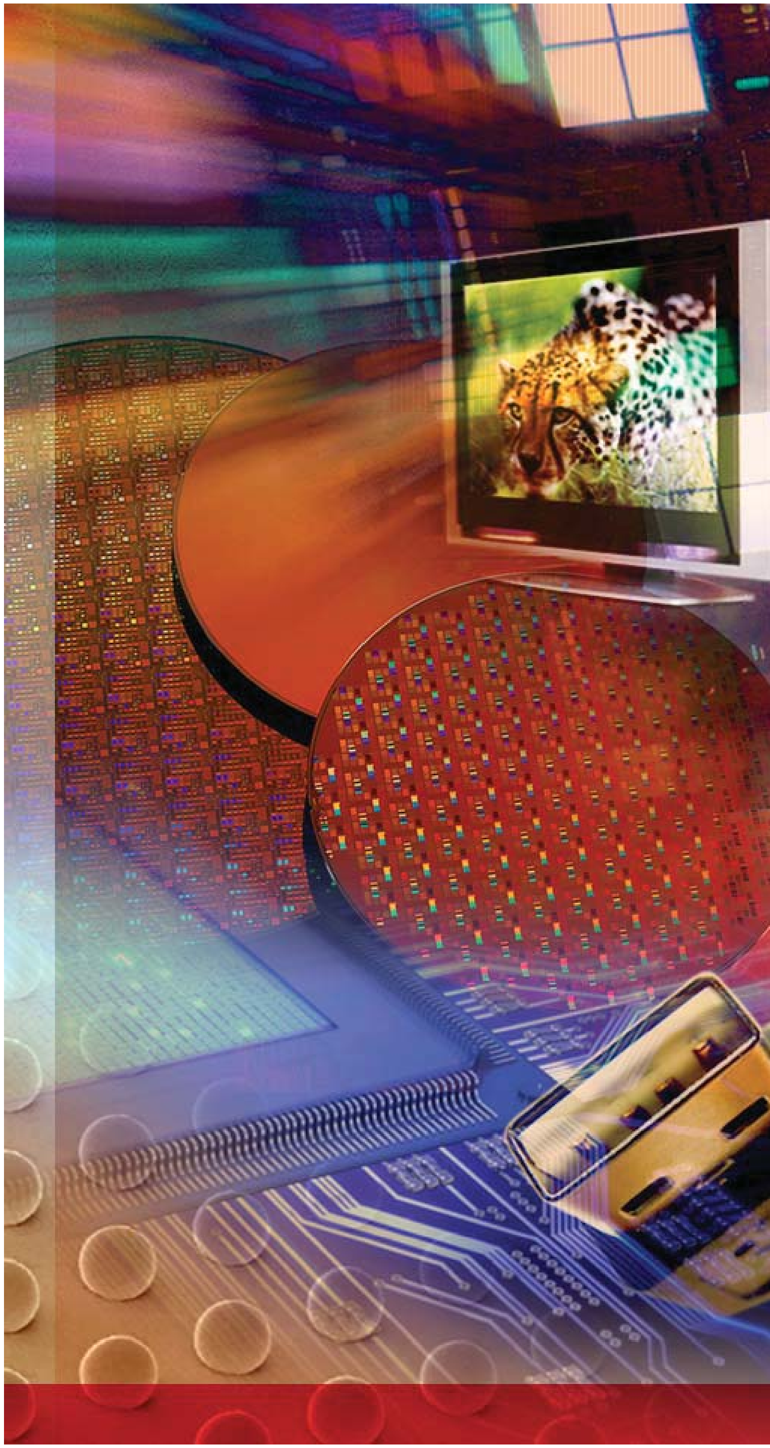
ALD and CVD Ni using Ni Amidinate Precursor

Huazhi Li[1], Deo V. Shenai[1], Zhefeng Li[2] and Roy G. Gordon[2]
1. Rohm and Haas Electronic Materials LLC, Microelectronic Technologies,
60 Willow Street, North Andover, MA 01845, U.S.A.
2. Department of Chemistry and Chemical Biology,
Harvard University, 12 Oxford Street, Cambridge, MA 02138, U.S.A.

Nickel silicide (NiSi) is emerging as the choice material for contact applications in semiconductor device processing for the 65nm technology node and beyond. As the dimensions of microelectronic circuits are being reduced, the non-conformal nature of sputtered Ni contact layers has started to cause problems. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are identified as the methods that can produce thin conformal contact layers (<10 nm). In this presentation we demonstrate the effectiveness of novel nickel amidinate (Ni AMD) as a good precursor in both ALD and CVD Ni thin films due to its high thermal stability and high reactivity. Ni AMD has acceptable vapor pressure (> 0.1 Torr at 90 ºC) for both ALD and CVD applications. Its solubility in common commercial solvents is excellent, which allows it to be used in direct liquid injection (DLI) mode. Our results confirm that when this precursor reacts with ammonia as second reagent in ALD, it readily forms Ni3N films. These NiNx films can be converted to conductive NiSi films with annealing under reducing environment such as using hydrogen. The conformality of both ALD and CVD films was confirmed inside holes with 40: aspect ratio.



