Assessment of Task and Peak Exposures to Solvents in the Microelectronics Fabrication Industry

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Short-term exposures to six solvents used in microelectronic fabrication clean rooms were assessed. The solvents measured were: 2-ethoxyethyl acetate, n-butyl acetate, xylene, isopropanol, acetone, and propylene glycol monomethylether acetate. Short-term exposures during production and maintenance tasks were measured using both charcoal tubes to obtain average task exposures and direct reading instrumentation to obtain real-time peak levels. All measured samples were considerably below current government or consensus standards for short-term exposures. Pharmacokinetic modeling was used to evaluate the toxicological significance of the highest real-time peaks measured, which in these clean rooms were to the solvent acetone. The model suggested that the peaks measured were below acetone levels associated with reproductive health risks in animals. Hallock, M.F.; Hammond, S.K.; Kenyon, E.; Smith, T.J.; Smith, E.R.: Assessment of Task and Peak Exposures to Solvents in the Microelectronics Fabrication Industry. Appl. Occup. Environ. Hyg. 8(11):945-954; 1993.

Introduction

The purpose of this study was to conduct an assessment of short-term exposures to reproductive toxins in several facilities manufacturing microelectronic components. Increased concern regarding exposure to reproductive toxins has been generated by the report of Pastides *et al.*,[1] which suggested a possibility of adverse reproductive health effects in a small group of women working in semiconductor clean rooms. Eight-hour, time-weighted average levels of solvents and acids used in clean rooms have been previously characterized by the National Institute for Occupational Safety and Health[2,3] industrywide evaluations and many companies and have generally been found to be close to or less than limits of detection (LOD). However, odors and episodes of irritation are routinely reported from both production and maintenance operations, suggesting that intermittent peak exposures to chemicals are occurring.

The overall study assessed exposure to selected solvents, mineral acids, and physical agents. This article presents the results of short-term air sampling for solvents. The solvents selected for evaluation were: 2-ethoxyethyl acetate (2EEA), *n*-butyl acetate (NBA), xylenes, isopropanol (IPA), acetone, and propylene glycol monomethyl ether acetate (PGMEA). Results for mineral acids and physical agents are presented separately.[4,5]

Methods

Selection of Solvents To Be Sampled

The chemicals to be sampled were selected by a team of industrial hygienists and toxicologists. A four-step selection process was used: (1) identify the materials used at fabrication room workstations; (2) perform walk-through mapping to determine how the materials are used and estimate potential for exposure; (3) perform a toxicologic literature review to determine if there is evidence of reproductive or other effects associated with the materials; and (4) merge the exposure data with the toxicity information and assess the potential for hazards.

A preliminary list of chemicals and workstations used was obtained from three fabrication rooms at two sites. Walk-through surveys were then conducted to verify information and observe operations and tasks at individual work stations. A fabrication room workstation description form was used to collect the following information at each station: (1) chemicals used; (2) description of operator activities including minor maintenance activities performed such as loading chemicals, unloading waste containers, cleaning machine parts, as well as the duration and frequency of each task; (3) description of maintenance activities involving chemical exposures and the duration and fre-

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quency of each task; and (4) description of engineering controls such as enclosures, automation, and local exhaust ventilation.

All of the above information was used to make an assessment of the potential for peak exposures during tasks at each workstation. Categorical information collected was entered into a workstation database to generate lists of workstations at which specific chemicals were used.

Approximately 200 workstations were surveyed during the walk-throughs. A list of 115 chemicals was compiled and evaluated for reproductive toxicity using the *Registry for Toxic Effects of Chemical Substances*[6] and primary literature sources. The final selection of chemicals to be sampled was made by a team of industrial hygienists and toxicologists and was based on toxicity, potential for peak exposures, and extent of use. Initially five solvents were selected for sampling (2-EEA, NBA, xylenes, IPA, acetone). At the request of the company, PGMEA, which is increasingly being substituted for 2-EEA, was also added to the list of solvents.

Air Sampling for Solvents

Short-term exposures to solvents occurring during production and maintenance tasks were measured using both charcoal tubes, to obtain average task exposures, and direct-reading instrumentation, to obtain real-time peak levels. A total of 105 short-term tasks were sampled simultaneously by charcoal tube and direct-reading instrumentation. In addition, 50 full-shift personal and area samples were collected.

Task and full-shift personal and area samples were collected using 150-mg charcoal tubes (Lot 120, SKC, Eighty Four, Pennsylvania) and Gilian air sampling pumps. Air flow was set at 250 cc/min for task samples and 200 cc/min for full-shift samples. Pump air flow was calibrated at the beginning and end of each sampling day using high precision laboratory rotameters calibrated against a primary standard (Gilibrator bubble meter, Gilian, West Caldwell, New Jersey).

Full-shift personal samples were collected in the breathing zone of fabrication room operators with charcoal tubes clipped to collars of clean room suits. Full-shift area samples were collected at workstations throughout the fabrication rooms. Task charcoal tube and direct-reading instrument samples were collected in the breathing zone of operators by clipping both sampling probes to a rod hand-held in the breathing zone of the worker by the industrial hygienist conducting the sampling.

Real-time profiles of solvent concentration were measured using a direct-reading instrument, the TIP (Total Ionizables Present), manufactured by Photovac (Huntington, New York). The TIP contains a photoionization detector consisting of a 10.6 eV ultraviolet (UV) lamp and current detector: solvents are ionized by UV light and measured by an electrometer. A small air sampling pump pulls air through the detector chamber at a rate of about 500 cc/min. The response time to 90 percent maximum value was reported by the manufacturer to be 3 seconds.

