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RESEARCH BRIEF

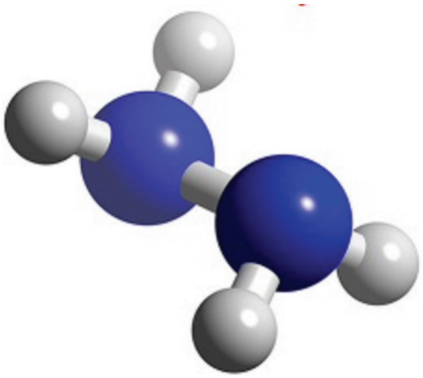
The Emergence of Hydrazine (N_2H_4) in Semiconductor Applications

by Jeffrey Spiegelman and Daniel Alvarez

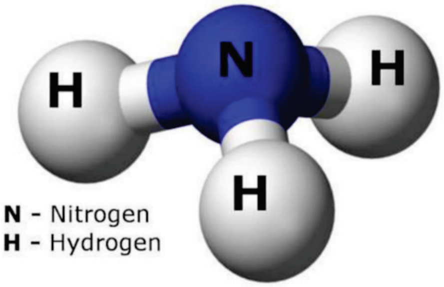
Purpose

Historically, metal-nitride MOCVD and ALD films have been fabricated with Ammonia (NH_3). However, lower thermal budgets and shrinking 3-dimensional structures are needed for next generation semiconductor devices. These challenges have exposed limitations with ammonia which could be overcome by replacing ammonia with hydrazine (N_2H_4). Purity of commercially available hydrazine has delayed its adoption. RASIRC Inc. has recently developed a new formulation of hydrazine called BRUTE® Hydrazine which is safer and meets purity requirements for semiconductor manufacturing. Prior to Brute Hydrazine, the body of technical data applicable to semiconductor processing was limited and scattered. This paper provides an overview of the growing activity in the thin film use of Brute hydrazine as well as early references on laboratory grade hydrazine for historical completeness.

Hydrazine



Ammonia



Increasing Need for More Reactive Nitrogen Sources

Emerging devices such Logic and Advanced Memory require high quality thin (5-20 Å) electrode and barrier films. Difficult thermal budget constraints are now being placed on well-known materials such as SiN_x, TiN_x and TaN_x.[1-3] Deposition temperature limitations have dropped to 350°C and below while very low resistivity (<150 micro-ohm/cm) for TiN and TaN must still be achieved. Although metal and nitride films grown using plasma assisted processes (PE-ALD) and (PE-CVD) at low temperatures exhibit enhanced properties, the damage induced by plasma on sensitive substrates is one of the common drawbacks,[4,5] as well as inability to support HAR or three-dimensional structures like horizontal vias and deep trenches.

III-V Nitride devices require a more reactive nitrogen source to reduce deposition temperatures and increase compositional stability.[6] Growth rates for InGaN films deposited with ammonia at reduced temperatures are prohibitively slow and grossly inefficient in ammonia usage. A more reactive nitrogen source can enable acceptable deposition rates at 500-650° C, where alloy stability is significantly increased and nitride source to precursor ratio can be reduced.

In addition to growing thin nitride films, hydrazine can also act as a reducing agent for several late transition-metals. This work is highly relevant to the use of hydrazine as a surface cleaning agent as well as a potential adder for metal ALD.[7]

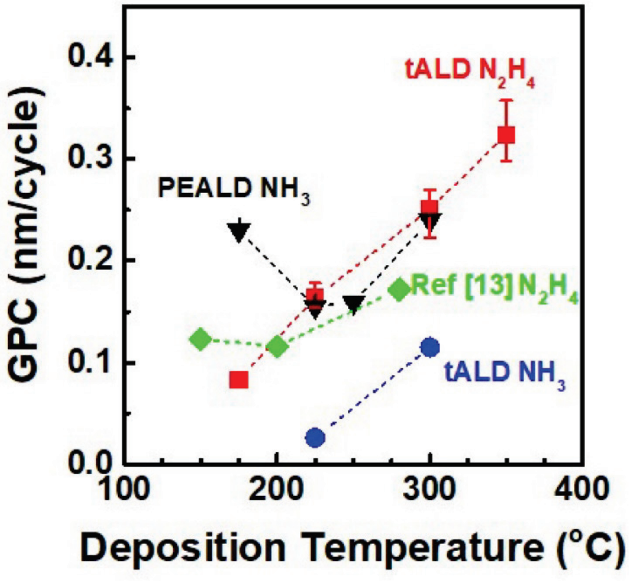


Figure 1: Low Temperature Thermal ALD growth rate with Hydrazine comparable to PEALD with Ammonia.

