The Semiconductor Industry Association (SIA) submits these comments to the U.S. Environmental Protection Agency (EPA) on the Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal: N-Methylpyrrolidone (NMP) (CAS number 872-50-4).

SIA is the trade association representing leading U.S. companies engaged in the design and manufacture of semiconductors. Semiconductors are the fundamental enabling technology of modern electronics that has transformed virtually all aspects of our economy, ranging from information technology, telecommunications, health care, transportation, energy, and national defense. The U.S. is the global leader in the semiconductor industry, and continued U.S. leadership in semiconductor technology is essential to America’s continued global economic leadership. More information about SIA and the semiconductor industry is available at www.semiconductors.org.

As discussed in EPA’s scoping document on NMP, the semiconductor industry uses NMP in its manufacturing processes. Semiconductor fabs are located in 21 states throughout the country (see Attachment 1). This document provides a summary of our industry’s manufacturing process, our uses of NMP, and information on the conditions of use relevant to EPA’s scoping exercise.

I. Background on Semiconductor Manufacturing

A. Overview of the Semiconductor Manufacturing Process

Semiconductor device fabrication is the process used to create integrated circuits that are present in electrical and electronic devices. An overview of semiconductor manufacturing process can be found in OECD emissions scenario documents.1 The fabrication process (see Figure 1) begins with a wafer of semiconductor material varying in size from 150-300mm in diameter and includes a sequence of photographic and chemical processing steps during which electronic circuits are gradually created on the wafer substrate. These electrical circuits are made one layer at a time by the combination of putting a layer on the surface of the wafer and using a patterning process to then remove designated parts of the layer to leave behind a specific shape. Advanced semiconductors may contain billions of transistors on a layer of silicon the size of a square centimeter, so manufacturing must be rigorously controlled and conducted with great precision to achieve features at the nanoscale.

The production of semiconductors is reliant on the use of photolithography chemical formulations in specialized manufacturing tools that pattern integrated circuits with line widths that may be only 10 nanometers or less in width. (As a point of reference, a water molecule is

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roughly 0.5 nanometer in diameter.) Thus, photolithography requires a highly precise and
exacting technology that is entirely dependent on the use of very precise chemical formulations
in highly specialized manufacturing tools. Photoresist formulations are typically comprised of 5
to 10 or more individual chemical components, including a polymeric resin, radiation sensitive
compound, and solvent that must work together in concert to receive a light image and delineate
the desired integrated circuit pattern on the wafer surface.

The patterning process, which is one of the most critical aspects of wafer fabrication as it sets
the dimensions of the device, consists of a photolithography step, etching step, and stripping
step.

- During the photolithography step, the wafer is coated with a layer of photoresist and
  subsequently covered with a mask that defines the specific patterns to be retained or
  removed in subsequent processes. In a typical processing scheme, the photoresist
  polymer formulation is applied to a spinning wafer, and then subjected to a pre-exposure
  bake to drive off a proportion of the solvent to impart dimensional stability to the film.
- The coated wafer substrate is then exposed thru a patterned photomask, with actinic
  radiation from a light source of specified wavelength. Reflectivity of the semiconductor
  material during light exposure can be problematic. To absorb light and reduce
  reflections during the exposure, a layer of anti-reflective coating is typically utilized. An
  anti-reflective coating applied after the photoresist is referred to as a top antireflective
  coating (TARC) agent and an anti-reflective coating applied before the photoresist is
  referred to as a bottom anti-reflective coating (BARC) layer.
- After exposure, the coated wafer substrate undergoes a development process whereby
  the previously exposed regions are selectively dissolved and removed from the
  photoresist film. This leaves the wafer surface with a patterned coating of photoresist,
  where in selected regions the resist material is completely removed, and where in the
  remaining areas the photoresist forms a protective coating. The open areas of the
  substrate may then be subjected to additive processes like physical vapor deposition,
  chemical vapor deposition, diffusion, ion implant or plating; or subtractive process like a
  plasma etch.
- In deposition, thin layers or films are added to the wafer surface to change its electrical
  properties or to serve as masks.
- In etching, specific areas of a deposited film are chemically removed so that an
  underlying material is exposed or another material may be deposited. Etching may be
  performed in a wet process using solutions of acids, bases or oxidizers, or in a dry
  process using various gases in a plasma.
- In Doping/Diffusion, atoms with one less electron than silicon (such as boron) or one
  more electron than silicon (such as phosphorus) are introduced into the area exposed by
  the etch process, to alter the electrical character (conductivity) of the silicon.
- Subsequent to the etch or deposition process, the residual photoresist and anti-reflective
  coating must be removed from the wafer surface. This final step, known as the
  photoresist strip step, must be accomplished in a manner that completely and uniformly
  removes the residual photoresist, without adversely impacting the surfaces of the
  materials comprising the underlying wafer substrate (Dean et al, 1992; Lee et al, 1994).
  One method to remove the photoresist and BARC involves the use of a liquid NMP
  solvent. Additional information on the use of NMP in semiconductor manufacturing is set
  forth below.
- Cleaning occurs in various parts of the process flow and is also an important part of the
  wafer fabrication process as semiconductor devices are highly susceptible to various
kinds of contamination such as particles, metal ions, chemicals, bacteria, and airborne molecular contaminants.

