The Growth and Characterization of Aluminum Nitride (AlN) Nanowires

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Dr. Usha Philipose
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The Growth and Characterization of Aluminum Nitride (AlN) Nanowires

Abstract

Nanotechnology is a rapidly growing field, with nanowires driving the advancement of our modern electronics. Aluminum nitride (AlN) wires stand out from other group III-V semiconductors due to their large piezoelectric coefficient and high thermal conductivity. Due to the nature of aluminum (Al), growth of these wires has proven problematic, and optimizing their different characteristics even more so. I intend to grow AlN wires at a lower temperature than other researchers have in order to prevent some of the defects from forming. I will also be growing on sapphire, a substrate better suited to the well arrayed growth of the wires than silicon (Si).

Introduction

Nanowires are at the forefront of advancement in electronics due to their versatility and cost effectiveness when compared to bulk materials.\(^1\) Aluminum nitride (AlN) nanowires have many interesting properties in comparison to other wide bandgap group III-V nitride semiconductors. They have a comparatively high thermal conductivity at low temperatures and a high resistivity along with the largest piezoelectric coefficient of the group. AlN nanowires are therefore very attractive for use in electromechanical and optoelectronic devices.\(^2\) They have shown promise in surface acoustic wave devices, such as those used in cell phones to keep unwanted frequencies out, and in the touch screen displays that have become commonplace in our electronics. AlN nanomaterials, including wires, have been found to trap hydrogen very well because of their structural makeup. The growth of AlN nanowires however can be difficult to achieve because of the difference in the free energy of formation of aluminum oxide (Al\(_2\)O\(_3\)) versus that of AlN, making Al\(_2\)O\(_3\) the favored product. At a growth temperature of 773 K, the
Gibbs free energy of formation for Al₂O₃ is -1432.6 while that for AlN is -219.2. Any oxygen in the system would therefore bond to the Al, preventing the formation of AlN. In this research project, I plan to grow AlN nanowires and then dope them (possibly in order to create a ferromagnetic material) and to test their optoelectronic properties. I will be using both a vapor-quasiliquid-solid (V-Q-S) growth method and a vapor-solid (V-S) one. As with many of the experiments I am basing my work off of I will be using ammonia (NH₃) as my source of non-diatomic nitrogen (N) and Al powder. I hope with my research to not only contribute to my field in the basic way of offering up a novel way to manufacture and optimize AlN wires, but also to address the large gap between theory and application that exists.

**Literature Review**

**Nanowire Production**

In my prior work I used aluminum chloride (AlCl₃) and NH₃ to attempt the growth of AlN wires, without success. Pouget and Lecompte discuss the reaction that occurs between AlCl₃ and NH₃. They go into an in depth discussion on the possible outcomes of the reaction, the unwanted along with the steps needed to get to AlN, and how often undesired reactions are what is found to have occurred. They conclude that the low amounts of AlN being formed is due to the other chemical compounds, such as ammonia chloride (NH₄Cl) and Al₂O₃, taking preference as the favored and more concentrated reactions. Wu, et. al. proposed the use of Al powder and NH₃ as their sources in order to avoid the unwanted reactions that occur when AlCl₃ is present. They show that by using nickel (Ni) as a catalyst one can grow longer and thinner wires than without. Both Mohammad, et. al. and Golovin, et. al. provide information on the actual steps of the reaction that is occurring inside the furnace, on a microscopic level.
appears the description provided by Mohammad, et. al. is the more correct one in my case, stating that the method of growth will be by a V-S or V-Q-S reaction.\textsuperscript{11}

Experimental Methods

Yang, et. al. discuss the possibility of doping the wires with manganese (Mn) in order to allow them to express ferromagnetic properties at, and possibly above, room temperature (around 300 K), making them a possible candidate for use in spintronics.\textsuperscript{12} This relatively Curie temperature of AlN would allow for more practical applications than the low temperatures that other materials possess. Huang, et. al. explains some of the interesting optical properties of AlN nanowires, and how these properties are different than those of the bulk material.\textsuperscript{13} The experiment that I will be attempting to recreate grows the wires on a sapphire substrate rather than Si.\textsuperscript{14} Zhao, et. al. point out that the lattice spacing of sapphire is much closer to that of AlN than Si, thereby making it the ideal material to grow these wires on. Because of this small size difference, well arrayed nanowires that are nearly vertical can be grown without the help of a catalyst, allowing for fewer defects and thinner tips on the wires. Like many of the other experiments, they used Al powder and NH\textsubscript{3} to produce their wires, with much success.\textsuperscript{15}

Vapor-Liquid-Solid Growth

In vapor-liquid-solid (V-L-S) growth the nanowires are formed in a series of steps that build upon each other. The steps I will be discussing can be seen in Figure 1, and though this process can be generalized to many different types of wires, I will be referring to the reactions occurring in the growth of mine. In the first step, a bead of Al will form upon the surface of the substrate while the N is flown as a gas over the surface, the vapor stage. The N will then mix into the Al and begin to form AlN, starting the liquid stage of the process. AlN has a much higher melting point than that of its components so it will fall out of the "bead" as it forms, creating a
solid. This AlN deposit will build up vertically forming the nanowire, with the bead at its tip. As the solid stage continues the wire will grow in length, and if left long enough, in width. Because of the AlN, the process can be referred to as V-S or V-Q-S, as pointed out by Mohammad, et. al., since the AlN prevents there from ever being a true liquid stage.\textsuperscript{16}