The TIP responds differentially to different solvents depending on their ionization potential and will detect most solvents with an ionization potential of less than 10.6 eV. The TIP cannot distinguish individual solvents in a mixture: the concentration measured will be a composite of the individual components. The response factors relative to *o*-xylene, as reported by the manufacturer, were: *p*-xylene = 0.94; *m*-xylene = 2.00; IPA = 0.15; NBA = 0.33. For other study solvents, we measured relative response using known concentrations of solvents generated in Tedlar bags; bag solvent concentrations were verified by gas chromatography/mass spectrometry (GC/MS). These response factors relative to *o*-xylene were: acetone = 0.51; 2EEA = 0.42; PGMEA = 0.41.

Charcoal tube samples taken simultaneously with TIP samples were used to verify solvent composition. If a mixture was present, percent solvent composition measured by GC/MS and TIP relative response factors could be used to calculate individual solvent concentrations. In practice, almost all of the tasks detected by the TIP had predominantly one solvent (> 90%) as determined by GC/MS analysis and were treated as a single solvent measurement for data analysis.

The LOD of the TIP for benzene has been reported by the manufacturer to be 0.5 ppm. LODs for study solvents have not been experimentally determined by the manufacturer but were estimated to be between 0.5 to 1 ppm. We verified that the TIP could detect 1 ppm of all study solvents by generating 1 ppm of each solvent in Tedlar bags.

During a sampling period, a photoionization instrument such as the TIP will experience moderate decreasing signal drift due to electronic fluctuations and buildup of solvent film on the UV lamp. To monitor and correct for zero drift, the TIP was zeroed at the beginning and end of each sampling period using hydrocarbon free air. To monitor for span drift, the TIP was calibrated at the same time with certified 30 ppm *o*-xylene. The two TIP units used in this study showed a mean (± standard error) zero drift of −0.1 ppm (± 0.04) and span drift of − 16.7 percent (± 0.7) for 27 sampling sessions of 178 minutes average duration. Any drift that occurred during a sampling session was corrected in the data analysis by using the mean of presampling and postsampling session calibration values.

Real-time TIP solvent concentration data was collected using a Ranger 2 datalogger (Rustrack, East Greenwich, Rhode Island) that monitored and stored TIP output voltage at 250-msecond intervals. The data were downloaded from the data logger into a laptop computer after each 2- to 3-hour sampling session. Pronto software (Rustrack) was used to plot real-time concentration profiles and convert plots into spreadsheet databases for calculations. Data were corrected for the mean voltage drift that occurred during the sampling session and the relative response of the solvent being measured.

Laboratory Analysis of Solvents

The selected solvents had different affinities for charcoal and so required different desorption methods. Two protocols (A and B) were consequently developed for solvent analysis. Air samples were collected using paired charcoal tubes because of the separate desorption and analyses required for the six solvents. After collection, samples were stored on ice or at −20°C prior to analysis.

One tube (A) from each pair was desorbed in 1 ml of a 5 percent dichloromethane solution in methanol (vol/vol; the second tube (B) was desorbed in a 1 percent sec-butanol solution in carbon disulfide (vol/vol). The charcoal was vibrated for 30 minutes during desorption. Tube A was analyzed for acetone, 2-EEA, NBA, and PGMEA. Tube B was analyzed for IPA, *o*-xylene, *m*-xylene, and *p*-xylene. A total of 195 charcoal tubes, including blanks, were analyzed for solvents. For selected samples the front and the back sections were desorbed and analyzed separately, and for the remainder, the front and back sections were combined for desorption and analysis.

All analyses were performed on Hewlett-Packard (HP, Atlanta, Georgia) Model 5890 gas chromatograph with an HP Model 5970 mass selective detector (MSD). The injector and detector temperatures were 200°C and separations were performed on a 30-m DB-Wax fused silica capillary column. For all solvents except acetone, the initial temperature of 50°C was held for 5 minutes, then increased at 7°C/min to 65°C, and then the temperature program rate was increased to 16°C/min to a final temperature of 150°C. The temperature program for acetone analysis started at 50°C, which was held for 2.05 minutes, and then increased at 45°C/min to 200°C. Helium served as the carrier gas at 1 ml/min. Each injection of 3 ul was split with a ratio of 50:1. The MSD was operated in the selected ion mode to enhance sensitivity. The GC/MS LOD for most of solvents was 0.05 ug/ml; it was 0.2 ug/ml for acetone. These correspond to air detection limits ranging between 0.004 to 0.034 ppm for a task sampled at 250 cc/min for 10 minutes.

Pharmacokinetic Modeling

It is difficult to define potentially hazardous peak exposures to solvents because adverse effects are determined by tissue concentration which, in turn, is a complex function of exposure, uptake, distribution, and elimination of solvent. The pharmacokinetic model we used was presented elsewhere but is summarized here for convenience.[7] The time course of solvent concentration in body compartments in response to peak exposures of solvents were modeled with a five compartment physiological model where the compartments were: (1) vessel-rich group (VRG); (2) muscle group (MG); (3) fat group (FG); (4) lungs; and (5) liver.

