Chemically Speaking LLC

Hexachlorodisilane

NY SESHA Chapter Seminar, E. Ngai

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Silicon nitride and Silicon dioxide are some of the most widely used dielectric materials in Si microelectronics processing and can be deposited by CVD and ALD methods

Used as silicon source for memory

Replacing dichlorosilane

Advantageous Deposition Rates at Lower Temperatures

The change from amorphous to polycrystalline growth takes place at 600-650^{o}C. At 600^{o}C deposited films are amorphous but crystallize during the growth process.

Low‐k Silicon Nitride Films Formed by Hexachlorodisilane and Ammonia

Very thin barrier layer SiOCN is grown in one recipe by ALD by sequentially pulsing

- HCDS
- NH_3
- O_2
- C_3H_6

Major Systems That Grow SiOCN Layers

Use HCDS Low Temperature

- TEL Indy
- Hitachi Kokusai Electric

Others

- Higher temperatures
- Other Silicon Compounds

DCS is liquefied gas that must be cooled to 0^{o}C (600 torr) for ALD while HCDS is heated to 100^{o}C (187 torr)

The use of hexachlorodisilane (Si_2Cl_6) as an alternative to silane for growth of polycrystalline silicon films has been investigated. Films were grown at atmospheric pressure in both hydrogen and nitrogen carrier gases over a temperature range of 450-900'C. Deposition rate data indicate the existence of two growth regimes at high and low temperatures and in the presence or absence of hydrogen. The change from amorphous to polycrystalline growth takes place at 600-650+C. At 600oC deposited films are amorphous but crystallize during the growth process. The chlorine content of high-temperature films was found to be less than 0.01 at.%.

SiOCN Layer, combined with ammonia to deposit thin layers of the barrier material silicon nitride

A low‐temperature process with good step coverage of silicon nitride (SiN) formed by low‐pressure chemical vapor deposition (LPCVD) has been successfully developed by using hexachlorodisilane (HCD). HCDS‐SiN showed a higher deposition rate than the conventional LPCVD technique performed at temperatures above 700°C. SiN films can be deposited down to 250°C using HCD. Deposition characteristics, film composition, and film properties under integrated circuit fabrication processes are measured mainly in terms of deposition temperature dependence. A low‐k HCD‐SiN film, formed at 450° C with a permittivity of 5.4, was applied on Cu films as an oxidation and diffusion barrier layer. The film shows excellent barrier properties and is advantageous for realizing high - performance very large scale integrated devices with Cu interconnects

Major Manufacturers

- Wacker
- Air Liquide
- Dow Chemical
- REC Silicon
- Nova Chem

Chlorosilane redistribution

By definition the chlorosilanes are classed as both a compressed gas and as a liquid

Monochlorosilane (MCS)	$SiClH_3$	Gas
Dichlorosilane (DCS)	$SiCl_2H_2$	Gas
Trichlorosilane (TCS)	$SiCl_3H$	Liquid
Silicon Tetrachloride (SiCl)	$SiCl_4$	Liquid
Methyltrichlorosilane (MTCS)	$SiCH_3Cl_3$	Liquid
Hexachlorodisilane (HCDS)	Si_2Cl_6	Liquid

As a result they might be classed differently even though they have the same hazards

Chemical and Physical Properties

- Si_2Cl_6, Chlorosilane
- CAS# 13465-77-5
- UN#2988 Chlorosilanes, water reactive, flammable, corrosive, n.o.s. (Hexachlorodisilane)
- Molecular Weight 268.89
- Liquid with Vapor Pressure of 12 mm hg @104^oF (40^oC)
- Liquid Density of 1.56 gm/cc @ 70^oF (21^oC)
- Corrosive Liquid with PEL of 5 ppm, IDLH of 100 ppm all as HCl, LC_{50} ppm
- Shipping Labels Dangerous When Wet, Corrosive Liquid, Flammable Liquid
- Boiling Point, 1 atm. : 293^oF (145^oC)
- Freezing Point, 1 atm.: 29.8^oF (-1.2^oC)
- Critical Temperature. :NA^oF (NA C)
- Hexachlorodisilane has a vapor density of. NA low vapor pressure
- Autoignition 302^oF (>150^oC)
- Flashpoint 80^oC (175^oF) Decomposition causes flammable gas
- Flammability (LFL-UFL) NA
- Thermal Stability Hexachlorodisilane is thermally stable up to 400^oC. (Wacker Study) Not very reactive in air – can be distilled in air without obvious oxidation
- Water Solubility Hexachlorodisilane reacts violently
- Odor Hexachlorodisilane is reported to have a sharp irritating odor
- Latent Heat of Vaporization NA
- Other reactions
- Most powerful deoxygenation agent – can abstract oxygen from many organics
- Water Reactive, Worker Safety (OSHA)

