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# Gas Safety for TFT-LCD Manufacturing

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## 1. Introduction

The fabrication of TFT-LCD panel includes the growing and etching of a-silicon and silicon nitride films. These fabrication processes utilize significant amounts of silane, phosphine, ammonia, chlorine, boron trichloride, nitrogen trifluoride, fluorine, and hydrogen which are highly flammable, reactive, corrosive, and/or toxic. The amount used and scale of the supply system for these gases are far larger than for other tech industries such as the semiconductor and photovoltaic industries. Accidental leaks and fires of these gases are the major safety concern in the TFT-LCD fabs.

This paper first reviews the hazardous properties of the gases used in the TFT-LCD manufacturing processes. The best practices for handling these hazardous gases are then described. Finally, the past incidents and emergency response actions are also reviewed.

## 2. Hazardous properties of specialty gases

The TFT-LCD manufacturing processes utilize significant amount of gases for thin-film deposition and etching. These include silane, phosphine, ammonia, and hydrogen for polycrystalline silicon and silicon nitride thin film deposition in a plasma-enhanced chemical vapor deposition (PECVD) reaction chamber. In addition, nitrogen trifluoride or fluorine is used in the PECVD chamber cleaning. Chlorine and sulfur hexafluoride are used in the dry etching of thin film. The hazards of these gases can be classified as pyrophoric, flammable and oxidizing gases. There are other bulk gases such as nitrogen, argon and helium which are used for inerting or purging and will not be discussed here owing to their low risks.

### 2.1 Silane

Silane or silicon tetrahydride ( $\text{SiH}_4$ ) is the most common silicon source used in TFT-LCD manufacturing. It is a highly flammable gas and has a very wide flammable range, from 1.37% to 96%. Silane is colorless and odorless although it has been reported to have a prudent odor and a reported time weighted threshold limit value (TLV-TWA) of 5 ppm by ACGIH. However, this data is based on analogy of another hydride gas Germane rather than the actual toxicological data. In fact, silane has no odor and its toxicity is low with a high median lethal concentration ( $\text{LC}_{50}$ ) of 9,600 ppm for rat at 4 hours exposure. The prudent odor comes from the impurity of trichlorsilane during early silane production.

Silane is used as a compressed gas. However, silane has a critical temperature of  $-3.4^{\circ}\text{C}$ . It is possible that liquefaction may occur in cold storage or during expansion cooling from compressed sources. A silane supply system must be designed properly to prevent unexpected pressure surge from liquefaction and vaporization.

Silane is also a pyrophoric gas that normally ignites upon contact with air. Silane has a reported autoignition temperature of  $-50\sim-100^{\circ}\text{C}$ . Autoignition of silane in air has also been reported down to  $-162^{\circ}\text{C}$ , depending on the oxygen concentration of the mixture (Baratov et al., 1969). However, the autoignition temperature only denotes the temperature above which a given fuel-air mixture will autoignite in a closed vessel. It however does not refer to details of the autoignition process and how autoignition is affected by flow. The major potential hazard of silane is however not in its pyrophoricity but rather in its unpredictable ignition behavior in accidental releases. A silane release from a pressure source has been known not to lead to spontaneously ignition (Koda, 1992) and frequently delayed ignition occurs when the release is shut-off resulting in a "pop". In a semi-confined space with gas accumulation, the pop can lead to a gas explosion with significant damage (Ngai et al., 2007).

The mechanism of delayed ignition has been studied by Tsai et al. (2011) which demonstrated that silane release without prompt ignition was most likely caused by quench of the reactive kernel from the flow strain or scalar dissipation accompanied by the large velocity and concentration difference between the release gas and the ambient air. With diminishing release velocity, the flow strain reduces along with quench of the reactive kernel and ignition then occurs at a critical exit velocity. The ignition at reducing velocity may ignite the released gas and create a significant combustion or explosion. The critical exit velocity of indefinitely delayed ignition lies between  $0.3\text{ m/s}$  to  $4.3\text{ m/s}$  for vent diameter of  $2.03\sim 4.32\text{ mm}$  as shown in Figure 1. These velocities are at least two orders of magnitude smaller than the velocity from a pressurized source which in most cases reaches sonic velocity. Furthermore, Figure 1 also highlights that the critical velocity is also decreases with decreasing vent size.

There are factors other than vent size affecting the critical exit velocity. Among them, the temperature, moisture and silane combustion powder are the most noticeable factors. At higher temperature, the reactive kernel is stronger and thus the critical exit velocity is larger (Liang et al., 2010). Removing the moisture in the air also results in significantly higher critical exit velocity indicating an inhibitory role of moisture on silane ignition (Liang et al., 2010). The inhibitory action of moisture on the silane autoignition in air is also in consistent with other fuel such as hydrogen and methane. Silane combustion produces white to brown powders as shown in Figure 2. These powders are also known to promote ignition but its exact role remains to be studied.