**Prior Work**

**Methodology**

This past summer I was given the opportunity to attend a research experience for undergraduates (REU) through the National Nanotechnology Infrastructure Network (NNIN). In this work, a chemical vapor deposition (CVD) system employing NH\textsubscript{3} and AlCl\textsubscript{3}, as the sources of N and Al respectively, was used. Si substrates were used as seed material and some were coated with thin layers of various metals as catalysts. Also some samples were partially coated with Al and kept upstream to promote growth on the Si. The setup of a typical run can be seen in Figure 2. Growth temperatures ranged between 1000-1100°C with pressures of 100 torr and flow rates between 100-500 sccm. In order to keep oxygen in the system to a minimum, the system was flushed during both heat up and cool down with a flow of nitrogen gas at a rate of 100 sccm. Growth times, measured only when the machine was fully heated up, varied but most runs lasted 120 minutes.

**Results**

A film of AlN and some micro-scale deposits of AlN were found on silicon and nickel coated silicon samples by looking at them in a scanning electron microscope (SEM). Their compositions were confirmed by energy-dispersive X-ray spectroscopy (EDX), and these AlN deposits can be seen in Figure 3. However no AlN nanowires were found on any samples, even those with catalysts. Chlorine deposits were also found on the surface of some samples, and
NH₄Cl deposits were found in the reaction tube. This reaction was expected since AlCl₃ was the source of Al, and it had little effect on experimental outcomes. However, the main reason for the lack of AlN growth was aluminum oxidation. A very large deposit of Al₂O₃ was formed in the quartz tube used for heating and on the substrates, indicating the extent of oxygen in the system. The composition of the Al₂O₃ was confirmed using EDX. Figures 4 and 5 show deposits of Al₂O₃ on some samples and the almost artistic way in which they grew due to the changing growth conditions.

Challenges

The main challenges that I faced in this experiment related directly to the oxygen affinity of Al. The formation of Al₂O₃ kept AlN from forming, and thereby kept us from succeeding. Because of the temperature of the system, and the fact that it was being constantly pumped down to be kept at a low pressure, we can assume that all oxygen was present in the system itself. This oxygen could have come from the Si substrates, as SiO₂ forms almost immediately on the surface and therefore is always present. The AlCl₃ could also have bound to oxygen, bringing it in that way. There was no oxidizing environment in our system, so no oxygen that was present would be carried away that way.

Proposed Solutions

To prevent the oxidation of Al in my current experiment, precautionary methods are being taken. Si will no longer be used, in favor of sapphire, which will not oxidize. AlCl₃ will also no longer be used, and is being replaced by Al. Before the Al is to be used it will be etched and cleaned in order to remove any oxidation on its surface. H₂ will be used as both the purge and carry gas to create an oxidizing environment within the system in order to take away any oxygen that has found its way into the system and was not pumped out.
Methodology/Experimental

Synthesis

Many of my sources did not follow an experiment but were rather research papers, and though they did give me insight into my experiment they are not something for me to mimic or try to reproduce. There are of course some actual experimental papers included in my research, and it is from these I will build my own experiment. The method I will use is that Qing Zhao, et al. used to successfully grow their wires. I will grow my AlN nanowires in a CVD machine, using NH$_3$ and Al powder (99.9 % pure) as my sources. I will be using a clean sapphire substrate to grow on, as its lattice spacing is closer to the size of AlN than Si is. This substrate will be placed in the center of the CVD oven. An alumina boat containing the Al powder will be placed just upstream of the substrate so that it may combine with the nitrogen from the NH$_3$ and then deposit the AlN on the surface of the sapphire. A schematic diagram of my setup can be seen in Figure 6. Before actual growth of the wires, the system will be pumped with hydrogen (H$_2$) in order to remove all of the oxygen. I will grow at just under 1000 degrees Celsius for a length of time that has yet to be determined, though it will most likely stay under 90 minutes. During this time I will flow the NH$_3$ (5 sccm) through the system, carried by H$_2$ (100 sccm). At this temperature the NH$_3$ will have broken down, providing the N that I had mentioned before and hydrogen to form a reducing environment. The H$_2$ as a carry gas helps to move the gasses through the system.

Characterization

I will structurally clarify the wires using a SEM and run tests using EDX to confirm that they are made up of AlN. I can then test the transport properties using Agilent B1500A. From there I can create basic current-voltage graphs, and I can also use the data to calculate both the
resistance and resistivity of the wires. Testing of optical properties will occur in Dr. Neogi's lab here at UNT with the aid of his graduate students.

**Ethical and Safety Risks**

**Risks**

Due to the nature of NH₃ and H₂, I have provided the material safety data sheets (MSDS's) for them in Appendix B. The sheets I have included are not from the same company as the materials I have, they do however contain the same data. Though these chemicals can be toxic, we will be using them in very small or very dilute amounts, minimizing risk. The CVD machine I will be using requires a very high heat and low pressure, as well as a constant flow of gas through the system. I have also taken the collaborative institutional training initiative (CITI) courses that may be relevant to my work at any time in the process of achieving my thesis, and have included the proof of completion in Appendix B as well. These courses help me to understand the questions of ethics that I may encounter.

