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WHITE SMOKE EMISSION FROM A SEMICONDUCTOR MANUFACTURING PLANT

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Semiconductor manufacturing involves processes which emit various gaseous and particulate pollutants. One of the common problems in the industry is the emission of white smoke from stacks of wet scrubbers. This study analyzed the physical and chemical characteristics of the white smoke in one of the semiconductor plants in Taiwan. It was observed that the medium diameter of the emitted particles is about 0.1 µm, which will grow further into 0.1-1.0 µm size range due to the condensation of water vapor onto these particles under certain meteorological conditions. These 0.1-1.0 µm particles are responsible for the white smoke since they have a high light scattering efficiency. In the waste stream from the wet scrubber, the main chemical species were found to be silica, monomeric silica, ammonium, and chloride for particulate pollutants, and ammonium and chloride for gaseous pollutants. A wet Electrostatic Precipitator (ESP) installed behind the wet scrubber was shown to be able to eliminate white smoke emission due to efficient removal of submicrometer particles. ©1997 Elsevier Science Ltd

INTRODUCTION

Semiconductor manufacturing processes emit various gaseous and particulate pollutants. Acidic gaseous pollutants are normally treated using wet scrubbers which are not efficient for submicrometer particle removal. Many plants in the semiconductor industry have white smoke emission problems from the wet scrubbers. Under unfavorable meteorological conditions, the plume opacity often becomes greater than the regulated 20% level (TEPA 1995). This white smoke problem, which was also mentioned in Dumas (1994), is often associated with high concentrations of acidic gases or fine particles as described in Damle et al. (1987).

The formation of white smoke happens in the plume after a distance downstream of the stack. In the first zone, the plume is diluted and cooled by the wind. In the second zone, the volatile species and water vapor will condense on the surfaces of existing particles emitted from the stack since the temperature of the plume decreases below the dew point. This phenomenon, which is often referred to as heterogeneous condensation or nucleation, leads to particle growth. Further downstream of the stack, the temperature of the plume may become lower than the nucleation temperature in the third zone. The volatile chemicals will become self-nucleated and small particles are formed due to homogeneous nucleation. In these last two zones of the plume, efficient light scattering particles in the 0.1-1 µm diameter range are formed, and the plume opacity may be increased beyond the regulated 20% level. The peak plume opacity often increases with an increasing concentration of acidic gases or fine particles (Damle et al. 1987). To overcome the white smoke problem, it is often necessary to reduce the concentration of either acidic gases or fine particles, or both, depending upon the cost of treatment and availability of technology.

