

Factors controlling material deposition in the CVD of nickel sulfides, selenides or phosphides from dichalcogenoimidodiphosphinato complexes: deposition, spectroscopic and computational studies

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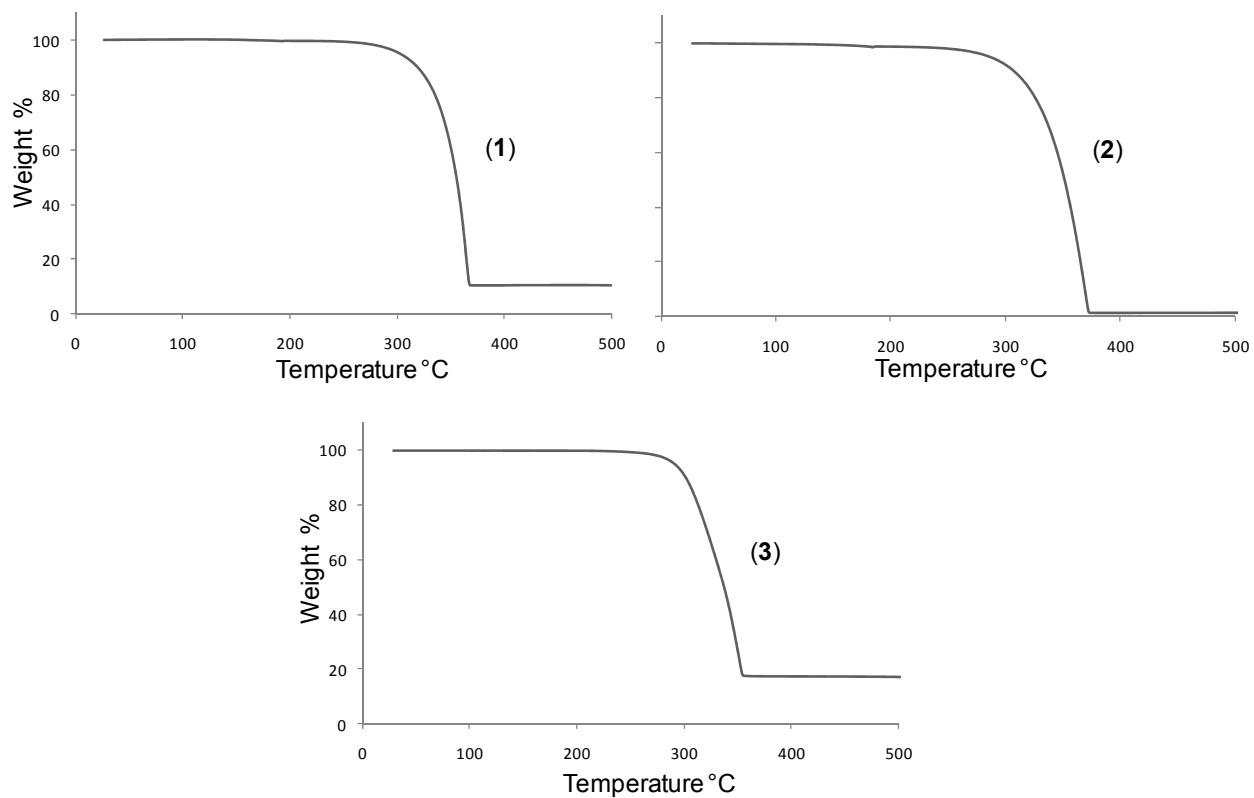


Fig. S1 TGA plot of precursors $[\text{Ni}\{\text{Pr}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Pr}_2\}_2]$ (1), $[\text{Ni}\{(\text{SP}\text{Pr}_2)_2\text{N}\}_2]$ (2) and $[\text{Ni}\{(\text{SeP}\text{Pr}_2)_2\text{N}\}_2]$ (3) heated at 10 °C/min under N_2 .