The following table provides primary references for the areas of hydrazine ALD/CVD relevant to Semiconductor device applications. Additional relevant references on related films are also included.

Precursor and Temperature	Film	Reference
Al surface nitridation 200C-450C	AlN	Taylor et.al. U.S. Patent 6465350, **2002**
TMA MOCVD 300C-400C	AlN	Fujieda, S. *et. al.* *Adv. Func. Mat.* **1996**, 6(3), 127-134
TDEAA 150C-225C	AlN	Abdulagatov, A.I. *et. al.* *Russian Microelectronics*, **2018**, 47(2), 118–130.
TMA 175C-350C	AlN	Jung, Y.C. *et. al.* *Materials* **2020**, 13, 3387; https://doi:10.3390/ma13153387
TDMAA 225C-400C	AlN	Ueda, S.T. *et. al.* *Appl. Surf. Sci.* **2021**, 554, 149656
BCl_3 , 350C	BN	Wolf, S. *et. al.* *Appl. Surf. Sci.* **2018**, 439, 689–696
Surface Clean 200C	Cu	Hwang, S.M. *et. al.* *ECS Trans.* **2019**, 92, 265
Surface Clean 100C-300C	Cu, Co	Hwang, S.M. “Effect of Surface Cleaning Efficacy on Vapor-Phase Cleaning of Cu and Co Using Anhydrous N_2H_4” *AVS ALD/ALE* ***2021*** *Session: Area Selective ALD* AS4-1
TMG, 400C-800C	GaN	Fujieda, S. *et. al.* *Jpn. J. Appl. Phys.* **1987**, 26, 2067-2071
TMG, TMI, 600C-900C Theoretical	GaN, InGaN	*Koukitu, A. et. al. phys. Stat. sol. (b)*, **1999**, 216(1), 707-712
TMG Theoretical	GaN	Goddard, W. *et.al.* *J. Phys. Chem. C* **2015**, 119(8) 4095–4103
[Ru(DMBD)$(CO)_3$] 200C. Metal Deposition	Ru	Cwik, S. *et. al.* *J. Vac. Soc. Sci. & Tech. A* **2020, 38**, 012402; https://doi.org/10.1116/1.5125109
SiH_4 550C-1050C	SiN	Yoshioka, S. *et. al.* *J. Electrochem. Soc.* **1967**, *114*, 962–964.
SiH_4/W hot wire 300C	SiN	Matsumura, H. **1989** Jpn. J. Appl. Phys. 28 2157
Si_2H_6, Si_3H_8 350C-550C	SiN	Kanoh, H. et al. “Low-Temperature Chemical-Vapor-Deposition of Silicon Nitride” *Journal de Physique IV Proceedings*, **1991**, 02 (C2), pp.C2-831-C2-837.
Si surface Nitridation. 300C-500C	SiN	*Abyss, J.A. et. al.* *J. AIChE* **1995**, *41*, 2282–2291
Si_2Cl_6 285C	SiN	Edmonds, M. *et. al.*, *J. Chem. Phys*. **2017,** 146, 052820; https://doi.org/10.1063/1.4975081
Si_2Cl_6 320C-410C	SiN	Kondusamy, A. *et. al.* “Low Temperature Thermal ALD of Silicon Nitride Utilizing a Novel High Purity Hydrazine Source”, *Electrochem. Soc. AiMES* ***2018****, Meet. Abstr.* G02-993
Si_2Cl_6 410C-650C	SiN	Le, D.N. *et al* “Thermal Atomic Layer Deposition of Silicon Nitride Using Anhydrous Hydrazine and Ammonia” AVS ALD **2021**, Session AF9.
TBTDET 150C-250C	TaN	Burton, B.B., *et. al.* *J. Electrochem. Soc.* **2008**, 155, D508
TBTDET 100C-300C	TaN	Wolf, S. *et.al.* *Appl. Surf. Science*, **2018**, 462, 1029-1035
TDMAT 200C	TiN	Wierda, D.A. *et. al.* *Electrochemical and Solid-State Letters*, **1999**, 2 (12) 613-615
$TiCl_4$ 200C-350C	TiN	Abdulagatov, A.I. *Ph.D. Thesis,* Univ. of Colorado, **2012***, UMI No. 3549153*
$TiCl_4$ 300C-400C	TiN	Wolf, S. *et.al.* *Appl. Surf. Science*, **2018**, 462, 1029-1035
$TiCl_4$ 300C-400C	TiN	Kuo, C.H. *et. al.* “Low Resistivity Titanium Nitride Thin Film Fabricated by Atomic Layer Deposition on Silicon” *AVS ALD 2021,* Session AM5-9.
$TiCl_4$ 250C-400C	TiN	Alvarez, D. *et. al.* “Comparative Study of Titanium Nitride ALD using High Purity Hydrazine vs Ammonia” *Electrochem. Soc.* ***2020*** *Meet. Abstr.* ***MA2020-02*** *1668*
BTBMW 300C	WN	Bernal-Ramos, K. *Ph.D. Thesis*, Univ. of Texas, Dallas, **2014**, *UMI No. 3668896*
BTBMW 250C-350C	WN	Le, D.N. *et.al.* “Atomic Layer Deposition of Nanometer Thick Tungsten Nitride Using Anhydrous Hydrazine for Potential X-Ray Optics Application” *AVS ALD/ALE* ***2021*** *Session: AF10-15*