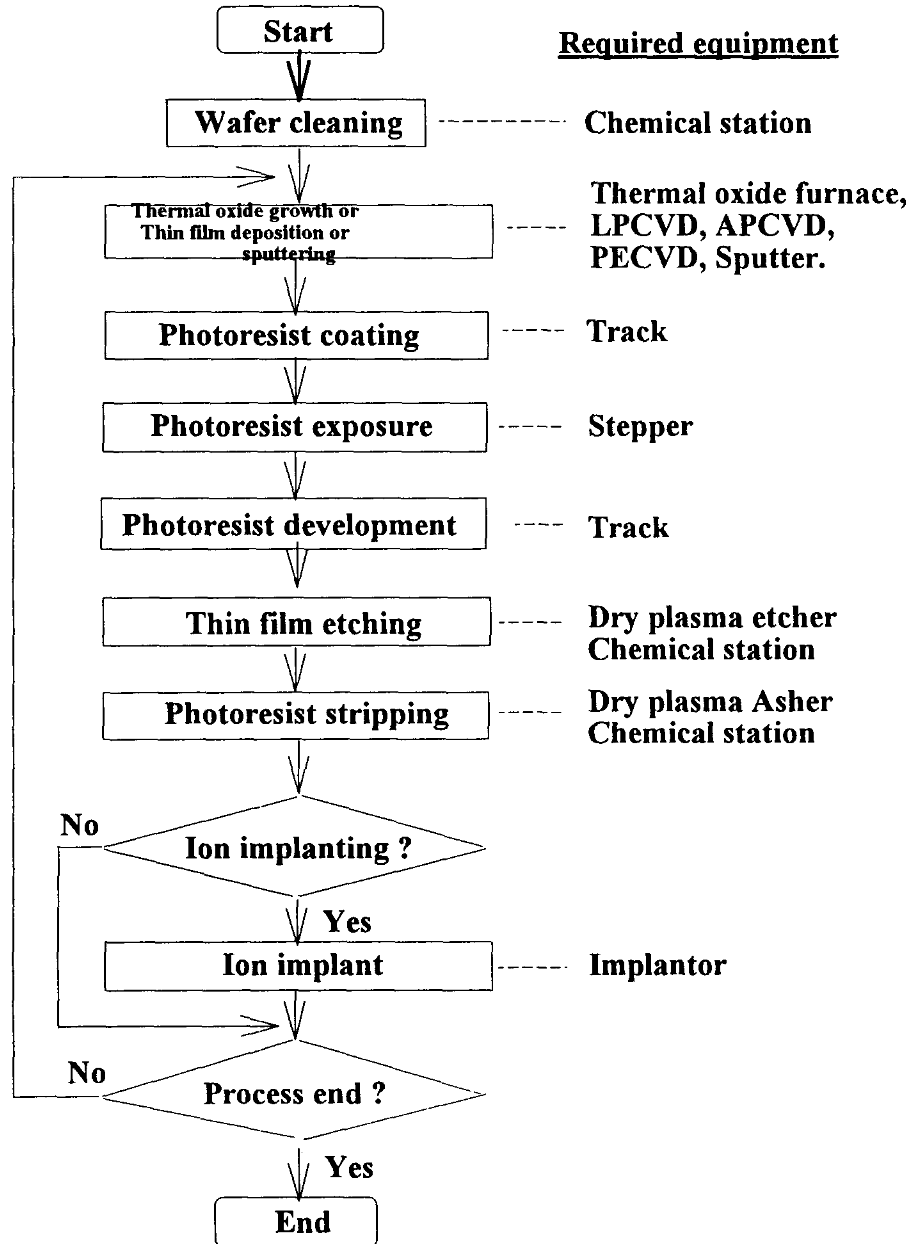

Fig. 1. Flow chart of semiconductor manufacturing process.

The flow chart of the semiconductor manufacturing process per mask level is shown in Fig. 1. It starts from wafer cleaning, thermal oxidation (or thin film deposition, sputtering), photoresist coating, photoresist exposure, photoresist developing, thin film etching, photoresist stripping, and ion implanting if necessary. Line width for the manufacturing of the 16 mega dynamic random access memory (DRAM) is currently about 0.35 μm. The process may involve over 20 mask levels until an integrated circuit (IC) is produced. The wafer cleaning process is to remove gaseous and particulate contaminants on the wafer surface to increase the breakdown voltage of the gate oxide. The thermal oxide growth process is to grow SiO_2 on the wafer in the thermal oxidation furnace. Thin film deposition is to deposit films such as Si_3N_4 and polysilicon on the wafer in the chemical vapor deposition (CVD) facility. Sputtering is to deposit metal on the wafer. The processes of photoresist coating, photoresist exposure, and photoresist development are to define the mask on the wafer. The thin film etching process is to define patterns of the device and the photoresist stripping process is to remove the mask on the defined patterns. Ion implanting is an optional process which is used to control the concentration and depth of impurities precisely by ion beam on the wafer.

The main sources of pollutants can be classified into five different types based on equipments as follows:

1) Chemical stations and tracks are widely used in wafer cleaning, isotropic film etching, and photoresist stripping process. Because many kinds of chemicals are used, volatile species including inorganic compounds (such as HF, H_2SO_4, NH_4OH, HCl, HNO_3, and H_3PO_4) and organic compounds (such as organosilicon, hydrocarbon, organophosphate compounds, and amines) are emitted. Besides creating environmental problems, once these airborne pollutants enter the clean room, they may also contaminate the wafer and reduce the product yield. For example, they degrade the quality of thermal oxidation due to surface reactions with dangling bonds on the Si surface to form Si-C defect centers (Muller et al. 1994). Furthermore, fine particles such as droplets of H_2SO_4, ammonium salts NH_4F, NH_4Cl, $(NH_4)_2SO_4$, and NH_4NO_3 will be generated by gas phase chemical reactions.

