New Ni Amidinate Source for ALD/CVD of NiN_x, NiO and NiSi

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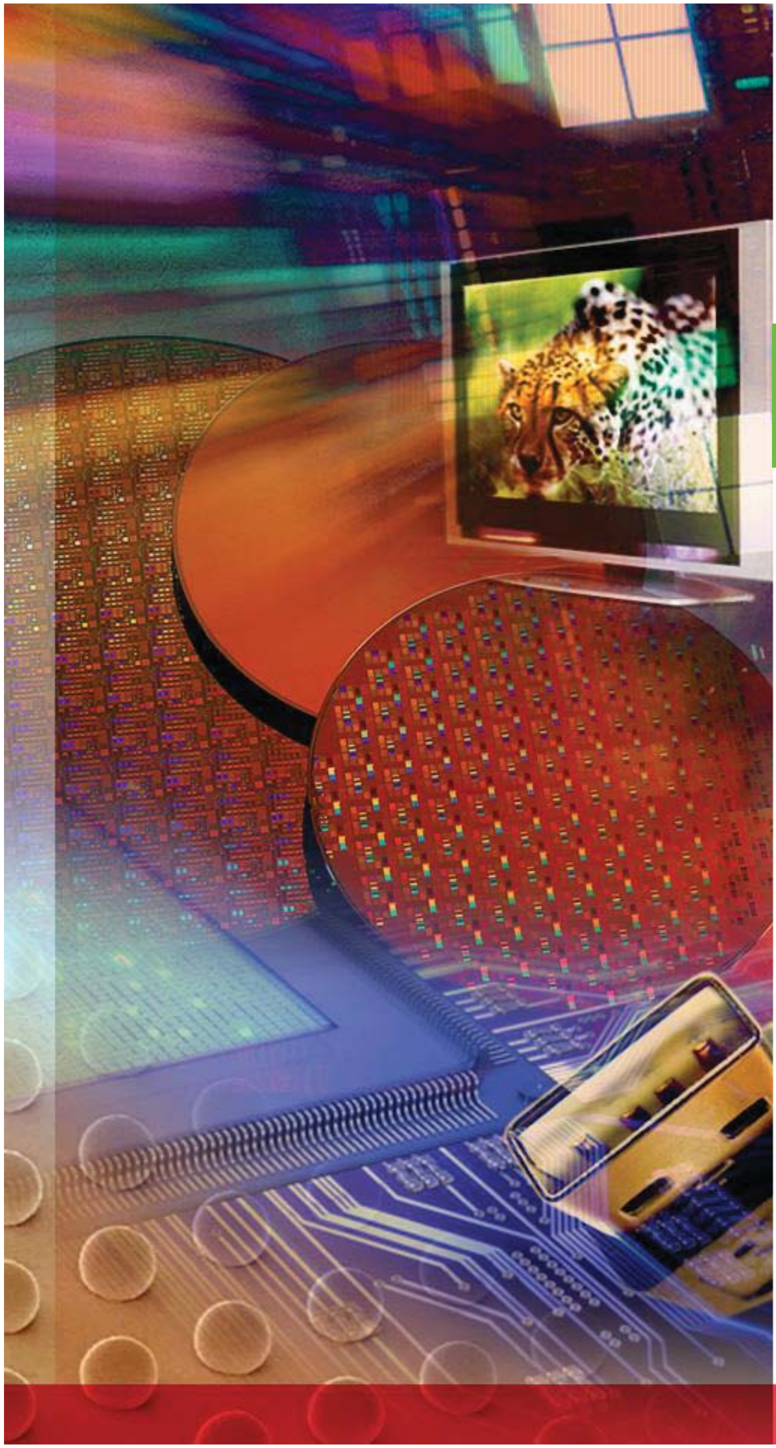
Ni materials in the form of NiN_x, NiO or NiSi have been found to be particularly important in memory as well as logic applications. Nickel silicide (NiSi) is emerging as the choice material for contact applications in semiconductor devices with 45nm technology node and beyond.[1] Recent research shows that the resistance switching characteristics of NiO thin film, in combinations with a metal-insulator-metal (MIM) structure, offer potential applications for the next generation nonvolatile resistive random access memory devices.[2] As the feature sizes of microelectronic circuits are shrinking, more complex structures are going to be adopted by the industry. Atomic layer deposition (ALD) is the preferred technique that can produce ultra-thin conformal layers (<10 nm). Nickel amidinate (Ni-AMD) has been demonstrated as an excellent precursor for both ALD and CVD Ni thin films due to its greater thermal stability and high reactivity.[3] We report our results on deposition of NiO, NiN_x and its conversion into NiSi using Ni-AMD, and discuss the chemistry of forming NiO, NiN_x and NiSi films with vapor depletion and direct liquid injection (DLI) using various organic solvents that enhance the deposition process.