**Resolutions**

All gas cylinders are anchored to the wall to prevent an accident. The H₂ tank is equipped with a flame arrestor to prevent any flare ups. Because we will be working with NH₃ and we are unsure what gas will be vented out, the entire setup is under a vent hood and proper exhaust system. Protective clothing is also to be worn at all times in the lab, and proper safety protocol in the event of a potentially harmful situation are known to all persons who are in the lab at any time. Though I do not foresee working with live subjects, I do see that my work will be based off of the work of other people and that I may be collaborating with scientists from outside the U.S., because of this I must be careful to avoid plagiarism or skewed data and familiarize myself with export policies in relation to data and materials.
**Costs**

In order to do this research the raw materials must first be acquired. This means the purchase of Al powder, NH$_3$, and sapphire disks, which the department has provided the funding for through Dr. Philipose and her lab. I will be using the machines that the university already has possession of in order to grow and test my nanowires, so no new machines will need to be purchased in pursuit of this experiment. Some alterations to the current setup of the lab are required, and the materials needed to accomplish this must be bought. In order for me to work in the lab over the summer, which has become a possibility, I will need to find funding for my project, allowing me to stay here and focus my abilities on the work being done in the lab. I hope to receive a subsidy from the department of physics where I will be working, and will most likely take up another job to help pay for living expenses and the costs of any courses I would be taking at the same time.

**Timeline**

I have already begun work in Dr. Philipose's lab, and as this is the continuation of the project I had done over the summer I already know what needs to be done technically to achieve my goals. By Christmas break we will have all the materials needed to grow our wires and have our experiment planned out so that we can quickly begin work in the spring. After the winter break I will attempt to grow the AlN wires for the first time. Once that has been established I will begin work on growing better arrayed wires with fewer defects. At this point I will have enough data to present my findings at Scholars Day. By the start of the summer I hope to have the wires so that I may then begin running tests on them and deciding where my thesis needs to go from there. If funded over the summer, I will be working on the possibility of doping the wires to make them ferromagnetic or considering taking advantage of their optical properties in possible
laser applications. The final year of my thesis I will be finalizing any reports that I may be attempting to publish and tying up any loose ends from my research so that I leave with a fully finished project. A visual representation of what I plan to accomplish and when can be seen in Figure 7.

**Dissemination Plan**

I will begin to share my findings with the public by first presenting my data at Scholars Day in the spring. I will also take my completed paper on my research and present it for inclusion in the Eagle Feather publication. Once all my research is done, and if it is felt that my work has presented something novel or innovative to the field, I will apply for publication in at least one peer reviewed journal relative to my topic. I will also take my findings to various conferences in my field, both at the student and professional level.

**Conclusions**

In research I have found that mistakes and failures contribute more to progress than when success is easily found. Over the summer I had tried to form AlN through a reaction between AlCl$_3$ and NH$_3$ and had no success. The paper on the reactions of the two chemicals allowed me to see what had gone wrong, and how my chances stood at succeeding with that method. Because of this I have decided to put aside that reaction and to grow my wires by using pure Al powder and NH$_3$ and growing on a sapphire disk rather than Si. In order to carry my thesis from theory to application, I then propose to follow some method of doping to bring out properties that can be directly useful, such as using Mn to induce ferromagnetism in the wires. The articles on V-L-S growth allow me to have a better understanding of the physics behind what I am doing so that I can further increase my chances of success. The various experiments that I have read will allow me to run my experiment more smoothly, as I will be able to alter variables to ratios that have
already been proven to work. Though not cited in this paper, I have included those experiments in my bibliography for reference. Looking into the optical properties that AlN has, and the different ways those properties can be manipulated, has helped to prepare me for once we have the wires and begin to test their properties, as well as explain some of the benefits of nano over bulk.  

I hope to spread my research through both publication and conferences. Though there are some ethical and safety concerns, they have all been addressed in a way that allows me to feel more than comfortable working in the lab and on this project. This thesis, and the distribution of my findings, will hopefully be complete by the end of spring semester 2013 in order for me to graduate and continue on to get my doctoral degree.
Notes


4. S. Noor Mohammad; "For nanowire growth, vapor-solid-solid (vapor-solid) mechanism is actually vapor-quasisolid-solid (vapor-quasisolid-solid) mechanism"; *The Journal of Chemical Physics*, 131 (December 2009).


7. Pouget and Lecompte


11. Mohammad


13. Huang.


15. Zhao


17. Zhao.

18. Zhao.
Appendix A: Figures

Figure 1: Step flow growth of nanowires

Figure 2: Schematic diagram of CVD setup used at Howard University. The NH$_3$ is fed in through the left from a tank hooked to a mass flow controller, and all gasses are pumped out the right and vented out.
Figure 3: Large growth of AlN on Ni coated Si

Figure 4: Al₂O₃ spheres and nanowires
Figure 5: Another example of $\text{Al}_2\text{O}_3$ spheres growing off a large $\text{Al}_2\text{O}_3$ mass

Figure 6: Current CVD setup. The $\text{NH}_3$ and argon are fed in through the left from tanks hooked to a mass flow controller, and all gasses are pumped out the right and vented out through the exhaust system.
Figure 7: Timeline for thesis development
Appendix B: CITI Certification, MSDS

CITI Collaborative Institutional Training Initiative (CITI)

UNT RCR FOR PHYSICAL SCIENCES Curriculum Completion Report
Printed on 12/8/2011

Learner: Alicia Herro (username: 10635326)
Institution: University of North Texas (Denton, TX)
Contact Information: Department: Physics
Email: aliciatherro@gmail.com

UNT RCR FOR PHYSICAL SCIENCES: This course is for investigators, staff and students with an interest in focus in Physical Science research. This course contains text, embedded case studies AND quizzes.

