AIRBORNE CHEMICAL CONTAMINATION OF A CHEMICALLY AMPLIFIED RESIST

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ABSTRACT

We have found that the performance of the t-BOC/onium salt resist system is severely degraded by vapor from organic bases. This effect is very pronounced and can be observed when the coated wafers stand for 15 minutes in air containing as little as 15 parts per billion (ppb) of an organic base. The observed effect, caused by this chemical contamination, depends on the tone of the resist system. For negative tone systems the UV exposure dose, required to obtain the correct linewidth, increases. While for the positive tone system, one observes the generation of a skin at the resist-air interface. Both effects are caused by the photogenerated acid being neutralized by the airborne organic base. There are a wide variety of commonly used materials which can liberate trace amounts of volatile amines and degrade resist performance. For example, fresh paint on a laboratory wall can exhibit this detrimental effect. These effects can be minimized by storing and processing the resist coated wafers in air that has passed through a specially designed, high efficiency carbon filter. The implementation of localized air filtration, to bathe the resist in chemically pure air, enabled this resist system to operate in a manufacturing environment at a rate of 100 wafers/hour.

1. INTRODUCTION

In the early 1980's Fréchet, Ito and Willson described the use of photogenerated acid to yield a sensitive, negative tone DUV resist[1-3]. The chemistry of this system (known as Chemical Amplification) is shown in Figure 1 and consists of two distinct steps; 1) photolysis of an onium salt to generated acid and 2) acid catalyzed thermolysis of a t-butyl carbonate to yield a phenolic hydroxyl group. The basic concepts behind Chemical Amplification have been extended to several other imaging systems[4], and currently represent the predominant approach to designing modern DUV/E-beam/X-Ray resists. Chemically amplified resists are not only being investigated by resist research groups, but are also being used by manufacturing & development groups. At this conference last year, Maltabes et al. described using the t-BOC/onium salt resist system in the production of 1-megabit DRAM chips[5]. Also, Holmes et al. described the use of a proprietary DUV chemically amplified resist on a 16-megabit DRAM, pilot-line operation[6].

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In the course of evaluating the t-BOC/onium salt system for use on the manufacturing floor, we observed that the lithographic characteristics of freshly coated wafers differed from wafers which were exposed 8, 12 or 24 hours after coating. When processed in the negative tone, this change in lithographic performance appeared to be a decrease in DUV exposure sensitivity. That is, the longer the coated wafers stood before DUV exposure, the greater the dose required to obtain correct image size. Or conversely, if the DUV exposure dose is held constant, the longer the coated wafers stood, the more the image size changed. This change in linewidth with time can be large (0.4 μm in 30 minutes) and is shown in Figure 2(●). When processed in the positive tone, one also observes a change in performance if the coated wafers are allowed to stand for some time before the DUV exposure. For the positive tone system, and a short delay time between coating and DUV exposure, one observes the formation of a "lip" at the top of the relief image. A longer delay time yields a thin skin at the resist-air interface. This thin skin is shown in Figure 3.

The chemistry of this resist system, shown in Figure 1, affords a reasonable rationalization for this observed degradation in resist performance. The central feature of any chemically amplified resist is the use of a small number of photogenerated acid molecules to initiate a catalytic reaction. The gain associated with these systems is substantial and McKean et al. have reported that 1 acid cleaves approximately 1000 carbonate units[7]. This long catalytic chain yields a sensitive DUV photoresist. However, because of the long catalytic chain any basic impurity which reduces the activity of the photogenerated acid will also degrade lithographic performance. Hence an explanation for the data in Figure 2(●) is that the coated resist films contain a basic impurity which inhibits the photogenerated acid. Furthermore, as the linewidth change in Figure 2(●) increases with time, it appears that the basic inhibitor concentration within the film, also increases with time. This observation is consistent with resist films absorbing the basic inhibitor from the surrounding environment.

In this paper we will show that storing coated resist films in typical clean room air degrades the lithographic performance. But, storing the coated resist films in clean room air that has been scrubbed by a high efficiency carbon filter, preserves lithographic performance and yields a stable manufacturing process. We believe that the carbon filter is removing volatile organic base from the clean room air and we will present data to support this theory.

2. RESULTS AND DISCUSSION

2.1 Effect of Adsorbed Water

One common base that exists in clean room air is water. Water is a stronger base than the t-butylcarbonate group, hence if water was adsorbed from the air and present in the resist film it would effectively compete for the photogenerated acid. To evaluate the possibility that atmospheric water was responsible for the linewidth control problem described in the introduction, we used radiotracer techniques to quantify water uptake. Standard 125 mm silicon wafers were coated with 1.3 μm's of the t-BOC/Ph_3S-SbF_6 resist and baked. The coated wafers were placed into a small desiccator which had been previously saturated for 24 hours with tritiated water (^3H_2O, specific activity = 1.00 mCi/g). Also a control wafer which was not coated with resist was placed in the desiccator at the same time. At various time intervals two wafers were removed from the test chamber. One wafer was subjected to the standard lithographic sequence of DUV exposure, bake, and anisole spray development[5]. The linewidth of image on the test wafer was compared to that obtained with a freshly coated wafer. The other wafer, which was removed from the desiccator, was allowed to air dry for 1 minute and then submerged in anisole to harvest the film. Standard liquid scintillation counting techniques were used to measure the radioactivity level of this solution.

