Supporting Information

Section A. Supplemental discussion comparing data sources on chemical use and emissions in semiconductor fabrication

In general, three analytical tools are available to check the reliability of external data: process modeling, mass balance, and consistency with other sources. Process modeling involves creating physical/chemical simulations of a process that at least roughly characterize materials use and emissions. While it is possible to apply this technique to certain sub-processes, a realistic simulation of the overall flow of semiconductor fabrication, even if possible with publicly available information, is well beyond the scope of this work. Mass balance analysis checks the internal consistency of process data through verification that input mass equals output. This tool is only applicable to the data from the Electronics Industries Association of Japan (EIAJ) (11). The total chemical input to the national industry of Japan is around 90,000 metric tons while the total output of sludge, acids, and bases is 174,000 metric tons (11). Two possible explanations of the difference are inclusion of water added in output (e.g. in sludges) and/or incomplete listing of input materials. At any rate, it is clear that EIAJ and other organizations should clarify the reporting of process data to account for the discrepancy. Mass balance analysis is not possible for any other of the data sets due to incompleteness.

The data sets suitable for direct consistency checking are EIAJ and TRI. The two emissions figures for some categories should be close: While TRI reports for the US and EIAJ for Japan, both describe national emissions of industries with similar structure, technology and economic scale. However, the EIAJ figure is 13 times higher than TRI, a surprisingly large difference. As noted already, the structure of the TRI is probably responsible for this: many toxic emissions could fall below the reporting threshold, while some inputs fall outside the list of tracked substances. Given the diversity of chemical use in fabrication facilities, TRI is a poor tool to track emissions. For example, considering the anonymous firm data for a sample facility, only 11 of the 40 chemicals used meet the TRI reporting requirements and the facility would report an aggregate chemical use of 23 grams/cm^2 under TRI, 60% of the real total. For sectors such as semiconductors that undergo rapid technological change, TRI may not even correctly indicate the direction of an overall trend. If a facility switches from using a chemical whose emissions fall above the threshold to several that fall below, the reported TRI emissions could fall when, in fact, total emissions *increased*.

Considering time as a variable, the differences between UNEP, MCC and anonymous figures suggest radical declines in quantities of chemical inputs over time. A specific technological change that may account for the bulk of this improvement is the switch from wet to dry etching processes. In the UNEP/UNIDO data, chemicals needed for wet etching account for 83% of overall use. The more recent anonymous firm data, however, reflects the use of dry etching processes. In additional to process optimization, increased recycling of inputs accounts for a significant degree of the reduction in net inputs (11).

Section B. Input/output data on wafer fabrication processes

Table B.1 Chemical inputs of Japanese semiconductor industry (1996 data)
(source: Electronics Industry Association of Japan, 1997 (11))

Process	**Substance**	**Amount (tons/year)**
Washing	Acids (e.g. sulfuric, hydrofluoric, nitric)	34,000-50,000
	Alkali (e.g. NaOH, KOH)	1,400-2,000
	Organic solvents	16,000-25,000
Lithography	Photoresists (e.g. ortho-diazoketone, isoprene)	2,700-3,500
	Developing agents (e.g. xylene, isopropyl alcohol, ethylene glycol)	9,400-12,000
CVD	Silicon containing gases (e.g. monosilane, silicon tetrachloride)	45-60
	Boron, phosphorous compounds (e.g. diborane, phosphine)	8-10
Etching (dry)	fluorine compounds (e.g. HF, NH_4F)	290-380

Table B.2: 1997 Aggregate emissions of Japanese semiconductor industry
(source: Electronics Industry Association of Japan, 1997 (12))

Waste stream	**Main source Processes**	**Amount (tons)**	**Share**	**Treatment method**
Sludge	Water treatment	64,989	25%	Landfill or use as cement ingredient
Oil	Vacuum pumps	41,844	16%	Incineration or purify for reuse
Acids	Etching	68,668	26%	Neutralization, precipitation, landfill
Alkali	Lithography	41,111	16%	Microorganisms
Plastic	Assembly, Packaging	22,495	9%	Conversion to Fuel or landfill
Metal	Lead frame, soldering	16,352	6%	Reuse
Ceramics, glass	Various (quartz vessels)	2,720	1%	Crush, then landfill
Other		5,396	2%	
Total		263,576		

