Anhydrous Hydrazine Gas Delivery for Atomic Scale Fabrication

Low temperature, high reactivity nitride source for ALD and MOCVD processes

RASIRC BRUTE Hydrazine delivers anhydrous hydrazine (N_2H_4) gas into atomic layer deposition (ALD) processes in a repeatable method. BRUTE Hydrazine includes a vaporizer preloaded with hydrazine and a proprietary organic solvent.

By loading anhydrous hydrazine dissolved in proprietary solvent, it allows:

- Lower flammibility (Flash Point = 47°C)
- · Lower toxicity
- · Stable anhydrous, high purity solution
- For thorough example view Table 1

BRUTE Hydrazine can be used for a variety of metal nitride deposition processes at temperatures below 400°C:

- High purity, low resistivity TiN and other metal nitrides, using either metal organic or halogenated precursors
- Low temperature, thermal deposition of sidewall spacer/ etch stop (SiN)
- · High conformality, thermally deposited AIN
- TiN, Ru, Cu, and Co can be cleaned and reduced as an initiation step for passivation and ALD

RASIRC BRUTE Hydrazine Benefits

- Higher reactivity than NH₃ enables lower temperature ALD applications (200-400°C)
- Penetrates high aspect ratio structures to achieve uniform films
- Lower temperature allows for gate-first processing
- Replacement for N₂ plasmas for uniform SiN spacers and etch stops
- Proprietary delivery process, ensuring higher purity
- · Only semiconductor grade hydrazine on the market
- Higher growth rate than ammonia (NH₃)
- Vaporizer orders available for HVM 1.2L or R&D 250ml and 100mL ampoules (<u>Figure 1</u>)

Background

Plasma and ammonia have been used for growing nitride films in the past. These methods work poorly with next generation materials that require lower thermal budgets and feature high aspect ratio structures. Plasma cannot uniformly coat the side walls of high aspect ratio structures and can cause surface damage. Ammonia has limited reactivity at the low process temperatures required for new materials and metal-organic precursors.

Hydrazine has been proposed as a nitride source, but residual water in commercially available hydrazine leads to imperfect films containing oxygen. BRUTE Hydrazine is the only semiconductor grade hydrazine on the market, delivering a high concentration of hydrazine with minimal water. With BRUTE Hydrazine, thin nitride films can be effectively created at lower temperatures and higher purity in comparison to ammonia.

How it Works

BRUTE Hydrazine provides a stable, reliable flow of anhydrous hydrazine gas from a liquid source in a sealed vaporizer. The liquid source combines anhydrous hydrazine and a proprietary solvent that acts as a stabilizer.

The BRUTE Hydrazine vaporizer converts source liquid hydrazine to gas while leaving behind the non-volatile solvent. Hydrazine vaporizes into the headspace of the vaporizer. The resulting hydrazine gas is swept to process via vacuum draw or by an optional carrier gas that flows through the headspace.



Figure 1: BRUTE Hydrazine Ampoules

Table 1: BRUTE Hydrazine Physical & Chemical Properties Compared to Commercial Hydrazine

| | Hydrazine | BRUTE® Hydrazine | |
|---------------------------------------|---|---|--|
| Gas Molecule | E Z E | H N N | |
| Color | colorless | colorless | |
| Odor | ammonia, amine odor | ammonia, amine odor | |
| рН | strong base | 16.3, strong base | |
| Melting/Freezing Point | -2℃ | -25°C | |
| Boiling Point | 114°C | 116.2°C | |
| Flash Point (with ignition source) | 38°C | 46.7°C | |
| Flammability Limit | 1.8 – 100vol% | 3.3 − 51vol% (@125°C) | |
| Relative Density (g/cm³) | 1.0036 (@25°C) | 1.05 (@20°C) | |
| Vapor Pressure 16 torr (@25°C) | | 14 torr (@20°C) | |
| Water Solubility | miscible | miscible | |
| Auto Ignition Temperature | 270°C on glass | 217°C on glass | |
| Decomposition Temperature N/D | | 150.3℃ on SS | |
| TLV (ACGIH TWA) 0.01 ppm | | 0.01 ppm | |
| NFPA Rating | Health — 4 Flammability — 4 Instability — 3 | Health — 3 Flammability — 2 Instability — 1 | |

Table 2: BRUTE Hydrazine Product Grade Breakdown

| BRUTE Grade | Maximum Moisture Content* | Certification | |
|---------------------|---------------------------|-------------------------------------|--|
| BRUTE Hydrazine 7.0 | Less than 100 ppb | Each vessel verified for compliance | |
| BRUTE Hydrazine 8.0 | Less than 10 ppb | Each vessel verified for compliance | |

^{*}Contact RASIRC for testing parameters

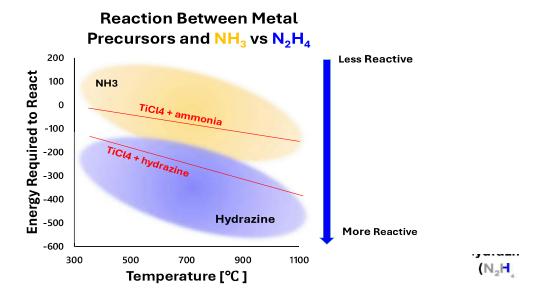


Figure 2: Hydrazine has a lower activation energy than ammonia, making it more viable for low temperature ALD reactions.