The results from the liquid scintillation counting are shown in Table 1. The lithographically processed wafers only exhibited a linewidth change after 26 hours in the test chamber. This data shows

two important trends. First, the water content within the t-BOC film does not increase with time. Second, linewidth change was observed after 26 hours in the test chamber but not observed after 4 hours. However, the water content of the 26 hour sample was less than the 4 hour sample. In view of these two observations, we believe atmospheric water is not responsible for the linewidth change observed with the t-BOC resist.

Table 1

Wafer	Time in Chamber	Water Content (μg)
Silicon	1 Hr	0.254
Resist	1 Hr	0.210
Resist	2 Hr	0.196
Resist	4 Hr	0.219
Resist	7 Hr	0.077
Resist	10 Hr	0.055
Resist	15 Hr	0.044
Resist	26 Hr	0.083

2.2 Effect of Carbon Filtered Air

Water is not the only basic substance commonly found in air. There are also a variety of volatile nitrogen containing compounds. For example, low molecular weight alkyl amines (the essence of decomposing fish) can be easily detected by the human nose in most open air fish markets. The manufacture of semiconductor devices utilizes a variety of nitrogen containing reagents which may give rise to volatile basic compounds. For example tetramethyl ammonium hydroxide (TMAH) solutions, a commonly used metal-ion-free developer, has a distinctly "fishy" aroma due to alkyl amine. Hence, there is reason to suspect that an airborne organic base, may be responsible for the observed linewidth shift.

To investigate this possibility, we have used a high efficiency carbon filter as a source of pure air. The carbon filtration unit consists of a fan, a active carbon filter bed, and a HEPA filter. Laboratory air is drawn into the filter housing and passed over the specially designed, low leakage active carbon bed to remove organic components. The air then passes through a series of particle filters before it is ready for use.

Coated wafers that are allowed to stand in carbon filtered air behave differently from coated wafers which stand in typical clean room air. For this study 125 mm silicon wafers were coated with the t-BOC/Ph_3S-SbF_6 resist and baked. One set of coated wafers was allowed to stand under a laminar flow hood. The other set of wafers was placed in an open container approximately 1 meter away. This container was continuously purged with clean room air that passed through the carbon filtration unit (see Figure 4). At various time intervals, one coated wafer from each set was removed from its test environment and subjected to the standard lithographic process. The linewidth of the developed image was measured by SEM (5-sites per wafer) and the final results are shown in Figure 1. The data in Figure 2 shows that the two test environments are substantially different. The wafers that stood under the laminar flow hood exhibit a rapid linewidth change with time. While the wafers which stood in the carbon filtered air show constant linewidth. The data in Figure 2 is consistent with the theory proposed in the introduction section, that an airborne organic contaminant is responsible for the observed linewidth shift.

2.3 Effect of Artificially Generated Contaminated Air

The data in section 2.2 argues that the carbon filtration unit is removing some airborne organic contaminate, but does not identify the chemical nature of that contaminate. We have addressed this issue by allowing resist coated wafers to stand in air that was intentionally doped with organic vapor. A variety of compounds were screened with a static contamination test chamber. In this experiment a resist coated 125 mm wafer was allowed to stand for 30 minutes in a closed 2 liter vessel containing 10 μl of the test reagent. The coated wafer was then subjected to the standard lithographic process and examined for linewidth changes. The results were clear. Common solvents such as acetone, ethylacetate, or pentane did not induce linewidth changes. But amines like triethylamine, pyridine, or N-methylmorpholine induced massive linewidth change. In fact the coated wafers which were treated with amine vapor did not produce any image when given a standard UV exposure dose.

The static test chamber is acceptable for gross screening experiments, but does not allow for quantitative work. The static chamber has two major limitations. First, the test compounds are liquids (at room temperature) and may not completely vaporize. Hence, the exact amine concentration in the chamber air is unknown. Second, it's technically difficult to reduce the contaminant concentration to the part per million (ppm) range simply because one is required to deliver a small volume of amine. Consider the following calculation:

> *From the ideal gas law, a 2 l test chamber at 300°K and 1 atmosphere will contain approximately 8.1 x 10^{-2} moles of gas. Rounding to 1 significant figure, the 2 l test chamber contains 10^{-1} moles of gas. Hence one must add 10^{-7} moles of contaminate to generate a ppm concentration level. Assuming a molecular weight of 100 g/mole, one must add 10^{-5} grams or 0.01 mg of contaminate to the chamber. For a liquid with a density of 1 g/ml, this corresponds to 0.01 μl.*

Given these difficulties with a static test chamber, we have used a dynamic system to examine contaminant concentrations in the part per billion (ppb) range. This test chamber is shown in Figure 5. In this test chamber, a carbon filtration unit is used to provide a source of chemically clean air. The contaminating agent is placed into the glass U-tube and carried into the carbon filtered air stream by nitrogen gas. The contaminant concentration is calculated in a simple fashion. The glass U-tube is weighed before and after 24 hours of operation to obtain the contaminant flow rate (g/min). The flow rate in g/min is converted to moles/min, which by the ideal gas law is converted to (liters of gas)/min. The flow rate of the carbon filtration unit was measured at 30 ft^3/min. The ratio of these two flow rates determines the contaminant concentration. A key feature of the dynamic flow system is the ability to deliver a slow contaminant flow rate (typically 50-200 mg/24 hours) into a fast moving stream of carbon filtered air.