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ALD and CVD of NiN Using Nickel Amidinate Source

Huazhi Li and Deo Shenai

Dow Electronic Materials,

The Dow Chemical Company, North Andover, MA 01845

Zhefeng Li and Roy Gordon

Dept of Chemistry and Chemical Biology,

Harvard University, Cambridge, MA 02138

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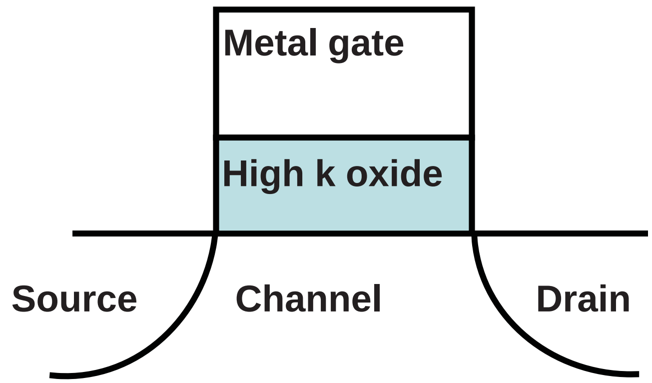
Background and Motivation for ALD/CVD NiSi



- ***NiSi is widely used in CMOS for source and drain contact metal.***
- ***NiSi offers the advantage of substantially low resistance than other metals.***
- ***With the complexity of structures involved at 32 nm and beyond,***
  - ***ALD is considered as preferred technique than CVD for NiSi***
  - ***Good precursors of acceptable stability and reactivity are needed***
  - ***Better precursors needed for depositions by both ALD and CVD***
- ***Most of the commercial Ni precursors have limited stability and reactivity***
  - ***e.g. $Ni(PF_3)_4$, $Ni(CO)_4$ and $Ni(acac)_2$.***
- ***New ALD/CVD results using NiAMD precursor are presented in this work***

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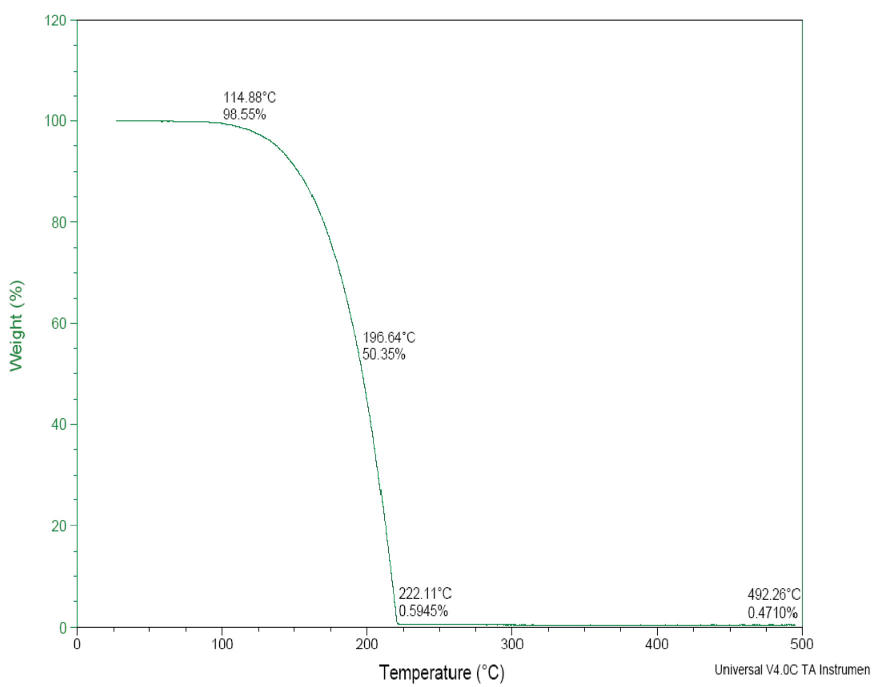
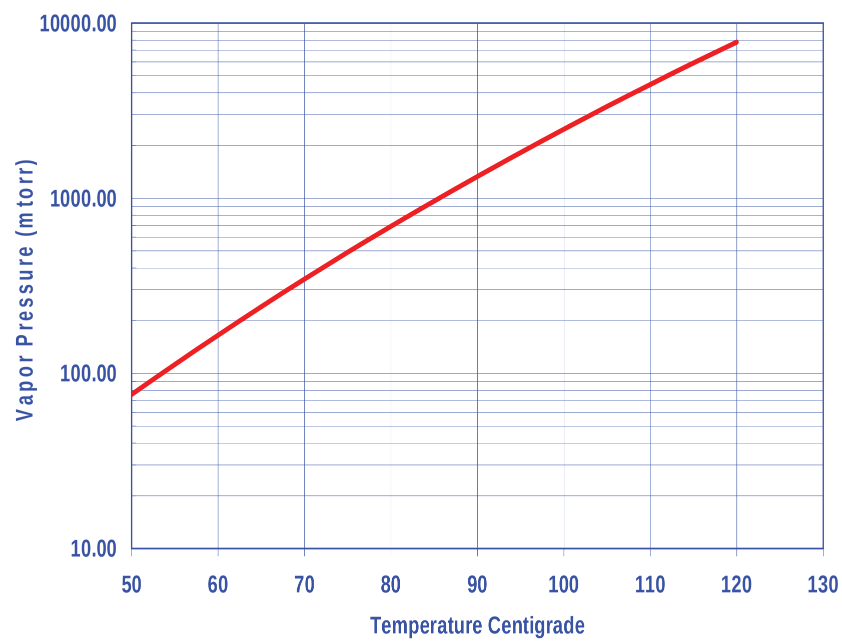
Ni Amidinate Precursor for ALD and CVD

