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Formation of Cobalt Disilicide on 3D Structures from Highly Conformal Cobalt Nitride Thin Films by Low-temperature Chemical Vapor Deposition from a Liquid Cobalt Amidinate Precursor

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Abstract

Silicides have been widely studied and used for the low-resistance contacts, gate electrodes and local interconnections in metal-oxide-semiconductor field effect transistors (MOSFET) for decades. Although nickel silicide (NiSi) offers lower resistivity, the greater thermodynamic stability of cobalt disilicide ($CoSi_2$) makes it more suitable for structures which high processing temperatures are needed. Traditionally, $CoSi_2$ has been prepared by annealing of sputtered or evaporated cobalt films on silicon substrates. Industry is moving towards 3D transistors to continue the pace of technology advancement, however, cobalt films made by physical vapor deposition methods (sputtering or evaporation) are non-conformal over the complex 3D architectures and thus fail to meet the challenge. In this presentation, we will demonstrate the formation of $CoSi_2$ by in-situ annealing of highly-conformal cobalt nitride films inside holes with aspect ratios over 30 to 1. The cobalt nitride films are prepared by chemical vapor deposition (CVD) using a cobalt amidinate precursor and a reactant mixture of NH_3 and H_2 at low substrate temperatures. We studied the reaction of cobalt nitride films with silicon under different annealing conditions. Morphological stability and interfacial smoothness are crucial for application of cobalt disilicide as a material for contacts, gates or local interconnects. We developed a method to measure the roughness of $CoSi_2$/Si interfaces by selective backside etching followed by atomic force microscopy. Using this method, we optimized the deposition and processing conditions to make smooth interfaces between $CoSi_2$ and various crystalline orientations of silicon.

Formation of $CoSi_2$ from Highly Conformal CoN Thin Films by Low-Temperature CVD from a Liquid Cobalt Amidinate Precursor

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Introduction & Motivation

■ Metal silicide thin films are integral parts of all microelectronics devices. They have been used as ohmic contacts, Schottky barrier contacts, gate electrodes, local interconnects, and diffusion barriers.

■$TiSi_2$
√ Good thermal stability
□ Strong Linewidth Dependence

■NiSi
√ Low resistivity in narrow dimensions
□ High temperature degradation

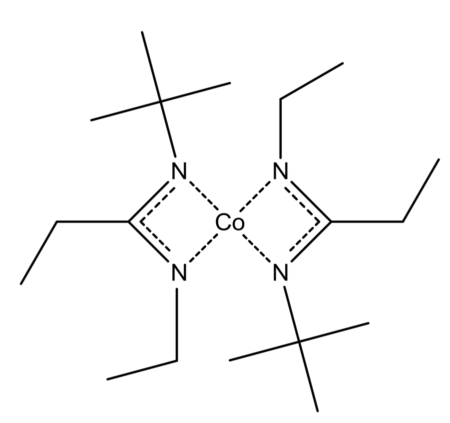
■**$CoSi_2$**
√ High Thermal Stability (up to 900°C), desirable for DRAM application
√ Weak Linewidth Dependence
Challenges:
--Sensitive to oxygen contamination, both at the surface and in the annealing atmosphere

■ Conventionally, $CoSi_2$ was formed by RTA treatments of sputtered or evaporated Co deposited on silicon. Poor step coverage of these PVD Co films prevents its use in future non-planar transistor or nanoscale CMOS devices.
■ Highly conformal cobalt/cobalt-containing thin film for silicide formation is desired for novel device structures.

