3M™ Novec™ Engineered Fluids
For Vapor Drying of Semiconductor Wafers

Precision Drying

The nonflammable, “drop-in” alternative to IPA. Safe for delicate films and photoresists.

Solvent technology for drying of semiconductor wafers

The Marangoni effect describes the behavior of liquid on the wafer surface resulting from a surface tension gradient at the gas/liquid interface. This effect results in liquid on the wafer surface being pulled back into the immersion bath as the wafer is removed from the tank. Because IPA has a much lower surface tension (22 dynes/cm) than water (73 dynes/cm), when IPA from the vapor dissolves into the water at the gas/liquid interface, a surface tension gradient is created.

IPA in nitrogen has been the mainstay of wafer drying for nearly 20 years[1,2] but this process has limitations for advanced semiconductor devices. Due to the low flashpoint of IPA, it is necessary to limit the amount of IPA in nitrogen to less than 2% to maintain a nonflammable condition. It has also been reported[3,4] that IPA can remain on a wafer surface after a drying process, leaving a residue that could form Si-C bonds during a subsequent high temperature process, thereby degrading thin oxide reliability.

3M™ Novec™ Engineered Fluids offer an alternative to IPA, with physical properties that overcome current drying limitations. 3M™ Novec™ 7100 and 71IPA Engineered Fluids are both nonflammable and are compatible with materials of construction in IPA vapor drying systems. Novec fluids have low water solubility and high vapor pressures that prevent residue formation on surfaces subsequent to the drying step.

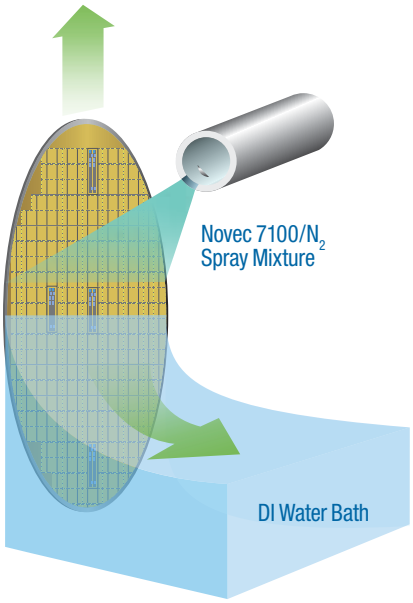
A sustainable, high-performance alternative to IPA

As semiconductor features become smaller, more complex and densely packed, there is growing concern about the use of aggressive solvents such as IPA in certain applications. Even the slightest amount of unwanted etching can cause serious defects that increase the chance of device failures and rejects. Applications such as multilayer photoresists and double patterning of photoresists have delicate features that are soluble in IPA. The use of solvents such as IPA can lead to critical dimension changes, adversely impacting device yield. Novec fluids do not etch photoresists.

Novec 7100 fluid, methoxy-nonafluorobutane ($C_4F_9OCH_3$), is a clean, colorless and low-odor fluid with an outstanding balance of safety, performance and environmental characteristics. A combination of unique physical properties, including low surface tension, low viscosity and high vapor pressure, makes Novec 7100 fluid ideal for use in surface tension gradient drying. And because Novec fluids are nonflammable, they can be used under a wider range of process conditions compared to IPA, which has flammability limits of 2% in air.

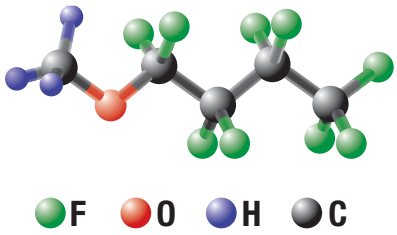
Novec 7100 fluid is low in toxicity. It also has zero ozone depletion potential and low global warming potential. Because it does not contribute to the formation of photochemical smog, it is exempt from the definition of a volatile organic compound (VOC).

Marangoni Dry Mechanism



Surface tension gradient draws water away from surface

Structure of Novec 7100 Fluid



Typical Physical Properties

	Novec 7100	Novec 71IPA	IPA
Boiling point (°C)	61	55	82
Vapor pressure (torr)	200	207	44
Surface tension (dynes/cm)	13.6	14.5	22
Viscosity (cPs)	0.58	.75	2.27
Density (g/ml)	1.52	1.48	0.79
Flashpoint (°C)	None	None	12
Flammability Limits (%) in nitrogen	None	None	<2%

As shown here, Novec 7100 and Novec 71IPA fluids (71IPA contains 4.5% w/w IPA) have lower surface tensions compared to IPA but significantly higher vapor pressures. Because of this and because they are nonflammable, Novec 7100 and 71IPA fluids can be run at much broader concentration ranges than IPA.

Environmental and Safety Properties and Exposure Guidelines

	Novec 7100
Exposure Guidelines (ppm) (8 hr. time-weighted average)	750
Acute LC_{50}, ppm	>100,000
Ozone Depletion Potential (ODP)	0.0
Atmospheric Lifetime, yrs.	4.1
Global Warming Potential (GWP)[1]	297
Hazardous Air Pollutant	No
VOC (U.S. EPA definition)	No

[1] GWP–100 year integrated time horizon; CO_2 = 1.0

For Environmental and Safety Properties and Exposure Guidelines for Novec 71IPA fluid please contact your 3M technical service representative.