- **Dielectric Deposition and Metallization** - Following completion of the "front end," the individual devices are interconnected using a series of alternating metal depositions and dielectric films, with their respective patterning.
- **Passivation** - After the last metal is patterned, a final insulating layer (passivation) is deposited to protect the circuit from damage and contamination. Openings are etched in this film to allow access to the top metal later by electrical probes and subsequent wire bonds.
- **Assembly** - A diamond saw slices the wafer into single chips. Sizes can vary from 1 x 1 mm to 76 x 56mm. Each chip is then assembled into an appropriate package that provides the contact leads for the chip. In one type of interconnect a wire bonding machine attaches wires, a fraction of the width of a human hair, to the leads of the package.

*Figure 1. Integrated Circuit Production Process Flow Diagram from #EPA 440/1-83/075 (1983) updated with information from 1998 Guidance Memo and current semiconductor manufacturing processes.*
B. Semiconductor Manufacturing – Fab Cleanrooms and Equipment

The fabrication of semiconductors is conducted in specialized buildings known as “fabs” that involve the use of cleanrooms, and a hierarchy of design features that isolate workers and wafers from chemicals. The fab cleanroom design approach protects manufacturing personnel, and is also critical to semiconductor wafer product quality. Figure 2 illustrates schematically the design of a typical 300mm fab. The fab consists of a cleanroom where the manufacturing operations are conducted, and an isolated ancillary space which contains chemical and air handling equipment, emission controls, and other infrastructure, and which is often located in an area within the building known as a “sub-fab”.

The fabrication of an integrated circuit on a silicon wafer involves a sequence of hundreds of additive, subtractive, photolithography, and cleaning steps that is accomplished by shuttling wafers between specialized manufacturing “tools” within which the individual unit operations are conducted on the wafer. The manufacturing tools, engineers and operators are located within the cleanroom, but the tools are supplied with chemicals, power, and other utility services from the subfab or other ancillary space.

As also indicated on Figure 2, fresh air is brought into the fab thru an air conditioning unit that controls the fab air temperature and humidity, and recirculated through ultra-low particulate air (ULPA) filters before being exhausted to the building exterior. In a typical 300mm wafer manufacturing fab built in 2000, the entire volume of air in the fab cleanroom is replaced every 7 minutes, and the entire volume of air in the cleanroom is recirculated through the ULPA filters at a rate of once every 0.64 minute. This extensive level of air circulation and replacement provides an exceptional level of fab air cleanliness.