Highly conformal Co_4N film by Low-Temperature CVD

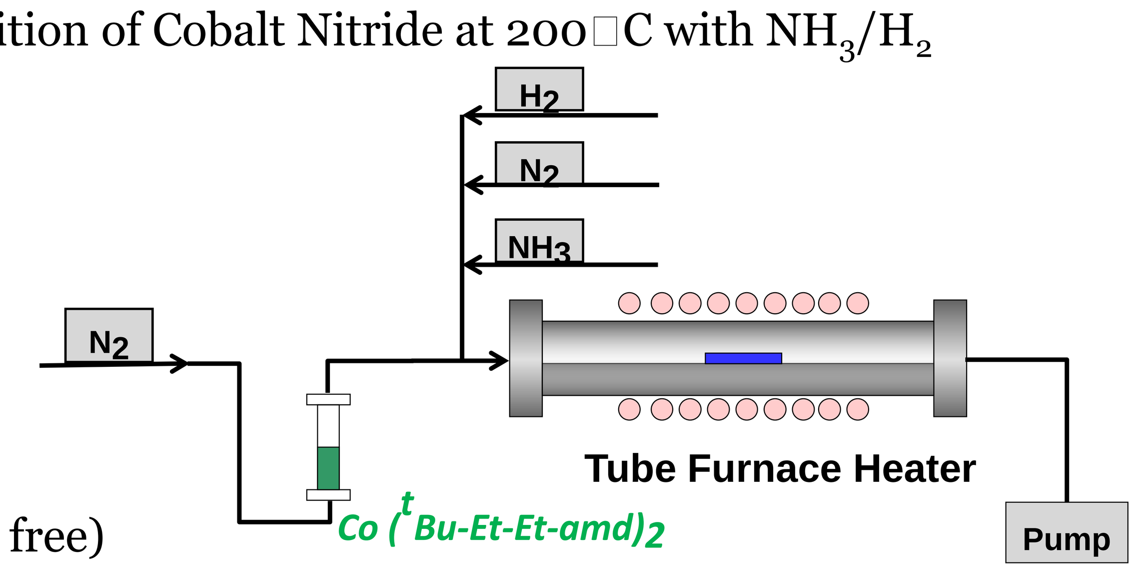
■ Volatile liquid cobalt amidinate precursor

bis(N-tert-butyl-N'-ethyl-propionamidinato)cobalt(II)

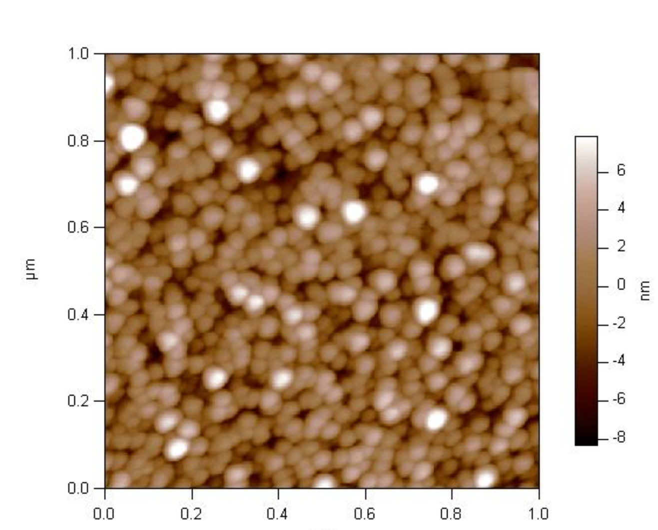


■Color: dark blue/green liquid compound at room temperature
■Melting Point: -17 °C
■Bubbler Temperature: 85 °C
■Vapor Pressure: 262mTorr at 85 °C
❑High thermal stability for years
❑Clean evaporation < 1% residue