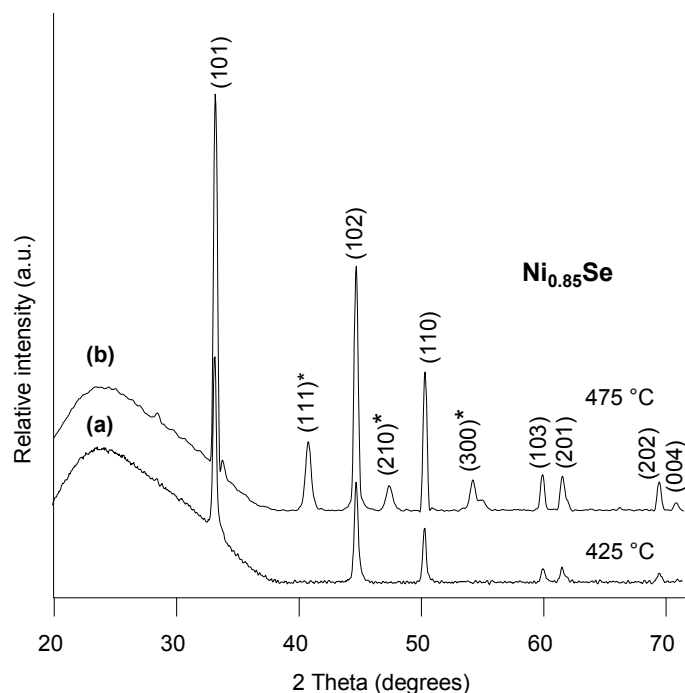


Fig. S2 XRD patterns of nickel selenide ($\text{Ni}_{0.85}\text{Se}$) films deposited on glass from (1) at flow rate of 240 sccm and deposition temperatures of (a) 425 °C and (b) 475 °C, "*" - Ni_2P peaks.

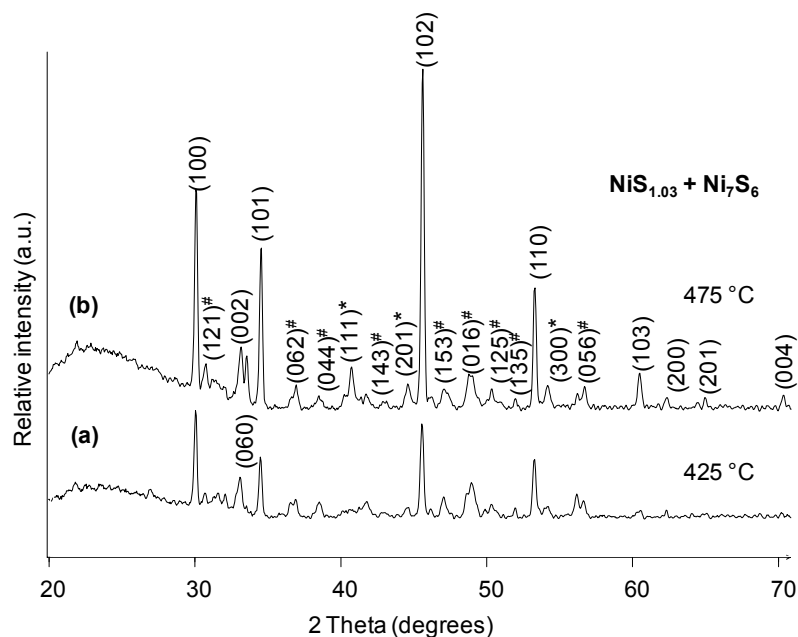


Fig. S3 XRD patterns of nickel sulfide ($\text{NiS}_{1.03}$) films deposited on glass from (2) at flow rate of 200 sccm and deposition temperatures of (a) 425 °C and (b) 475 °C, "#"- Ni_7S_6 , and "*" - Ni_2P peaks.