2) Thermal oxidation furnace is to grow the thermal oxide SiO_2 used for the gate capacitance of device through the reaction of SiH_4, O_2, and/or H_2O. Trans-1,2-Dichloroethylene (Trans-LC) is also involved as a source of chloride in silicon oxidation and quartz tube cleaning (Newboe 1993). Typical pollutants are the residual gases such as SiH_4, organic chloride, and particles such as SiO_2.

3) CVD can be classified as low pressure CVD (LPCVD), atmospheric pressure CVD (APCVD), and plasma enhanced CVD (PECVD) according to the level of vacuum and the type of reaction in the tool. Many residual gases, acidic gases, and fine particles are seen to emit from the CVD system. The generation of fine particles such as SiO_2 and NH_4Cl is mainly due to gas phase chemical reactions (Lee et al. 1994).

4) Plasma-assisted dry etching, a critical technology for anisotropic etching processes, uses fluorocarbons (FCs), chlorofluorocarbons (CFCs), and other gas mixtures. Other than FCs and CFCs, main etching gases are Cl_2 and HBr for polysilicon film, SF_6 nitride film, BCl_3 and Cl_2 for metal film such as TiN/Al/TiN. CF_4 is the first feed gas used to etch silicon dioxide for semiconductor fabrication; it provides the source of atomic fluorine to gasify silicon. Pollutants such as SiF_4, CO, CO_2, COF_2, and F_2 are generated in addition to residual reactive gases. The organic chloride, which is carcinogenic or mutagenic, will be generated in O_2 environment due to its reaction with photoresist.

5) Pollutants of the ion implanter are particles and residual gases such as PH_3/H_2 and AsH_3/H_2.

The air pollution control system of the semiconductor manufacturing plant under this investigation is shown in Fig. 2. Initially, only two wet scrubbers were installed to treat exhaust gases. The wet scrubber #2 has two inlets from the exhaust line of equipments. The wet scrubbers use the NaOH absorbent to remove acidic vapors and halides from chemical stations, chemical vapor deposition tools, and dry plasma etchers (Brookman et al. 1988). Organic and pyrophoric pollutants from ion implanters and tracks are removed by combustion in a burn box (Elliot et al. 1990) before entering the wet scrubber #2. The burn box is a simple enclosure where phrophoric and organic pollutants are burned efficiently in the presence of air. Because of white smoke problems, a wet electrostatic precipitator (ESP) was later installed at the exit of the scrubbers to remove fine particles. The ESP consists of nozzles to spray water as absorbent. This hopefully increases the diameter of particles by condensation process to facilitate their removal. Fine particles are then charged by electrodes and collected on the collection plates, which are washed down regularly by another set of nozzles. This study focuses on the white smoke related inorganic fine particles and acidic gases.

EXPERIMENTAL METHODS

In this study, at first fine particles less than 1.0 μm in diameter were measured by a scanning mobility particle sizer (SMPS, Model 3034C, TSI Inc., St. Paul, MN, USA) system at both the inlet and exit of the wet scrubber. This is to determine the number distribution of particles before and after the emission is treated by the wet scrubbers. The SMPS system, shown in Fig. 3, includes an electrostatic classifier (TSI Model 3071A, TSI Inc., St. Paul, MN, USA), a condensation particle counter (CPC, TSI Model 3020), SMPS software, and a computer. The system is capable of measuring particles ranging from 0.007 to 1.0 μm in diameter, and 2 to 10^7 particles/cm^3 in number concentration. The measurement cycle time was 60 s in this study. An impactor with 577 nm cut aerodynamic diameter was installed at the inlet of the SMPS. A detailed description of the SMPS system can be seen in Wang and Flagan (1990).

Particles were also sampled by an in-line filter holder at a constant flow rate for chemical analysis by ion chromatography. Teflon filters were used. In case anions, cations, silica, and monomeric silica were to be analyzed, samples were extracted by 0.2 mL alcohol and 6 mL $HClO_4$ in the parafilm sealed beaker by ultra-