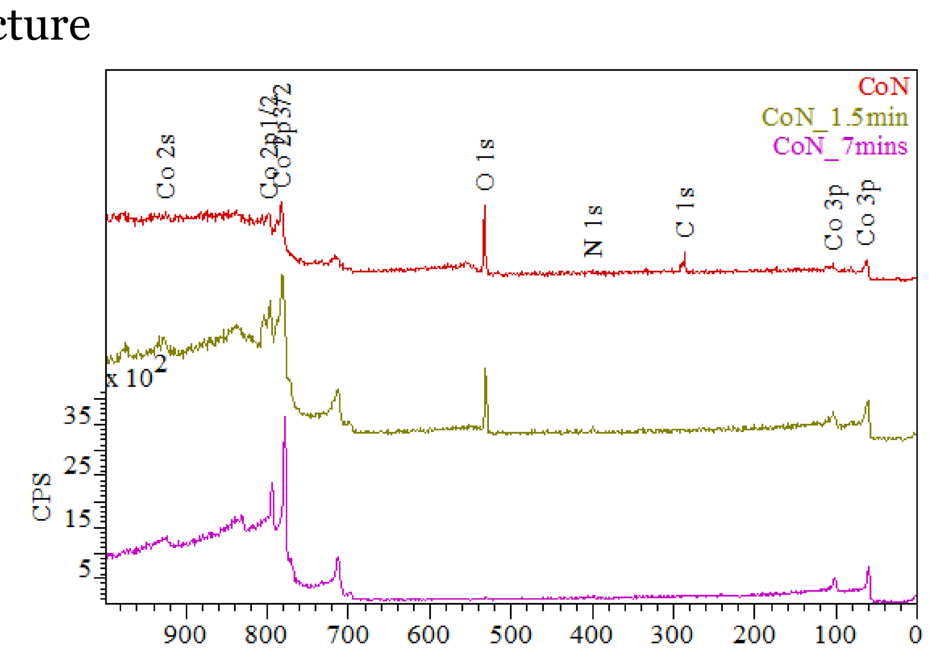
■ Chemical Vapor Deposition of Cobalt Nitride at 200°C with NH_3/H_2



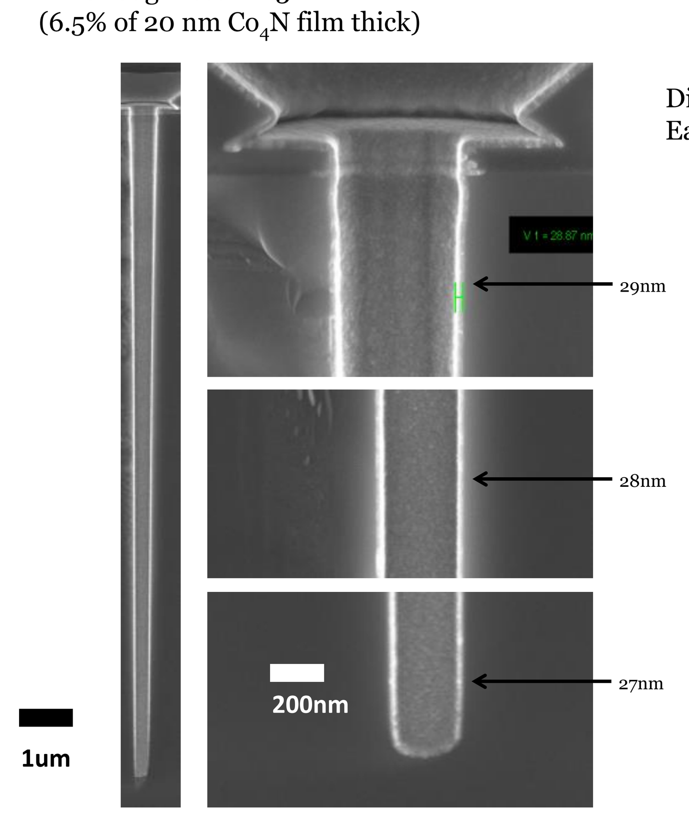
■ High quality Co_4N film
■ Smooth
■ High purity (Carbon free)
■ Excellent Step Coverage
■ Face centered cubic (fcc) structure