*Figure 2. Schematic of airflow in a typical Fab.*
In all semiconductor manufacturing, regardless of the level of sophistication of the factory, equipment systems operate with intrinsic controls that minimize or eliminate chemical liquid or vapor exposure potential during normal equipment operations. The equipment must be maintained frequently, which requires the operating parts of the equipment to be placed in stand-by (non-operating mode) and the opening of protective enclosures. During these maintenance activities, workers utilize protective equipment to reduce the potential for employee exposure. Older manufacturing equipment (150mm and older) is generally less sophisticated with varying degrees of protective equipment controls. In those cases, more PPE is used to protect the employee during operations. Even in these cases a high degree of engineering controls are used to ensure employee exposure is minimized including exhaust, interlocks, and monitoring. In all cases where engineering controls are not available, administrative controls are used to minimize the potential for exposure.

During fabrication, the wafers are highly susceptible to even minute amounts of contamination, and so the wafers are moved in and out of tools by robotics, placed robotically into enclosed boxes, known as front opening unified pods (FOUPs), and shuttled between tools via a computer controlled, automated transport system. Figure 3, shows manufacturing tools aligned along one of many corridors within a typical 300mm fab, and Figure 4 an automated transport system that shuttles FOUPs between tools.

Figure 3. Photo of typical 300mm wafer manufacturing cleanroom.
II. Uses of NMP in the Semiconductor Industry

A. Overview of Semiconductor Uses of NMP

In the highly-controlled semiconductor manufacturing process, the semiconductor industry uses NMP in manufacturing for three main purposes:

1. Dedicated solvent in certain photolithography formulations, including photoresists, Bottom Anti-Reflective Coatings (BARC) and polyimides
2. Solvent pre-wet of wafers prior to application of spin on polymer
3. Component of photoresist stripper formulations.

In addition to the main uses of NMP, this chemical may also be used in similar photolithography applications such as mask making and related manufacturing processes that involve the attachment of the chip to chip packaging. Small quantities of NMP are used in analytical laboratories such as failure analysis labs for organic surface deconstruction to inspect device features. Lab use occurs in exhaust hoods with appropriate personal protective equipment such as gloves and eye protection.

It is important to emphasize that there is no NMP left in the final product, which is a finished wafer that is then cut into individual semiconductor devices for assembly, test, and packaging.

1. Dedicated solvent in formulations

The industry uses NMP as a dedicated solvent in formulations such as polyimides and Bottom Anti-Reflective Coatings (BARC). NMP solvates the active material. BARC is deposited on the
semiconductor wafer in a fully enclosed process tool at ambient temperature and pressure. Wafers coated with BARC are baked at elevated temperature in a fully enclosed tool. Polyimide deposition occurs in a semi-closed or fully enclosed process tool (process operated at atmospheric pressure and temperature from room temperature to elevated temperature). Wafers coated with Polyimide are baked at ~380°C in a fully enclosed tool. No NMP is present in the final polyimide film.

2. Solvent pre-wet on wafers

The quantity of photoresist dispersed in the wafer can be reduced if the wafer surface is pre-wet with a solvent such as NMP that is compatible with the solvent used in the resist. Using the casting solvent contained in the resist for pre-wetting prevents process variability and ensures uniform film thickness and composition.

3. Cleaning of organic contamination and removal of organic layers

As part of the semiconductor manufacturing process, manufacturers use NMP for resist removal or the stripping of metal covered silicon layers, post metal dry etch clean, and the removal of other organic matter on wafers/devices. Depending on the process requirements, NMP is used in either pure form or in specially formulated mixtures. The majority of processes occur in automated and fully or semi-enclosed systems. Maintenance activities are conducted by workers wearing PPE.

B. Importance of NMP in Semiconductor Manufacturing

The chemical NMP is an essential component in many of these steps. In one application, NMP is used as a solvent in photoactive polymer systems, wherein it must be chemically compatible with the polymer and photosensitive compounds, provide exactly the right viscosity, cohesion, and adhesion for the photo resist formulation to spin coat the wafer, volatize from the applied resist to the desired extent during the bake step, retain the necessary transparency to the photoresist during the light exposure step, facilitate the activation of the photoreactive compounds, and be compatible with the development step. In some applications NMP is used to pre-wet the wafer in order to facilitate an efficient coating of the wafer surface with the photoresist. Another important application is in the photoresist strip step where depending on the particular photopolymer formulation, NMP may be essential to effectively dissolving and removing the residual photoresist step prior to the next cycle of patterning.

