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Potential occupational health hazards in the microelectronics industry

by Joseph LaDou, MD¹

LA DOU J. Potential occupational health hazards in the microelectronics industry. *Scand j work environ health* 9 (1983) 42–46. The microelectronics industry is a major user of a wide variety of chemicals and other toxic materials. In the recent past semiconductor manufacturers have located in many countries and brought a new set of challenging clinical problems to occupational physicians. California, an area with a significant history in the statistical study of health and safety in the microelectronics industry, presents some evidence of potential health hazards in the semiconductor manufacturing process. The Semiconductor Industry Study done in California in 1981 explains the application of many toxic materials in the semiconductor manufacturing process, including a variety of solvents, acids, and metals such as arsenic. The Study documents the extensive use of dopant gases, primarily arsine, phosphine and diborane. Further study is necessary to assure the health and safety of microelectronics workers, particularly in the application of dopant gases.

Key terms: arsine, diborane, dopant gases, occupational illness, phosphine, semiconductor, systemic poisoning.

The microelectronics industry is rapidly becoming a major industry throughout the world. It began only 35 years ago with the development of the transistor, a small, low-power amplifier which replaced the large, inefficient vacuum tube (5). The industry found large and ready markets in the computer industry and for solid-state integrated circuits for consumer products made possible by the transistor. Today the industry produces a vast number of electronic circuits and devices for military and space agencies, the computer and data communications industries, and industrial and consumer applications.

The initial development of microelectronic devices occurred primarily in California, which today continues to lead the industry in technological advances and consumer applications. The explosive growth of this industry, stemming from a series of scientific discoveries and rapid manufacturing process developments, has resulted in a world market of more than USD 16 billion in sales and in a workforce of more than one-half

million. The manufacture of semiconductors and related microelectronic devices has been reviewed in the literature although state-of-the-art techniques are maintained in relative secrecy (2, 4, 6, 8).

Statistical evidence of health hazards

To date, the high technology manufacturing techniques of this industry have produced some as yet unexplained health and safety statistics in the state of California. These statistics are derived from state Workers' Compensation Insurance records from information supplied by the many hundreds of companies engaged in microelectronics manufacturing and distribution. Although the electronics industry has traditionally had a lower combined incidence of occupational illness and injury than heavier industries, workers in semiconductor manufacturing in California have consistently exhibited an unusually high incidence of occupational illness, whereas they have shown a low incidence of occupational injury. Table 1 compares the rate of injury and illness in California for all private industry, the electronics industry, and the semiconductor segment of the electronics industry. The data indicate that the electronics industry has a higher rate of occu-

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Table 1. Occupational injury and illness rates for private-industry, electronics, and semiconductor workers.^a

	Injury and illness incidence rate per 100 full-time employees				Occupational illness incidence rate per 100 full-time employees			
	1977	1978	1979	1980	1977	1978	1979	1980
Private industry	10.3	10.5	10.6	10.1	0.3	0.3	0.3	0.3
Electronics industry	7.9	8.3	8.0	7.7	0.6	0.6	0.5	0.5
Semiconductor manufacturing	7.6	9.1	8.0	7.6	1.3	1.3	0.8	1.3

^a Data summarized from California work injuries and illnesses, Department of Industrial Relations, Division of Labor Statistics and Research, San Francisco, California, 1980, 1981 and 1982.

pational illness than other industries and that the semiconductor segment accounts for a large part of the difference.

These findings may reflect the widespread use of toxic materials in the industry, which has developed process applications for many metals, chemicals, and gases in a wide variety of combinations and environmental settings. One statistical category of occupational illness termed "systemic poisoning" is increasing each year among electronics workers engaged in semiconductor manufacturing in California. Table 2 compares the incidence of this illness among all manufacturing workers and electronics workers. The latter exhibit a large increase in this category of occupational illness, primarily because of the high incidence among semiconductor workers.

It should be emphasized that systemic poisoning includes a number of other disease possibilities and that the data cited are derived from First Report of Injury forms which seldom reflect a final medical diagnosis in complex cases of toxic exposure. Thus, rather than accurately indicating the incidence of systemic

Table 2. Systemic poisoning as the percentage of occupational illness for manufacturing, electronics, and semiconductor workers.^a

	1977	1978	1979	1980
Manufacturing industry	17.8	19.0	19.2	19.2
Electronics industry	29.8	31.4	35.5	38.8
Semiconductor manufacturing	37.2	42.9	42.1	46.9

^a Data summarized from California work injuries and illnesses, Department of Industrial Relations, Division of Labor Statistics and Research, San Francisco, CA, 1980, 1981 and 1982.