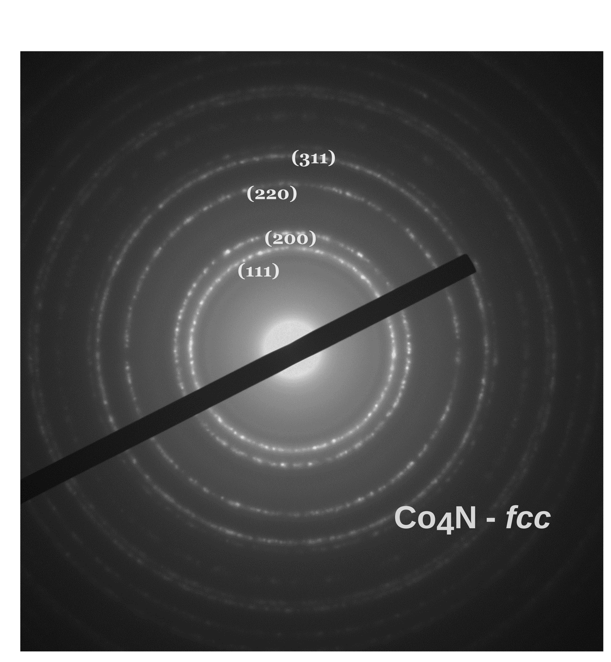
RMS roughness = 1.3 nm
(6.5% of 20 nm Co_4N film thick)



Disappearance of Carbon 1s peak in XPS after 1.5min sputtering
Easily oxidized with air exposure. Avoid vacuum break during silicidation.



Thickness profile along a 14 μm deep hole (a/r=30)