The presence of a critical exit velocity for prompt ignition of silane release has important implications in the safety of silane operations. First of all, almost all current silane uses in the semiconductor, TFT-LCD, and photovoltaic industries are supplied in the form of pressurized cylinders with pressure up to  $12.5\text{ MPa}$ . The high pressure silane is then regulated to  $0.8\text{ MPa}$  for the supply tube into the cleanroom and then further regulated down to  $0.3\sim 0.45\text{ MPa}$  before feeding into the process chamber. Thus, almost all potential leak points in silane utilization have pressure and possible leak velocity higher than the reported critical velocity for prompt ignition. In addition, the potential leak points are the cylinder valve, tubing, and tube connections (Huang and Ngai, 2006). The potential release size will be much smaller than  $2.03\text{ mm}$ , except for a catastrophic full bore tube rupture. Thus, delayed ignition should be considered as the usual case rather than a rare case in most silane operations.

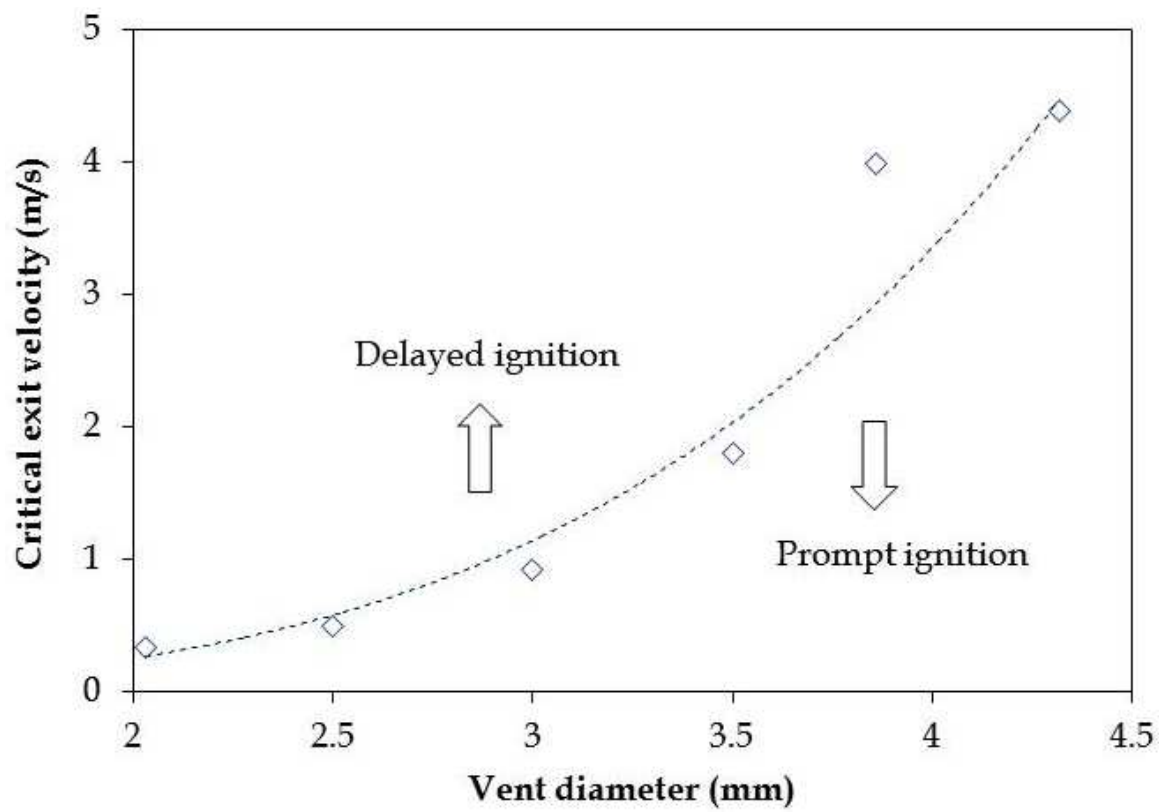


Fig. 1. Critical exit velocity for delayed/prompt ignition as a function of vent diameter.



Fig. 2. Typical silane combustion powder.

## 2.2 Phosphine

Phosphine ( $\text{PH}_3$ ) is a highly toxic and pyrophoric liquefied compressed gas. Phosphine is used primarily as a phosphorus dopant (N-type dopant) in the TFT LCD industry. It is typically supplied as a mixture with hydrogen.

Pure phosphine is a colorless, pyrophoric liquefied gas. Although pure samples of phosphine are odorless, the gas often has an odor of garlic or decaying fish due to the presence of substituted phosphine and diphosphine ( $\text{P}_2\text{H}_4$ ). It is a highly toxic gas with a PEL of 300 ppb, an  $\text{LC}_{50}$  of 20 ppm for rat at 1 hour exposure.