In resist removal and cleaning, NMP is a very efficient polar solvent and is capable of removing both organics (resists and organic residues), and polymers generated in dry etch. It can be combined well with other active cleaning agents (removing other impurities such as metals and other polymers) and it is compatible with metallic layers (Al, W, Cu). Thus, NMP removal and cleaning processes are robust and have a wide process window so that a single tool and chemistry can be used for a broad spectrum of process conditions.

In its use as a dedicated solvent in formulations such as polyimides and bottom antireflective coatings (BARCs), NMP has desirable physical and chemical properties. It has excellent wetting and evaporation characteristics. It is extremely suitable for polyimide deposition (tuned processing) because its chemical structure is similar to that of polyimides. Polyimides are applied as protection layer in discrete devices and particular sensors, where essential parts of
the device structure must be directly accessible to the outside world. As a solvent, NMP affords reproducibly uniform and hermetically closed polyimide protection layers.

The use of NMP in semiconductor photolithography polymer and resist strip formulations is the product of a long and thoughtful research and development process that encompasses a considerable body of intellectual property (Dean et al, 1993; Quinlen et al, 2014, and references therein).

The molecular structure and physicochemical properties of NMP are unique, and enable it to work in concert with the other components of a carefully matched photoresist systems (Saint Clair and Saint Clair, 1987). In particular, NMP is a polar organic chemical, with very low vapor pressure (0.34 mm Hg), comparatively high flash point (96 C), low freezing point (–23.6 C) and high boiling point (204.3 C). The molecular structure of NMP provides a particular combination of dispersive, polar, and hydrogen bonding forces as quantified by its Hanson solubility parameters, that enable unique interaction with certain polymers and other ingredients in photoresists (Cowie, 1994). Solvents and polymers which have similar solubility parameters are likely to be mutually soluble, and provide an important indication of efficacy. Although NMP has recognized toxicity characteristics, its physicochemical properties are conducive to carefully controlled use, that minimizes the potential for human exposure or environmental emissions. The vapor pressure of NMP at 20 C is 0.34 mm Hg (torr) (45.33 Pa), which makes it a relatively low volatility compound. By comparison, the vapor pressure of water at 20C is 17.5 mmHg (2,333.1 Pa), and tetrachloroethylene is 14 mm Hg. Relative to butyl acetate, a standard benchmark, NMP has an evaporation rate of only 0.06. Similarly, the relative high flash point (96 C), and ignition temperature (270 C) helps mitigate fire hazard.

C. Absence of Alternatives for Semiconductor Uses of NMP

The semiconductor industry has previously used a number of alternative chemicals in photoresist and photoresist stripping applications such as dimethylformamide, dimethylacetamide, certain glycol ethers, and halogenated solvents. Each of these chemicals, however, raise concerns about toxicity potential and other concerns. These other chemicals are described in the patent and general literature. It is well known, for instance, that NMP was selected as a more benign alternative to methylene chloride and other halogenated solvents for many applications (Detinger et al, 2002; Poet et al, 2016). As described below, however, NMP provides unique functionality, and at this time there are no proven sustainable NMP-free alternatives that yield the same performance in many critical applications.

Typical photoresist strippers are comprised of complex formulations that include some combination of organic solvents, reducing agents, oxidizing agents, organic bases, and corrosion inhibitors among others (Quinlan et al, 2014). The various alternatives which have been used include halogenated hydrocarbons, such as methane chloride and tetrachloroethylene; amines derivatives, such as dimethylformamide and dimethylacetamide; glycol ethers such as ethylene glycol monomethyl ether; and ketones such as methyl ethyl ketone and acetone, among others (Dean et al, 1992). The suitability of a particular alternative depends on the effectiveness and compatibility of the solvent for the particular photoresist polymer system; compatibility with the underlying substrate material; and the ease with which occupational exposures, environmental discharges, and safety risks can be controlled. Some NMP based strippers, for instance were developed expressly to replace conventional halogenated solvent based strippers like methylene chloride and tetrachloroethylene which have high volatility and toxicity, and for which occupational exposure and emissions controls, and disposal are difficult (Detinger et al, 2002). In contrast, NMP has relatively low volatility making it
easier to control fugitive emissions, is readily destructed in conventional thermal oxidizers used to treat exhaust emissions, and is relatively biodegradable. Likewise, some alternative organic solvents like the ketones have high volatility, low flash points. Acetone, for instance has a boiling point of 56 C, and a flashpoint of -20 C, and thus is inherently more difficult to control vapor emissions and fire hazard.