References:

1. J. Foggiato, W. S. Yoo, M. Ouaknine, T. Murakami, and T. Fukada, *Mater. Sci. Eng. B*, 2004, **114-115**, 56.
2. C. B. Lee, B. S. Kang, A. Benayad, M. J. Lee, S.-E. Ahn, K. H. Kim, G. Stefanovich, Y. Park, and I. K. Yoo, *Appl. Phys. Lett.* 2008, **93**, 042115.
3. Zhefeng Li, Roy G. Gordon, Huazhi Li, Deo V. Shenai, and Christian Lavoie, *J. Electrochem. Soc.* 2010, **157** (6) H679.



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Motivation to Develop New ALD/CVD Ni Amidinate Source

- Emerging three-dimensional semiconductor device architectures are going to become one of the ultimate solutions for Si device scaling in the long run. These novel complex device structures and the integration of new materials require the development of appropriate thin film deposition technologies, including the synthesis of novel metal precursors and the design of new material deposition systems, in order to obtain high quality thin films with desirable characteristics (e.g. excellent step coverage in high-aspect-ratio holes).

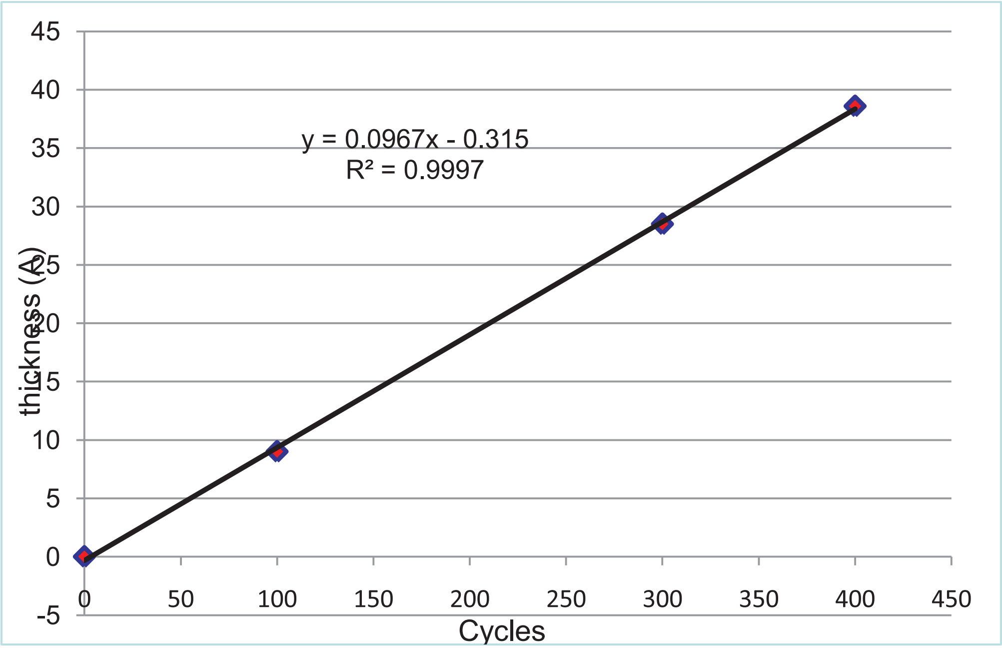
- Nickel silicide has low resistivity (14 μΩ.cm) and low contact resistance to silicon, good thermal stability, and is quite compatible with CMOS processes. It has become an indispensible part of the advanced microelectronic devices.