Discussion on Specific Films

Titanium Nitride (TiN) is a critical film in semiconductor manufacturing. Commonly TiN is utilized as an electrode material as well as a low resistivity barrier layer. Early CVD work by Wierda demonstrated low temperature (50C-250C) TiN CVD by hydrazine and TDMAT. Optimal results were obtained when 1.9% hydrazine was combined with ammonia. This may be attributed to a different mechanistic pathway or ammonia dilution of oxygen containing contaminants. Wolf later demonstrated low temperature (300C) TiN ALD with the use of $TiCl_4$. This result was then optimized by Kuo in the same lab, where resistivities well below 180 micro-ohm/cm were achieved by reducing oxygen contamination in the film through improved hydrazine purity. A comparative study of Hydrazine vs Ammonia for $TiCl_4$ was reported by Taiyo Nippon Sanso, where the two nitrogen sources showed highly disparate growth rates and film properties. Hydrazine demonstrated viability at the 250C-400C range for low temperature semiconductor applications.

Silicon Nitride (SiN) is a widely used material in semiconductor devices. SiN is commonly used as an etch stop, a dielectric layer, an encapsulation layer, and as a barrier layer on organic devices. As early as 1967, hydrazine and Silane CVD was demonstrated at 550C. This work was then followed-up by Kanoh with higher silanes in the 350C-550C range. In a very interesting approach, Abyss demonstrated Si surface nitridation with hydrazine at temperatures as low as 300C. More recently, Edmonds cleverly used hydrazine/hexachlorodisilane ALD to place a thin SiN passivation layer on SiGe at 285C. Extensive studies have been carried out by the Kim group at UT Dallas in the range of 320C-650C. Below 400C, thermal ALD leads to films with good composition, but unfavorable low density and high wet etch rates. This can be overcome with addition of Argon plasma densification. At 480C and above, thermal ALD films are grown with high density, low wet etch rates, and reduced hydrogen incorporation. When compared to ammonia grown films in the same temperature range, the hydrazine ALD films are superior up to temperatures >600C where films properties become more similar.

Gallium Nitride and Indium Gallium Nitride (GaN, InGaN) grown with hydrazine have had few publications in the last 20 years despite interest in reduction of ammonia usage and poor indium incorporation. These films are central in LEDs and emerging power devices. Fujieda demonstrated that overall chemical consumption can be greatly reduced with hydrazine vs ammonia for GaN deposition in the 400C-800C range. Koukitu followed this up with a theoretical thermodynamic study showing how the use of hydrazine can reduce deposition temperature and stabilize composition for GaN and InGaN films. In 2015, Goddard elucidated the likely mechanisms for hydrazine vs ammonia is GaN deposition.