The concentration of an organic agent within a given compartment is given by the general form:

$$\frac{dC_i}{dt} = \frac{Q_i}{V}(C_{art} - C_i/N_i) \quad (1)$$

where C_i is the concentration of the ith compartment, C_{art} is the arterial concentration coming from the lungs, Q_i is the blood flow rate through the compartment, V_i is the tissue volume, and N_i is the blood/tissue partition coefficient. The expressions for the lung and liver compartments are more complex because of air/blood exchange and metabolic clearance, respectively.

TABLE I. Compartmental Parameters of the Acetone Model

Compartment	Volume (L)	Perfusion Rate (L/min)	Partition Coefficient
Lungs and blood	6.2		300 Blood/air
Air flow		9.6[A]	
Blood flow		7.4[A]	
Liver	1.7	1.5	1.0 Liver/blood[B]
Vessel rich	7.1	3.0	1.0 VRG/blood
Skin and muscles	35.0	2.6	1.0 Muscle/blood
Fat group	12.4	0.26	1.0 Fat/blood

[A]Air and blood flowing through the lungs depend on the exercise rate; the model was set at light exercise (20 W).
[B]There are no measured partition coefficients for acetone partitioning into tissues from blood; the value was set at 1.0 based on acetone's high water solubility.
VRG = vessel-rich group.

Volatile organic agents may enter the lung compartment by inhalation of contaminated air or with venous blood coming into the lungs. The agent leaves the lungs by exhalation or with arterial blood going to the tissues. The concentration of the agent in the lung compartment is equal to that of arterial blood leaving the lungs and is given by:

$$\frac{dC_{art}}{dt} = \frac{(Q_{alv}C_{air} + Q_{tot}C_{ven} - Q_{alv}C_{art} - Q_{tot}C_{art}/N_{arb})}{V_{lung} + V_{art} + V_{rsd}/N_{arb}} \quad (2)$$

where C_{air} is the air concentration in the worker's breathing zone, Q_{alv} is the alveolar rate, Q_{tot} is the total blood flow through the lungs, C_{ven} is the mixed venous blood concentration (blood flow weighted sum of concentrations leaving the tissues), and N_{arb} is the air/blood partition coefficient. The three volumes are the following: V_{lung} is lung tissue, V_{art} is arterial blood, and V_{rsd} is the residual functional capacity (air in lungs).

The expression for the concentration in the liver compartment is:

$$\frac{dC_{liv}}{dt} = \frac{Q_{liv}}{V_{liv}}(C_{art} - C_{liv}/N_{liv}) - K_{met}C_{liv} \quad (3)$$

where the metabolic rate is assumed to be approximately

TABLE II. Characteristics of Solvents Used in Fabrication Rooms

Chemical	Use	VP,mm Hg at 68°F	PEL (ppm)	STEL (ppm)
Acetone	Cleaning, coater rinse	180	750 (OSHA) 250 (NIOSH)	1000 (OSHA)
IPA	Cleaning	33	400 (OSHA)	1000 (OSHA)
PGMEA	Photoresist component	4	None	None
2EEA	Photoresist component	2	100 (OSHA) 5 (ACGIH)	None
Xylenes	Photoresist component	8	100 (OSHA)	150 (OSHA)
NBA	Photoresist component	10	150 (OSHA)	200 (OSHA)

See text for abbreviations.

TABLE III. Characteristics of Study Fabrication Rooms

Rooms	Class	Airflow Pattern	Photoresist Composition	FR Volume (ft^3)	Total CFM	Percent Fresh Air	Total Air Changes Per Hour	Fresh Air Changes Per Hour
1	1000	Ceiling to side wall, returns via chase	Two positive resists: 60% PGMEA, 60% 2EEA plus 5% NBA and xylene, acetone as rinse	68,000	37,300	28	33	9
2	100	Ceiling to side wall, returns via chase	Positive resist: 70% PGMEA, PGMEA as rinse	150,000	600,000	8	240	19
3	10	Ceiling to floor, returns via chase	Positive resist: 60% PGMEA, PGMEA as rinse	180,000	909,160	7	303	21

See Table II for abbreviations.

linear and unsaturated, K_{met}. The rate of metabolism was estimated by fitting the model to data on venous blood and breath levels obtained by Brown *et al.*[8] in a chamber study of human volunteers exposed to 250 ppm acetone. A value of 0.6 min^{-1} was chosen for K_{met}, which gave a good fit (<10% difference) to the three points for the 250 ppm data.

The tissue volumes and blood perfusion rates for each compartment at 20 W exercise (Table I) have been estimated by others.[7] The partition coefficients for tissue to blood distribution of acetone in the six compartments were assumed to be 1.0 on the basis of acetone's high water solubility; thus the estimates of blood and tissue concentration are approximate.

This model accounted for inhalation uptake, hepatic metabolism, and changes in respiration and organ blood flow when solved by numerical integration over small time increments. Volumes, blood perfusion rates, and partition coefficients specific for each compartment were used. Since the partition coefficients for tissue to blood were assumed to be 1.0 on the basis of high water solubility, but were not measured, the estimates of tissue concentration are approximate. The model gave a good estimation of the time course of tissue concentration and approximated the absolute magnitude.

Results

Description of Solvent Use in Fabrication Rooms

Table II lists characteristics of the six solvents, their major uses, and the current government or consensus 8-hour permissible exposure limits and 15-minute short-term exposure limits (STELs). Most of the current standards are based on acute health effects (dizziness, irritation, narcosis) with the exception of the American Conference of Governmental Industrial Hygienists 8-hour recommended exposure level for 2EEA, which is based on reproductive health effects.