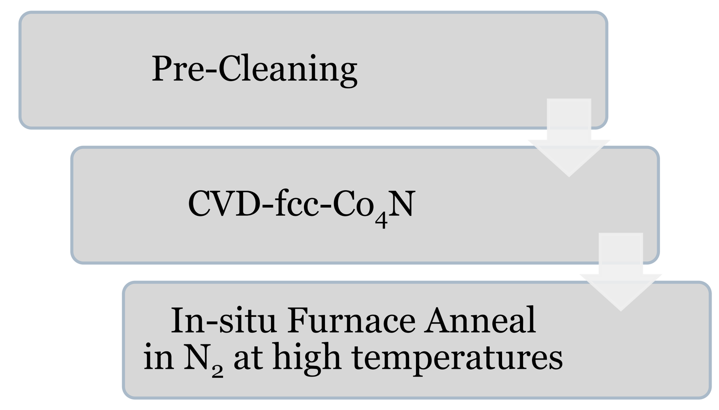
fcc-Co_4N peaks observed by TEM

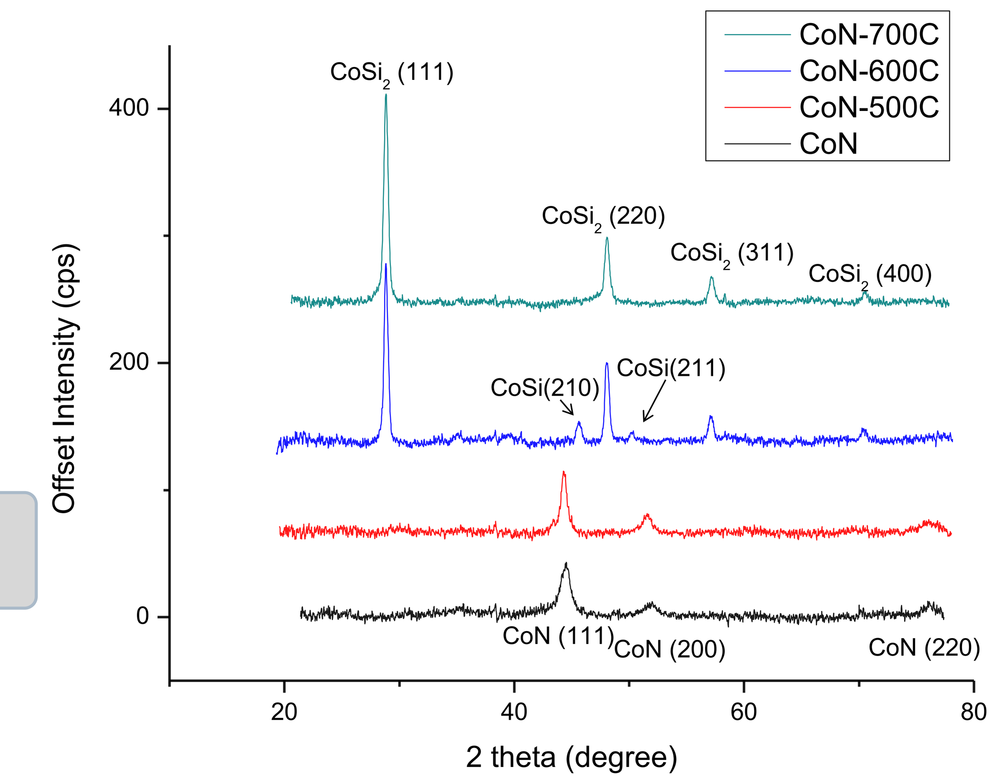
CVD-Co_4N silicidation

■ Resistivity decreases to 20 μΩ·cm after annealing, close to the value reported for bulk $CoSi_2$.

Co_4N	In-situ Annealing → 700°C, ramp rate: 15°C/sec	$CoSi_2$
30 nm		110 nm
140 μΩ·cm		20 μΩ·cm