Stage 1. RCR Passed on 11/21/11 (Ref #7035620)

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For this Completion Report to be valid, the learner listed above must be affiliated with a CITI participating institution. False information and unauthorized use of the CITI course site is unethical, and may be considered scientific misconduct by your institution.

Paul Braunschweig, Ph.D.
Professor, University of Miami
Director Office of Research Education
CITI Course Coordinator

Return
CITI Collaborative Institutional Training Initiative (CITI)

Export Controls Curriculum Completion Report
Printed on 12/8/2011

Learner: Alicia Hero (username: 10633528)
Institution: University of North Texas (Denton, TX)
Contact Information: Department: Physics
Email: alicia hero@gmail.com

CITI Export Controls Course: After completing this module the learner should be able to: 1. Describe the three major sets of regulations that regulate the export of materials, technology, technical data, and software from the United States. 2. Define and use key terms and concepts critical to understanding U.S. export regulations. 3. Understand why it is important for researchers in U.S. institutions of higher education to have a core knowledge of U.S. export regulations.

Stage 1 Stage 1 Passed on 11/21/11 (Ref # 7035822)

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Paul Breunig, Ph.D.
Professor, University of Miami
Director, Office of Research Education
CITI Course Coordinator

Return
ANHYDROUS AMMONIA: (MSDS) Material Safety Data Sheet

Tanner Industries, Inc. divisions: National Ammonia, Northeastern Ammonia, Hamler Industries, Bower Ammonia & Chemical
735 Davisville Road, Third Floor, Southampton, PA 18966; 215-322-1238

Corporate emergency telephone number: 800-643-6226
Chemtrec: 800-424-9300

Overview:
:: Description
:: Spill or Leak Procedures
:: Statement of Health Hazard
:: Special Protection and Procedures
:: Physical Data
:: Special Precautions
:: Emergency Treatment
:: Labeling and Shipping
:: Fire and Explosion Hazard Data
:: Other Regulatory Requirements
:: Chemical Reactivity
:: Disclaimer

Description
Chemical Name: Ammonia, Anhydrous
CAS Registry No: 7664-41-7
Synonyms: Ammonia
Chemical Family: Inorganic Nitrogen Compound
Formula: NH₃
Molecular Weight: 17.03 (NH₃)
Composition: 99+% Ammonia

Statement of Health Hazard
Hazard Description
Ammonia is an irritant and corrosive to the skin, eyes, respiratory tract and mucous membranes. Exposure to liquid or rapidly expanding gases may cause severe chemical burns and frostbite to the eyes, lungs and skin. Skin and respiratory related diseases could be aggravated by exposure.
  • Not recognized by OSHA as a carcinogen
  • Not listed in the National Toxicology Program
  • Not listed as a carcinogen by the International Agency for Research on Cancer

Exposure Limits for Ammonia: Vapor
OSHA  50 ppm  35 mg / m³ PEL  8 hour TWA
NIOSH 35 ppm  27 mg / m³ STEL  15 minutes
  25 ppm  18 mg / m³ REL  10 hour TWA
  300 ppm IDLH
ACGIH 25 ppm  18 mg / m³ TLV  8 hour TWA
  35 ppm  27 mg / m³ STEL  15 minutes
Toxicity: LD 50, (Oral / Rat), 350 mg / kg

Physical Data
Boiling Point: -28°F at 1 atm
pH: N/A
Specific Gravity of Gas (air = 1): 0.596 at 32°F
Specific Gravity of Liquid (water = 1): 0.682 at -28°F (compared to water at 39°F)
Percent Volatile: 100% at 212°F
Appearance and Odor: Colorless liquid or gas with pungent odor
Critical Temperature: 271.4°F
Gas Specific Volume: 20.78 ft³/lb at 32°F and 1 atm
Vapor Density (air = 1): 0.0481 lb/ft³ at 32°F
Liquid Density: 38.00 lb/ft³ at 70°F
Approximate Freezing Point: -108°F
Weight (per gallon): 5.15 pounds at 60°F
Vapor Pressure: 114 psig 70°F
Solubility in Water (per 100 pounds of water): 86.9 pounds at 32°F,
51 pounds at 68°F
Surface Tension: 23.4 Dynes / cm at 52°F
Critical Pressure: 111.5 atm

Emergency Treatment
Effects of Overexposure
Eye: May cause severe irritation, eye burns or permanent eye damage.
Skin: Irritation, corrosive burns, blister formation may result. Contact with liquid may produce a caustic burn and frostbite.
Inhalation: Exposure may result in severe irritation and / or burns of the nose, throat and respiratory tract. It may cause bronchospasm, pulmonary edema or respiratory arrest. Extreme exposure may result in death from spasm, inflammation or edema. Brief inhalation exposure to 5,000 ppm may be fatal.
Ingestion: Ingestion is unlikely since the material is a gas under normal atmospheric conditions. If ingested, it may cause burns and severe pain of the mouth, throat, esophagus and stomach or may be fatal.