- Atomic layer deposition (ALD) and chemical vapor deposition (CVD) techniques are able to deposit very conformal films over high-aspect-ratio holes. Thus we developed ALD/CVD Ni amidinate source which affords high reactivity and good thermal stability. It reactivity with water and ammonia was presented.

ALD Growth of NiO_x using Ni AMD and H_2O

ALD Process Information

- Source Temp: 80 ºC
- Substrate Temp: 200 ºC
- Co-Reactant: H_2O
- Pressure: 2 -3 Torr
- ALD rate: 1.0 Å/cycle



Reduction of NiOx using H_2 Gas Annealing

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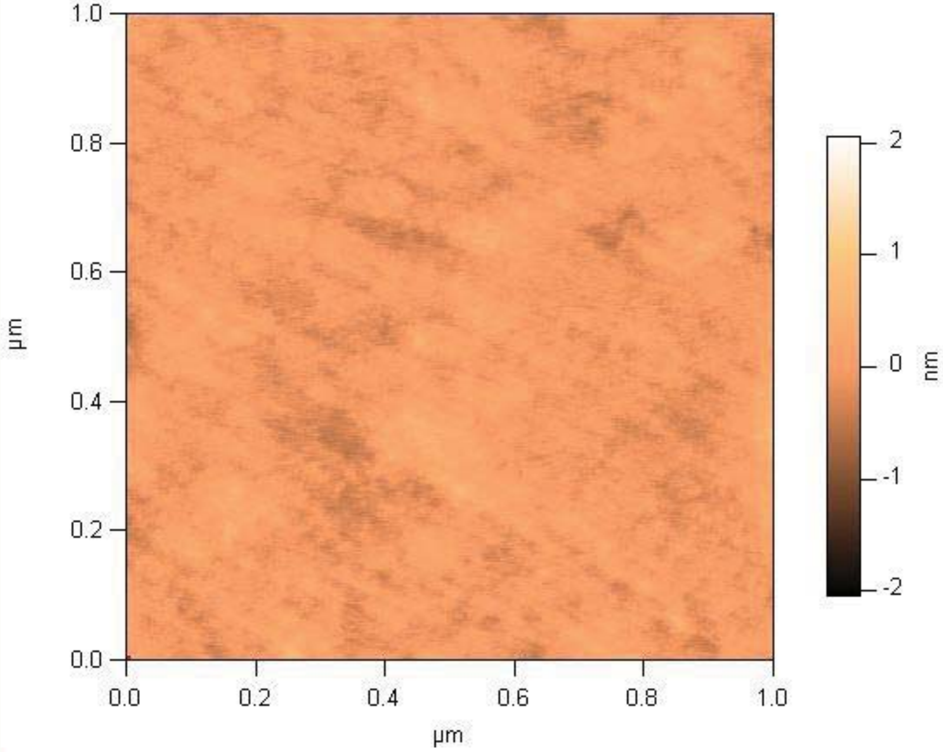
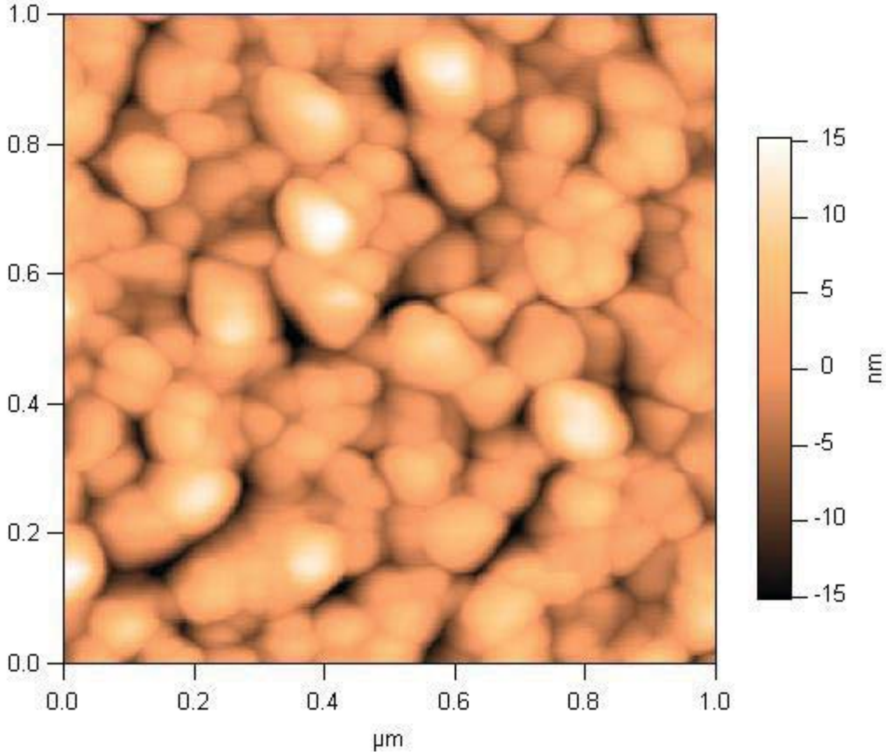