Phosphine has a low auto-ignition temperature  $<0^\circ\text{C}$  so it may ignite spontaneously on contact with air. Autoignition of phosphine released into air is also subjected to effects by temperature, moisture, and flow strain just like silane. For example, autoignition of phosphine is reported to occur only in dry air but not in moist air (Brittton, 1990). However, there is still a lack of detailed studies on the exact conditions for these effects. It also has an extremely wide flammable range of 1.6% – 95% in air. It burns in air with an orange flame forming white phosphorous pentoxide as a byproduct as shown in Figure 3(a), which is a severe respiratory irritant. Under certain conditions, phosphine will form red phosphorus as a byproduct in a fire as shown in Figure 3(b).

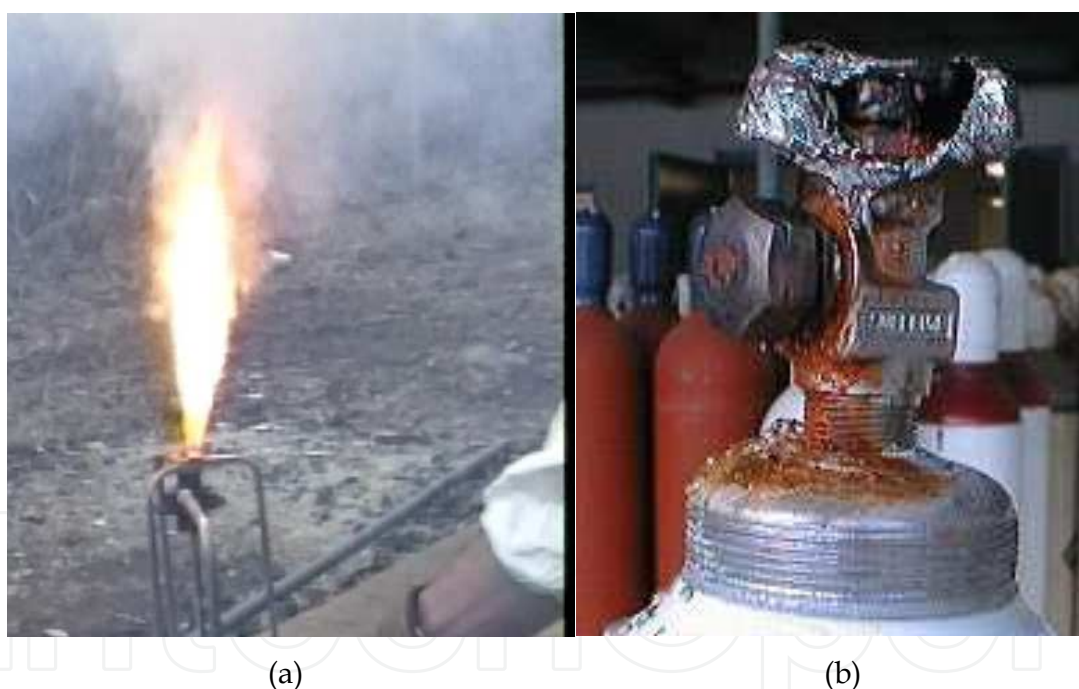


Fig. 3. Typical phosphine combustion flame and powder. (a) Orange flame and white phosphorous pentoxide powder (b) Red phosphorus powder.

Acute exposures to phosphine cause respiratory tract irritation that attacks primarily the cardiovascular and respiratory systems causing peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema. Inhalation is the primary exposure route, and there is no known dermal exposure route. Symptoms may include restlessness, irritability, drowsiness, tremors, vertigo, double vision (diplopia), ataxia, cough, dyspnea, retrosternal discomfort, abdominal pain, and vomiting. There is no antidote for phosphine exposures; treatment is supportive. Guidance on proper medical treatment is available from the US Health

Department Agency for Toxic Substances and Disease Registry (ATSDR) sheet on phosphine.

Transportation regulations prohibit the supply of pure phosphine in cylinders larger than 50 liters since it is highly toxic. As a dopant, phosphine is supplied to the process as a low concentration mixture in order to precisely control the diffusion rate for the TFT-LCD processes. As a mixture, the gas is no longer classified as highly toxic, therefore it is supplied in bulk high cylinders of 450 liters or larger.

Some gas suppliers are also supplying gas mixing systems which will dynamically blend the phosphine from a pure source cylinder with hydrogen. A single cylinder will supply 200 cylinders of 0.5% concentration.