Given the unique chemical functionality of NMP, in conjunction with the exceptional complexity of its interaction with photoresist formulations, the development and qualification of more benign alternatives would take many years, presuming that it is feasible. Moreover, it is likely that there would be no single solution.

III. Controls in Semiconductor Manufacturing

A. Controls Employed with Uses of NMP

Each of the uses of NMP in the semiconductor industry are subject to significant levels of control. The controls employed in the semiconductor industry associated with each use is summarized in Table 1. The wafer fabrication activities listed in this table would normally be conducted within robotically operated enclosed tools, where engineering controls (chamber containment) provide exposure control during normal operations.

Table 1. Summary of general NMP use in the semiconductor wafer manufacturing processes.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>NMP use</th>
<th>Purpose</th>
<th>Exposure control(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface preparation</td>
<td>Yes</td>
<td>Clean and dry wafer surfaces</td>
<td>Enclosed chamber within robotically operated tool</td>
</tr>
<tr>
<td>Photolithography</td>
<td>Yes</td>
<td>Solvent for certain photoresist polymer formulations, including Bottom Anti-Reflective Coatings (BARC)</td>
<td>Enclosed chamber within robotically operated tool</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solvent pre-wet of wafers prior to application of spin on polymer</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solvent for polymeric polyimide dielectrics</td>
<td></td>
</tr>
<tr>
<td>Etch</td>
<td>No</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Strip</td>
<td>Yes</td>
<td>Component of photoresist stripper formulation</td>
<td>Enclosed chamber within robotically operated tool</td>
</tr>
</tbody>
</table>

\(^2\) Figures 3, 4, and 5 are representative photographs of the enclosed tools and the clean rooms in which the tools are used.
1. Processing in Enclosed Equipment

NMP is used in semiconductor manufacturing in wafer fabs and assembly-packaging operations. Semiconductor manufacturing tools are typically designed, built, and certified to industry specifications for environmental, health, and safety controls, known as SEMI S2.³ Relevant tool design requirements that protect semiconductor workers include (SEMI S2-0703a, April 11, 2003 version):

- Chemical emission to the workplace environment during normal equipment operation must result in ambient air concentrations that are less than 1 % of the relevant Occupational Exposure Limit (OEL) in the worst-case personnel breathing zone.
- Chemical emissions during maintenance activities must result in ambient air concentrations that are less than 25 % of the relevant Occupational Exposure Limit (OEL) in the worst-case personnel breathing zone during maintenance activities.
- Chemical emissions during equipment failures must result in ambient air concentrations that are less than 25 % of the relevant Occupational Exposure Limit (OEL) in the anticipated worst-case personnel breathing zone during a realistic worst case system failure.

Typically, the conformance of a particular tool with the SEMI S2 standards is demonstrated by third party testing at the time a tool is designed and offered for sale. Often the occupational exposure conformance testing validation that is provided at the time of tool purchase, has been conducted using a tracer gas test such that the extent of chemical isolation between the tool chamber and operator can be bridged to any specific chemical that is used in the tool. A typical 300mm coater/developer tool is shown in Figure 5.