Emergency Aid: Remove patient to uncontaminated area
Eye: Flush with copious amounts of tepid water for a minimum of 20 minutes. Eyelids should be held apart and away from eyeball for thorough rinsing. Seek medical attention.
Skin: Flush with copious amounts of tepid water for a minimum of 20 minutes while removing contaminated clothing, jewelry and shoes. Do not rub or apply ointment on affected area. Clothing may initially freeze to skin. Thaw frozen clothing from skin before removing. For liquid ammonia contact, seek immediate medical attention. For severe vapor contact or if irritation persists, seek medical attention.
Inhalation: Remove to fresh air. If not breathing, administer artificial respiration. If trained to do so, administer supplemental oxygen, if required. In case of severe exposure or if irritation persists or if breathing difficulties arise, get medical attention.
Ingestion: If conscious, give large amounts of water to drink. May drink orange juice, citrus juice or diluted vinegar (1:4) to counteract ammonia. If unconscious, do not give anything by mouth. DO NOT INDUCE VOMITING! Seek medical attention.

NOTE TO PHYSICIAN:
Respiratory injury may appear as a delayed phenomenon. Pulmonary edema may follow chemical bronchitis. Supportive treatment with necessary ventilation actions, including oxygen, may warrant consideration.

Fire and Explosion Hazard Data
Flashpoint: None
Flammable Limits in Air: LEL/UEL 16% to 25% (listed as 15% to 28% in the NIOSH Pocket Guide to Chemical Hazards.)
Extinguishing Media: Dry Chemical, CO₂, water spray or alcohol-resistant foam if gas flow cannot be stopped
Auto Ignition Temperature: 1,204°F (If catalyzed), 1,570°F (If un-catalyzed)

Special Fire-Fighting Procedure
Must wear protective clothing and a positive pressure SCBA. Stop source if possible. If a portable container (such as a cylinder or trailer) can be moved from the fire area without risk to the individual, do so to prevent the pressure relief valve of the trailer from discharging or the cylinder from rupturing. Fight fires using dry chemical, carbon dioxide, water spray or alcohol-resistant foam. Cool fire-exposed containers with water spray. Stay upwind when containers are threatened. Use water spray to knock down vapor and dilute.

Unusual Fire and Explosion Hazards
- Outdoors, ammonia is not generally a fire hazard. Indoors, in confined areas, ammonia may be a fire hazard, especially if oil and other combustible materials are present. Combustion may form toxic nitrogen oxides.
- If relief valves are inoperable, heat exposed storage containers may become explosion hazards due to over pressurization.

Chemical Reactivity
Stability
Stable at room temperature. Heating a closed container above room temperature causes vapor pressure to increase rapidly. Anhydrous ammonia will react exothermically with acids and water. Will not polymerize.

Conditions to Avoid
Anhydrous ammonia has potentially explosive reactions with strong oxidizers. Anhydrous ammonia forms explosive mixtures in air with hydrocarbons, chlorine, fluorine and silver nitrate. Anhydrous ammonia reacts to form explosive products, mixtures or compounds with mercury, gold, silver, iodine, bromine, silver oxide and silver chloride.

Avoid anhydrous ammonia contact with chlorine, which forms a chloramine gas, which is a primary skin irritant and sensitizer. Anhydrous ammonia is incompatible with acetaldehyde, acrolein, boron, chloric acid, chlorine monoxide, chlorites, nitrogen tetroxide, perchlorate, sulfur, tin and strong acids.

Avoid contact with galvanized surfaces, copper, brass, bronze, mercury, gold and silver. A corrosive reaction will occur.

Hazardous Decomposition Products
Anhydrous ammonia decomposes to hydrogen and nitrogen gases above 450°C (842°F). Decomposition temperatures may be lowered by contact with certain metals, such as iron, nickel and zinc and by catalytic surfaces such as porcelain and pumice.

Spill or Leak Procedures
Steps to be Taken
Stop source of leak if possible, provided it can be done in a safe manner. Leave the area of a spill by moving laterally and upwind. Isolate the affected area. Non-responders should evacuate the area, or shelter in place. Only properly trained and equipped persons should respond to an ammonia release. Wear eye, hand and respiratory protection and protective clothing; see PROTECTIVE EQUIPMENT. Stay upwind and use water spray downwind of container to absorb the evolved gas. Contain spill and runoff from entering drains, sewers, and water systems by utilizing methods such as diking, containment, and absorption. CAUTION: ADDING WATER DIRECTLY TO LIQUID SPILLS WILL INCREASE VOLATILIZATION OF AMMONIA, THUS INCREASING THE POSSIBILITY OF EXPOSURE.

Waste Disposal
Listed as hazardous substance under CWA (40 CFR 116.4, 40 CFR 117.3). Reportable Quantity 100 pounds. Classified as hazardous waste under RCRA (40 CFR 261.22 Corrosive #D002). Comply with all regulations. Suitably diluted product may be utilized
on agricultural land as fertilizer. Keep spill from entering streams, lakes, or any water systems.

Special Protection and Procedures

Protective Equipment
At a minimum, splash proof, chemical safety goggles, ammonia resistant gloves (such as rubber) and ammonia-impervious clothing should be worn to prevent contact during normal operations, such as loading, unloading and transfers. A face shield and boots can be worn as additional protection. Refer to 29 CFR 1910.132 through 1910.138 for OSHA personal protective equipment requirements.

For a hazardous material release response, Level A or Level B ensemble including positive-pressure SCBA should be used.

Eye Protection
Chemical splash goggles should be worn when handling anhydrous ammonia. A face shield can be worn over chemical splash goggles as additional protection. Do not wear contact lenses when handling anhydrous ammonia. Refer to 29 CFR 1910.133 for OSHA eye protection requirements.