Bond Dissociation Energy

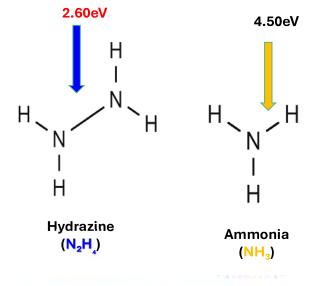
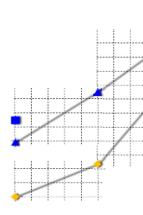


Figure 3: The low dissociation energy of hydrazine's nitrogen-nitrogen bond makes it more reactive and provides more amine groups than ammonia.



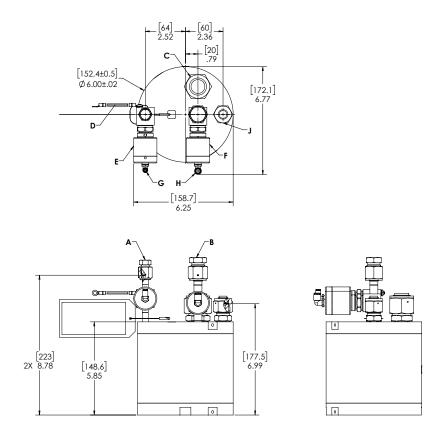


Figure 4: BRUTE Hydrazine 1000 Vaporizer. Vaporizer PN #100857. (mm denoted in brackets; corresponding inches denoted without brackets)

Table 3: Vaporizer Connections (1000)

| | Description | Size/Type |
|---|------------------------------|---|
| Α | Inert Gas Inlet | 1/4″ Female VCR |
| В | Process Gas Outlet | 1/2″ Female VCR |
| С | Fill Port | 3/4" Male VCR (DO NOT USE) |
| D | Grounding Cable | 18" cable with M5 terminal ring (included) - RASIRC PN: 201990 |
| Е | Inlet Valve | Normally Closed Pneumatic Valve (70 to 110 psig actuation pressure) |
| F | Outlet Valve | Normally Closed Pneumatic Valve (70 to 110 psig actuation pressure) |
| G | Inlet Valve Pneumatic Input | 5/32" Push Connect |
| Н | Outlet Valve Pneumatic Input | 5/32" Push Connect |
| J | Dip Tube | 1/2" Male VCR (DO NOT USE) |

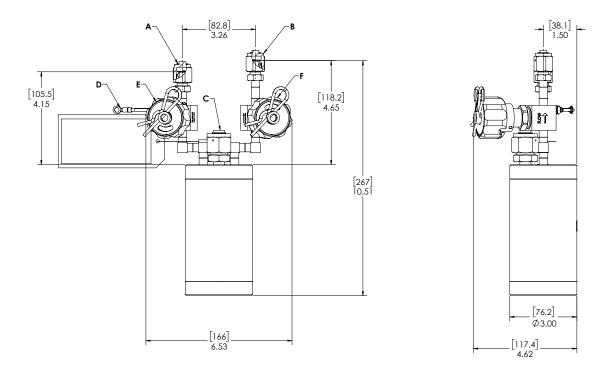


Figure 5: BRUTE Hydrazine 250 Vaporizer. Vaporizer PN #100834. (mm denoted in brackets; corresponding inches denoted without brackets)

Table 4: Vaporizer Connections (250)

| | Description | Size/Type |
|---|--------------------|--|
| А | Inert Gas Inlet | 1/4" Male VCR |
| В | Process Gas Outlet | 1/4" Male VCR |
| С | Fill Port | 1/2" Male VCR (DO NOT USE) |
| D | Grounding Cable | 18" cable with M5 terminal ring (included) - RASIRC PN: 201990 |
| Е | Inlet Valve | Manual LOTO Valve |
| F | Outlet Valve | Manual LOTO Valve |