Acetone and IPA were used in the fabrication rooms for the general cleaning of parts, machines, and work surfaces. Acetone was also used as a wafer edge bead rinse in photoresist coaters. PGMEA, 2EEA, NBA, and xylene were used primarily as components of photoresists. Table III presents information on the photoresists used and ventilation characteristics of the three fabrication rooms. Fabrication room

TABLE IV. Results of Full-Shift Solvent Personal Samples

Rooms	Operator	Number of Samples	Solvent Level (ppm)*				
			Acetone	PGMEA	2EEA	Xylene	NBA
1	Coater operator	2	1.80 ± 0.49	0.053 ± 0.010	0.007 ± 0.000	< 0.000	< 0.000
	Aligner operator	2	0.69 ± 0.005	0.006 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	< 0.000
	Inspector	2	0.93 ± 0.14	0.003 ± 0.001	0.001 ± 0.000	< 0.000	< 0.000
2	Coater operator	3	0.32 ± 0.027	0.004 ± 0.001			
	Aligner operator	3	0.15 ± 0.024	0.004 ± 0.001			
	Maintenance technician	2	1.80 ± 0.79	0.022 ± 0.009			
3	Coater operator	7	0.55 ± 0.011	0.016 ± 0.000			

*Mean ± standard error.
See Table II for abbreviations.

TABLE V. Results of Full-Shift Solvent Area Samples

Rooms	Sample Location	Number of Samples	Solvent Level (ppm)*				
			Acetone	PGMEA	2EEA	Xylene	NBA
1	Photo bay, at Coater	2	0.86 ± 0.29	0.16 ± 0.067	0.064 ± 0.030	0.005 ± 0.002	0.003 + 0.002
	Photo bay, other work stations	3	0.59 ± 0.015	0.005 ± 0.001	0.002 ± 0.000	< 0.000	< 0.000
	Adjacent bays	4	0.27 ± 0.061	0.003 ± 0.001	0.001 ± 0.000	< 0.000	0.000
2	Photo bay, at coater	4	0.21 ± 0.021	0.005 ± 0.000			
	Photo bay, other work stations	1	0.14	0.004			
	Adjacent bays	2	0.072 ± 0.000	0.003 ± 0.001			
3	Photo bay, at center	2	0.13 ± 0.003	0.008 ± 0.000			
	Photo bay, other work stations	1	0.14	0.007			
	Adjacent bays	2	0.10 ± 0.004	0.004 ± 0.000			

*Mean ± standard error.
See Table II for abbreviations.

1 used positive photoresists containing either 2EEA or PGMEA as the major solvent. Typical photoresist compositions were: 60 percent 2EEA, 5 percent NBA, 5 percent xylenes, and 30 percent resins or 70 percent PGMEA and 30 percent resins. Fabrication rooms 2 and 3 used only PGMEA based photoresists. In the last 2 years the industry has seen a trend toward substitution of PGMEA for 2EEA in photoresists because of the latter's potential reproductive health effects.

All three fabrication rooms were organized into work bays separated by finger service chases that contained support equipment. Air was recirculated from the ceilings back through the service chases either via side walls or through the floor. Fabrication room 1 was the oldest and had the fewest fresh air changes per hour.

Each fabrication room contained one to three coaters that automatically dispensed photoresist onto wafers. Each wafer was automatically conveyed into the bowl of the coater, 3 to 5 ml of photoresist was dispensed onto the center of the wafer from a tube, and the wafer was spun at high speed to distribute the photoresist evenly across the wafer surface. The underside of the wafer was then rinsed with 15 to 30 ml of another solvent (either acetone or PGMEA) to remove any beads of photoresist from wafer edges. The wafer was then conveyed into an in-line bake plate oven or removed from the coater and baked in a separate oven unit to harden photoresist resins.

Extensive engineering controls limited release of photoresist solvents into fabrication room air. Coater bowls were more than 90 percent enclosed by plexiglass covers and had local exhaust ventilation (LEV). LEV was also generally applied to inline bake plates, photoresist waste containers, and cabinets containing photoresist supply bottles. Nonetheless photoresist odors were occasionally detected.

Odors were not generally detected inside clean room work areas (except during certain tasks) but were prevalent in the chase areas behind the coaters. In these fabrication rooms, air entered and flowed downward from ceilings and exited through the lower portion of side walls or through floors; it was recirculated back upward through service chases before returning through banks of high-efficiency particulate air filters. Solvents released from coaters would tend to be carried downward by clean room air flow and into service chases behind the coaters and eventually recirculated back into the fabrication room.

The production rates (i.e., number of wafers coated per day) were similar for all fabrication rooms during the period that solvent sampling was conducted. Typical rates were 160 wafers per shift. If 3 to 5 ml of photoresist and 15 to 30 ml of rinse were applied per wafer, this means that ap-

TABLE VI. Results of Solvent Task Samples: Coater Operation

Rooms	Task	Number of Samples	Mean Task Duration (Minutes)	Solvent Level (ppm)*				
				Acetone	PGMEA	2EEA	Xylene	NBA
1	Loads wafer cassettes	2	11.2	0.29 ± 0.009	< 0.002 ± 0.000	< 0.002 ± 0.000	< 0.009 ± 0.001	< 0.003 ± 0.000
	Unload wafer cassettes	4	14.3	0.79 ± 0.077	0.034 ± 0.008	0.043 ± 0.018	< 0.009 ± 0.001	< 0.003 ± 0.000
2	Load wafer cassettes	6	9.6	0.026 ± 0.003	< 0.003 ± 0.000			
	Unload wafer cassettes	6	10.3	0.027 ± 0.002	< 0.003 ± 0.000			
3	Load wafer cassettes	4	10	0.60 ± 0.119	0.019 ± 0.002			
	Unload wafer cassettes	6	10	0.34 ± 0.064	< 0.002 ± 0.000			

*Mean ± standard error.
See Table II for abbreviations.