Table 3. Chemicals used by 42 companies manufacturing semiconductors in 1979.^a

	Amount	
	Kilograms	Liters
<i>Solvents</i>		
Isopropanol (2-propanol)		499,392
n-Butyl acetate		348,106
Freons		322,784
Xylene		280,884
Acetone		243,186
Methanol		196,100
Petroleum distillates		96,101
Trichloroethylene		86,070
1,1,1-Trichloroethane (methyl chloroform)		61,733
Methylene chloride (dichloromethane)		14,420
Tetrachloroethylene (perchloroethylene)		4,996
Ethylene glycol		3,028
Methyl ethyl ketone (2-butanone)		2,763
Hexamethyldisilazane (10 %) (HMDS)		2,081
Ethanol		492
Toluene		227
Chlorobenzene		37
<i>Acids</i>		
Sulfuric acid	70,470	1,500,374
Hydrofluoric acid	15,390	786,485
Hydrochloric acid	5,985	1,274,031
Phosphoric acid	7,560	122,444
Ammonium fluoride	2,475	339,817
Acetic acid	1,485	1,288,224
Nitric acid	2,025	511,959
Boric acid	360	37
Citric acid	4	378
Buffered oxide etch (hydrofluoric acid & ammonium fluoride)		88,947
Fluoboric acid		302
<i>Caustics</i>		
Sodium hydroxide	243,045	
Ammonia	39,015	
Potassium hydroxide	16,051	
Ammonium hydroxide	3,658	

^a Data summarized from pages 33–34 of the report of Wade & Williams (11).

poisoning, the data merely indicate an area for suspicion about the semiconductor work environment.

The semiconductor industry study

In 1980 the California Department of Industrial Relations asked 53 semiconductor companies to provide information on their use of a large number of materials. Forty-two companies responded. This small sampling of the hundreds of semiconductor manufacturers in California included many of the major companies in the industry. Consequently the quantities of chemicals shown in table 3 are very probably indicative of the amount used overall in this segment of the electronics industry.

Table 4 indicates the types and quantities of gases and liquids that have been used widely in the manufacture of semi-

conductors in recent years. The occurrence of health complaints among semiconductor workers parallels an increase in doping techniques in which arsenic, phosphorus, and boron are deposited on the surface of silicon wafers either in diffusion furnaces or by ion implantation or other advanced techniques. Dopant gases provide the dopant ions required in these processes, and arsine (AsH_3), phosphine (PH_3), and diborane (B_2H_6) – the hydrides of arsenic, phosphorus, and boron – are being used increasingly in the semiconductor industry. These gases are usually diluted to a low concentration before the doping, but some techniques now utilize higher concentrations, which of course increase the potential for toxic exposure. Table 5 summarizes the use of these highly poisonous gases, as well as other gases commonly used, in the semiconductor industry.

Table 4. Gases and liquids used by 42 companies manufacturing semiconductors in 1979.^a

	Amount (l)
Gases	
Hydrogen chloride	23,657,762
Unspecified concentration (probably pure hydrogen chloride)	23,591,987
5 % hydrogen chloride	65,775
Silane	7,185,035
Unspecified concentration (possible range 1.5–100 % silane)	4,428,680
1.5–100 % (specified)	2,756,355 (= 1,750,002 l of pure silane)
Phosphine	5,990,056
Unspecified concentration (possible range 0.0005–100 % phosphine)	4,652,729
0.0022–10 %	1,337,326 (= 66,030 l pure phosphine)
Ammonia (assumed 100 %)	4,346,694
Arsine	1,815,635
Unspecified concentration (possible range 0.0005–100 % arsine)	1,305,530
0.002–2 %	510,105 (= 10,343 l pure arsine)
Diborane	750,705
Unspecified concentration (possible range 0.0005–1 % diborane)	666,793
0.0023–1 %	83,912 (= 646 l pure diborane)
Boron trifluoride (assumed 100 %)	42,423
Krypton 85 (assumed 100 %)	283
Liquids	
Silicon tetrachloride (assumed 100 %)	2,377,942
Trichlorosilane (assumed 100 %)	1,433,793
Boron tribromide (assumed 100 %)	1,200,930

^a Data summarized from page 35 of the report of Wade & Williams (11).