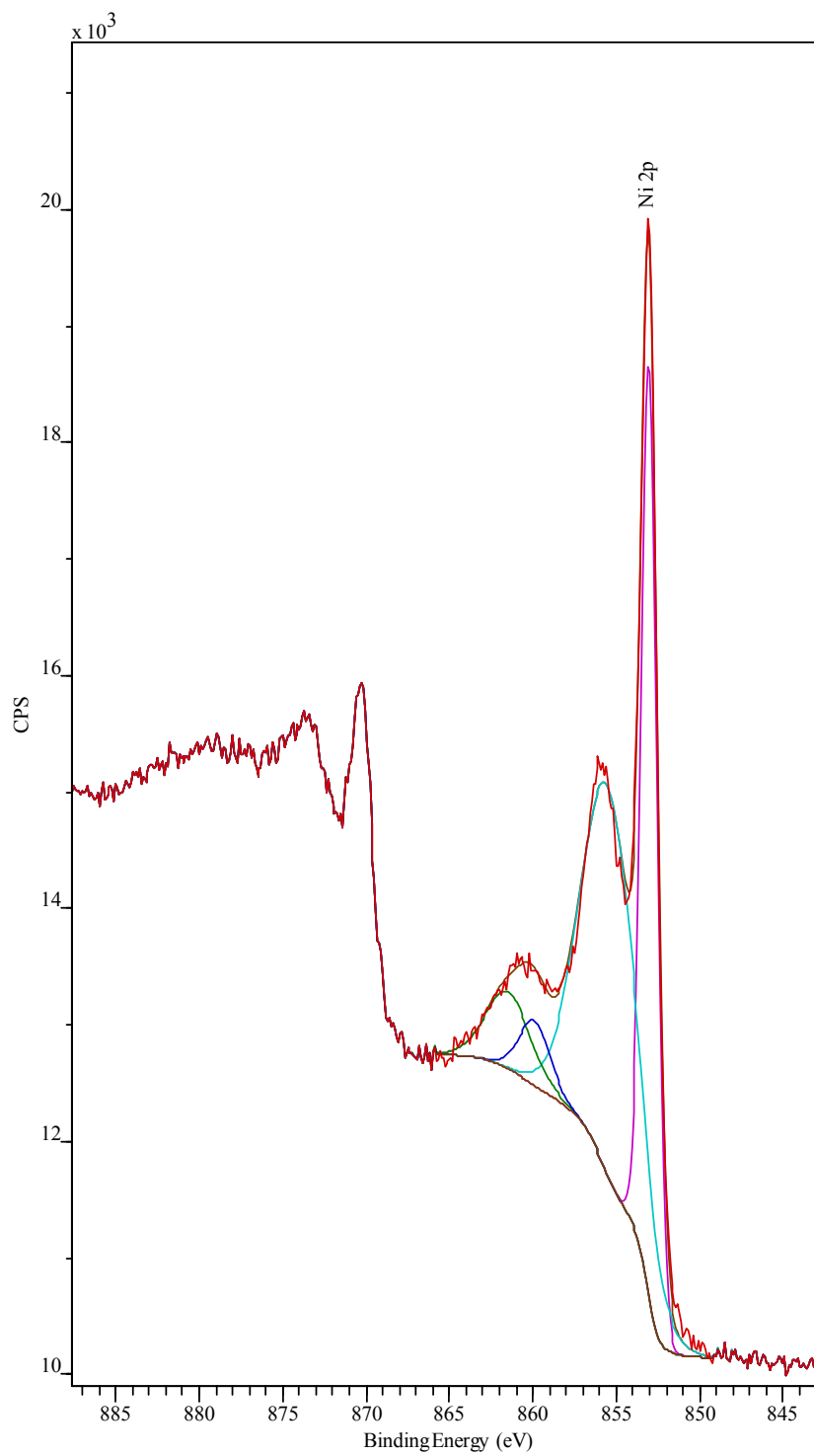


Fig. S4 XPS spectrum of Ni2p region.