TABLE VII. Results of Solvent Task Samples: Coater Maintenance

Rooms	Task	Number of Samples	Mean Task Duration (Minutes)	Standard Level (ppm)*	
				Acetone	PGMEA
2	Photoresist bottle change	3	5.5	0.21 ± 0.050	< 0.017 ± 0.005
	Line purge and acetone rinse	5	4.7	0.72 ± 0.25	< 0.006 ± 0.001
	Waste jug change	1	2.0	0.087	0.36
3	Photoresist bottle change	1	3.0	0.33	< 0.006
	Line purge and acetone rinse	1	0.5	1.1	< 0.039
	Waste jug open pour	3	6.7	0.39 ± 0.12	0.084 ± 0.033

*Mean ± standard error.
See Table II for abbreviations.

proximately 1 L of resist and 5 L of rinse were used in the fabrication room per shift.

Results of Full-Shift Sampling

The sampling period for full-shift samples ranged from 6 to 8 hours. A total of 28 area samples and 22 personal samples were taken.

The results of the personal samples are summarized in Table IV. The values presented are the arithmetic means of solvent concentration in parts per million (±standard errors). Table cells with no reported values indicate that analysis of the solvent was not performed because it was not in use in that area.

All operators sampled were working in photo bays on the day of sampling. Coater operators loaded and unloaded wafer cassettes into coaters. Aligners and inspectors worked at other workstations at distances between 5 to 25 feet from coaters. The maintenance technicians sampled were all performing preventive maintenance or repairs on the coaters and generally used acetone to clean parts; some also cycled photoresist through tubing as part of repairs.

The solvent levels measured were very low. Acetone and IPA levels ranged between 0.5 to 3 ppm. PGMEA and 2EEA ranged between 1 and 50 ppb and xylene and NBA levels were generally undetectable. All the levels measured were less than 1 percent of current standards for 8-hour exposures. Fabrication room 1 levels were marginally higher than the other fabrication rooms. Maintenance technicians generally had higher levels than coater operators who in turn were higher than aligners or inspectors.

The results of area samples are summarized in Table V. Samples taken at the coaters were held at breathing zone height above the coaters by clipping sampling probes to a ring stand. Samples at other workstations in photo bays or in adjacent bays were generally taken at inspection stations or computer terminals where solvents were not used.

Acetone levels ranged between 0.1 to 9.0 ppm and IPA levels between 0.5 to 0.7 ppm. PGMEA and 2EEA levels ranged between 1 to 164 ppb. Xylene and NBA levels were mostly undetectable (< 0.1 ppb for an 8-hour sample). Fabrication room 1 acetone and PGMEA levels were marginally higher than the other fabrication rooms.

Samples taken in adjacent bays at approximately 50 to 100 feet from coaters were similar and only marginally lower than samples taken at workstations in photo areas at distances of 10 to 20 feet from the coaters. This is due to general fabrication room air flow patterns and the mixing of air from different parts of the fabrication room before recirculation.

Results of Task Solvent Sampling

A total of 105 tasks were sampled for solvent levels. For most tasks both charcoal tube and TIP samples were taken. The results are summarized in Tables VI through VIII.

Table VI presents the results for coater production operation tasks sampled by charcoal tube. Samples were taken at all coaters in a fabrication room at both load and unload ends of the coater. Coater operation consists of two tasks: loading cassettes of wafers onto coater conveyors at one end of the coater and unloading cassettes from the opposite end. Loading also involves the selection of the correct application program and usually observation of application of resist onto the first wafer to check operation; the total procedure takes approximately 2 to 3 minutes. The load end is generally next to the coater bowl. Unloading wafer cassettes from the opposite end takes less time (less than 1 minute). The unload end of the coater is next to the in-line bake plate.

For these tasks only, actual sampling time was longer than task time to maximize levels of detection. This decision was based on initial sampling with the TIP which showed that levels were below 1 ppm. The mean task duration ranged between 9 to 14 minutes, generally covering the period during which one cassette of 5 to 6 wafers was processed. Sampling probes were clamped to ring stands at 2 feet above the top to the coater to sample breathing zone position.

The levels measured by charcoal tube sampling (Table VI) were low and similar to personal and area sample results presented previously. PGMEA and 2EEA levels range between < 2 to 43 ppb while the other resist solvents were generally nondetectable. Acetone levels ranged between 0.03 to 0.8 ppm. All TIP samples in these locations were nondetectable (less than 1 ppm). All measured levels were less than 1 percent of current STELs.