Table 5. Properties of gases used in semiconductor chemical vapor deposition.^a

Gas	Flammable (% in air)	Pyrophoric % in air (auto ignition°C)	Lethal in a few minutes (ppm)	Lethal in a few hours (ppm)	Irritant level (ppm)	Approximate odor level (ppm)	8-Hour permissible exposure level (ppm)	Comments
Arsine (AsH ₃)	Yes	7°C	250	6	—	1	0.05	Highly poisonous
Phosphine (PH ₃)	Yes	40–50°C	2,000	100	8	2	0.3	Highly poisonous
Diborane (B ₂ H ₆)	0.8–88 %	37–52°C	160?	?	—	3	0.1	Highly poisonous
Ammonia (NH ₃)	15–28 %	650°C	30,000	—	25	5	50	Reacts strongly with chlorides
Nitrous oxide (N ₂ O)	Supports combustion	Non- pyrophoric	?	—	100	10	—	Anesthetic, possible nerve damage
Nitrogen/dinitrogen tetroxide (N ₂ /N ₂ O ₄)	Supports combustion	Non- pyrophoric	200?	—	60	10	5C	
Oxygen (O ₂)	No	Non- pyrophoric	Nonlethal	—	—	—	—	Keep separate from reducers; supports fierce combustion
Carbon dioxide (CO ₂)	No	Non- pyrophoric	Asphyxiant	20,000	—	—	5,000	Irritant
Silane (SiH ₄)	Yes	(0.5 % SiH ₄ /H ₂)	Nonlethal	Nonlethal	?	—	0.5	Forms fine silica dust and vigorous flame
Dichlorosilane (SiH ₂ Cl ₂), trichloro- silane (SiHCl ₃)	Yes	(4 % SiH ₄ /N ₂)						
Silicon tetrachloride (SiCl ₄)	No	—	?	8,000	10	1	—	Decomposes to hydrogen chloride and silicon dioxide in air
Hydrogen (H ₂)	4–80 %	585°C	Asphyxiant	—	Non- irritant	Non- odorous	—	Store < 56,678 l in building
Nitrogen (N ₂)	No	—	Asphyxiant	—	Non- irritant	Non- odorous	—	
Hydrogen chloride (HCl)	No	—	1,300	1,000	10	1	5	Noxious
Hydrogen fluoride (HF)	No	—	100?	?	30	?	3	Noxious

^a Data summarized from page 146 of the report of Wade & Williams (11).

Discussion

It is a matter of concern that semiconductor manufacturers are using large quantities of the previously mentioned toxic gases in a variety of manufacturing processes and in an even wider variety of settings (1, 3, 6, 7, 8). The gases are delivered in metal cylinders, and, although many hundreds of companies frequently use them, there are no uniform warning labels or uniform codes of color demarcation on the cylinders. Plant engineers and safety professionals do not agree on how the cylinders should best be handled. They must either be stored out of doors or in the work area, where they are connected to diffusion furnaces, ion implanters, or other devices by stainless steel gas lines. Some engineers feel that the cylinders should be kept outside the plant and fed into the plant by gas lines, while others argue that the safest method is to move the cylinders into the work areas and store them there.

Although semiconductor health and safety personnel consider the use of arsenic as a dopant to be an obvious health hazard, the California Industrial Relations Department survey indicates that gallium-arsenide is being used increasingly as a wafer material for higher speed micro-electronic devices (3, 7, 9, 10). This wider use of arsenic was studied by state investigators using industrial hygiene monitoring, and some instances of airborne contaminant levels in excess of those allowed for inorganic arsenic were disclosed.²

Recommendations

The semiconductor industry represents a major challenge to the occupational

² A review of the 1981 Semiconductor Industry Study is beyond the scope of the present paper. Those interested may obtain a copy of the report from CalOSHA Communications, 525 Golden Gate Avenue, Third Floor, San Francisco, CA 94102, USA.

physician. The industry and its products are of very recent origin. Moreover, the technology often moves so rapidly that new materials and processes replace old ones before sufficient information is obtained on the health hazards of either. Consequently, in cases of worker illness or injury in the semiconductor industry, occupational physicians should contact the individual's place of employment to determine from managers and supervisors the nature of the work and the conditions of the work environment. Finally occupational physicians involved in the semiconductor industry would be well advised to visit periodically the various manufacturing plants under their purview. The importance of further studies of the health and safety of microelectronics workers is evident from this early experience of the California semiconductor industry.

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