a satellite at 860.4 eV consistent with the pure nickel phosphide.[17] The two P 2p doublets at 129.9 and 133.5 eV can be assigned to phosphide and phosphate, respectively.[18] A small quantity of selenium (2.5%) is observed with peak positions at 54.0 and 55.0 eV corresponding to bound and elemental selenium. In the case of nickel selenide film the Ni $2p_{3/2}$ peak observed at 853 eV along with a satellite at 857.9 eV is in good agreement with the literature values.[19] Se(3d) peak at 53.9 eV is due to the metallic selenide. The Se(3d) spectra display no sign for the presence of selenium oxides (expected at >58 eV). Both nickel phosphide and nickel selenide films show the presence of O1s and C1s peaks which are largely due to contamination/oxidation of films because of exposure to atmosphere.

Since the deposition from this precursor resulted in two types of materials; nickel phosphide (n-type) and nickel selenide (p-type) at different temperatures, we thought it sensible to try to grow these materials as a heterostructure. A nickel phosphide film was deposited at 475 °C onto indium tin oxide (ITO)-coated glass substrate and then nickel selenide film was deposited onto the nickel phosphide layer at 400 °C. The XRD pattern (Figure 3a) showed characteristic peaks for both nickel selenide and nickel phosphide. The percentage of each phase in the film is calculated by Rietveld analysis which shows 70.48% of $Ni_{0.85}Se$ and 29.52% of Ni_2P. The SEM image (Figure 3b) clearly showed a mixture of nickel phosphide wires and nickel selenide blocks and not a heterostructure.

Another experiment was carried out by reversing the order of deposition; nickel selenide was deposited onto the ITO substrate at 400 °C followed by the deposition of nickel phosphide at 475 °C over the nickel selenide. The XRD pattern (Figure 3c) confirmed the presence of both nickel selenide and nickel phosphide. Rietveld analysis shows 83.05% of Ni_2P and 16.95% of $Ni_{0.85}Se$ in the film. The SEM image (Figure 3d) revealed the growth of two layers; nickel phosphide flakes grown over the nickel selenide blocks. Similar results were observed when the deposition was carried out onto a glass substrate.

In summary we have grown two different materials; nickel phosphide and nickel selenide from the same precursor just by varying the deposition temperature and also a heterostructure of $Ni_{0.85}Se/Ni_2P$. The possible reason for the formation of different products may be due to the structural flexibility of the isopropyl group which causes the enlargement of the P−N−P angle.[20] Current studies are focused on the mechanism for the formation of nickel phosphide or selenide films by pyrolysis GC−MS and computational studies.

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Supporting Information Available: Experimental details; synthesis of the precursor; SEM and EDX data of films deposited at 450, 425, and 375 °C; growth of $Ni_{0.85}Se/Ni_2P$ on glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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