Though little has been published for GaN/InGaN deposition with hydrazine, viability for III/V materials can be inferred from work published for AlN ALD with hydrazine. Fujieda reported MOCVD with trimethyl aluminum (TMA) in the 300C-400C range. More recently Jung reported ALD with TMA as low as 175C and compared to ammonia in the 175C-350C range. Abdulagatov made use of the nitride-based ligands with TDEAA/hydrazine ALD in the 150C-250C range. In a similar approach using TDMAA, Ueda has reported the deposition of crystalline AlN films as low as 350C with thermal ALD. With the addition of Argon plasma densification, crystalline films can be obtained as low as 225C, where crystallinity in AlN was optimized at 400C.

Copper, Cobalt and Ruthenium can be reduced *in situ* by Hydrazine. Furst provided a detailed review on hydrazine as a reducing agent for organic compounds.[8] Recently Hwang reported an extension of this reactivity to Cu surfaces. Gas phase reduction of Cu oxides to Cu metal with hydrazine at moderate temperatures (100C-300C) was reported. Here, hydrazine is introduced in short pulses, analogous to an ALD reaction. A similar report for Cobalt has also been presented by Hwang. Cwik working in the Winter group has recently released data showing the ability to grow Ru metal using hydrazine as a reducing agent in Ru ALD at 200C. Here hydrazine was found to be advantageous over substituted hydrazine derivatives.

Conclusion

Hydrazine is emerging as a replacement for ammonia in low temperature applications. Recent examples of different production-worthy nitrides have been reported for both ALD and MOCVD films. These positive reports have led to an increasing level of interest within the scientific community looking for solutions to new device structures and increased density.

Contact the Author

The author is available for additional technical discussion. Contact RASIRC to schedule an appointment.

References

1. Burton BB, Lavoie AR, George SM (2008) Tantalum nitride atomic layer deposition using (tert-Butylimido) tris(diethylamido)tantalum and Hydrazine. J Electrochem Soc 155, D508

2. Alvarez, D.; Spiegelman, J.; Andachi, K.; Holmes, R.; Raynor, M.; and Shimizu, H. Enabling Low Temperature Metal Nitride ALD Using Ultra-High Purity Hydrazine: ET/ID: Enabling Technologies and Innovative Devices. 2017 28th Annu. SEMI Adv. Semicond. Manuf. Conf., Saratoga Spring, NY, USA, 2017, 426–430.

3. Hwang, S.M.; Kim, H.S.; Le, D.N.; Ravichandran, A.V.; Sahota, A.; Lee. J.; Jung, Y.C.; Kim, S.J.; Ahn, J.; Hwang, B.K.; Lee, L.; Zhou, X.; and Kim, J. Plasma-Enhanced Atomic Layer Deposition of Nanometer-Thick SiNx Films Using Trichlorodisilane for Etch-Resistant Coating. ACS Appl. Nano Mater. 2021, 4, 2558–2564. https://doi.org/10.1021/acsanm.0c03203.

4. Kim, H.; Oh, I.-K.; Review of Plasma-Enhanced Atomic Layer Deposition: Technical Enabler of Nanoscale Device Fabrication. *Jpn. J. Appl. Phys.* **2014**, *53*, 03DA01. https://doi.org/10.7567/JJAP.53.03DA01.

5. Mussroot, J. *et.al. Microelectronic Engineering 86 (2009) 72-77. http://dx.doi.org/10.1016/j.mee.2008.09.036*

6. Ravinder Kour *et al* 2020 *ECS J. Solid State Sci. Technol.* **9**, 015011

7. Hwang, S. M.; Peña, L. F.; Tan, K.; Kim, H. S.; Kondusamy, A. L. N.; Qin, Z.; Jung, Y. C.; Veyan, J.-F.; Alvarez, D.; Spiegelman, J.; et al. Vapor-Phase Surface Cleaning of Electroplated Cu Films Using Anhydrous N_2H_4. *ECS Trans.* **2019**, *92,* 265–271.

8. Furst, A. *et. al. Chem. Rev.* **1965**, *65*, 51–68.