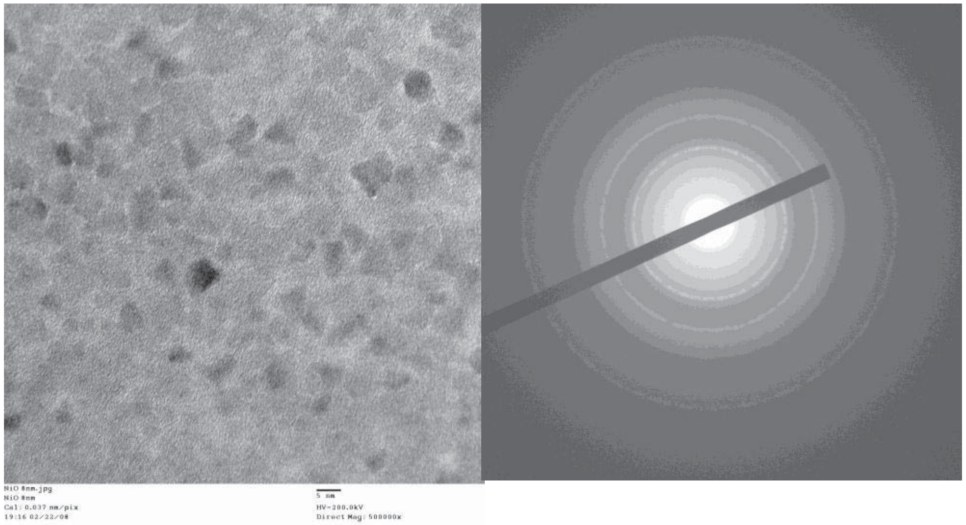
As-deposited NiOx:
RMS: 0.15nm
Sheet resistance: over range



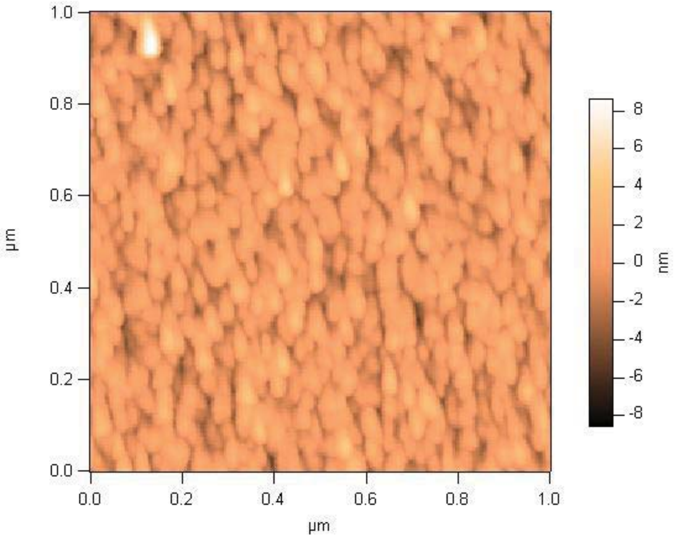
After reduction at 400 ˚C:
RMS: 4.68nm
Sheet resistance: ~10 ohms/□

