Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, TUNGSTEN

Tungsten has three readily prepared binary fluorides, tungsten hexafluoride [7783-82-6], tungsten pentafluoride [19357-83-6], and tungsten tetrafluoride [13766-47-7] (1, 2). The three lower oxidation state tungsten binary fluorides have been observed only in high energy systems (3). Several complex oxyfluorides are known including WOF_4 [13520-79-1] and WO_2F_2 [14118-73-1] (4). Only tungsten hexafluoride is made commercially. Tungsten hexafluoride is used as a tungsten source in chemical vapor deposition (CVD) for very large-scale integration (VSLI) devices.

1. Tungsten Hexafluoride

1.1. Physical Properties

Tungsten(VI) fluoride [7783-82-6], WF_6, is a colorless gas that condenses at ca 100 kPa (1 atm) and 17.1°C to a water-white liquid that may be colored owing to metallic impurities. Below 2°C it forms a white solid. Tungsten hexafluoride has a symmetrical octahedral structure at near room temperature and a phase of lower symmetry below −8.5°C (5). The Raman and uv spectra (6), as well as the ir spectrum (7) have been studied. The physical properties of tungsten hexafluoride are given in Table 1.

1.2. Chemical Properties

Tungsten hexafluoride is readily hydrolyzed by water to give tungsten trioxide and hydrogen fluoride. It is a strong fluorinating agent and reacts with many metals at room temperature. Tungsten hexafluoride reacts with the alkali fluorides KF, RbF, and CsF to form the complex salts K_2WF_8 [57300-87-5], Rb_2WF_8 [57300-88-6], and Cs_2WF_8 [57300-89-7], respectively (10). The alkali iodides and WF_6 react in sulfur dioxide to form the tungsten(V) compounds $NaWF_6$ [55822-76-9], KWF_6 [34629-85-1], $RbWF_6$ [53639-97-7], and $CsWF_6$ [19175-38-3] (11). Tungsten hexafluoride reacts with hydrogen and hydrogen-containing reducing agents at elevated temperature to form tungsten metal and hydrogen fluoride. This reaction is the basis of the primary use of tungsten hexafluoride in CVD (see Thin films). The CVD chemistry of WF_6 has been reviewed (12, 13). Reduction with hydrogen generally requires temperatures of 450–750°C and pressures of <100 kPa (14.5 psi) (14). Other gaseous reductants include GeH_4 (15), SiH_2F_2 (16), SiH_4 (17), and diethyl silane (18).

1.3. Manufacture and Economics

Tungsten hexafluoride is produced commercially by the reaction of tungsten powder and gaseous fluorine at a temperature in excess of 350°C (19). Tungsten hexafluoride is the principal product of the reaction, and there are no by-products when high purity tungsten powder and fluorine are used. U.S. production is several metric tons per year. Essentially all of the product is used in CVD. Air Products and Chemicals, Inc. (Allentown,

Table 1. Physical Properties of Tungsten Hexafluoride

Property	Value	References
boiling point, °C	17.2	8
triple point, °C, 55.1 kPa[a]	2.0	9
liquid density at 15°C, g/mL	3.441	8
transition point, °C, 32.0 kPa[a]	−8.2	9
heat of vaporization, kJ/mol[b]	26.5	9
heat of fusion, kJ/mol[b]	1.76	9
heat of transition, kJ/mol[b]	5.86	9
heat of sublimation, kJ/mol[b]		
above transition	32.4	9
below transition	38.3	9
entropy of vaporization, J/(mol·K)[b]	91.2	9
entropy of fusion, J/(mol·K)[b]	6.07	9
entropy of transition, J/(mol·K)[b]	22.1	9
specific heat at 25°C, J/(mol·K)[b]	118.92	9
vapor pressure equation	$\log P_{kPa} = a - b/T$	
liquid		9
T, °C	2.0 to 17.1	
a	6.760[c]	
b	1380.5	
solid		9
T, °C	−8.2 to 2.0	
a	7.883[d]	
b	1689.9	
T, °C	−60 to −8.2	
a	9.076[e]	
b	2006.0	

[a]To convert kPa to mm Hg, multiply by 7.5.
[b]To convert kJ to kcal, divide by 4.184.
[c]For P in mm Hg, $a = 7.635$.
[d]For P in mm Hg, $a = 8.758$.
[e]For P in mm Hg, $a = 9.951$.

Pennsylvania) and Bandgap Technology Corp. (Broomfield, Colorado) are the only U.S. producers. The 1992 price ranges from $300–$850/kg, depending on the purity.

Because of the development of electronic applications for WF_6, higher purities of WF_6 have been required, and considerable work has been done to improve the existing manufacturing and purification processes (20). Most metal contaminants and gaseous impurities are removed from WF_6 by distillation. HF, which has a similar vapor pressure to WF_6, must be removed by adsorption (see Electronic materials).

1.4. Specifications

The use of tungsten hexafluoride in CVD applications in the manufacture of high density silicon chips requires a high purity product, essentially free of all metallic contaminants. Several grades of WF_6 are available. Table 2 shows the specifications for three grades of WF_6.

Tungsten hexafluoride is shipped as a liquid under its own vapor pressure in nickel or steel cylinders in quantities of 45 kilograms per cylinder or less; however, it has been shown that the purity of WF_6 packaged in steel cylinders can degrade over time (21). It is classified as a corrosive liquid by the DOT.

Table 2. Specifications on Three Grades[a] of WF_6

Impurity	Electronic	VLSI	Megaclass
HF, ppmv	150	10	1
CO_2, CF_4, SF_6, SiF_4, ppmv each	10	0.5	0.5
N_2, ppmv	15	1	0.5
O_2 + Ar, ppmv	10	0.5	0.5
CO, ppmv	[b]	1	1
total metals, ppb[c]	1000	1000	1000
Cr, Fe, K, Na, ppb[c] each	10	10	10
U, ppb[c]	0.1	0.05	0.05
Th, ppb[c]	0.1	0.1	0.1

[a] Commercial grades offered by Air Products and Chemicals, Inc.
[b] No specifications given.
[c] By weight.

1.5. Handling and Toxicity

Tungsten hexafluoride is irritating and corrosive to the upper and lower airways, eyes, and skin. It is extremely corrosive to the skin, producing burns typical of hydrofluoric acid. The OSHA permissible exposure limits is set as a time-weighted average of 2.5 mg/kg or 0.2 ppm (22).

Monel and nickel are the preferred materials of construction for cylinders and delivery systems; however, copper, brass, steel, and stainless steel can be used at room temperature, providing that these metals are cleaned, dried, and passivated with a fluoride film prior to use. Studies have shown that fluorine passivation of stainless steel and subsequent formation of an iron fluoride layer prior to WF_6 exposure prevents reaction between the WF_6 and the stainless steel surface (23).

1.6. Uses

The primary use of WF_6 is for blanket and selective deposition of tungsten and tungsten silicide films in the manufacture of VLSI electronic devices. The important aspects of this application have been reviewed (24). Additionally, several conferences have been devoted to CVD using WF_6 (13, 20). Nonelectronic applications of tungsten hexafluoride include the CVD of tungsten to form hard tungsten carbide coatings on steel (25) and to fabricate solid tungsten pieces such as tubing or crucibles. Composite coatings of tungsten and rhenium are produced by the simultaneous chemical vapor deposition from these hexafluorides (26) and the addition of rhenium improves the ductility and high temperature properties of the deposit.

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