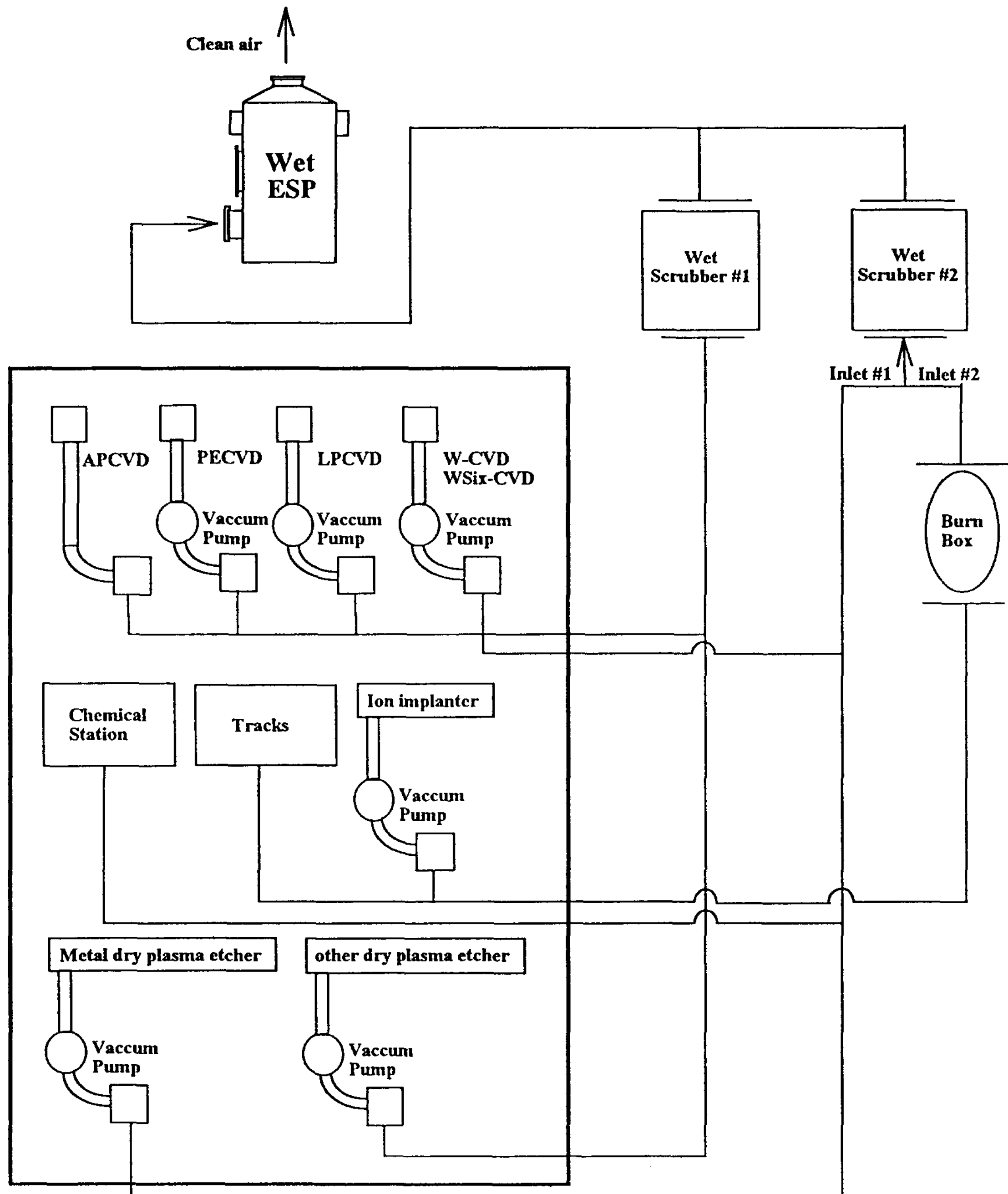

Fig. 2. Air pollution control system of the semiconductor plant.

sonication for 30 min. The concentration of anions and cations was measured by an Ion Chromatograph (IC, Model 4500i, Dionex Corp.). Silica was measured by a UV spectrometer with the calorimetric silica-molybdate test. The Dionex IC system is basically a two-column, separator-suppresser system which is equipped with a conductivity detector. For anions such as F^-, Cl^-, NO^{2-}, NO^{3-}, and SO_4^{2-}, a Dionex Ionpac-AG4 anion guard column, an Ionpac-AS4 anion separator column, and an AFS anion suppresser column were utilized. A 3 mM $NaCO_3$/2.4 μM $NaHCO_3$ eluant was used. For cations such as NH_4^+ and Na^+, an Ionpac-CG_1 cation guard column, an Ionpac-CS_1 cation separator column, and a CFS cation suppresser column were utilized. A 5 mM HCl eluant was used.