TABLE VIII. Results of Solvent Task Samples: Pouring and Cleaning

Rooms	Task	Location	Number of Samples	Mean Task Duration (Minutes)	Solvent Level (ppm)*		
					Acetone	IPA	PGMEA
1	Pour acetone into dispensing bottles	SC	2	1.2	42.3 ± 11.8		
	Pour acetone into coater cannister	SC	1	1.5	9.6		
	Pour acetone into tool reservoir	FR	1	1.3	2.4		
	Pour IPA into tool reservoir	FR	1	1.0		4.44	
	Clean coater bowl with acetone	FR	3	9.9	12.5 ± 1.1		0.042 ± 0.001
	Clean room bench with IPA	FR	1	6.0		16.6	
2	Pour acetone into dispensing bottles	FR	2	0.8	2.2 ± 0.98		
	Clean coater cup with acetone	FR	4	6.3	0.8 ± 0.20		<0.033 ± 0.001
	Clean room bench with acetone	FR	1	3.0	1.9		<0.006
3	Pour acetone into dispensing bottles	SC	1	4.0	273.0		
	Pour PGMEA into coater cannister	SC	4	4.0			2.3 ± 0.35
	Clean coater bowl with acetone	FR	1	16.0	2.8		
	Clean coater parts with acetone	FR	2	9.5	31.6 ± 10.4		0.042 ± 0.02
	Clean room bench with IPA	FR	2	3.3		5.8 ± 2.4	

*Mean ± standard error.
FR = fabrication room.
SC = service chase.
See Table II for additional abbreviations.

The results of Table VI suggest that coater operation releases only very low levels of resist solvents into fabrication room air during the 4 to 7 hours the coater may be in operation per shift. TIP samples of air exhausted from coater bowls during wafer coating (taken in local ventilation exhaust ducts in service chases) showed levels ranging between 200 to 1100 ppm (mean values). For example, a TIP sample taken during application of 3 ml of 2EEA followed by 20 ml of acetone measured a mean value of 1142 ppm in the exhaust duct. A sample taken during application of PGMEA resist and rinse measured 250 ppm in the exhaust duct. Coater exhaust samples demonstrate the large quantities of vapor captured and the potential for exposure if local exhaust ventilation is not present or is not functioning properly. The low concentrations observed in area, personal, and task samples at the three fabrication rooms demonstrated proper functioning of the coater LEV systems during the routine coater production operations sampled.

Table VII presents the results of coater maintenance tasks sampled by charcoal tube. Photoresist bottle changes were generally performed by coater operators; other tasks were performed by maintenance technicians. Photoresist bottle changes and waste jug removals occurred regularly (3 to 5 times per week over all shifts); the other tasks occurred infrequently (less than once per week).

Most of the maintenance tasks sampled involved open solvent containers but minimal pouring or application of solvent. Acetone levels ranged between 0.2 to 1.7 ppm; PGMEA levels ranged between <2 to 356 ppb. All levels were below 1 percent of current STELs. Most TIP samples were less than 1 ppm.

Currently, at all fabrication rooms, photoresist stock is replenished by switching tubing from empty to fresh bottles; no open pouring is involved and solvent air levels were consequently very low. Detectable levels of PGMEA were measured during resist waste jug changes that involved open pouring.

Table VIII presents the results of solvent cleaning and pouring tasks sampled by charcoal tube. Acetone or IPA was used to clean parts, machines, work surfaces in the fabrication room. If photoresist was on parts being cleaned, resist solvents could sometimes be detected. These tasks were performed either by fabrication room operators or by maintenance technicians.

Cleaning coater cups was performed at the end of each shift by coater operators. The plexiglass cover of the coater bowl was removed and approximately 1000 to 2000 ml of acetone was used to remove resist resin from inside the coater bowl. Local exhaust ventilation was kept on during the cleaning and as a result the mean task results were low. Mean acetone levels for cleaning tasks ranged between 0.8 to 12.5 ppm.

Some of the solvent cleaning was not done under local exhaust ventilation, such as fabrication room bench wiping. Measured levels were still low, however, due to downward laminar air flow patterns. All samples were below 3 percent of current STELs. The highest levels measured were for cleaning coater cup assemblies in fabrication room 3 (mean acetone level = 31.6 ppm). This task was performed on the floor of the fabrication room by a maintenance technician using approximately 1000 ml of acetone to wipe coater parts; a plastic basin would catch and hold acetone that dripped from parts. The results of TIP samples for these tasks are presented in the next section.

Table VIII also presents the results of solvent pouring tasks measured by charcoal tube. Open pouring occurred more frequently in the past; in the last 5 years, many cannisters and reservoirs have been plumbed into bulk delivery systems and are filled automatically. A limited amount of open pouring was still done, primarily of acetone and IPA.

TABLE IX. Results of Solvent Task Samples: Pouring and Cleaning

Rooms	Task	Location	Duration (Minutes)	Solvent Levels (ppm) TIP Mean	TIP Maximum Peak
1	Pour acetone into dispensing bottles	SC	1.7	8.4	52.9
	Pour acetone into dispensing bottles	SC	0.8	20.6	161
	Pour acetone into coater cannister	SC	1.5	77.2	616
	Pour acetone into tool reservoir	FR	1.3	0.6	12.7
	Clean coater bowl with acetone	FR	10.8	3.7	700
	Clean coater bowl with acetone	FR	7.0	1.0	201
	Clean coater bowl with acetone	FR	11.0	2.2	45.5
2	Clean coater cup with acetone	FR	5.7	0.4	31
	Clean room bench with acetone	FR	3.0	0.4	40.4
3	Pour acetone into dispensing bottles	SC	4.0	73.1	1133
	Pour PGMEA into coater cannister	SC	7.0	3.3	32.3
	Pour PGMEA into coater cannister	SC	2.0	2.2	25.0
	Pour PGMEA into coater cannister	SC	5.0	0.5	9.8
	Pour PGMEA into coater cannister	SC	2.0	2.4	17.5
	Clean coater parts with acetone	FR	2.0	8.0	122
	Clean coater parts with acetone	FR	6.8	62.5	1162
	Clean room bench with IPA	FR	5.5	0.6	12.5

See Table II for abbreviations.
FR = fabrication room.
SC = service chase.