- 400 ˚C annealing leads to conductive and rough Ni films; low temperature should be used for annealing

XRD of NiOx Films



As-deposited NiOx (~8nm) shows cubic NiO structure

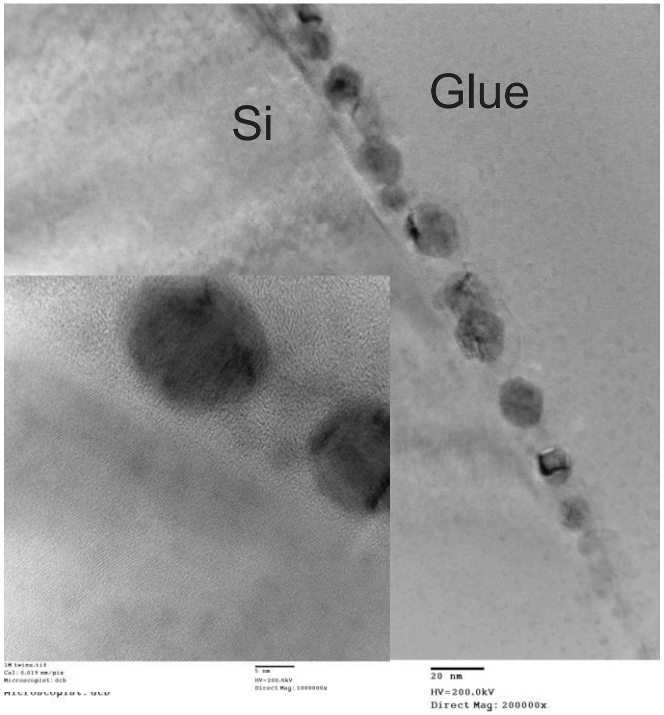


NiO reduced at 200 ˚C
RMS: 1.352nm

- 200 ˚C annealing leads to smoother and conductive Ni films

Conversion of NiOx to NiSi Films

$$\begin{tikzcd}
\text{NiO} \arrow[r, "1\text{atm } H_2", "200\ ^\circ\text{C}"'] \arrow[d] & \text{Ni} \arrow[r, "\text{RTA}", "550\ ^\circ\text{C}"'] \arrow[d] & \text{NiSix} \arrow[d] \\
29.3\text{ nm} & \text{SR}= 79.5\text{ohm}/\square & \text{SR}= 289\text{ ohm}/\square
\end{tikzcd}$$