3M™ Novec™ 7100 Engineered Fluid has been found to be acceptable as a cleaning and drying solvent by many major environmental regulatory bodies around the world. For instance, it is listed by the U.S. EPA as "Acceptable Without Restrictions." Novec fluids have zero ozone-depletion potential, short atmospheric lifetimes and are low in Global Warming Potential.

Process results

New research has shown that 3M™ Novec™ 7100 Engineered Fluid can address the performance limitations of IPA in wafer cleaning and drying – and can be used as a virtual drop-in replacement for IPA in surface tension gradient drying. Process development has been completed with Novec 7100 and 71IPA fluids. Novec 71IPA fluid is a blend of Novec 7100 fluid (95.5% w/w) and IPA (4.5% w/w).

In tests conducted by 3M, particle performance was evaluated using Novec 7100 fluid in a surface tension gradient vapor dryer. 200mm bare silicon wafers were processed in an automated wafer cleaning immersion system. Wafers were processed with a mixture of ammonium hydroxide, hydrogen peroxide and DI water (SC-1) followed by rinsing in DI water. The wafers were then dried with Novec 7100 fluid in nitrogen instead of IPA in nitrogen. Wafers defects were measured prior to and after drying on a KLA Tencor SP2 wafer inspection system, scanning defects with nominal sizes greater than or equal to 45nm. Figures 1 and 2 show the wafer maps before and after cleaning.

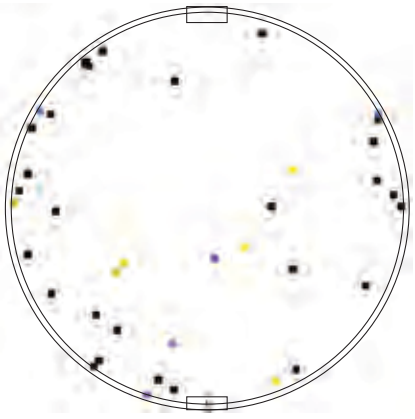


Figure 1. Pre-scan on SP2 showing 46 total defects.

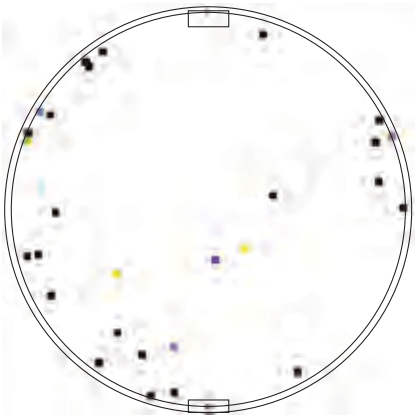
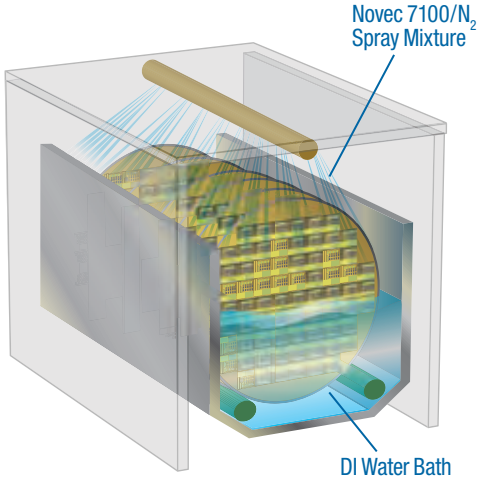


Figure 2. Post-scan on SP2 showing 37 total defects.

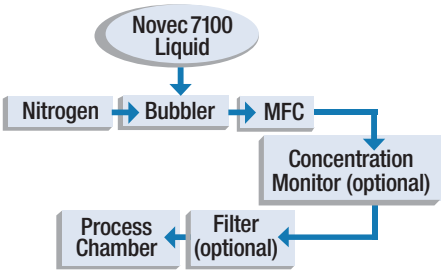
Converting from IPA to 3M™ Novec™ Engineered Fluids

Specific details will vary depending on the exact cleaning system used. The following are the steps necessary for a general cleaning system:

- Remove IPA via purging bubbler with filtered nitrogen
- Fill with Novec fluid and flush with filtered nitrogen
- Fill with Novec fluid
- System ready for testing

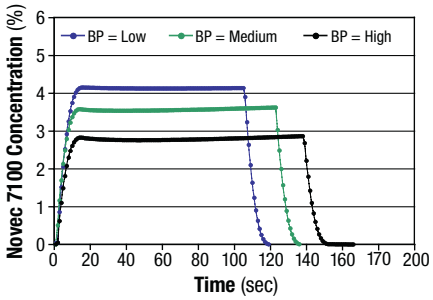


Vapor Generation



One common method to generate a vapor stream of drying agent in nitrogen is the bubbler method. A simplified configuration is shown here. In this configuration, nitrogen gas is bubbled into liquid Novec 7100 fluid, resulting in a mixture of Novec fluid and nitrogen that is then delivered to the process chamber. The nitrogen flow rate may be controlled by a mass flow controller (MFC) and/or a bubbler pressure (BP) regulator. Some systems offer a nitrogen heater to raise and control incoming nitrogen temperature.