Respiratory Protection
Respiratory protection approved by NIOSH for ammonia must be used when applicable safety and health exposure limits are exceeded. For escape in emergencies, NIOSH approved respiratory protection that consists of a full-face gas mask and canisters approved for ammonia or SCBA should be used. A positive pressure SCBA is required for entry into ammonia atmospheres at unknown concentrations or above 300 ppm (IDLH). Refer to 29 CFR 1910.134 and ANSI: Z88.2 for OSHA respiratory protection requirements. Also refer to 29 CFR 1910.111 for respiratory protection requirements at bulk installations.

Ventilation
Maintain adequate ventilation to keep ammonia concentrations below the applicable standards.

Special Precautions

Storage and Handling
Only trained persons should handle anhydrous ammonia. Store in cool (26.7°C / 80°F) and well-ventilated areas, with containers tightly closed. OSHA 29 CFR 1910.111 prescribes handling and storage requirements for anhydrous ammonia as a hazardous material. Use only stainless steel, carbon steel or black iron for anhydrous ammonia containers or piping. Do not use plastic. Do not use any non-ferrous metals such as copper, brass, bronze, tin, zinc or galvanized metals. Protect containers from physical damage. Keep away from ignition sources, especially in indoor spaces.

Work-Place Protective Equipment
Protective equipment should be stored near, but outside of anhydrous ammonia area. Water for first aid, such as an eyewash station and safety shower, should be kept available in the immediate vicinity. See 29 CFR 1910.111 for workplace requirements.

Disposal
See WASTE DISPOSAL. Classified as RCRA Hazardous Waste due to corrosivity with designation D002, if disposed of in original form.

Labeling and Shipping

Hazard Class: (US Domestic): 2.2 (Non-Flammable Gas) (International): 2.3 (Poison Gas) subsidiary 8 (Corrosive)

Proper Shipping Description:
• (US Domestic): UN1005, Ammonia, Anhydrous, 2.2, RQ, Inhalation Hazard
• (International): UN1005, Ammonia, Anhydrous, 2.3, (8), RQ, Poison-Inhalation Hazard Zone “D”
Placard: (US Domestic): Non-Flammable Gas, 
(International): Poison Gas, Corrosive (Subsidiary) 
Identification No: UN 1005 
Identification System Labels: 
Anhydrous Ammonia 
HEALTH = 3 
FLAMMABILITY = 1 
REACTIVITY = 0 
PERSONAL PROTECTION = H

Other Regulatory Requirements 
Under the Comprehensive Environmental Response, Compensation, and Liability Act of 
1980 (CERCLA), Section 103, any environmental release of this chemical equal to or 
over the reportable quantity of 100 lbs. must be reported promptly to the National 

The material is subject to the reporting requirements of Section 304, Section 312 and 
Section 313, Title III of the Superfund Amendments and Reauthorization Act (SARA) of 
extremely hazardous substance, 40 CFR 355, Title III, Section 302 - Ammonia, 
Threshold Planning Quantity (TPQ) 500 lbs.

EPA Hazard Categories - Immediate: Yes; Delayed: No; Fire: No; Sudden Release: 
Yes; Reactive: No.

Clean Air Act - Section 112(r): Material is listed under EPA's Risk Management Program 
(RMP), 40 CFR Part 68, at storage/process amounts greater than the Threshold 
Quantity (TQ) of 10,000 lbs.

The chemical is listed under Department of Homeland Security regulation 6 CFR Part 
27, Chemical Facility Anti-Terrorism Standards at storage / process amounts greater 
than the threshold quantity of 10,000 pounds.

This chemical is subject to 49 CFR 1580, Rail Transportation Security.

Disclaimer 
The information, data, and recommendations in this material safety data sheet relate 
only to the specific material designated herein and do not relate to use in combination 
with any other material or in any process. The information, data, and recommendations 
set forth herein are believed by us to be accurate. We make no warranties, either 
expressed or implied, with respect thereto and assume no liability in connection with 
any use of such information, data, and recommendations.

Revision: January 2011 Prepared By: JRP

Tanner Industries, Inc. 1-800-643-6226
# Material Safety Data Sheet

## Hydrogen

### Section 1. Chemical product and company identification

<table>
<thead>
<tr>
<th><strong>Product name</strong></th>
<th>Hydrogen</th>
</tr>
</thead>
</table>
| **Supplier**     | AIRGAS INC., on behalf of its subsidiaries  
259 North Radnor-Chester Road  
Suite 100  
Radnor, PA 19087-5283  
1-610-687-5253 |
| **Product use**  | Synthetic/Analytical chemistry. |
| **Synonym**      | Dihydrogen; o-Hydrogen; p-Hydrogen; Molecular hydrogen; H2; UN 1049; UN 1966; Liquid hydrogen (LH2 or LH2) |
| **MSDS #**       | 001026 |
| **Date of Preparation/Revision** | 4/26/2010. |
| **In case of emergency** | 1-866-734-3438 |