Open pouring of acetone in the service chases produced the highest task exposure levels, ranging between 9 to 273 ppm. The highest sample was still considerably below the 1000 ppm STEL for acetone. Pouring in fabrication rooms produced lower exposure levels (between 2 to 4.5 ppm of acetone and IPA). Fabrication room 3 fills coater cannisters with PGMEA edge bead remover by open pouring in the service chases; the mean level measured was 2.3 ppm. Pouring in service chases limits exposure to fabrication room personnel in general but increases the exposure of the operator performing the task. TIP samples for these tasks will be discussed in the next section.

Results of Peak Solvent Sampling

A total of 92 TIP samples were taken during solvent task sampling. Many task samples had levels quantitated as less than 1 ppm by charcoal tube samples. Of the 92 TIP samples, 35 measured levels above 1 ppm.

The highest peak samples occurred during solvent cleaning and open pouring. The highest values are listed in Table IX. Examples of real-time solvent concentration fluctuations of the two highest tasks are shown in Figure 1.

The results of Table IX demonstrate that task peak values can exceed mean values by up to two hundredfold. Two of the maximum peak values measured by the TIP were above 1000 ppm. However, an inspection of Figure 1 shows that these peaks did not last longer than a few seconds.

The toxicological significance of measured peak values was evaluated by pharmacokinetic modeling that is discussed in the next section. The TIP is a state-of-the-art direct reading instrument with a very fast response time. The response time of its detector (similar to a GC detector) is almost instantaneous. However, it takes about 3 seconds for its detection chamber to mix and fill with outside air and during this time period it can underestimate very rapid peaks. The ratio of all paired TIP and charcoal tube samples was 0.82 (N = 80). The ratio of TIP and charcoal tube samples for solvent levels detected by the TIP was 0.59 (N = 27). For dose modeling TIP values were multiplied by 1.69 to correct for peak underestimation.

Results of Pharmacokinetic Modeling

Only one of the solvents (acetone) appeared to warrant modeling because of observed high exposures. No high exposures were measured for the other solvents in use during the tasks monitored. The time course of acetone concentrations in the VRG, which includes the reproductive organs, was modeled using a task with high peak concentrations, shown in trace B of Figure 1. The task was cleaning coater parts in fabrication room 3. The mean ppm during this task was 26 ppm; the maximum peak observed was 1162 ppm. For modeling, the TIP data were averaged over 10-second periods to correspond to typical breathing cycles. The concentration of acetone in alveolar air was considered equal to the resultant data (Figure 2, solid square). The model then calculated the level of acetone in the VRG group that includes the central nervous system, kidneys, reproductive organs, and other tissues with high blood flow/volume rates (Figure 2, dashed line). Table I presents the compartmental parameters used in the model; sources for parameter values are Smith[7] and Perbellini *et al.*[9]

As shown, this task produced high air concentrations of acetone for very short time intervals (less than a minute). The second large peak shown in Figure 2 exceeded an air concentration of 1100 ppm for 40 seconds. These brief

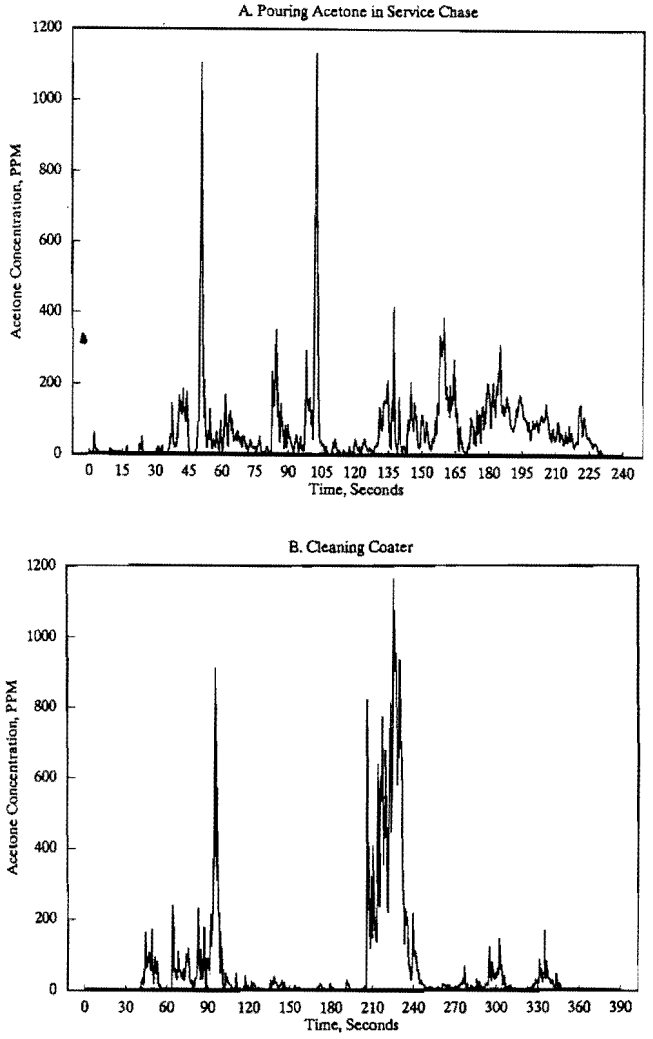

FIGURE 1. Real-time acetone concentration for two tasks as measured by the TIP.