Table B.3: Material inputs for fabrication of integrated circuits on 4 inch wafer
(source: United Nations Environment Programme/ United Nations Industrial Development Organization (15))

Activity	Sub-Activity	Input type	Conc.	Flow Rate	unit	Time	Unit	Unit Proc.
Lot initiation	Pre-Diffusion Clean	H2SO4	95%	58	cc/min	2	min.	Piranha
		H2O2	30%	145	cc/min	2	min.	4H2SO4:H2O2
		DIH2O	14M	3450	cc/min	4.5	min	Dump Rinse
		DIH2O	14M	2975	cc/min		Cont.	Cascade Rinse
		HF	49%	600	cc/min	1	min.	Dilute HF 11DIH2O:1HF
		DIH2O	14M	6600	cc/min			
		DIH2O	14M	297	cc/min		Cont.	Cascade Rinse
Diffusion	Boron Deposition (1100C)	BBr3	99.99%		Bubbler		Cont.	Boron Deposition From Liquid Source Dopant
		O2	99.99%	0.145	l/min	20	min.	
		N2	99.99%	5.6	l/min	20	min.	
		N2CaMix	99.99%	40	cc/min	20	min.	
		HF DIH2O	14M	2975	cc/min	10	sec.	Dilute HF Dip 11DIH2O:1HF
	Boron Diffusion (1150C)	Net O2	99.99%		Not Req.			Boron Diffusion And Oxide Cap
		H2	99.99%	5.2	l/min.	20	min.	
		O2	99.99%	2.8	l/min.	20	min.	
		N2	99.99%	4.1	l/min.	10	min.	
Moat Photo 1	RCA Clean	NH4OH	30%	100	cc/min	3	min.	RCA Clean
		HCL	60%	100	cc/min	3	min.	
		H2O2	30%	100	cc/min	7.5	min.	
		HF	49%	600	cc/min	1	min.	
		Hot DI Water	14M	500	cc/min	12.5	min.	RCA Rinse
	Pre-Bake	HMDS Isopropyl Alcohol	N/A N/A		Slow Dispense	10	sec.	Pre-Bake to Promote Resist Adhesion Primers

Table B.3 (continued): Material inputs for fabrication of integrated circuits on 4 inch wafer
(source: United Nations Environment Programme/ United Nations Industrial Development Organization (15))

Activity	Sub-Activity	Input type	Conc.	Flow Rate	unit	Time	Unit	Unit Proc.
Moat Photo 1(Cont)	Coating	Negative Photoresist	SC180			10	sec.	Resist Coating
	Soft Bake (Low Temp)	N2	99.99%	5.6	l/min.	30	min.	Soft Bake
	Exposure	Exposure Energy	45+-ml/km2					Alignment & Exposure
		Mask Sets	Emulsion & Iron Oxide					
		UV Lamps						
	Develop	N2	99.99%	4	l/min.	60	sec.	Rinse for Developer
		NBA	99.99%	500	cc/min	60	sec.	
		Xylene	99.99%	500	cc/min	60	sec.	Develop
		Waycoat PF Developer	99.99%	600	cc/min	60	sec.	
	Hard Bake (High Temp)	N2	99.99%	5.6	l/min.	30	min.	Hard Bake
Moat Etch	Etch	HNO3	70%	500	cc/min	12	min.	Moat Etch Comb. Solutions 5:3:3 5:HNO3:3HF:3CH3COOH
		HF	49%	500	cc/min	12	min.	
		CH3COOH	99%	500	cc/min	12	min.	
	Resist Strip	J100	Mixture	5.6	Liters		Cont.	Neg. Resist Strip
	Cleans	DIH2O	14M	3450	Cc/min	4.5	min.	Dump Rinse
		DIH2O	14M	2975	Cc/min		Cont.	Clean
Junction & Piranha Cleans	Piranha	H2SO4	95%	580	Cc/min	2	min.	Pre-Passivation Junction Clean
		H2O2	30%	145	Cc/min	2	min.	
		DIH2O	14M	3450	Cc/min	4.5	min.	Dump Rinse
		DIH2O	14M	2975	Cc/min		Cont.	Cascade Rinse