Nitrogen temperature, nitrogen flow rate and bubbler pressure are variables for controlling the final gas concentration. The optional concentration monitor measures the amount of Novec 7100 fluid used during a wafer drying sequence.



Note: BP refers to the bubbler pressure setting used to control Novec 7100 fluid in a nitrogen carrier gas. Increasing the bubbler pressure results in a decrease of Novec 7100 fluid in the vapor phase.

Resources

3M™ Novec™ Engineered Fluids are supported by global sales, technical and customer service resources, with technical service laboratories in the U.S., Europe, Japan, Taiwan, Korea and Singapore. Users benefit from 3M's broad technology base and continuing attention to product development, performance, safety and environmental issues. For additional technical information on Novec fluids in the United Sates, or for the name of a local authorized distributor, call 3M Electronics Markets Materials Division: 800-810-8513.

References

1. A. F. M. Leenaars, J. A. M. Huethorst, J. J. van Oekel, *Marangoni Drying: A New Extremely Clean Drying Process*. American Chemical Society, 1990. Volume 6, p. 1701-1703.
2. J. Marra, J. A. M. Huethorst, *Physical Principles of Marangoni Drying*. American Chemical Society, 1991. Volume 7, p. 2748-2755.
3. K. Miya, T. Kishimoto, A. Izumi, *Non-IPA Wafer Drying Technology for Single-Spin Wet Cleaning*. Electrochemical Society Proceedings, 2003. Volume 26, p. 57-63.
4. K. Motai, T. Itoga, T. Irie, *The Effect of Isopropyl Alcohol on the Electrical Characteristics of Thin Oxide*. Japanese Journal of Applied Physics, 1998. Volume 37, p. 1137-1139.

The 3M™ Novec™ Brand Family

The Novec brand is the hallmark for a variety of patented 3M products. Although each has its own unique formula and performance properties, all Novec products are designed in common to address the need for safe, effective, sustainable solutions in industry-specific applications. These include precision and electronics cleaning, heat transfer, fire protection, lubricant deposition and several specialty chemical applications.

3M™ Novec™ Engineered Fluids • 3M™ Novec™ Aerosol Cleaners • 3M™ Novec™ 1230 Fire Protection Fluid • 3M™ Novec™ Electronic Coatings • 3M™ Novec™ Electronic Surfactants

United States
3M Electronics Markets
Materials Division
800 810 8513

China
3M China Ltd.
86 21 6275 3535

Europe
3M Belgium N.V.
32 3 250 7521

Japan
Sumitomo 3M Limited
813 3709 8250

Korea
3M Korea Limited
82 2 3771 4114

Singapore
3M Singapore Pte. Ltd.
65 64508888

Taiwan
3M Taiwan Limited
886 2 2704 9011

Product Use: All statements, technical information and recommendations contained in this document are based on tests or experience that 3M believes are reliable. However, many factors beyond 3M's control can affect the use and performance of a 3M product in a particular application, including conditions under which the product is used and the time and environmental conditions in which the product is expected to perform. Since these factors are uniquely within the user's knowledge and control, it is essential that the user evaluate the 3M product to determine whether it is fit for a particular purpose and suitable for the user's method of application.

Warranty and Limited Remedy: Unless stated otherwise in 3M's product literature, packaging inserts or product packaging for individual products, 3M warrants that each 3M product meets the applicable specifications at the time 3M ships the product. Individual products may have additional or different warranties as stated on product literature, package inserts or product packages. 3M MAKES NO OTHER WARRANTIES, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO, ANY IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE OR ANY IMPLIED WARRANTY ARISING OUT OF A COURSE OF DEALING, CUSTOM OR USAGE OF TRADE. User is responsible for determining whether the 3M product is fit for a particular purpose and suitable for user's application. If the 3M product is defective within the warranty period, your exclusive remedy and 3M's and seller's sole obligation will be, at 3M's option, to replace the product or refund the purchase price.

Limitation Of Liability: Except where prohibited by law, 3M and seller will not be liable for any loss or damage arising from the 3M product, whether direct, indirect, special, incidental, or consequential regardless of the legal theory asserted, including warranty, contract, negligence or strict liability.

3M

Electronics Markets
Materials Division
3M Center, Building 224-3N-11
St. Paul, MN 55144-1000
www.3M.com/novec
1-800-810-8513

Please recycle. Printed in USA.
Issued: 5/09 © 3M 2009.

All rights reserved. 6761HB

60-5002-0400-7

3M and Novec are trademarks of 3M.
Used under license by 3M subsidiaries and affiliates.