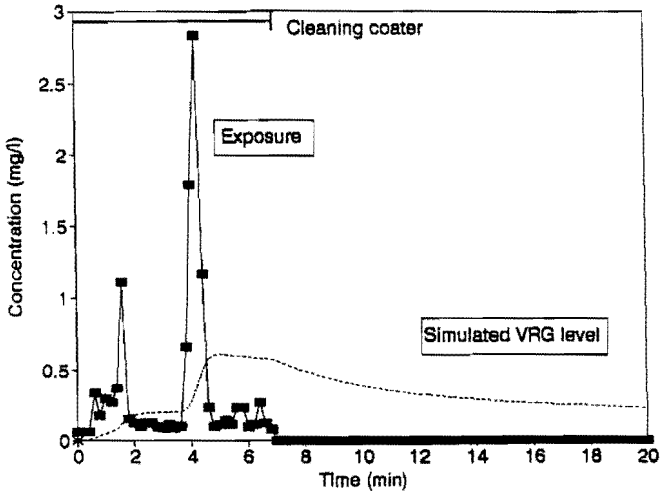

FIGURE 2. Time course of acetone inhalation exposure and VRG tissue concentration predicted by multicompartment model.

peaks will cause the concentration in the blood and VRG tissues to rise rapidly during the peak. After the peak passes, the tissue levels fall off much more slowly. The magnitude of the increase in the tissue concentration is determined by the magnitude and duration of the inhaled peak. Shorter less intense peaks, such as the first peak in Figure 2 (which reached 460 ppm for 10 seconds), produce smaller increases in tissue dose concentration.

The results of the multiple compartment model shown in Figure 2 estimated that a maximum VRG tissue concentration of about 0.6 mg/L was produced immediately after the cleaning task. The decline during the time period of 10 to 20 minutes following the task was caused by redistribution and removal by metabolism and exhalation. Thus during the 6.8-minute cleaning exposure that averaged 0.34 mg/L, acetone entered the body at an effective alveolar ventilation intake rate of 6 L/min (9.6 L/min × 0.6 absorption) so a total of 13.8 mg of acetone will be absorbed.

One published study observed postimplantation mortality associated with exposure of test animals to 31.5 mg/m^3 (0.0315 mg/L) for 24 hours.[10] Assuming the animals have approximately the same air/blood partition coefficients as humans (300) and the same blood/tissue coefficient for VRG (1.0), then the multicompartment model would predict steady-state blood and VRG tissue level of acetone after 24 hours exposure to be 9.3 mg/L (300 × 0.0315 mg/L). Since this was the lowest exposure associated with any evidence of reproductive health effects in animals, this blood level is an estimate of the minimum blood level that might be associated with such adverse effects in humans. This approach should be used with caution because there are large species differences for reproductive effects. However, it suggests the approximate order of magnitude for a minimum effect level. The blood levels calculated from the highest human exposures observed in the fabrication rooms (0.6 mg/L) were fifteenfold below this marker.

This modeling suggests that the highest peak exposure observed would produce an estimated blood and reproductive tissue concentrations much lower than the estimated levels in the animal experiment. Clearly, multiple peak exposures at the 1000 ppm level, if sufficiently frequent, could produce tissue levels as high as those projected in the animal study. However, these routine cleaning operations are infrequent (generally only several times per week) and on average produce much smaller peak exposures.

Discussion and Recommendations

The observed solvent levels were considerably below all current legal and recommended standards. A pharmacokinetic model also suggested that levels of one solvent, acetone, associated with the highest exposures were considerably below levels associated with adverse reproductive outcomes in animal studies.

The low levels observed were most likely the result of the state-of-the-art engineering controls used at these fabrication rooms to contain and control exposures on coaters and other equipment. These controls include local exhaust

ventilation on coater bowls, photoresist supply bottles, and coater waste containers, bulk delivery of chemicals to eliminate open pouring, and the substitution of less hazardous for more hazardous materials (e.g., the substitution of PGMEA for 2EEA). Unfortunately, the odor threshold for PGMEA is much lower (probably less than 1 ppm) than that of 2EEA and the perception of hazard by the operators has actually increased.

There are a number of actions that could be taken to reduce exposures. These would reduce the incidence of odors and the discomfort of the operators. These actions include the following:

1. Reduce open pouring in fabrication clean room areas and service chases. Pouring and filling reservoirs (operations frequently performed) should be performed in solvent hoods whenever automated delivery of chemicals is not feasible.
2. Distilled water should be substituted for IPA for wiping clean room work surfaces.
3. Machine cleaning with solvents should be performed under local exhaust ventilation whenever possible. Where possible, parts can be removed and cleaned in hoods. Duplicate parts can be used to minimize production down time.
4. Photoresist odors are routinely noticed in service chases and occasionally in clean room areas. Tests with smoke sticks have indicated small leaks occurring in coater cup assemblies. Complete enclosure of coater cabinets and installation of LEV would contain odors originating from coater cups and other sources.
5. Routine surveys of ventilation should be performed. The low levels measured throughout this study were due to the good performance and optimum adjustment of LEV systems in use. Routine surveys had been instituted only in the last several years and should be continued.

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