^{*}VCR is a registered trademark of Swagelok

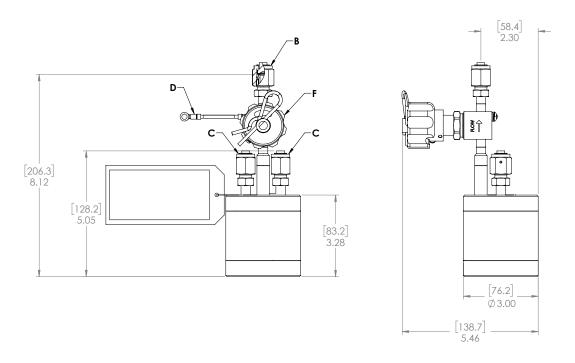


Figure 6: BRUTE Hydrazine 100 Vaporizer. Vaporizer PN #101300. (mm denoted in brackets; corresponding inches denoted without brackets)

Table 5: Vaporizer Connections (100)

| | Description | Size/Type |
|---|--------------------|--|
| В | Process Gas Outlet | 1/4″ Male VCR |
| С | Fill Port | 1/4" Male VCR (DO NOT USE) |
| D | Grounding Cable | 18" cable with M5 terminal ring (included) - RASIRC PN: 201990 |
| F | Outlet Valve | Manual LOTO Valve |

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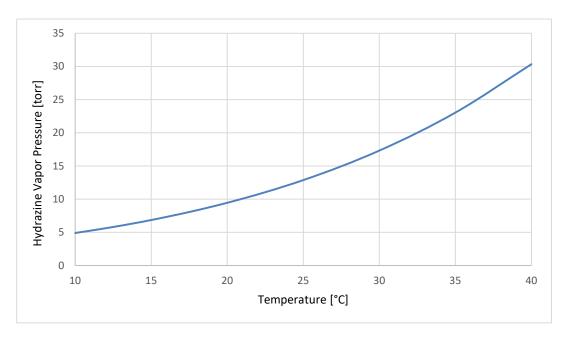


Figure 7: Theoretical vapor pressure curve of BRUTE Hydrazine.

Table 6: Facilities Specifications

| Operating Conditions | Temperature: 10-40°C (Heaters must have secondary interlock) Max Pressure: 1500 torr | |
|---|---|--|
| Carrier Gas | 1000 Vaporizer: 0-5 SLM (user supplied MFC) 250 Vaporizer: 0-500 sccm (user supplied MFC) 100 Vaporizer: vacuum draw only Filtered to 0.003 μm Purified to <1 ppb water, <1 ppm other contaminants Nitrogen or inert gas (NO OXYGEN) | |
| Vapor Pressure (See <u>Figure 7</u> for graph) | 31 torr at 40°C 13 torr at 25°C | |
| Tools & Supplies Required (1000g) | PPE (see SDS) (1) 1/4" SS VCR gasket no silver plating (Swagelok PN: SS-4-VCR-2-VS) (1) 1/2" SS VCR gasket no silver plating (Swagelok PN: SS-8-VCR-2-VS) 3/4", 5/8", 15/16", and 1 1/16" wrenches | |
| Tools & Supplies Required (250g) | PPE (see SDS) (2) 1/4" SS VCR gaskets no silver plating (Swagelok PN: SS-4-VCR-2-VS) 3/4" and 5/8" wrenches | |
| Tools & Supplies Required (100g) | PPE (see SDS) (1) 1/4" SS VCR gaskets no silver plating (Swagelok PN: SS-4-VCR-2-VS) 3/4" and 5/8" wrenches | |
| Pneumatic Gas (only applies to 1000 Vaporizer) | Clean Dry Air or Inert Gas Filtered to 0.1 µm Operating Pressure: 0.48 to 0.76 MPa (70-110 psig) | |

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Table 7: BRUTE Hydrazine Chemistry

| Name | Mass Loading | Chemistry Part Number | Vaporizer Part Number |
|----------------------|--------------|-----------------------|-----------------------|
| BRUTE Hydrazine 7.0* | 1000g | 110166-1000g7.0 | 100857 |
| BRUTE Hydrazine 7.0 | 250g | 110166-250g7.0 | 100834 |
| BRUTE Hydrazine 7.0 | 100g** | 110166-100g7.0 | 101300 |
| BRUTE Hydrazine 8.0* | 1000g | 110166-1000g8.0 | 100857 |
| BRUTE Hydrazine 8.0 | 250g | 110166-250g8.0 | 100834 |
| BRUTE Hydrazine 8.0 | 100g** | 110166-100g8.0 | 101300 |

^{*}Contact RASIRC to fill OEM specific 5-valve vessels

How to Order

To place an order for **BRUTE Hydrazine:** Contact RASIRC at sales@rasirc.com

About RASIRC

RASIRC products generate and deliver water vapor, hydrogen peroxide, and hydrazine gas to enable critical processes.



^{**100}g chemistry fills are not tested to certify compliance to the 7.0 or 8.0 moisture specs