CVD-Co_4N silicidation

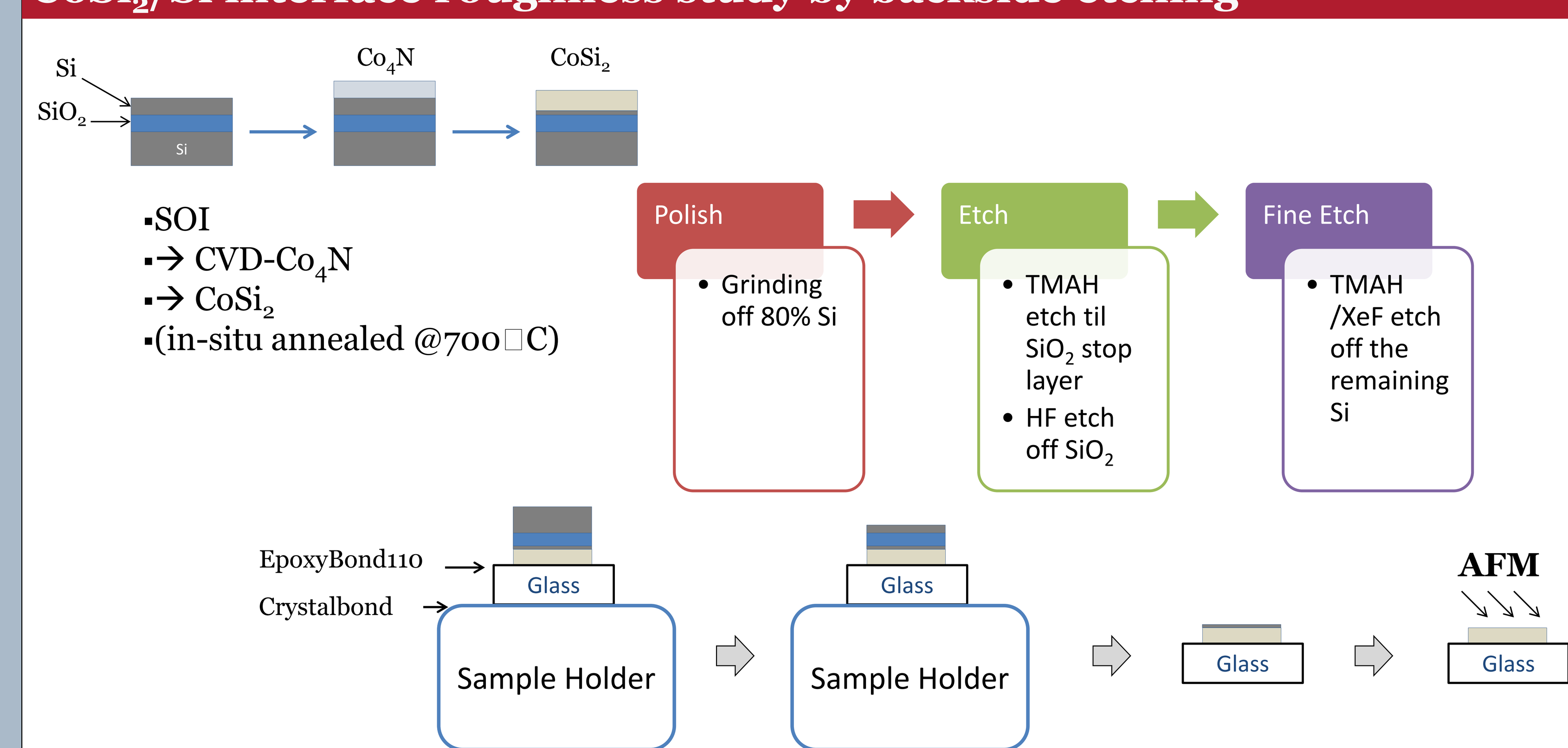


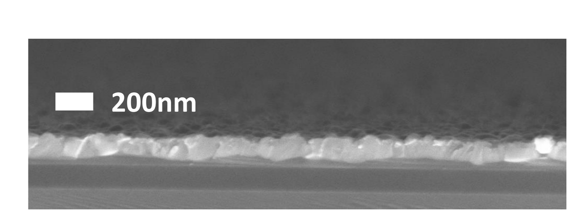


XRD phase analysis of CVD-Co4N film on Si(100) substrates after in-situ Furnace Anneal at 500°C, 600°C, 700°C

■ Face centered cubic Co_4N is stable up to 500 °C
■ A mixture of CoSi and $CoSi_2$ phases shows up after annealing at 600 °C.
■ CoSi converts to low-resistivity $CoSi_2$ by annealing at 700 °C.
■ Polycrystalline $CoSi_2$, dominated by components with (111) and (220) orientations, is grown when reacting cobalt nitride films with Si (100).
■ Retardation of $CoSi_2$ phase formation temperature.
❑ the formation temperature of the $CoSi_2$ layer was higher than that of layers formed from the pure Co film due to the retardation of Co/Si diffusion process by the nitrogen incorporation in the film.

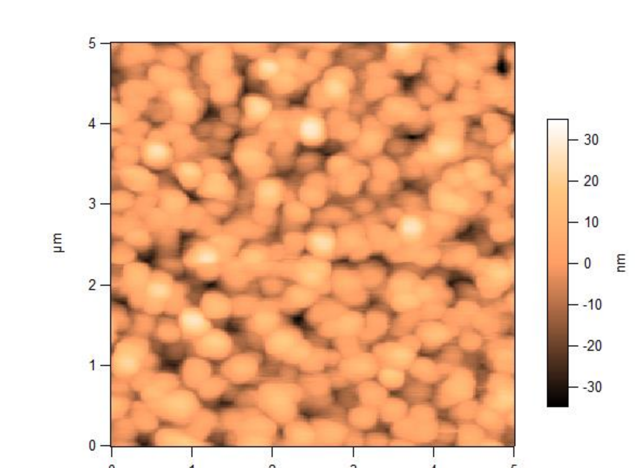
$CoSi_2$/Si interface roughness study by backside etching





	Interfacial roughness percentage*	Surface roughness percentage*
In-situ annealing @ 700°C		
SOI	8.3%	11.1%
In-situ annealing @ 600°C		
SOI	11%	11.2%

*interfacial/surface roughness rms divided by the total film thickness



AFM image of $CoSi_2$/Si interface by backside etching method.
The $CoSi_2$ is formed on SOI substrate by annealing Co_4N film in N_2 at 700°C

■ $CoSi_2$/Si interfacial roughness is reduced after converting CoSi to $CoSi_2$ completely.

Conclusions

■ Highly conformal Co_4N films have been successfully deposited from CVD processes using bis(N-tert-butyl-N'-ethyl-propionamidinato)cobalt(II) and NH_3/H_2 as the co-reactants at a low temperature of 200°C.
■ Thin fcc-Co_4N films have been successfully converted to continuous $CoSi_2$ films with in-situ furnace annealing at 700 °C.
■ First time **quantitative** evaluation of $CoSi_2$/Si interfacial roughness.

Future Plan

■ Silicidation process can be optimized to achieve a smooth interface with the underlying Si and could potentially result in low junction leakage

Acknowledgments

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