TGA of Ni-AMD



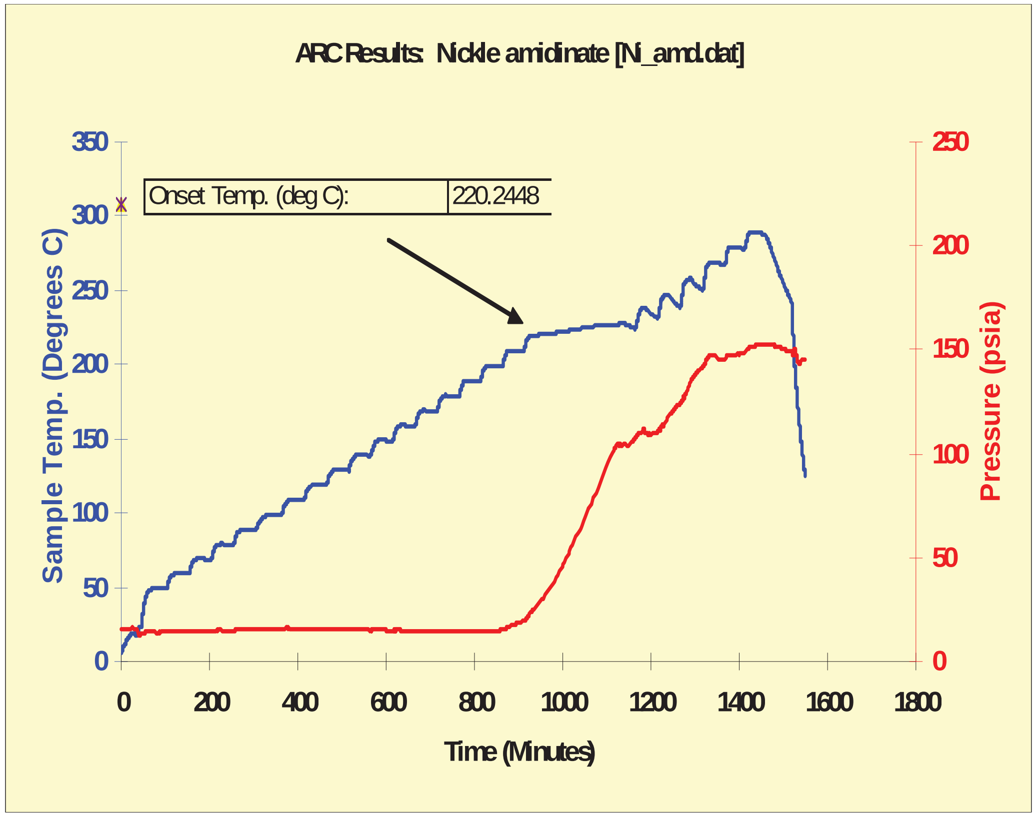
Vapor Pressure Curve for Ni-AMD



- *Low melting point solid (87 ºC) with good shelf life and thermal stability*
- *High vapor pressure (>1 Torr @ 90 ºC) offers advantage of high throughput*
- *Negligible evaporation residue as confirmed by TGA*

Thermal Stability of Ni AMD by ARC

Accelerating Rate Calorimetry (ARC) Studies on Ni-AMD



- *Onset of thermal decomposition is reported at around 220 ˚C*
- *Half life ($t_{1/2}$) at 130 ºC was found to be 96 hrs by NMR studies*