Pollutant gases at the exit and entrance of the scrubber were sampled by SKC™ silica gel for analyzing anions, or citric acid coated glass fiber filters for analyzing cations.

To determine if the ESP was effective for white smoke control, particle size distributions were measured by the SMPS at different operating voltages at both the entrance and exit of the ESP.

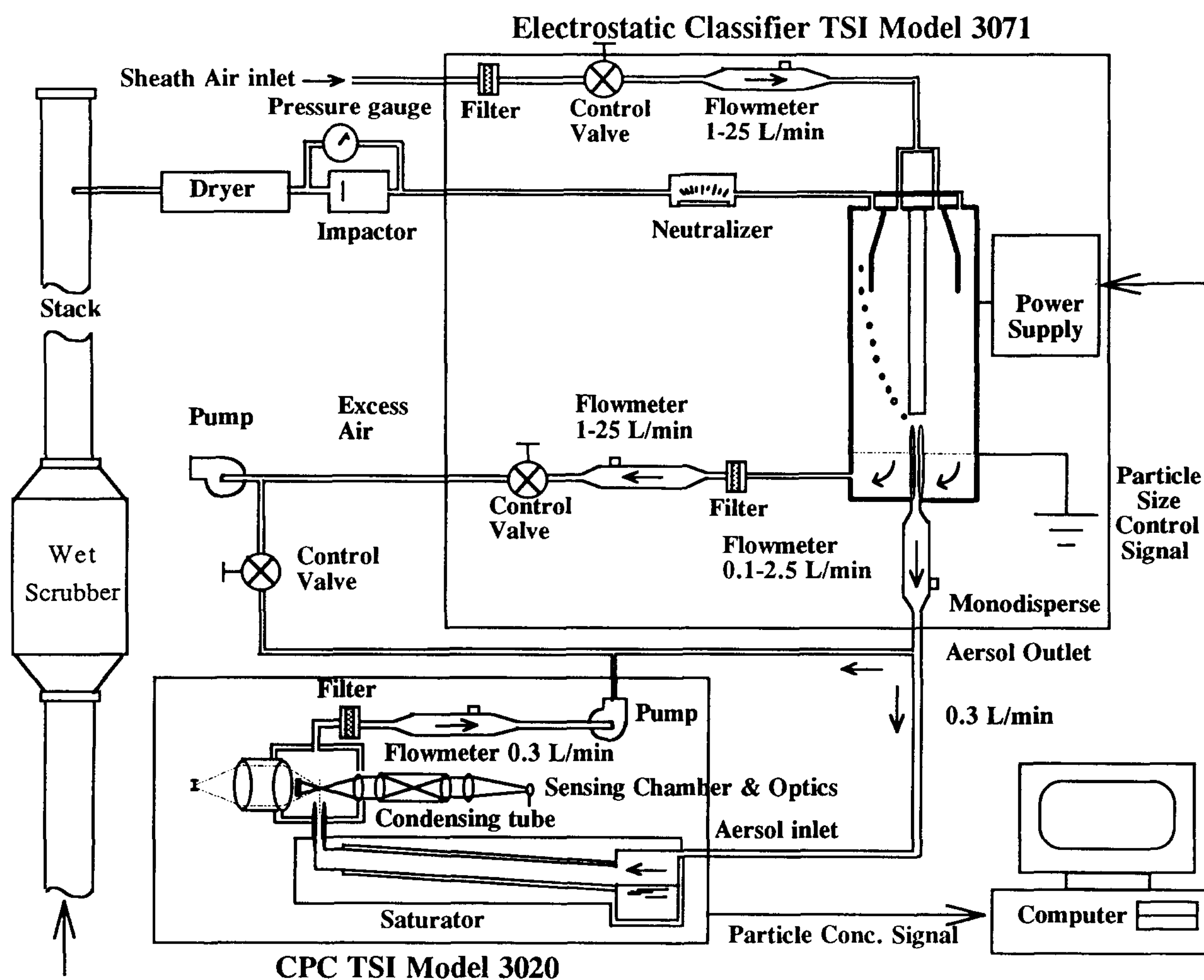

Fig. 3. Schematic diagram of the submicrometer particle measuring system.