### 2.3 Hydrogen

Hydrogen is a colorless, odorless, tasteless, highly flammable gas. It is also the lightest weight gas. It is much less dense than air and can disperse rapidly or accumulate in the upper sections of enclosed spaces

Hydrogen has a wide flammability range, 4% to 75% in air, and the small amount of energy required for ignition necessitate special handling to prevent the inadvertent mixing of hydrogen with air. Sources of ignition such as sparks from electrical equipment, static electricity, open flames, or extremely hot objects should be eliminated. Hydrogen and air mixtures within the flammable range can explode and may burn with an almost invisible flame. Although hydrogen is not pyrophoric like silane or phosphine, hydrogen release from a tube or a crack under high pressure may lead to spontaneous ignition. This is attributed to the low ignition energy, high blow-off velocity and the adiabatic compression from the shock wave of the release (Dryer et al., 2007)

Gaseous hydrogen may be supplied in cylinders or in tubes that are designed and manufactured according to applicable codes and specifications for the pressures and temperatures involved. The pressure rating and internal volume of a container determines the quantity of hydrogen it can hold. Cylinders may be used individually or can be manifolded together to allow for a larger gas storage volume. Tubes are mounted on truck-trailer chassis or in ISO frames for transportation and are referred to as tube trailers or tube modules, respectively.

### 2.4 Ammonia

Ammonia ( $\text{NH}_3$ ) is a toxic and corrosive liquefied compressed gas. It is used to grow a silicon nitride layer in the TFT-LCD industry. Pure ammonia is a white liquefied gas. It is a strongly irritating gas. It is a toxic gas with a PEL of 50 ppm and an  $\text{LC}_{50}$  of 7,338 ppm. Ammonia is lighter than air (specific gravity: 0.59) and is highly soluble in water. Ammonia is thermally stable.

Ammonia has a very narrow flammable range of 16% to 25% and minimum ignition energy (MIE) 40,000 times (680 mJ) higher than that of hydrogen (0.017 mJ). The common flammable gases such as propane have a MIE of 0.25 mJ which is still many times less than ammonia. The high lower flammable limit (LFL) and lighter than air vapor density makes it unlikely for an ammonia release to reach concentrations high enough to burn in open areas. It is thus classified as non-flammable for transportation purposes. The national building and fire regulations however classify it as flammable in storage and use.

As a flammable gas, ammonia is reactive with oxidizer gases such as nitrous oxide or oxygen. Since ammonia has an  $LC_{50}$  higher than 5,000 ppm (threshold for toxic gas), the United States classifies it as a non-toxic non-flammable gas. All other countries classify ammonia as a toxic gas. Ammonia is a severe irritant with a sharp pungent odor that will have an immediate effect on moist tissues, eyes, upper respiratory system and skin. Guidance on proper medical treatment is available from the US Health Department Agency for Toxic Substances and Disease Registry (ATSDR) sheet on Ammonia.

Ammonia is very corrosive to low alloy carbon steel, causing stress corrosion. Ammonia is also corrosive to viton, zinc and copper. Bulk ammonia is supplied in low or high pressure bulk containers (250 liter - 950 liter). Some facilities use 40,000 lb ISO Modules that are sited like the nitrogen trifluoride or silane modules for continuous supply. It is vaporized for use on demand.

### 2.5 Nitrogen trifluoride

Nitrogen trifluoride ( $NF_3$ ) is a colorless, odorless, nonflammable, oxidizing compressed gas. Nitrogen trifluoride is the most common reactor cleaning gases used in the TFT-LCD industry because of its advantages, such as high etching rates, high selectivity, carbon-free etching, and minimal residual contamination. It is first decomposed in a remote plasma chamber into a reactive fluorine before fed to the reaction chamber where it is used to react solid deposits on the reactor walls to form gaseous byproducts such as silicon tetrafluoride.

Nitrogen trifluoride is not toxic, it has an  $LC_{50}$  of 6,700 ppm (1 hr. rat). It is not hazardous by skin contact and is a relatively minor irritant to the eyes and mucous membranes. Exposure of rats to a 100 ppm concentration for 7 hrs per day, 5 days per week over a 19 week period caused minor pathological changes to the liver and kidney. No other effects were noted. The ACGIH established the current TLV-TWA of 10 ppm based on 1/10 of this value. Some countries classify nitrogen trifluoride as a toxic gas because it has a TLV-TWA <200 ppm.

Under ambient temperatures and pressures, nitrogen trifluoride is inert. However it can become an extremely reactive under certain conditions. It is a strong oxidizer that is violently explosive at elevated pressures with flammable gases such as hydrogen or silane. Purification of nitrogen trifluoride using a solid absorbent media such as molecular sieve is to be avoided. Fires and explosions have occurred.

Nitrogen trifluoride is reported to be a significant greenhouse warming gas with a Greenhouse Warming Potential (GWP) >10,000 as compared to carbon dioxide. Properly design remote plasma cleaning system will react 100% of the nitrogen trifluoride, so it has a GWP comparable to fluorine under these conditions.