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ALD and CVD Ni Conditions

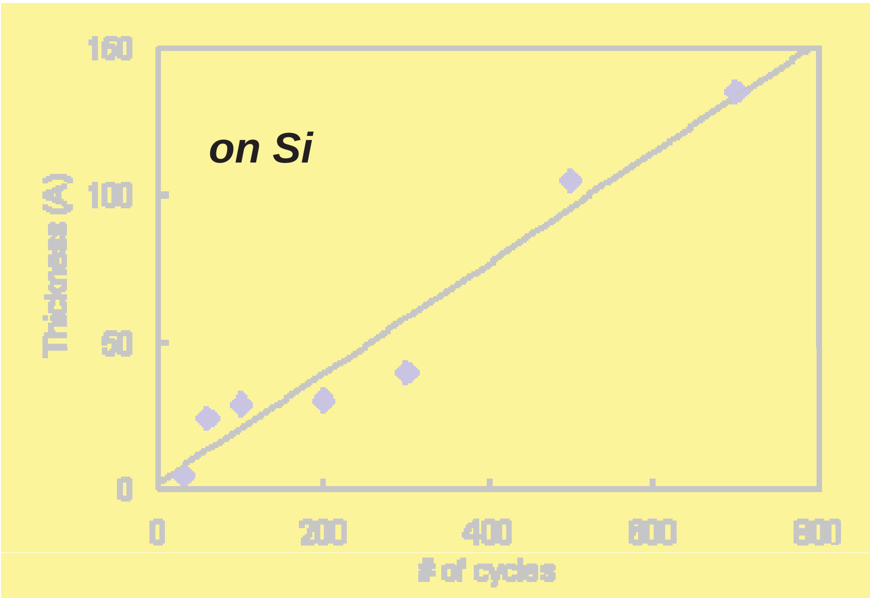
ALD/CVD conditions

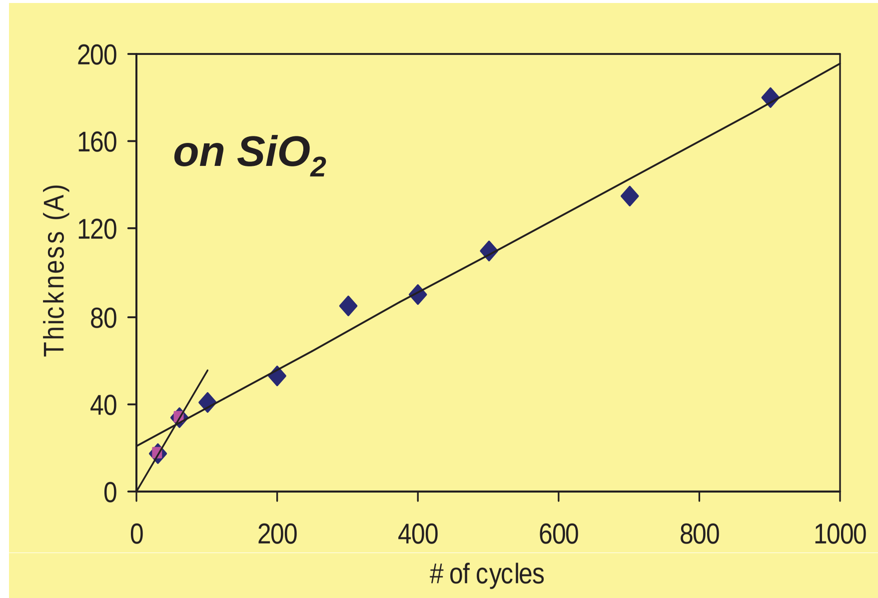
- ***Bubbler temperature for ALD/CVD: 90-100 ℃ (molten source)***
- ***ALD/CVD substrate temperature: 275 ℃.***
  - ***In ALD mode, the second reactant is NH_3.***
  - ***In CVD mode, the second reactant is H_2/NH_3.***
- ***Silicidation carried out using rapid thermal annealing (RTA):***
  - ***at 550 ºC, using forming gas at 5 Torr for 5 min.***

Physical properties of Ni-AMD

Name	Nickel Bis(*N,N'*-ditertialbutylacetamidinate)
XP number	XP-07239
Formula	BDTBANi, $Ni(tBu_2\text{-amd})_2$, $((tBu)NC(CH_3)N(tBu)_2Ni$
Molecular Weight	397.27
Appearance	brown solid
m.p. (ºC)	87 ºC
Density (g/ml)	0.65
Thermal Stability	greater than 2 months at 90 ºC
Shelf life	More than 12 month