RESULTS AND DISCUSSION

Particle size distribution measured by the SMPS at the outlets of the wet scrubber #1 is shown in Fig. 4. It shows that the particle count median diameter is about 0.1 μm with the cumulative submicrometer particle number concentration up to 3.0 x 10^5 #/cm^3 at the outlet of the wet scrubber #2. Because of negative pressure at the inlet of the wet scrubber, the particle size distribution was unable to be measured there.

Results of fraction of soluble anions, cations, silica, and monomeric silica of particles are shown in Table 1. Both total inlet and outlet mass concentrations for stacks #1 and #2 are found to be about 10 mg/m^3 determined independently by open face filter holders. This indicates that fine particles are not removed by scrubbers. Main components of particles are seen to be ~30% silica, ~15% monomeric silica, ~10% ammonium, and ~10% chloride as shown in the table at the inlet of the wet scrubbers. Silica is seen to be the major component in particles since it is the basic material of the semiconductor manufacturing process. The source of silica and monomeric silica comes from CVD, dry plasma etchers, and chemical stations or tracks.

Ammonium and chloride come from the nitride CVD (Lee et al. 1994), chemical stations, and metal dry plasma etchers. In the case of nitride CVD, the highest concentration of NH_4Cl is found to be near the interface between the reaction chamber and the exhaust line due to the contraction of the cross section area at the interface and the temperature drop there. In the chemical stations, the NH_4Cl results from the chemical reaction of NH_3 in the ammonium peroxide mixing (APM) solution, which is used to remove particles, and HCl in the hydrochloride peroxide mixing (HPM) solution, which is used to remove metallic impurities. In the case

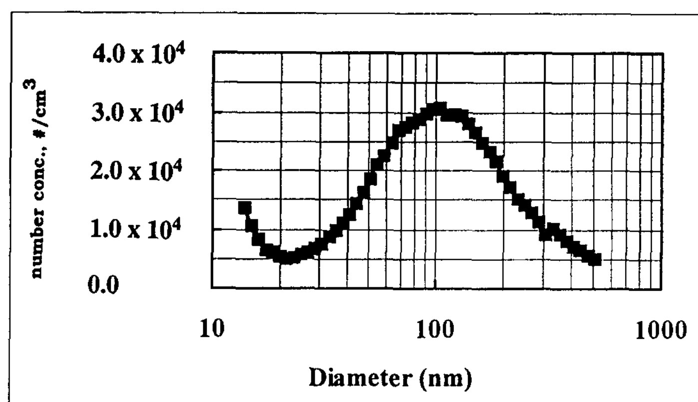

Fig. 4. Particle size distribution at the exit of wet scrubber #1.

Table 1. Concentration (g/kg) of inorganic anions and cations in particles.

Stack # Composition	#1 inlet	#1 outlet	#2 inlet 1	#2 inlet 2	#2 outlet	ESP outlet
NH_4^+	0.617	1.26	0.383	1.052	1.182	0.639
Na^+	0.0058	0.00056	0.13	0.023	0.013	<DL
F^-	0.055	0.0187	0.035	0.279	0.226	0.074
Cl^-	0.413	1.454	0.256	1.118	1.084	0.521
NO_2^-	<DL	<DL	<DL	<DL	<DL	<DL
NO_3^-	<DL	0.035	<DL	0.056	0.163	1.055
SO_4^{2-}	0.0085	0.00085	0.0018	0.0097	<DL	0.055
SiO_2	3.159	3.371	2.851	2.931	3.276	<DL
Si^{4+}	1.474	1.590	1.330	1.368	1.529	<DL
Total	5.733	7.731	4.987	6.837	7.459	2.345

DL: detection limit.

Table 2. Concentration (mg/m^3) of inorganic anions and cations in gaseous pollutants.

Stack # Composition	#1 inlet	#1 outlet	#2 inlet 1	#2 inlet 2	#2 outlet
NH_4^+	2.68	0.74	3.29	1.54	1.22
F^-	0.12	0.04	0.05	0.05	0.15
Cl^-	0.19	1.37	0.55	0.20	0.17
NO_2^-	<DL	<DL	0.12	1.25	<DL
NO_3^-	<DL	<DL	<DL	<DL	<DL
SO_4^{2-}	<DL	<DL	5.75	<DL	0.03

DL: detection limit.

of metal dry plasma etchers, raw materials like BCl_3 and Cl_2 are used and by products like $AlCl_3$, HCl, and $TiCl_4$ will be generated. Also, main components of particles in the ESP are ammonium and chloride as shown in Table 1. Furthermore, the main components of effluent gases are ammonium and chloride as shown in Table 2. This implies high concentrations of ammonium and chloride existing in solid particles.