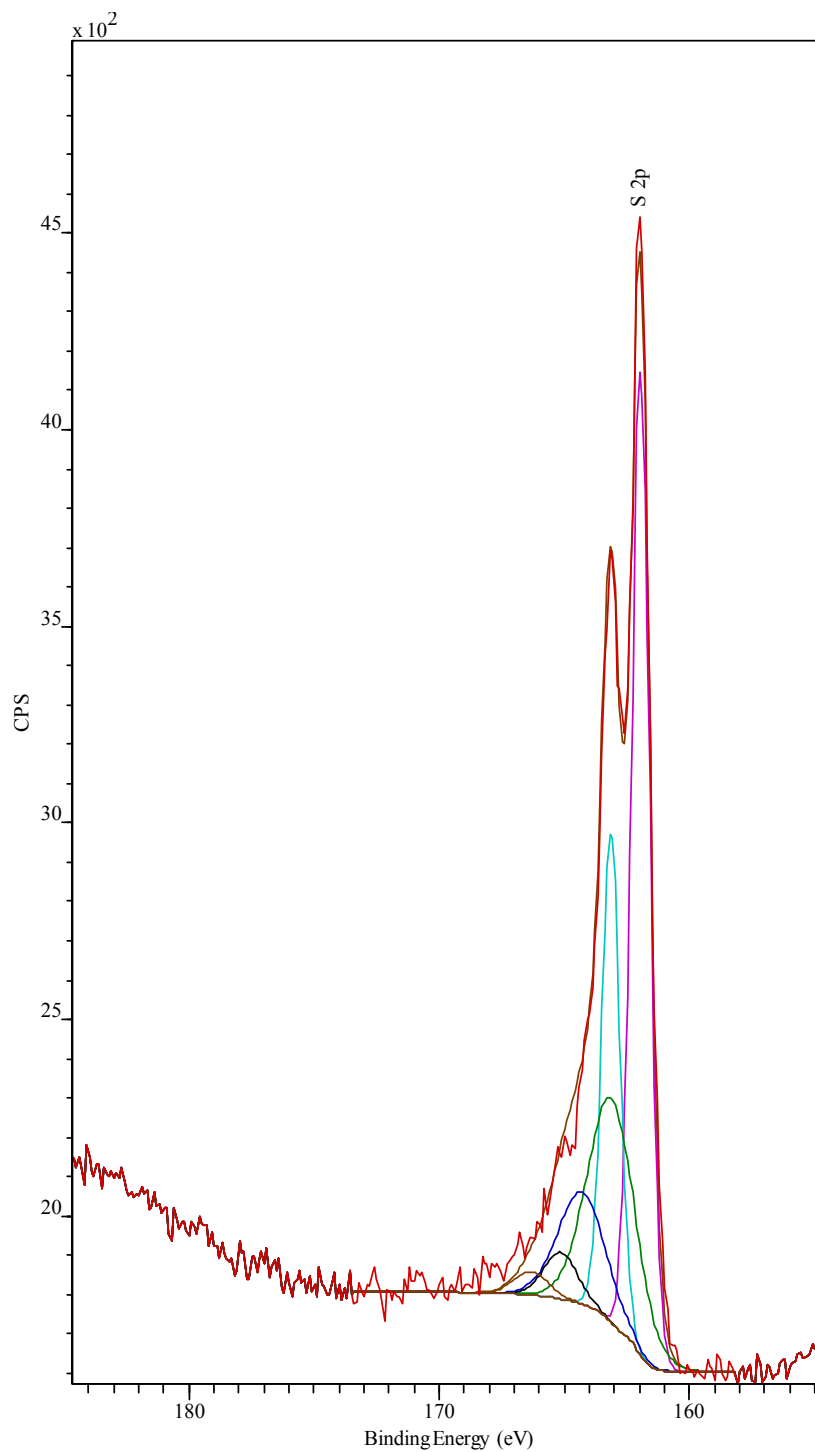


Fig. S5 XPS spectrum of S2p region.