### 2.6 Chlorine

Chlorine ( $Cl_2$ ) is a toxic and corrosive liquefied compressed gas. It is also an oxidizing gas. Chlorine is used primarily as an etching gas in the TFT-LCD industry. Pure chlorine is a yellow-green liquefied gas. It is a strongly irritating and highly toxic gas with a PEL of 0.5 ppm and an  $LC_{50}$  of 293 ppm. Chlorine is much heavier than air (specific gravity: 2.49) and is slightly soluble in water. Chlorine is thermally stable.

Chlorine is a severe irritant with a pungent odor that will have an immediate effect on moist tissues, eyes, upper respiratory system and skin. Chronic exposure will corrode teeth, in

some cases it will cause flu-like symptoms. Guidance on proper medical treatment is available from the US Health Department Agency for Toxic Substances and Disease Registry (ATSDR) sheet on chlorine.

Chlorine is an oxidizer gas that is equivalent to a 60% concentration of pure oxygen or almost 3 times that of air. As an oxidizer chlorine is reactive with flammable gases such as silane or hydrogen. In some cases it can be explosive, even in concentrations as low as 3% when mixed with these gases. Pure chlorine has also autoignited flammable materials.

Similar to ammonia, bulk chlorine is supplied in low or high pressure bulk containers (250 liter - 950 liter). It is vaporized for use.

## 2.7 Fluorine

Fluorine is a highly toxic gas with extreme oxidation and corrosion potentials. It has a sharp, pungent odor that can be detected by most people at very low levels (0.1 ppm). It has a TLV-TWA of 1 ppm and an LC<sub>50</sub> of 185 ppm (1 hr. rat). Chronic fluorine exposures at low levels may cause fluorosis or abnormal calcium accumulation in bone structure. Fluorine is highly reactive with moisture, forming hydrofluoric acid which is extremely corrosive to human tissue. Fluorine will have an immediate effect on the eyes and respiratory system.

Medical treatment of exposure is specific and specialized. Releases into air can form varying concentrations of hydrofluoric acid, depending on conditions. When the aqueous hydrofluoric acid concentration is below 50%, it has delayed (up to six hours) symptoms of exposure. In a fire, fluorine will react to form other toxic fluoride compounds.

Fluorine is the most reactive of all elements and the most powerfully known oxidizing agent. Fluorine is able to react with almost all elements and compounds depending on pressure and temperature, with the exception of lighter noble gases (e.g. helium, argon), inorganic fluorides of the highest valency, and perfluorinated organic compounds. It reacts with many organic substances even at room temperatures and often accompanied by combustion and possible explosion (European Industrial Gases Association, 2011). Therefore special steps, such as special cleaning and passivation procedures, must be taken to protect systems.

Fluorine reacts vigorously at ambient temperatures with most metals. The reaction intensity depends upon the surface area of the metal. Powdered metals or fine wires may react violently. Most inorganic materials react with fluorine; water forms hydrofluoric acid, and salts convert to fluorides. Contact with organic materials generally results in ignition or violent explosion.

Due to its extreme reactivity, national transportation regulations typically limit the total amount of fluorine in a 50 liter cylinder to 3 kg or to a pressure of 30 bar. Pure fluorine cylinders can be fairly reactive at 30 bar. Some users use a mixture which is less reactive. Testing by Air Products and Chemical Inc. (2004) has shown that fluorine is 2.5 times more reactive than oxygen, when it is mixed in a 20% concentration with nitrogen it will not ignite a 1/4" carbon steel rod at 13,790 kPa.

Testing by Ngai (2005) has shown that pure fluorine even at a pressure as low as 1 atm (101 kPa) can cause 316 stainless steel tubing to burn. Pure fluorine did not react immediately with the raw chicken. To better simulate human skin, some human hair was placed on the chicken skin. This immediately ignited and started the skin on fire as shown in Figure 4. The reaction was so hot that it ignited the stainless steel tubing, which sprayed the chicken with molten stainless steel. This continued to react until the fluorine flow was stopped (Ngai, 2005).