ALD of $NiN_{0.1}$ on Si and SiO_2



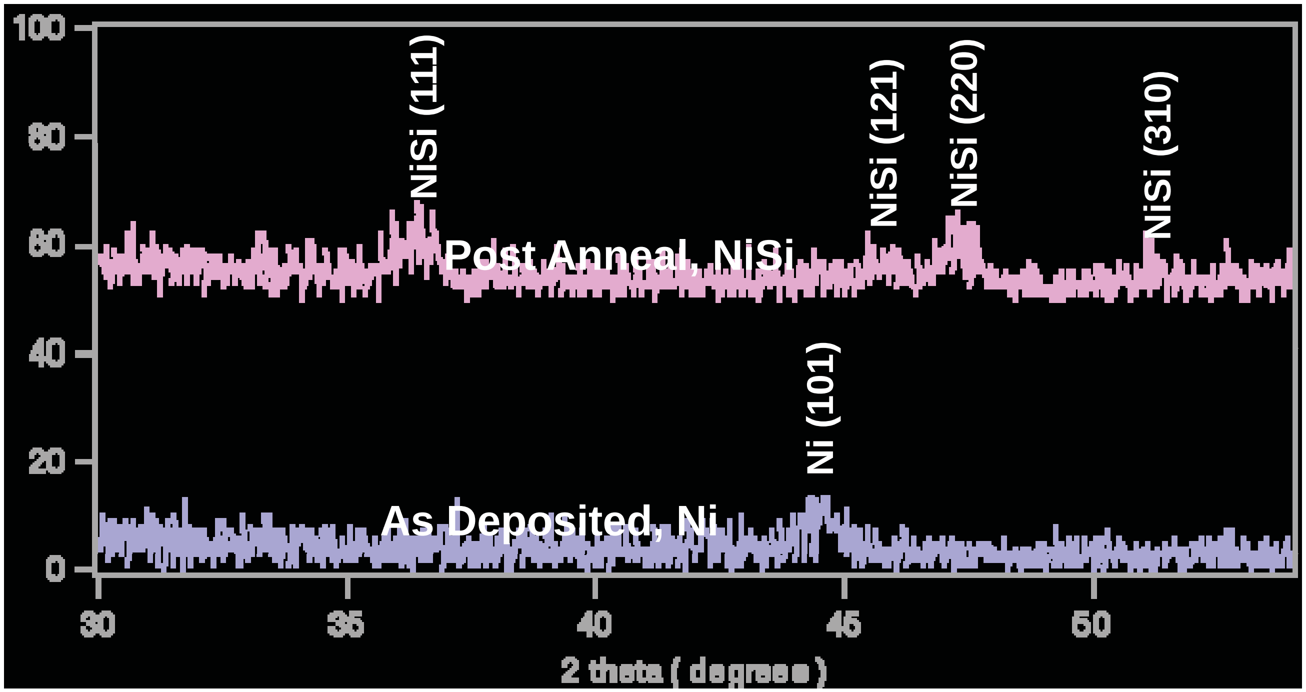


ALD rate;
~ 0.2 Å/cycle

ALD rate;
~ 0.6 Å/cycle (before 60 cycles)
~ 0.2 Å/cycle (after 60 cycles)

- ***Higher growth rate is achieved initially on SiO_2 substrate than on Si.***
- ***After ~60cycles, comparable growth rates are achieved on Si and SiO_2.***