### Section 2. Hazards identification

<table>
<thead>
<tr>
<th><strong>Physical state</strong></th>
<th>Gas or Liquid.</th>
</tr>
</thead>
</table>
| **Emergency overview** | WARNING!  
GAS: CONTENTS UNDER PRESSURE.  
Extremely flammable  
Do not puncture or incinerate container.  
Can cause rapid suffocation.  
May cause severe frostbite.  
LIQUID: Extremely flammable  
Extremely cold liquid and gas under pressure.  
Can cause rapid suffocation.  
May cause severe frostbite.  
Do not puncture or incinerate container.  
Contact with rapidly expanding gases or liquids can cause frostbite. |
| **Routes of entry** | Inhalation |
| **Potential acute health effects** |  
**Eyes**: Contact with rapidly expanding gas may cause burns or frostbite. Contact with cryogenic liquid can cause frostbite and cryogenic burns.  
**Skin**: Contact with rapidly expanding gas may cause burns or frostbite. Contact with cryogenic liquid can cause frostbite and cryogenic burns.  
**Inhalation**: Acts as a simple asphyxiant.  
**Ingestion**: Ingestion is not a normal route of exposure for gases Contact with cryogenic liquid can cause frostbite and cryogenic burns.  
**Potential chronic health effects**: CARCINOGENIC EFFECTS: Not available.  
MUTAGENIC EFFECTS: Not available.  
TERATOGENIC EFFECTS: Not available. |
| **Medical conditions aggravated by over-exposure** | Acute or chronic respiratory conditions may be aggravated by overexposure to this gas. |

See toxicological information (section 11)
Section 3. Composition, Information on Ingredients

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS number</th>
<th>% Volume</th>
<th>Exposure limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1333-74-0</td>
<td>100</td>
<td>Oxygen Depletion [Asphyxiant]</td>
</tr>
</tbody>
</table>

Section 4. First aid measures

No action shall be taken involving any personal risk or without suitable training. If it is suspected that fumes are still present, the rescuer should wear an appropriate mask or self-contained breathing apparatus. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.

**Eye contact**: Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.

**Skin contact**: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.

**Frostbite**

**Inhalation**: Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

**Ingestion**: As this product is a gas, refer to the inhalation section.

Section 5. Fire-fighting measures

**Flammability of the product**: Flammable.

**Auto-ignition temperature**: 399.85 to 573.75°C (751.7 to 1064.8°F)

**Flammable limits**: Lower: 4%  Upper: 75%

**Products of combustion**: No specific data.

**Fire hazards in the presence of various substances**: Extremely flammable in the presence of the following materials or conditions: oxidizing materials.

**Fire-fighting media and instructions**: Use an extinguishing agent suitable for the surrounding fire.

Apply water from a safe distance to cool container and protect surrounding area. If involved in fire, shut off flow immediately if it can be done without risk.

Contains gas under pressure. In a fire or if heated, a pressure increase will occur and the container may burst or explode.

**Special protective equipment for fire-fighters**: Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Section 6. Accidental release measures

**Personal precautions**: Immediately contact emergency personnel. Keep unnecessary personnel away. Use suitable protective equipment (section 8). Shut off gas supply if this can be done safely. Isolate area until gas has dispersed.

**Environmental precautions**: Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers.

**Methods for cleaning up**: Immediately contact emergency personnel. Stop leak if without risk. Note: see section 1 for emergency contact information and section 13 for waste disposal.

Section 7. Handling and storage

**Handling**: High pressure gas. Do not puncture or incinerate container. Use equipment rated for cylinder pressure. Close valve after each use and when empty. Protect cylinders from physical damage; do not drag, roll, slide, or drop. Use a suitable hand truck for cylinder movement.

Never allow any unprotected part of the body to touch uninsulated pipes or vessels that contain cryogenic liquids. Prevent entrapment of liquid in closed systems or piping without pressure relief devices. Some materials may become brittle at low temperatures and will easily fracture.
Hydrogen

Section 8. Exposure controls/personal protection

Engineering controls: Use only with adequate ventilation. Use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits.

Personal protection:

Eyes: Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts.

Skin: Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.

Respiratory: Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

The applicable standards are (US) 29 CFR 1910.134 and (Canada) Z94.4-93

Hands: Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Personal protection in case of a large spill: Self-contained breathing apparatus (SCBA) should be used to avoid inhalation of the product.

Product name: Hydrogen  
Oxygen Depletion [Asphyxiant]

Consult local authorities for acceptable exposure limits.

Section 9. Physical and chemical properties

- Molecular weight: 2.02 g/mole
- Molecular formula: H2
- Boiling/condensation point: -253.2°C (-423.8°F)
- Melting/freezing point: -259.2°C (-434.6°F)
- Critical temperature: -240.1°C (-400.2°F)
- Vapor density: 0.07 (Air = 1)  
- Specific Volume (ft³/lb): 14.0845
- Gas Density (lb/ft³): 0.071

Section 10. Stability and reactivity

Stability and reactivity: The product is stable.

Incompatibility with various substances: Extremely reactive or incompatible with the following materials: oxidizing materials.

Hazardous decomposition products: Under normal conditions of storage and use, hazardous decomposition products should not be produced.

Hazardous polymerization: Under normal conditions of storage and use, hazardous polymerization will not occur.
Section 11. Toxicological information

**Toxicity data**

**Other toxic effects on humans**
No specific information is available in our database regarding the other toxic effects of this material to humans.

**Specific effects**

**Carcinogenic effects**
No known significant effects or critical hazards.

**Mutagenic effects**
No known significant effects or critical hazards.

**Reproduction toxicity**
No known significant effects or critical hazards.

No specific information is available in our database regarding the other toxic effects of this material to humans.

Section 12. Ecological information

**Aquatic ecotoxicity**
Not available.

**Environmental fate**
Not available.

**Environmental hazards**
No known significant effects or critical hazards.

**Toxicity to the environment**
Not available.

Section 13. Disposal considerations

Product removed from the cylinder must be disposed of in accordance with appropriate Federal, State, local regulation. Return cylinders with residual product to Airgas, Inc. Do not dispose of locally.