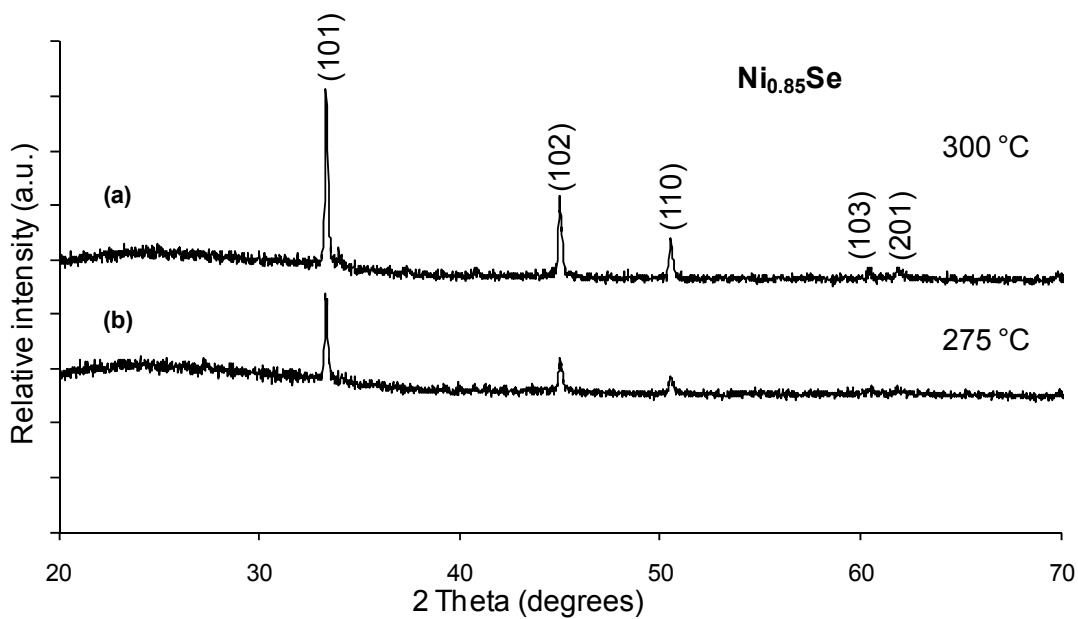


Fig. S6 XRD patterns of nickel selenide ($\text{Ni}_{0.85}\text{Se}$) films deposited on glass by LPCVD from (3) at substrate temperature of $425\text{ }^\circ\text{C}$ and T_{prec} (a) $300\text{ }^\circ\text{C}$ and (b) $275\text{ }^\circ\text{C}$.

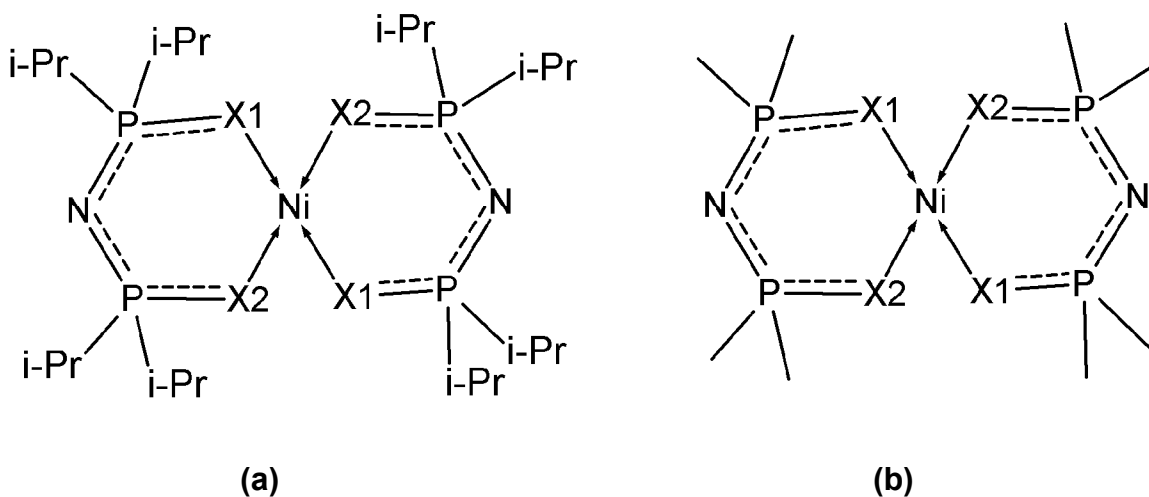


Fig. S7 (a) Precursor structure $[\text{Ni}\{\text{i-Pr}_2\text{P}(\text{X1})\text{NP}(\text{X2})\text{i-Pr}_2\}_2]$ [$\text{X1}=\text{S}$, $\text{X2}=\text{Se}$ (1); $\text{X1}=\text{X2}=\text{S}$ (2); $\text{X1}=\text{X2}=\text{Se}$ (3)] and (b) model used in the calculations.