XRD of ALD $NiN_{0.1}$ on Si

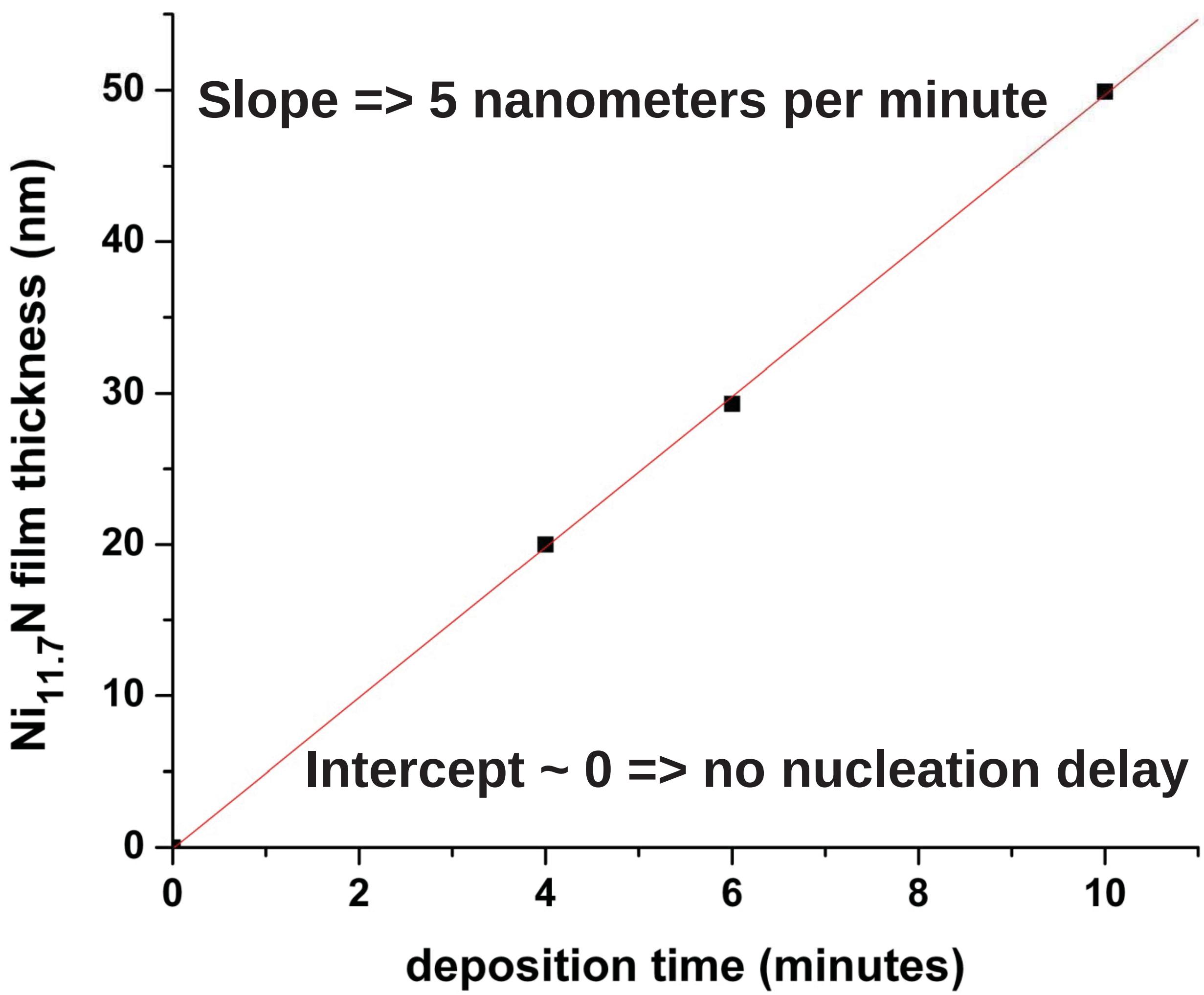


Nitrogen expelled and pure NiSi formed

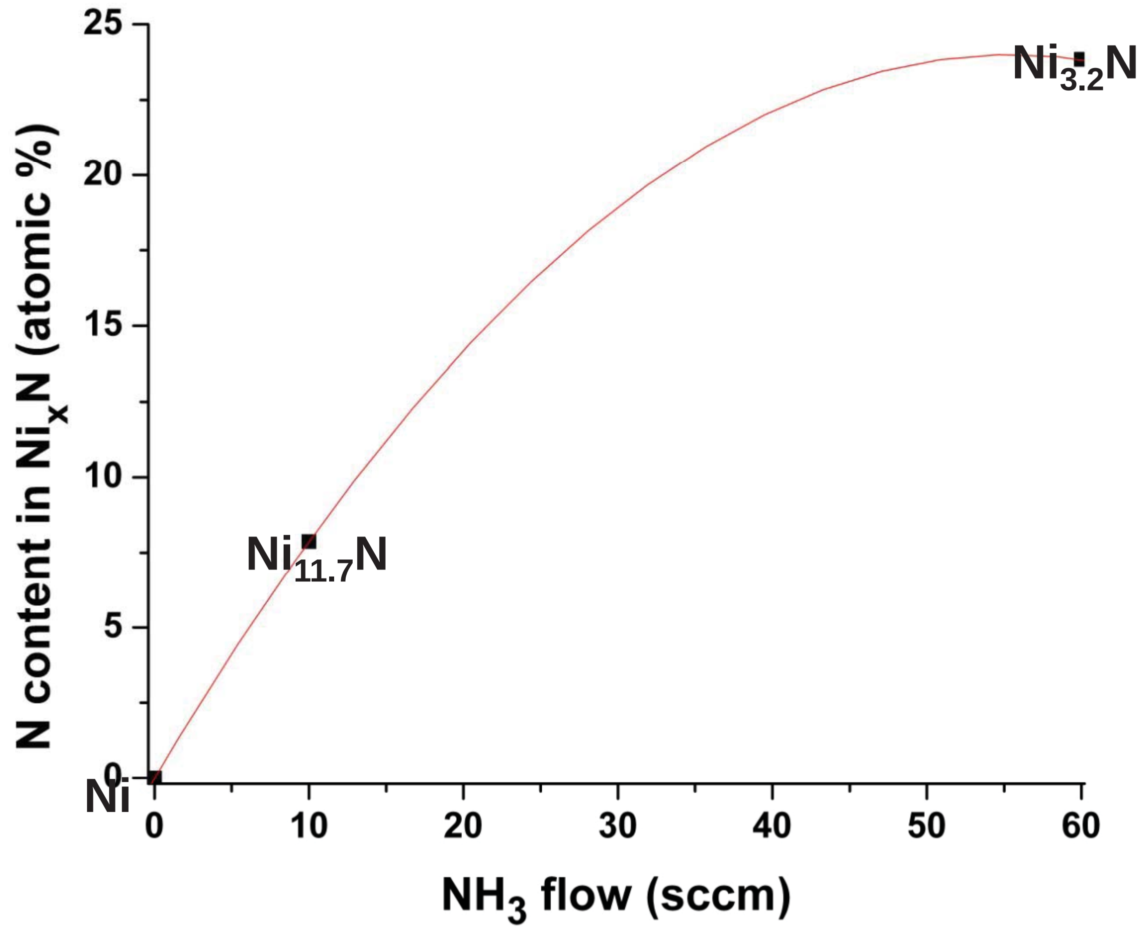
⇨ ***Sheet Resistance of NiSi after annealing ~4.2Ω/sq***