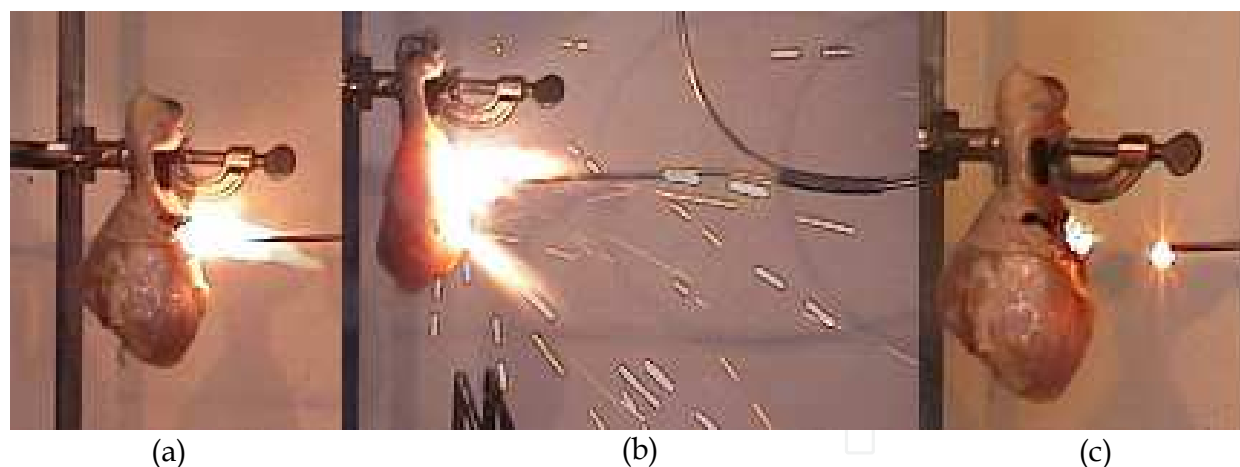


Fig. 4. Reaction of fluorine and chicken skin. (a) The hair on the skin reacts with the fluorine and ignites the chicken skin. (b) Skin burns hot enough to ignite the stainless steel tubing, which is sprayed at the chicken. (c) The tubing continues to react until the flow is stopped.

Despite its toxicity and reactivity, fluorine is being increasingly used as a reactor cleaning gas owing to less energy requirement, lower Greenhouse Warming Potential, and faster clean time (Stockman, 2009). To supply pure fluorine, small generators are being installed and managed by gas suppliers. These limit the amount of fluorine stored. A typical fluorine generator is an electrolytic cell which dialysis hydrogen fluoride to form fluorine and hydrogen (Stockman, 2009).

### 3. Best practice for handling

#### 3.1 Silane

The first step in safe handling of silane is to comply with relevant regulatory & industrial standards such as Compressed Gas Association (CGA), Semiconductor Equipment and Materials International (SEMI), National Fire Protection Association (NFPA), Factory Mutual (FM), European Industrial Gas Association (EIGA), Asian Industrial Gas Association (AIGA), Transportable Pressure Equipment Directive (TPED), Transportation of dangerous goods (ADR), SEVESO, ATEX, etc. The installation and operation practices are however not necessarily detailed in the above codes or standards. Rufin (2011) has presented a comprehensive list of best practices for silane supply system. The key features are summarized below.

From the perspectives of preventing silane explosion, the most effective measure is preventing the accumulation of unignited silane through the use of forced ventilation or open air storage. It is also important to detect an unignited release by installing a gas sensor. Flame (UV/IR) detector is also needed for detecting leaks with autoignition. Sprinklers are needed for cooling the cylinders and system. Operators must be also be protected by barriers and flame resistant protection suit.

Other minor but equally important issues include:

- Welding for all indoor distribution systems
- Joule-Thomson compensation for high flow >50 L/min
- Automation and remote control
- Prevention of “domino effect” by steel plate or firewall between sources

- Normally closed pneumatic shut off valves
- Dedicated purge sources with automated purge cycles
- High pressure test and He outboard leak test
- Emergency remote shut down

For high flow rate greater than 50 L/min, large pressure drop will produce liquid silane mixture causing failure and leaks mostly in regulators. Thus, use of 2 regulators in series and heaters to compensate Joule-Thomson expansion cooling and prevent condensation.

### 3.2 Fluorine

As fluorine reacts with almost everything, corrosion of materials in contact with fluorine is dependent upon the fluoride formed with the material. If the fluoride is volatile or in the form of loose flakes, new material will constantly be exposed to the fluorine and will be continuously eroded until it burns through the material. For this reason material selection is extremely important. Materials that form a good fluoride coating will be protected from further attack.

Systems for fluorine service must not only be fabricated of the proper material, the design of the system must consider the following factors:

- Adiabatic compression - Adiabatic compression and heating is caused by the rapid pressurization of a system where the gas absorbs the energy and the gas temperature rises. This heating occurs at the point of compression or the point where the flow of gas is stopped, such as at a valve or regulator seat. Depending on the material in use where the hot gas impinges, the heat may be sufficient to ignite the material.
- High flow - High flow velocity increases the potential for a particle to impinge onto a surface with sufficient force to ignite it. A common area where this occurs is at a direction of flow change such as an elbow.
- Reactive materials - If the valve or regulator has a seat made of a nonmetallic material, it may be more prone to ignition because nonmetals typically have lower ignition temperatures than metals.
- Drying - removal of moisture from the system surface is essential
- Cleaning - to remove contaminants such as oil and particles from the system. These can be ignited easily generating sufficient heat to propagate a reaction to the system.
- Passivation - Fluorine passivation of metals is a pretreatment of the components in order to stabilize the wetted surfaces of the system by formation of a self-limiting protective fluoride film on the surface of the metal. The typical film thickness range from thickness of 5 Å (0.0005 microns) to 50 Å (0.005 microns) depending on the metal (Air Force Rocket Propulsion Laboratory, 1967).
- Friction - from a component that is malfunctioning or operating poorly can generate heat. Friction between two materials generates fine particles, which may ignite from the heat generated.