Table B.3 (continued): Material inputs for fabrication of integrated circuits on 4 inch wafer

(source: United Nations Environment Programme/ United Nations Industrial Development Organization (15))

Activity	Sub-Activity	Input type	Conc.	Flow Rate	Unit	Time	Unit	Unit Proc.
Photo-Glass	Passivation Expose & Develop	Lead Boro Silicate Glass	99.99%		N/A		N/A	Glass
		Negative Photo Resist	SC450		Slow Dispense	30	sec.	Glass Suspending Mode
		IPA	99.99%	500	Cc/min	30	sec.	Biscosity Adjust
	Glass Fire	N2	99.99%	5.6	l/min.	30	min.	Glass Fire
Pre-Metal Clean	HF Dip	HF	49%	600	Cc/min	1	min.	HF Dip
		DIH2O	14M	6600	cc/min	1	min.	
		DIH2O	14M	2975	cc/min		Cont.	Cacade Rinse
Front Metal	Evaporation	AL-Si	99%Al	Evaporation Rate is Function of Energy		30	min.	Aluminium Front Metal
		AL-Cr Liquid Nitrogen Vacuum Pump Oil	99%Al					
	Aluminum Photolithography 2 Similar Waste Stream As Moat Photo 1							Aluminum Photolithography 2
	Aluminium Etch	H2PO4	49%	500	cc/min	10	min.	Top Metal Aluminium Etch
		CH3COOH	99%	500	cc/min	10	min.	
		HNO3	70%	500	cc/min	10	min.	

Table B.3 (continued): Material inputs for fabrication of integrated circuits on 4 inch wafer

(source: United Nations Environment Programme/ United Nations Industrial Development Organization (15))

Activity	Sub-Activity	Input type	Conc.	Flow Rate	Unit	Time	Unit	Unit Proc.
Back Metal	Back Lap	ALO, Slurry, Freon, Wax	15 micron CFC-113	300	cc/min	45	min.	Wafer Back Lap Thinning
	Back Metal Evaporation	Cr Ni Au Liqid Nitrogen	99% 99% 99%		Thickness and process Dependent	30	min. Average	Back Metal Contact
Dicing	Wafer Saw	Si DIH2O Tape	Wafers 14M Plastic	3000	cc/min	3	min	Sawing
	Ultra Pure Water	DIH2O	14M	Depends on plant				Ultarapure Water Generation

Table B.4: TRI Emissions from US Semiconductor Industry, 1997)

(source: US Environmental Protection Agency (13))

Chemical Name	# Facilities Reporting Chemical Release	Total Releases (metric tons)	# Facilities Reporting Chemical Transfers	Total Transfers (metric tons)	Recycling (metric tons)	Energy Recovery (metric tons)
Sulfuric Acid	125	46.48	125	843.76	472.31	0.00
Hydrochloric Acid	78	3.50	78	169.29	9.85	0.00
Hydrogen Fluoride	71	31.97	71	164.92	0.24	0.00
Phosphoric Acid	69	13.51	69	229.01	90.91	0.00
Nitric Acid	57	24.12	57	109.00	9.50	0.00
Acetone	53	461.00	53	655.52	62.27	488.93
Ammonia	42	96.81	42	458.42	0.30	0.00
Glycol Ethers	27	153.05	27	581.41	63.23	477.02
Xylene (Mixed Isomers)	25	119.43	25	405.55	14.23	331.22
Ethylene Glycol	16	5.73	16	262.85	6.91	46.37
Methanol	16	75.79	16	374.14	12.60	325.64
Freon	10	52.07	10	20.75	16.79	2.57
1,1,1-Trichloroethane	8	38.21	8	46.27	34.21	3.64
Methyl Ethyl Ketone	6	58.90	6	127.20	0.00	125.50
Tetrachloroethylene	4	25.25	4	55.84	4.64	24.09
Ammonium Nitrate	3	0.00	3	101.96	0.00	0.00
(Solution)		0.00		0.00	0.00	0.00
Ammonium Sulfate	3	0.11	3	732.03	55.45	0.00
(Solution)		0.00		0.00	0.00	0.00
Lead	3	0.00	3	33.90	26.88	0.00
Phenol	3	1.27	3	44.11	0.00	43.04
Toluene	3	26.70	3	10.44	0.00	2.71
Trichloroethylene	3	16.32	3	27.15	27.15	0.00
Copper	2	0.01	2	0.08	0.00	0.00
Ethylbenzene	2	0.67	2	7.79	0.00	7.64
Methyl Isobutyl Ketone	2	4.58	2	9.77	0.00	5.54
1,2-Dichlorobenzene	2	22.47	2	43.53	0.00	42.55
1,2,4-Trichlorobenzene	2	2.96	2	15.31	0.00	0.00
Antimony Compounds	1	0.01	1	8.23	0.00	0.00
Chlorine Dioxide	1	0.00	1	0.00	0.00	0.00
Cobalt Compounds	1	0.00	1	1.72	0.00	0.00
Isopropyl Alcohol	1	0.00	1	4.62	4.62	0.00
(Manufacturing)		0.00		0.00	0.00	0.00
Lead Compounds	1	0.00	1	3.01	0.00	0.00
N-Butyl Alcohol	1	0.05	1	5.39	0.00	0.65
Nickel Compounds	1	0.00	1	1.80	1.62	0.00
Nitrilotriacetic Acid	1	0.00	1	0.00	0.00	0.00
P-Xylene	1	0.20	1	4.72	0.00	0.00
Zinc Compounds	0	0.00	1	121.50	0.00	0.00
Totals		1281.18		5680.98	913.70	1927.12