*Figure 5. Typical coater/developer tool in which NMP solvent pre-wet and NMP containing photoresist application would take place.*

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³ SEMI (Semiconductor Equipment and Materials International) is a global industry association of companies that voluntary technical standards for the design of semiconductor tools, and equipment, and which many companies institute as a mandatory requirement in their tool procurement specifications.
B. Storage and Delivery

NMP-containing formulations can be purchased and stored in various size containers from 1 liter bottles to bulk tanks. Containers are stored in segregated storage areas in accordance with local fire code requirements. Regardless of the container size, NMP is stored and delivered into the manufacturing area using secondary containment and methods to prevent personnel exposure. For example, at one fab that uses large quantities of NMP (in excess of 100,000 lb/yr), bulk NMP is delivered by tanker truck and off loaded into double contained tanks which typically use a nitrogen blanket and conservation vent to prevent NMP vaporization from the tank. At this fab, NMP is transferred to process tools in double contained transfer lines, which are equipped with leak detection.

C. Waste Management and Controls

Used or waste NMP from semiconductor operations, which also contains residual photoresist, is either collected in a segregated collection system or mixed with other solvent-type waste streams in a mixed collection system. Waste NMP is usually managed offsite and is generally treated by thermal oxidation or blended for fuel recovery. Some sites use distillation to recover NMP from the waste stream. Residual quantities of NMP are also discharged as part of industrial wastewater streams, which undergo elementary neutralization prior to discharge to a publicly owned treatment works (POTW) for further treatment. The NMP in the wastewater streams is typically from rinse process steps in manufacturing where the NMP is a small component of a wastewater stream. Wastewater discharges are required to meet permit limits, which can be for NMP specifically or as part of a COD limit.

As discussed in the OECD document, fugitive emissions of NMP are expected to be minimal. Air emissions for tools using NMP are exhausted to dedicated solvent exhaust systems. In high volume manufacturing fabs, solvent exhaust emissions are typically controlled by abatement systems such as thermal oxidizers to ensure compliance with air permit limits for VOCs.

D. Worker Exposure

Semiconductor fabs employ stringent and often redundant controls to minimize the exposure of workers to chemicals of concern. The typical risk management measures and safety practices deployed at fabs to prevent NMP releases and worker exposure include the following:

- Chemical storage, dispense and handling
  - Segregated Storage per local codes
  - Automatic, ventilated, and fully enclosed supply and discharge systems
  - Personal protective equipment (PPE) worn during drum, canister and bottle change out (chemical resistant gown and chemical protective gloves, safety glasses, chemical resistant arm protection, and shoes)
  - Bottles are only used for small uses with PPE
  - General ventilation and local exhaust ventilation

- Routine fab, bumping or assembly manufacturing operations
  - Process tools are located in the clean room where a stringent clean regime is maintained as a requirement for production which also ensures no chemical releases
- Closed systems (wet benches with lids and local exhaust ventilation or fully closed spray processors)
- Continuous local exhaust ventilation under alarm
- Manual or automated chemical delivery

- Lab use – manual bath in vent hood, PPE
- Invasive maintenance
  - Tool emptied and purged prior to invasive maintenance
  - Maintenance occurs at room temperature under local exhaust ventilation. Wearing of proper PPE as determined at the local site level.
- Fabs employ professional industrial hygienists that evaluate and control potential workplace exposures.

Based on SIA member information available at this time, semiconductor workers are not exposed to levels above recommended limits. Attachment 2 sets forth confidential data compiled by the European Semiconductor Industry Association (ESIA) and submitted to the European Chemicals Agency (ECHA) in 2013. SIA believes that these data are representative of the exposure levels present in fabs in the U.S. SIA members are in the process of compiling IH monitoring data and will provide to EPA at a later date.

IV. Conclusion

The semiconductor industry uses NMP for specialized uses, where there are no known substitutes that meet our stringent performance requirements, and these uses are subject to extensive controls. As EPA continues its work on the scoping of NMP and the future risk evaluation, we look forward to working closely with EPA to properly characterize the uses and potential risks in the semiconductor industry. Given the conditions of use present in our industry, we call on EPA to exercise its authority to remove uses of NMP in the semiconductor industry during the scoping step of the risk evaluation process.
References


Attachment 2

[Note: The information contained in Attachment 2 has been designated as confidential business information (CBI) and is omitted from the public version of these comments.]