Results for particles analyzed by the EDS show the existence of Ti, Al, and C. Both Ti and Al may come from the metal plasma etcher which etches TiN material used for the barrier layers, as well as ARL and Al (+Si,Cu) materials. Carbon originates from the tracks, where organosilicon is widely used, and from the dry plasma ashers for the photoresist.

At the exit of the wet ESP, the particle size distribution was measured with respect to the operating voltage ranging from 0 to 50 kV. Results are shown in Figs. 5a-5f. The fractional and overall collection efficiency of particles vs the ESP operating voltage is

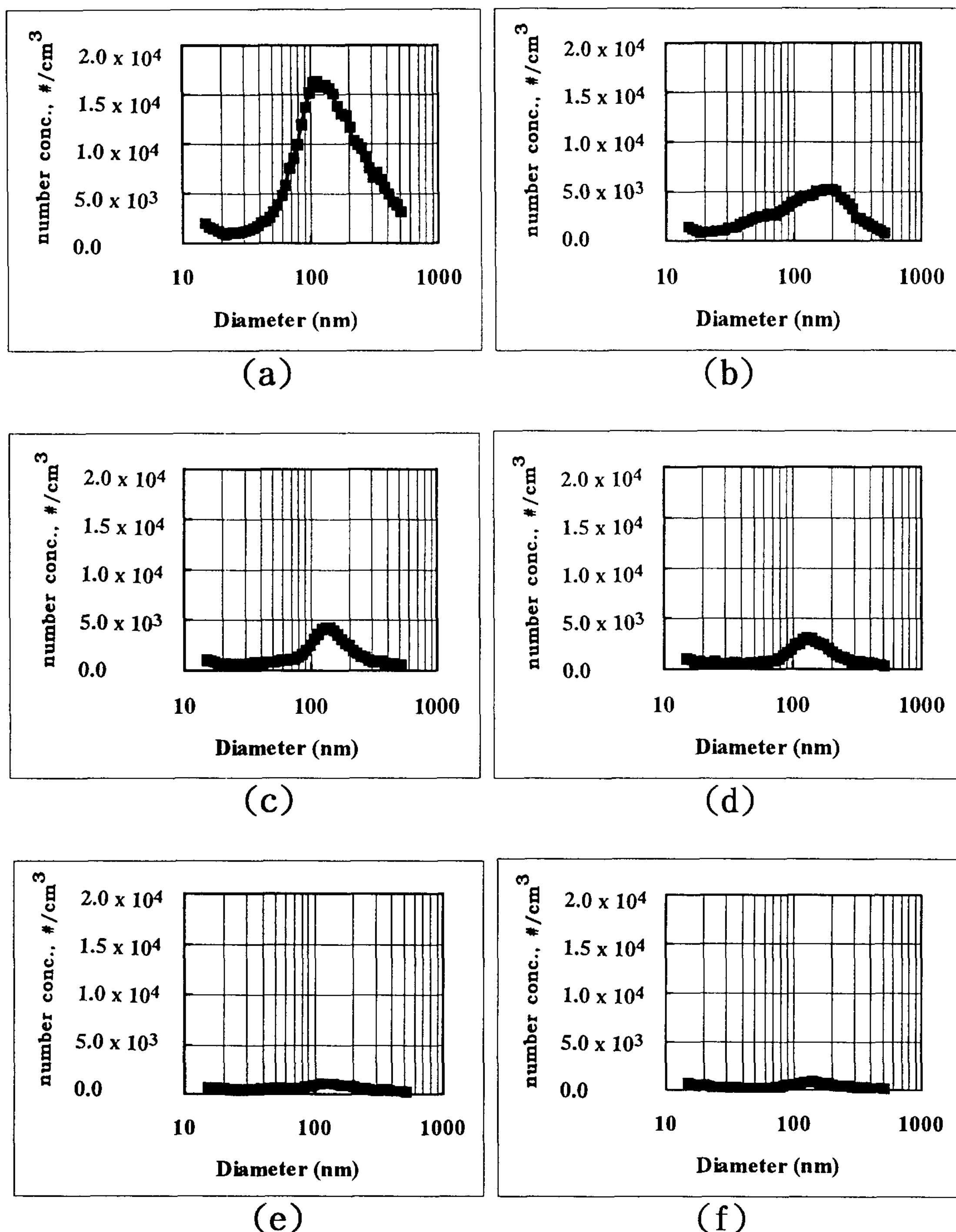

Fig. 5. Particle size distribution at the exit of the wet ESP vs operating voltage of the ESP: (a) zero KV; (b) 30 KV; (c) 35 KV; (d) 40 KV; (e) 45 KV; (f) 50 KV.

shown in Figs. 6 and 7, respectively. It is seen that the count median diameter remains unchanged and the cumulative submicron particle number concentration decreases as the operating voltage of the ESP increases. The white