Section C: Details of estimation of energy required for production of chemical inputs to fabrication of integrated circuits

Table C.1: Energy to produce subset of fabrication input chemicals (sources (38,16))

	energy (MJ/kg)	use (g/cm^2)	Fab. use (MJ/cm^2)
ammonia	43	0.012	0.0005
hydrochloric acid	22	0.0050	0.00011
hydroflouric acid	59	0.0010	0.000056
phosphoric acid 86%	77	2.4	0.16
hydroflouric acid .5%	59	3.4	0.0010
hydroflouric acid 5%	59	0.46	0.0013
hydroflouric acid 50%	59	0.25	0.0074
nitric acid 70%	18	1.2	0.015
sulfuric acid 96%	5	7.9	0.038
hydrochloric acid 37%	22	2.5	0.020
ammonia 30%	43	0.78	0.010
hydrochloric acid 30%	22	0.51	0.0033
sodium hydroxide 50%	28	0.65	0.0091
hydrogen peroxide	125	4.4	0.55
sodium hydroxide (for neutralizing wastewater)	28	7.6	0.21
Total		32.1	**1.0**

Section D: Reference tables

Table D.1 Wafer consumption by Region

(source: New Metals Databook (18) reporting Dataquest data)

Year	**World Total (billion cm^2)**	**N.America (billion cm^2)**	**Japan (billion cm^2)**	**Europe (billion cm^2)**	**Rest of Asia (billion cm^2)**
1998	28.44	7.37	10.92	3.93	6.23
1997	25.50	6.58	10.05	3.59	5.28
1996	24.20	6.37	9.69	3.36	4.77
1995	22.74	5.79	9.57	2.95	4.43
1994	18.79	5.13	8.25	2.34	3.08
1993	15.79	4.43	7.32	1.92	2.11

Table D.2 Densities of relevant chemical compounds

(sources: various)

Chemical	**Density (g/cm^3)**
HF 100%	1.858
NH_4F 100%	1.315
HF 1 vol + NH_4F 30 vol mixture	1.332516
H_3PO_4 Phosphoric acid 86%	1.69
HF .5%	Near 1
HF 5%	Near 1
HF 50%	1.19
HNO_3 70%	1.4
H_2SO_4 96%	1.84
HCl 37%*	1.18
NH_3 28%*	0.682
HCl 30%	1.18
NaOH 50%*	1.52
H_2O_2 30%	1.11
Isopropyl alcohol (developer)	0.79
Tetramethyl ammonium hydroxide (TMHA, developer)	1.01
methyl-3- methoxypropionate	1.04
acetone	0.78
hexamethyldisilazane (stripper)	0.77