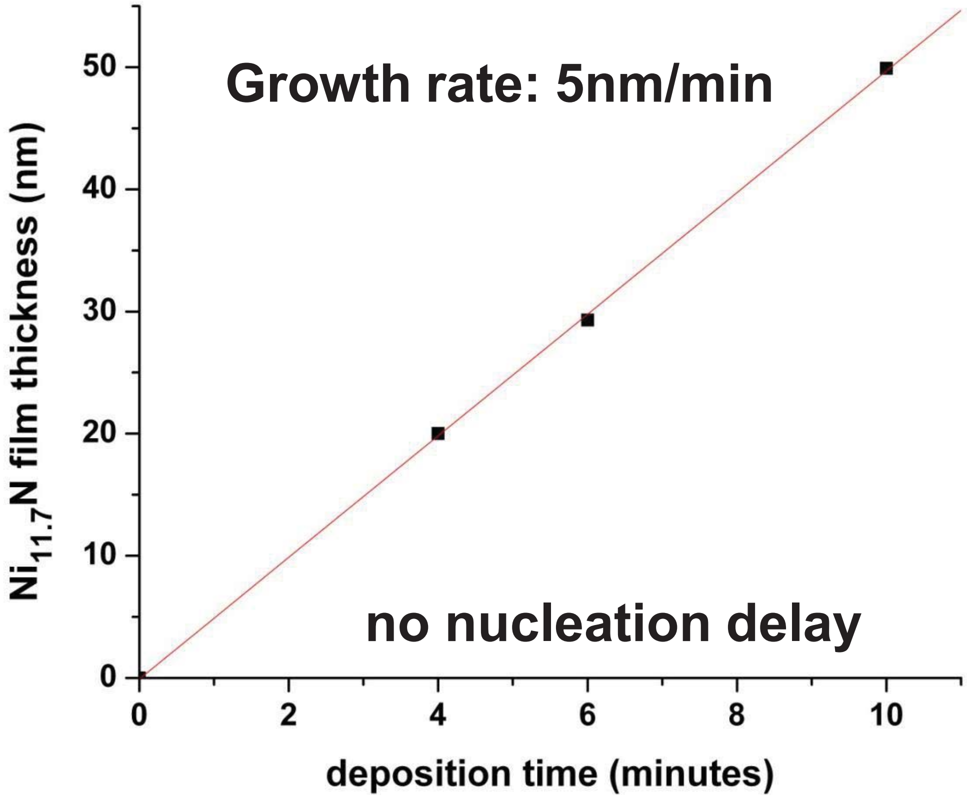


- Conversion of Ni films through NiO led to discontinuous NiSi films.

Direct Liquid Injection (DLI) CVD of NiNx with Ammonia

DLI CVD Process Information

- Dodecane solution
- Flow rate: 1.5 ccm
- Substrate Temp: 200 ºC
- Co-Reactant: NH_3/H_2
- Pressure: 1 - 10 Torr
- growth rate: 5 nm/min

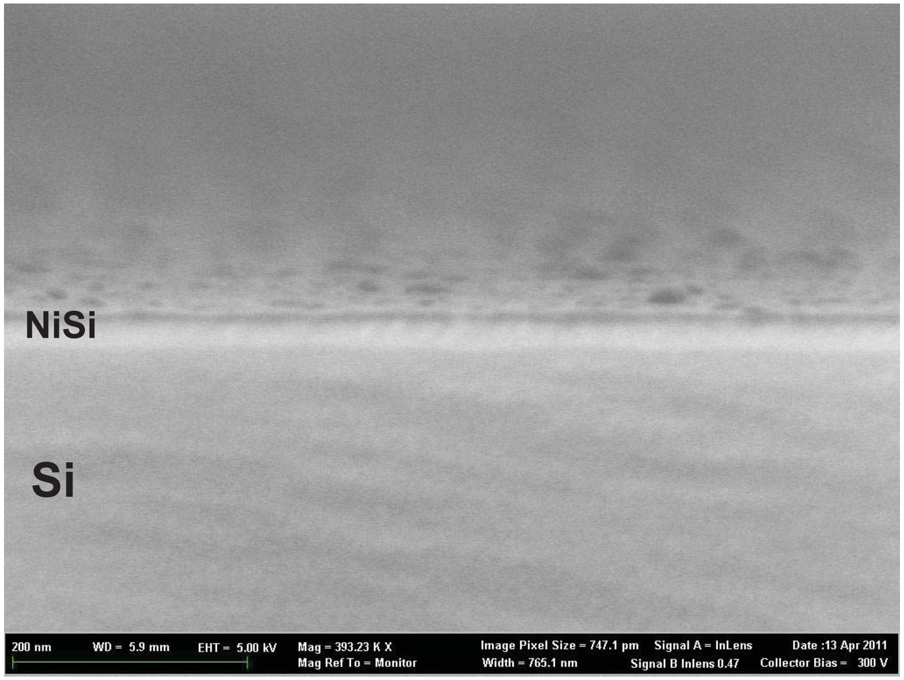


Conversion of NiNx to NiSi Films

$$\text{NiNx} \xrightarrow[\text{460 -500 °C, 1 min}]{\textit{in-situ}} \text{NiSix}$$