### 3.3 Other specialty gases

Silane and fluorine represent the two extremes, the flammable and the oxidizer, of the specialty gases used in TFT-LCD manufacturing. All other gases bear similar but less extensive practices and protection measures as these two gases. For example, gas detectors

are needed for all gases except for nitrogen trifluoride. Flame (UV/IR) detectors and sprinklers are needed for all flammable gases. High pressure test and He outboard leak test with emergency remote shut down are also typical practices for all gases.

## 4. Incidents and emergency response

### 4.1 Silane

There are numerous silane leaks in the forty years of silane use (Huang and Ngai, 2006) mostly resulted from poor procedures, practices, and equipment. The reactions from the leaks were reported to be a fire, minor “pops” to explosions. The “pops” can occur when a small amount of Silane trapped behind the valve cap or pigtail is released rapidly without prompt ignition. In a few cases they have been severe enough to cause eardrum rupture if the amount of accumulated silane is significant. Thus, the past silane leaks do support the fact that a leak with indefinitely delayed ignition is commonly observed in silane operations.

Although the release with indefinitely delayed ignition were mostly small and had finite impact, the unignited release may turn into large release with significant impact. The following major incidents were known where silane was released without immediate ignition and exploded after a delay:

- 1976, Germany, 1 fatality
- 1989, Japan, 1 fatality & 1 injury
- 1990, Japan, 1 fatality & 3 injuries
- 1992, US, 1 injury
- 1996, Japan, 1 fatality
- 2003, US, no injuries
- 2005, Taiwan, 1 fatality
- 2007, India, 1 fatality

Among these incidents, the incident in Taiwan in 2005 has been described in detail by Chen et al. (2006), Chang et al. (2007) and Peng et al. (2008). The cause of leak is a failed silane cylinder valve with loosened valve stem retainer. Silane leak from such a loosened retainer has been shown to have delayed ignition by Ngai et al. (2007). The operator in this case did not notice the unignited silane release from the loosened retainer and continued to turn the valve handwheel until eventually the retainer, valve stem, and valve diaphragm were all detached. The rapid silane release with ignition at end of release resulted in a fatal vapor explosion.

Emergency response to a silane incident is the most challenging one among all gas incidents (Ngai, 2011). The greatest danger is a leak and no fire. As ignition is inevitable at the end of leak, a pop or explosion should be expected. Use surveillance camera to make initial assessment if possible. Remotely review the gas detector response over time on a graph to insure that it is not sensor drift or electronic spike. Evacuation should be done first if there is a gas detector alarm but without visual confirmation of flame. The responders should wear full personal protection equipment, including fire proof suit, glove, hardhat, ear plug etc. and approach the leak with great care. The leak could ignite as the pressure decays in the source cylinder or an air flow disturbance is created. Assess the leak rate with a portable gas detector through the gas cabinet duct. For a small leak, it might be safe to remotely shutoff the supply but expect ignition and a pop at shutoff. Slow shutoff of the valve will minimize the amount of silane when it ignites. A leak with a

gas detector reading below the maximum scale, normally about 50 ppm, may be considered as a small leak. For a larger leak, activate sprinkler or apply water spray from a distance to the leak point to disperse the gas cloud and reduce the extent of potential explosion. Always prepare for possible explosion.

If the leak is burning, cool the adjacent area with a water spray. Do not spray water directly onto the fire as this could put it out and create an explosive environment. The heat could melt the fusible metal in the pressure relief device (PRD). The PRD will not activate unless the internal pressure reaches 27.6 MPa (4000 psig). Water spray from the deluge system onto the tubes will prevent this from ever reaching this temperature. A leak on fire can plug from the solids formed. Solids can also trap silane which can still be reactive. Even after a fire and the cylinder has vented to zero gauge pressure, there is still one atmosphere of gas in the cylinder. Emergency response teams typically will dilute the remaining silane by pressurizing the leaking cylinder with nitrogen to 0.79 MPa (100 psig) and venting 3 times. This will dilute the silane concentration to 2000 ppm. At this concentration and pressure, the cylinder can be shipped back as a non-hazardous package.