Chemical	Vapor Pressure 20°C, mm Hg
Concentrated Sulfuric Acid	0.001
ZyALD	1
50% Sodium Hydroxide	2
SAM 24	2
Ethylene Glycol	4
Hexachlorodisilane	3
Water	18
Propanol	18
50% Hydrofluoric Acid	25
Ethanol	68
Acetone	181
Trisilylamine	315
Trichlorosilane	516
Acetaldehyde	740

UN IDENTIFICATION NUMBER: UN 2987

PROPER SHIPPING NAME: Chlorosilanes, corrosive, n.o.s.

HAZARD CLASS NUMBER and DESCRIPTION: 8 (Corrosive)

PACKING GROUP: PG II

DOT LABEL(S) REQUIRED: Class 8 (Corrosive)

Hexachlorodisilane is a Chlorosilane that is a Water Reactive Liquid

Not all water reactive materials are classified as Dangerous When Wet

Hexachlorodisilane is a colorless liquid which is Water Reactive and Corrosive

Substances that are dangerous when wet because they undergo a chemical reaction with water. This reaction may release a gas that is either flammable or presents a toxic health hazard. In addition, the heat generated when water contacts such materials is often enough for the item to spontaneously combust or explode

Dangerous When Wet, Transportation (DOT) Division 4.3

a material that, by contact with water, is liable to become spontaneously flammable or to give off flammable or toxic gas at a rate greater than 1 L per kilogram of the material, per hour, when tested in accordance with UN Manual of Tests and Criteria

Water Reactive, Fire Codes (NFPA)

Materials that react violently with water, including the ability to boil water, or that evolve flammable or toxic gas at a sufficient rate to create hazards under emergency response conditions

Materials whose heat of mixing is at or above 100 cal/g and less than 600 cal/g

Water Reactivity Hazard Degree 2

Example used in NFPA is

Dichlorosilane. In contact with water, exothermic hydrolysis is accompanied by evaporation of the volatile liquid phase. Toxic dichlorosilane plus hydrogen chloride gases are released and spontaneous ignition of the Dichlorosilane can occur.

The definition by OSHA and DOT will only classify trichlorosilane and trimethylchlorosilane as Dangerous When Wet while silicon tetrachloride is just corrosive. While the NFPA definition classifies all Chlorosilanes as meeting the definition

The Silicones Environmental Health and Safety Council (SEHSC) petitioned the DOT to reclassify all chlorosilanes to be dangerous when wet and toxic, even if they do not meet the regulatory definition.

Acute Inhalation Toxicity

- Toxic by inhalation
- Corrosive, causes burns to eyes, skin and mucous membranes.
- Can cause burns to respiratory tract and mucous membrane.
- Exposure can result in pulmonary edema, which can be fatal.

The metal chlorides can have a more significant affect the respiratory system than HCl since some of it will enter into the upper airway before reacting to form HCl before reaching the lower airway

No TLV's, PEL's or IDLH values have been established for the Chlorosilanes

Since acute toxicity test data shows a good correlation with the equivalent HCl value, toxicologist have accepted the use of HCl equivalent values. For example trichlorosilane will form 3 moles of HCl which has LC_{50} of 3120 ppm (1 hr). TCS HCl LC_{50} equivalent is 1040 ppm which is very close to the test value

Hexachlorodisilane estimated LC_{50} – 520 ppm

For any liquid exposure, saturated clothing must be removed and any liquid removed from the skin before drenching the area in a Safety Shower or water spray. Liquid hydrolysis in water is highly exothermic and will cause severe thermal burns. The byproduct acid will also cause severe chemical burns.

The Chlorosilanes have a extremely low electrical conductivity (<<50 pS/m) and can accumulate significant static charge during the liquid transfer.