⇨ ***Resistivity of NiSi ~32μΩ-cm (lowest reported value ~14μΩ-cm)***

Deposition Rate of CVD NiN_x Films



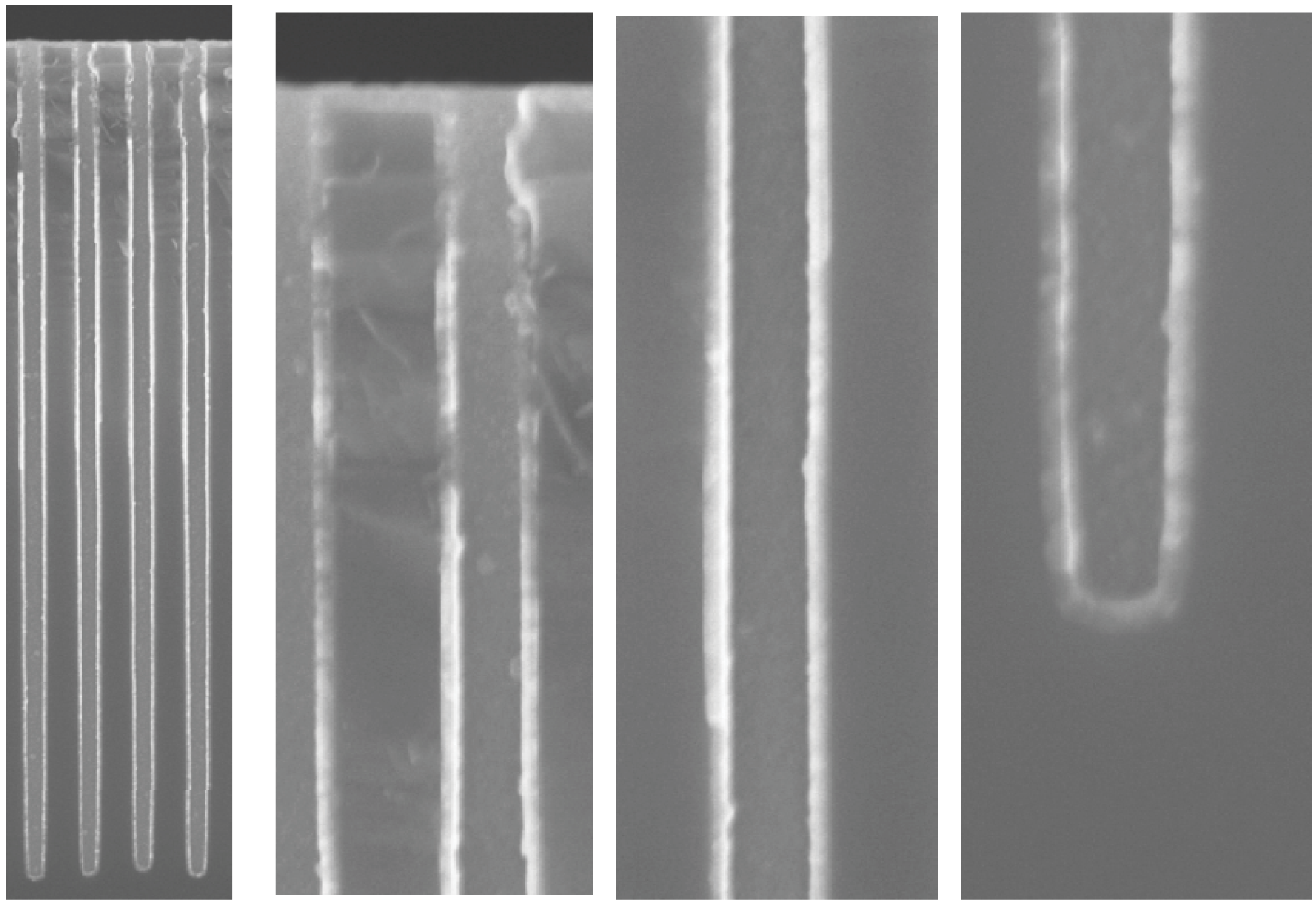
Composition of CVD NiN_x Films by RBS



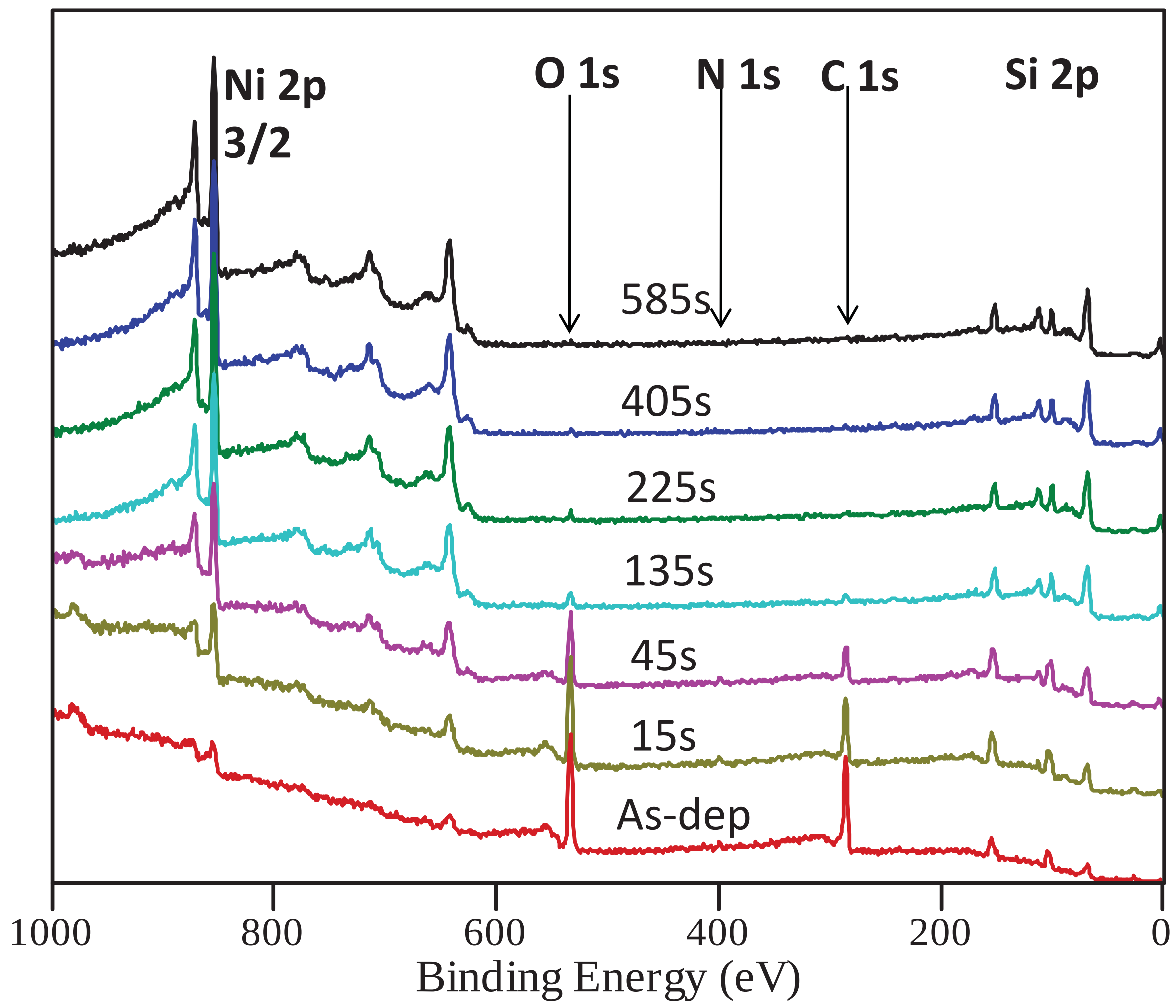
H_2 flow = 60 – NH_3 flow

N_2 flow = 60 sccm

Complete Step Coverage (>50:1 holes) by CVD



CVD NiSi Depth Profile by XPS



- ***XPS confirms high purity NiSi films with no C, N or O impurities***

Summary

- Ni-AMD has sufficient vapor pressure, good thermal stability, and excellent reactivity for ALD and CVD applications.
- ALD and CVD using NH_3 lead to Ni rich NiN_x on Si, which can be converted to pure NiSi after annealing under N_2.
- Complete step-coverage is achieved in CVD NiN_x with 50:1 aspect ratio holes at significantly higher growth rates than in ALD mode.
- High purity of NiSi films, as demonstrated by XPS, confirm NI-AMD to be a better source for ALD and CVD of Ni-comprising films