NiNx → 8 nm

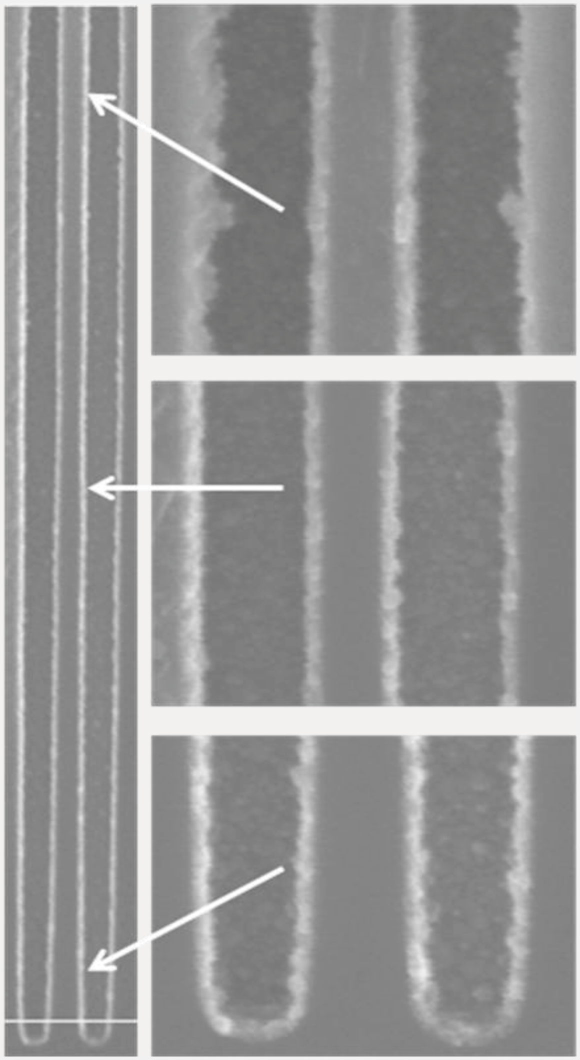
NiSix → Continuous film



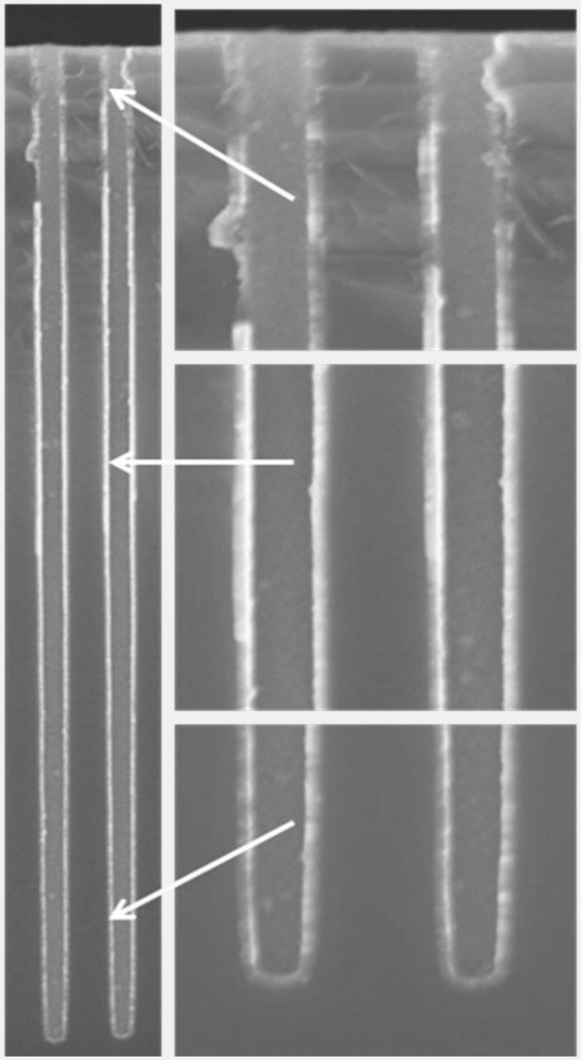
- Conversion of NiNx led to continuous NiSi films.