Static electricity discharges can ignite flammable liquids

Static electricity can be generated by, care must be taken for the following conditions

- Liquid flowing through pipes
- Liquid being discharged from a pipe
- Liquid falling freely through space
- Splash filling is particularly hazardous since it agitates the liquid

All vessels and piping should be electrically interconnected

All vessels and piping should be grounded

Piping should be conductive and not have a non conductive liner

Container UN1A1X1.8

Performance Packaging or DOT Cylinder Specification

- Manual or pneumatic valves
- Diptube
- VCR Outlet Connections
- Level sensor
- Center hex nut for filling

SEMI standard F96-0704 Specification for Port Configuration on Canisters to Contain Liquid CVD Precursors.

Male VCR on vapor line and female VCR on diptube

Container Refill

- Liquid emptied
- Valves taken apart
- Washed with dilute hydrofluoric acid
- Rinsed Deionized water in cleanroom
- Baked in oven in cleanroom
- Valves reassembled with new parts
- Filled in glovebox through large port

Bulk container supplies a process container that fills an in line ampoule before each run.

Bulk cabinet feeds a VMB to 4 tools

Ampoules are located at the tool in the Cleanroom

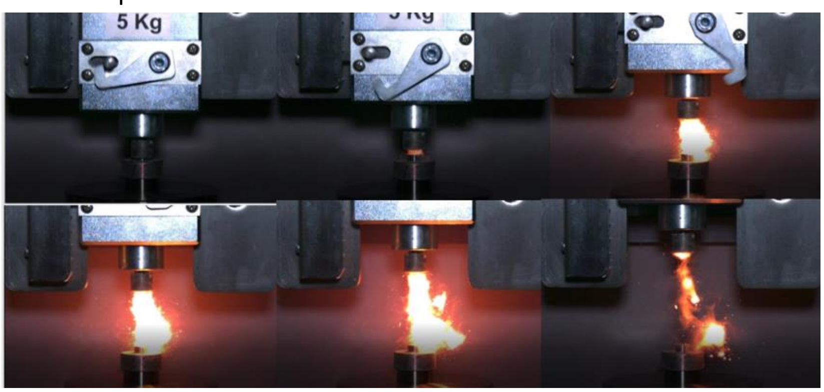
Incidents

TCS and water, MCTS with H_2 at high temperatures

Translusent gelatinous gel in foreline or vacuum pump

Exposure to air turns it into white/brown solid
Shock sensitive and/or flammable
Foreline deposits are extremely reactive with HF
Venting HCDS to atmosphere reacts to form shock sensitive gel

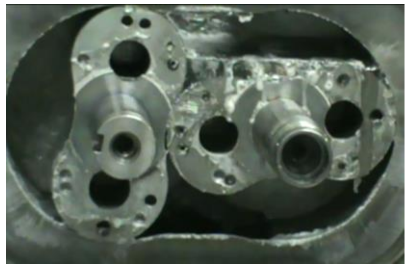
Testing by Prof Chen using Fall Hammer test to determine shock sensitivty
HCDS Hydrolysis or reaction with water may take place in four different processes:
Vapor-phase hydrolysis with HCDS vapor reacting with water vapor (moisture)
Liquid-phase hydrolysis with HCDS liquid reacting with liquid water
Two-phase hydrolysis with HCDS liquid reacting with water vapor (moisture)
Two-phase hydrolysis with HCDS vapor reacting with liquid water
The process strongly affects the rate of hydrolysis as well as possibly the structure of hydrolyzed deposit and/or other by-products that maybe attached to the final hydrolyzed deposit which in turns affect the shock sensitivity of the end products



concluded
Mechanism of shock sensitivity from HCDS hydrolyzed deposit is uncovered through extensive tests on hydrolysis and IR studies
The Si-Si bond in HCDS hydrolysis is preserved and can be cleaved by shock leading to intramolecular oxidation of neighboring Si-Si-OH bond to form networked Si-O-Si and H2
To prevent the formation of shock sensitivity deposit, it is necessary to either prevent the hydrolysis reaction or to inhibit the shock sensitivity through control of the deposit
It is impractical to prevent the hydrolysis as moisture is always present in air and can back diffuse easily into a vent line
Concentrated sulfuric acid is found to suppress shock sensitivity of the hydrolyzed powder