smoke emission was seen to disappear as the operating voltage increased beyond about 40 kV. It is, therefore, concluded that by removing only submicrometer particles using a wet ESP, white smoke emission in semiconductor plants can be eliminated.

Besides wet ESP, other air pollutant treatment systems have been suggested in the open literature to treat toxic exhaust gases in the semiconductor manufacturing industry. For example, the combustion-filter-scrubber system was shown to remove the toxic hydride

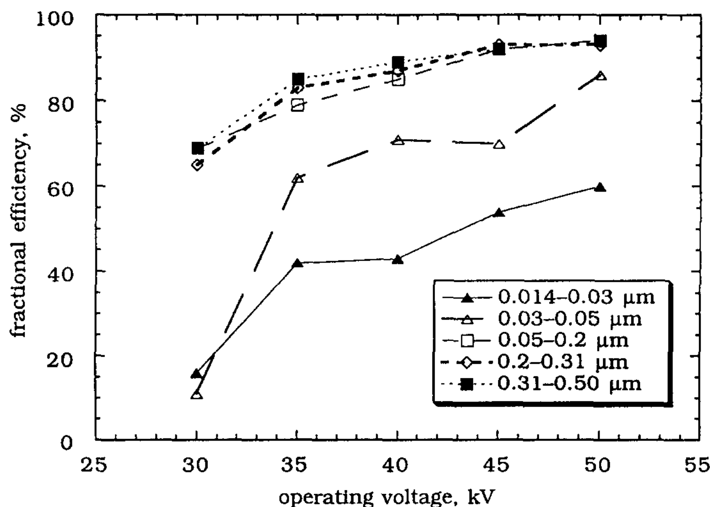

Fig. 6. Fractional collection efficiency of the wet ESP vs operating voltage.

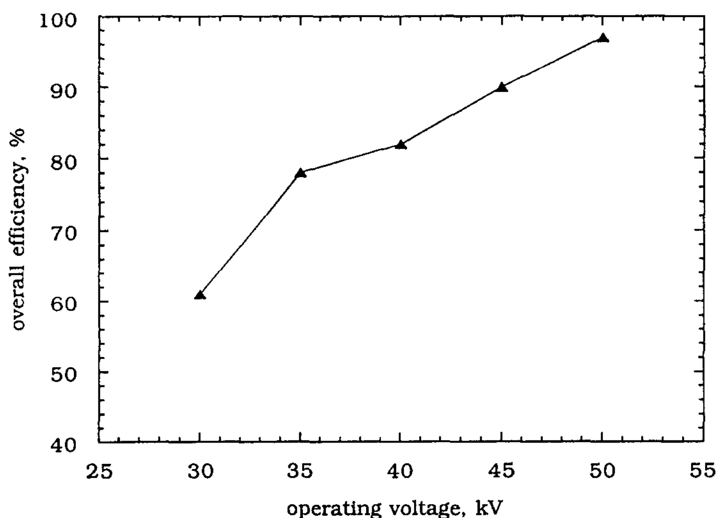

Fig. 7. Overall collection efficiency of the wet ESP vs operating voltage.

gases efficiently (Jordan et al. 1992). The gas reactor column (GRC) was claimed to remove toxic etching gases and other pollutants. But whether or not these devices are effective to eliminate white smoke emissions remains to be investigated.

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