Table S1. Reaction energies (kcal mol⁻¹) for the precursors (1), (2) and (3) computed at the B3LYP/TZVP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level.

	$\Delta_r E$	$\Delta_r G$
	(1)/(2)/(3)	(1)/(2)/(3)
INTA→INTB	70.2/-/75.61	61.8/-/59.1/
INTA→INTC	60.0/63.8/-	50.2/52.1/-
INTB→INTE	83.0/275.3/-	75.7/267.2/-
INTC→INTD	130.1/128.2/-	120.9/121.3/-
INTE→INTF	-34.5/-/-	-39.5/-/-
INTE→NiSe ₂ +2PNP	59.9	48.8
INTF→NiSe ₂ +2PNP	94.4	88.2
INTF→NiP ₂ +2SePN	118.7	103.7
NiSe ₂ → NiSe + Se	89.1	81.2
NiSe → Ni + Se	101.0	94.5
NiSe ₂ → NiSe ²⁺ + Se ²⁻	270.4	245.6
NiSe → Ni ²⁺ + Se ²⁻	369.9	361.9
NiS ₂ → NiS + S	99.9	94.5
NiS → Ni + S	111.7	104.6
NiS ₂ → NiS ²⁺ + S ²⁻	250.2	236.8

Table S2. Selected experimental (Exp), computed (DFT) bond-angles (degrees) and ring opening intermediates of precursors (1), (2) and (3)

	Precursor	Level	X1Ni X1 ^a	X2NiX 2 ^a	X1Ni X2 ^b	X1PN	X2PN	PNP
1	[Ni{Pr ₂ P(S)NP(Se)Pr ₂ } ₂]	Exp ¹	105	113	109	114	120	136
	[Ni{(CH ₃) ₂ P(S)NP(Se)(CH ₃) ₂ } ₂]	DFT	109	111	109	117	117	125
INTA	[Ni(SSePNP) ₂]	DFT	101	101	113	109	110	155
INTB	[Ni(SCH ₃ SePNP) ₂]	DFT	87	107	107	-	111	159
INTC	[Ni(SeCH ₃ SPNP) ₂]	DFT	97	106	109	110	-	157
2	[Ni{Pr ₂ P(S)NP(S)Pr ₂ } ₂]	Exp ²	109	-	110	118	-	-
	[Ni{(CH ₃) ₂ P(S)NP(S)(CH ₃) ₂ } ₂]	DFT	116	-	113	118	-	128
INTA	[Ni(SSPNP) ₂]	DFT	103	-	109	111	-	152
INTB	[Ni(SCH ₃ SPNP) ₂]	DFT	108 107 ^c	-	107	105 110 ^c	-	156
3	[Ni{Pr ₂ P(Se)NP(Se)Pr ₂ } ₂]	Exp ³	-	-	110	-	-	138
	[Ni{(CH ₃) ₂ P(Se)NP(Se)(CH ₃) ₂ } ₂]	DFT	-	107	114	-	117	127
INTA	[Ni(SeSePNP) ₂]	DFT	-	106	117	-	111	159
INTB	[Ni(SeCH ₃ SePNP) ₂]	DFT	108 109 ^c	-	106	106 110 ^c	-	158

'a' indicates the distance and angle between the atom in same ring; where X1, X2 = S or Se; 'b' indicates the angle between the atom in the different ring in the same complex, 'c' indicates the angle due to methylated X1 or X2.

References

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- 2 D. Cupertino, R. Keyte, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 2695.
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