#### 4.2 Hydrogen

The authors are aware of six hydrogen fires with one of the fires resulting in rupture of the hydrogen tube. The fire resulted from the detachment of an aging copper tube to the cylinder pack in a hydrogen filling station. The hydrogen ignited during tube detachment from a filling manifold and resulted in jet fire which impinged on a nearby tube trailer. The tube trailer was parked without protection of sprinkler system and two tubes were ruptured in less than 5 minutes of flame impingement. The most important emergency response after the tube explosion was continuous cooling and venting of hydrogen in the remaining tubes.

#### 4.3 Nitrogen trifluoride

There have been reported incidents of nitrogen trifluoride with flammable oils used in vacuum pumps. Systems for nitrogen trifluoride must be designed similar to the requirements for fluorine in 3.2. Adiabatic compression and heating can initiate the decomposition reaction of nitrogen trifluoride into reactive fluorine. Incidents have occurred with improperly designed or cleaned systems during routine activities such as pressurizing the system. Internationally the maximum fill limits for nitrogen trifluoride cylinders is 0.5 kg/liter. At 21°C the cylinder pressure will be 10.78 MPa. Quickly opening the cylinder valve into a system with a small dead volume will cause adiabatic compression and heating to 307°C. In the presence of a reactive nonmetal component or a contaminant, this can initiate the decomposition reaction. Given sufficient energy and pressure, the reaction can cause the metal system to also become involved. Figure 5 shows a burnt valve in a nitrogen trifluoride line caused by adiabatic compression.

#### 4.4 Chlorine

Chlorine is very corrosive to carbon steel and stainless steel. With the moisture in the air it forms hypochlorous (HClO) and hydrochloric (HCl) acids which will corrode the steel as shown in Figure 6. A corroded connection generally leads to leak. A good design supply system should pick up the leak by detector and shutdown the system. If the system is not



Fig. 5. A burnt valve in a nitrogen trifluoride line caused by adiabatic compression.



Fig. 6. Green hypochlorous and hydrochloric acids from chlorine corrosion.

designed properly, the chlorine may continuous to leak and affect the cleanroom. The author is aware of a chlorine leak from a tube connection in an IC fab that was not detected until one hour later. The chlorine cloud speaded and significantly affected the cleanroom and production tools.

#### 4.5 Other specialty gases

The authors are not aware of any phosphine, ammonia, or fluorine fatalities or fires related to semiconductor or TFT-LCD uses.

### 5. Conclusions

The TFT-LCD manufacturing processes utilize significant amount of gases ranging from highly flammable to strong oxidizer gases. Special cares must be taken in handling these specialty gases to prevent fire, explosion and toxic release.

This paper has reviewed the hazardous properties and potential incidents of these specialty gases. The best practices for handling these gases are then described. The emergency

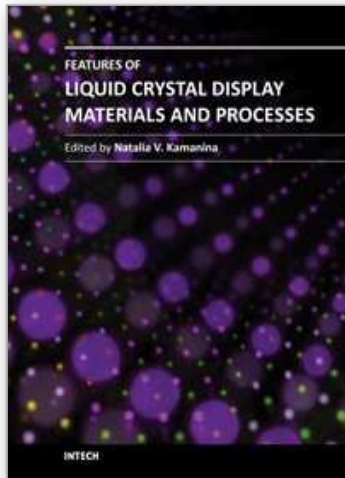
response actions are also reviewed. It is sincerely hope that the current summary may bring an integrated view on the complicated and delicate specialty gas supply system, and preventing future incidents from occurring.

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## **Features of Liquid Crystal Display Materials and Processes**

Edited by Dr. Natalia Kamanina

ISBN 978-953-307-899-1

Hard cover, 210 pages

**Publisher** InTech

**Published online** 30, November, 2011

**Published in print edition** November, 2011

Following the targeted word direction of Opto- and Nanoelectronics, the field of science and technology related to the development of new display technology and organic materials based on liquid crystals ones is meeting the task of replacing volume inorganic electro-optical matrices and devices. An important way in this direction is the study of promising photorefractive materials, conducting coatings, alignment layers, as well as electric schemes that allow the control of liquid crystal mesophase with good advantage. This book includes advanced and revised contributions and covers theoretical modeling for optoelectronics and nonlinear optics, as well as includes experimental methods, new schemes, new approach and explanation which extends the display technology for laser, semiconductor device technology, medicine, biotechnology, etc. The advanced idea, approach, and information described here will be fruitful for the readers to find a sustainable solution in a fundamental study and in the industry.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Eugene Y. Ngai and Jenq-Renn Chen (2011). Gas Safety for TFT-LCD Manufacturing, Features of Liquid Crystal Display Materials and Processes, Dr. Natalia Kamanina (Ed.), ISBN: 978-953-307-899-1, InTech, Available from: <http://www.intechopen.com/books/features-of-liquid-crystal-display-materials-and-processes/gas-safety-for-tft-lcd-manufacturing>

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