Section 14. Transport information

<table>
<thead>
<tr>
<th>Regulatory information</th>
<th>UN number</th>
<th>Proper shipping name</th>
<th>Class</th>
<th>Packing group</th>
<th>Label</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOT Classification</strong></td>
<td>UN1049</td>
<td>HYDROGEN, COMPRESSED</td>
<td>2.1</td>
<td>Not applicable (gas).</td>
<td></td>
<td>Limited quantity Yes.</td>
</tr>
<tr>
<td></td>
<td>UN1966</td>
<td>Hydrogen, refrigerated liquid</td>
<td></td>
<td></td>
<td></td>
<td>Packaging instruction Passenger aircraft Quantity limitation: Forbidden.</td>
</tr>
<tr>
<td><strong>TDG Classification</strong></td>
<td>UN1049</td>
<td>HYDROGEN, COMPRESSED</td>
<td>2.1</td>
<td>Not applicable (gas).</td>
<td></td>
<td>Explosive Limit and Limited Quantity Index 0.125</td>
</tr>
<tr>
<td></td>
<td>UN1966</td>
<td>Hydrogen, refrigerated liquid</td>
<td></td>
<td></td>
<td></td>
<td>ERAP Index 3000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Passenger Carrying Ship Index Forbidden</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Passenger</td>
</tr>
</tbody>
</table>
Hydrogen

### Mexico Classification
- UN1049: HYDROGEN, COMPRESSED
- UN1966: Hydrogen, refrigerated liquid

### Carrying Road or Rail Index Forbidden
- 2.1: Not applicable (gas).

“Refer to CFR 49 (or authority having jurisdiction) to determine the information required for shipment of the product.”

## Section 15. Regulatory information

### United States

**U.S. Federal regulations**
- TSCA 8(a) IUR: hydrogen
- United States inventory (TSCA 8b): This material is listed or exempted.
- SARA 302/304/311/312 extremely hazardous substances: No products were found.
- SARA 302/304 emergency planning and notification: No products were found.
- SARA 302/304/311/312 hazardous chemicals: hydrogen
- SARA 311/312 MSDS distribution - chemical inventory - hazard identification: hydrogen: Fire hazard, Sudden release of pressure
- Clean Water Act (CWA) 307: No products were found.
- Clean Water Act (CWA) 311: No products were found.
- Clean Air Act (CAA) 112 accidental release prevention: hydrogen
- Clean Air Act (CAA) 112 regulated flammable substances: hydrogen
- Clean Air Act (CAA) 112 regulated toxic substances: No products were found.

**State regulations**
- Connecticut Carcinogen Reporting: This material is not listed.
- Connecticut Hazardous Material Survey: This material is not listed.
- Florida substances: This material is not listed.
- Illinois Chemical Safety Act: This material is not listed.
- Illinois Toxic Substances Disclosure to Employee Act: This material is not listed.
- Louisiana Reporting: This material is not listed.
- Louisiana Spill: This material is not listed.
- Massachusetts Spill: This material is not listed.
- Massachusetts Substances: This material is listed.
- Michigan Critical Material: This material is not listed.
- Minnesota Hazardous Substances: This material is not listed.
- New Jersey Hazardous Substances: This material is listed.
- New Jersey Spill: This material is not listed.
- New Jersey Toxic Catastrophe Prevention Act: This material is not listed.
- New York Acutely Hazardous Substances: This material is not listed.
- New York Toxic Chemical Release Reporting: This material is not listed.
- Pennsylvania RTK Hazardous Substances: This material is listed.
- Rhode Island Hazardous Substances: This material is not listed.

### Canada

**WHMIS (Canada)**
- Class A: Compressed gas.
- Class B-1: Flammable gas.
- CEPA Toxic substances: This material is not listed.
- Canadian ARET: This material is not listed.
- Canadian NPRI: This material is not listed.
- Alberta Designated Substances: This material is not listed.
- Ontario Designated Substances: This material is not listed.
- Quebec Designated Substances: This material is not listed.
Section 16. Other information

United States
Label requirements: GAS:
CONTENTS UNDER PRESSURE.
Extremely flammable
Do not puncture or incinerate container.
Can cause rapid suffocation.
May cause severe frostbite.
LIQUID:
Extremely flammable
Extremely cold liquid and gas under pressure.
Can cause rapid suffocation.
May cause severe frostbite.

Canada
Label requirements: Class A: Compressed gas.
Class B-1: Flammable gas.

Hazardous Material Information System (U.S.A.):

<table>
<thead>
<tr>
<th>Health</th>
<th>Flammability</th>
<th>Physical hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

Liquid:

<table>
<thead>
<tr>
<th>Health</th>
<th>Fire hazard</th>
<th>Reactivity</th>
<th>Personal protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

National Fire Protection Association (U.S.A.):

Flammability
Health 0 4
Instability
Special

Notice to reader
To the best of our knowledge, the information contained herein is accurate. However, neither the above-named supplier, nor any of its subsidiaries, assumes any liability whatsoever for the accuracy or completeness of the information contained herein.
Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.
Appendix C: Bibliography


Mohammad, S. Noor; "For nanowire growth, vapor-solid-solid (vapor-solid) mechanism is actually vapor-quasisolid-solid (vapor-quasisolid-solid) mechanism"; *The Journal of Chemical Physics*, 131 (December 2009).