Step coverage of NiN_x in > 50:1 aspect-ratio holes

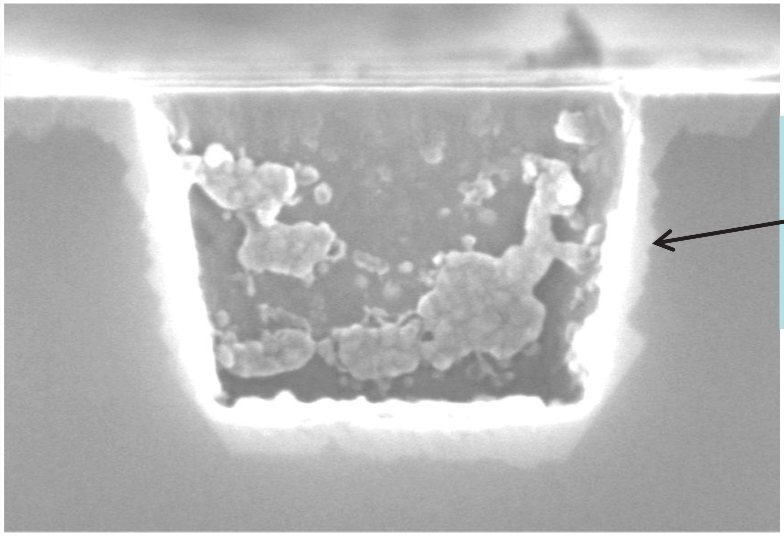
ALD



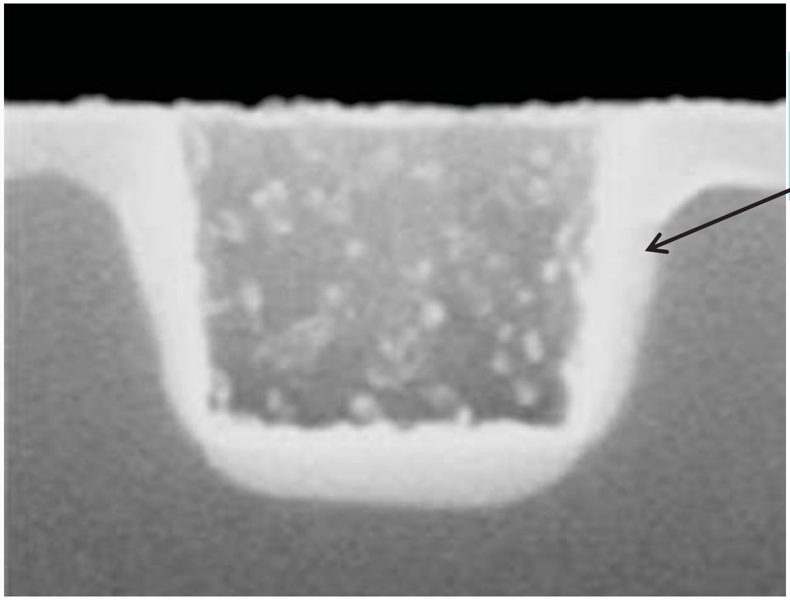
DLI-CVD



Reduced Interfacial Roughness of NiSi via NiNx



On Si surfaces other than the usual Si(100), NiSi from pure nickel metal forms **rough** interfaces



Solution: Nickel nitride (NiN$_x$) forms **smooth** NiSi/Si interfaces on all orientations of Si.

- **It is important to have smooth NiSi/Si interfaces under source/drain contacts for future 3D transistors. NiSi process through NiNx is an important enabler for this application.**

Summary

- Ni AMD material was developed for ALD/CVD Ni containing films.

- The ALD growth using Ni AMD and water led to cubic phase NiO films:
    a) the deposition rate reaches 1.0 Å/cycle.
    b) 200 °C annealing under H_2 lead to conductive Ni films.
    c) conversion of Ni films led to discontinuous NiSi films.

- DLI CVD of Ni AMD in dodecane with ammonia led to NiNx films:
    a) high growth rate of 5 nm/min was achieved
    b) Direct conversion of NiNx films led to continuous NiSi films.