Vacuum Pumps

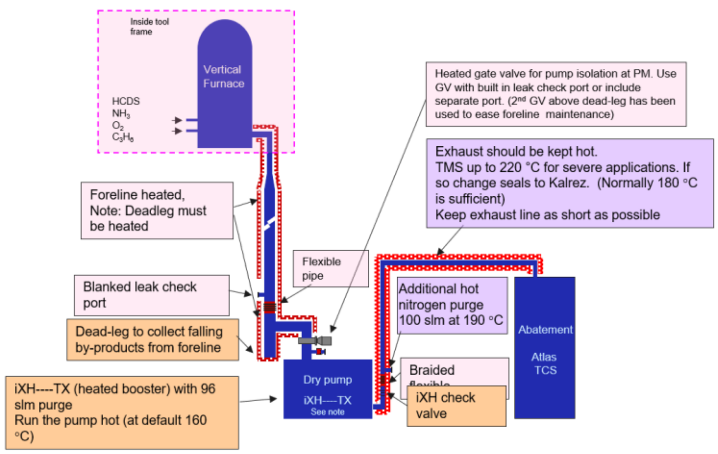
Over a dozen vacuum pumps have failed due to plugging with popping gel deposits

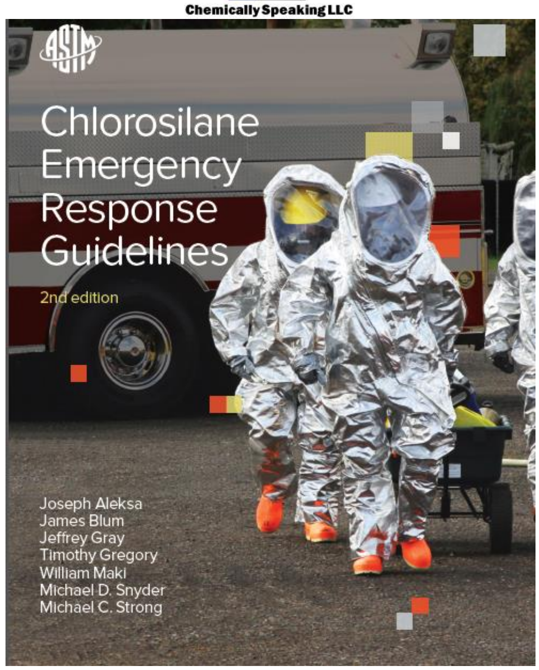


These ignited as they were taken apart

Recommend more frequent cleaning

Best known method for ALD SiOCN installation

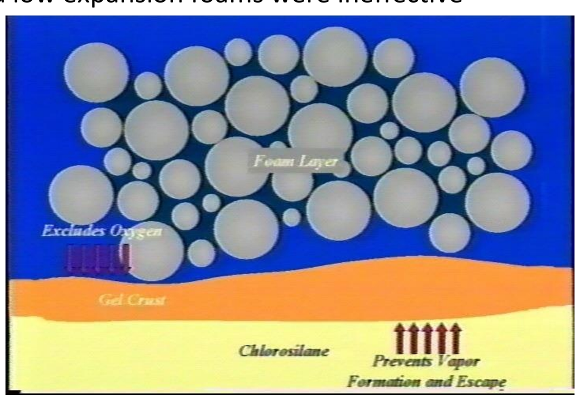




Foaming a Chlorosilane fire

Silicones Health Council in the United States in 1990 and testing in Taiwan 2007

Demonstrated the effectiveness of Alcohol compatible AFFF (Aqueous Film Forming Foam) at medium expansion. This must be applied properly in order to develop a continuous interface layer to suppress the TCS vapors from a spill. It is also capable of putting out a fire but must be properly applied and in a thick enough layer. High and low expansion foams were ineffective



Will be more effective on HCDS which has a vapor pressure of 3 mm Hg while TCS Is 517 mm Hg

Chemical and Flashover protection. Level A/B with Flashover

While the vapor pressure is low at 70^{o}F the liquid will quickly vaporize due to hydrolysis reaction from the moisture in air. It will leave behind a white deposit that might be reactive

Neutralizing with dilute alkaline can cause it to become reactive when dried

Overpack Container

To avoid static do not wear any synthetic undergarments
Position container so that the leak point is the highest vertical point
Depressurize container to reduce leak rate
Survey container using thermal imaging camera to make sure a reaction is not occurring within the container
UN1A2 Metal Overpack drum
Ground overpack
Clean and patch leak point, use Pig Putty
If possible purge air out of drum using a N2 wand
Place leaking container into metal drum
Fill area between the container and drum wall with vermiculite.
Note that HCDS will hydrolyze with the moisture (30%) on the vermiculite and heat up
Caution, dried vermiculite/HCDS is reactive