We have used this dynamic system to prepare contaminant concentrations in the ppb range. Even at this low concentration, amines have a potent effect on coated resist wafers. Figure 6 shows the results of allowing 125 mm wafers coated with the t-BOC/Ph_3S-SbF_6 resist to stand in air containing 15 ppb of N,N-dimethylaniline. In this study coated wafers stood in the contaminated air stream for 15 or 30 minutes. They were removed from the dynamic test chamber, exposed on a 1X UltraStep X-248E (2.8 mJ/cm^2), baked and developed with anisole. The SEM photographs, in Figure 6 show a significant linewidth shift for these wafers. Increasing the contaminant concentration to 28 ppb, increases the linewidth shift. Figure 6 shows SEM photographs of coated wafers which stood for 30 minutes in 15 ppb and 28 ppb N,N-dimethylaniline. Note that 30 minutes of 28 ppb severely alters image size. The data in Figure 6 is consistent with the theory proposed in the introduction section, that airborne organic contamination is responsible for the observed linewidth shift.

2.4 Effect of Construction Materials

As mentioned in section 2.2, there are numerous sources of volatile amine contaminants. For example, common household cleaning solutions, such as Windex® with Ammonia-D®, contain amine. Amines are also used as curing reagents in a variety of paints, adhesives, and sealants. Vapors emanating from curing construction materials are difficult to quantify. Hence we have used a static test chamber to screen them for detrimental effects. For this work, a sample of construction material was allowed to stand in a small desiccator for 2 hours, to generate a contaminated environment. A coated wafer was placed into the desiccator for 15 minutes, removed and processed on a PE-500 to yield a positive tone image. This positive tone image was examine for linewidth change as compared to a standard wafer. The SEM photographs in Figure 7 show the effect of urethane paint fumes. Note that the wafer treated with floor enamel vapor shows a linewidth shift and the formation of a "lip" at the resist-air interface.

We have used this technique to screen several construction materials and the results are shown in Table 2. In this study a "Pass" grade implies that the image size and shape remained constant.

Table 2

Material	**Result**
Fresh Urethane Paint	Fail
GE Silicon II Calking	Fail
Dow Corning 732 Sealant	Fail
PVC Glue	Fail
Floor Bond 600 Adhesive	Fail
Safety Label Adhesive	Pass
Freon TF	Pass

The test chamber, used to generate the data in Table 2, contains an unknown but undoubtedly high, contaminant level. Hence it represents a worst-case-analysis for construction materials. However, the data in Table 2 clearly show that a wide variety of common materials generate detrimental vapor.

2.5 Effect of Localized Air Filtration

In the previous sections we have demonstrated that carbon filtration of clean room air preserves linewidth, presumably by removing a volatile organic base from the air. One way to transfer this observation to the manufacturing floor would be to pass all clean room air through carbon filters. However, given the size of most manufacturing lines, this simple approach is not feasible. A more practical approach is to only filter the air surrounding the coated wafers.

In the 1-megabit DRAM process described by Maltabes[5], there are only two process steps in which the coated wafers require a carbon filtered environment. First, wafers which are coated & baked, and await exposure on the PE-500, need a filtered environment. Second, wafers in the PE-500 input cassette require carbon filtered air. Thus this process is amenable to localized air filtration. To implement this process we prepared a "holding-box" (approximately 1m x 1m x 1m), attached to a carbon filtration unit. This provided a contaminant-free storage environment for coated wafers awaiting UV exposure. The input cassette area of the PE-500 was enclosed with a polycarbonate box that was slightly larger than a standard 25 wafer cassette. This polycabonate box was attached to a carbon filtration unit and purged continuously with contaminant-free air. Filtering the air at these two locations dramatically improved the lithographic process. Specifically, the observed linewidth shift of the filtered process was

only 0.07 μm in 24 hours. Whereas in section 2.2 we showed that an unfiltered process could exhibit rapid linewidth changes of 0.4 μm in 30 minutes.

The 1-Megbit DRAM semirecessed oxide level was manufactured with the t-BOC/Ph_3S-SbF_6 and the localized carbon filtration process. The resist imaging step required defining a 0.9 μm image (using a PE-500) in a 1.6 μm thick layer of resist. The throughput of this process was 100 wafers/hour. While the raw cycle time through the PE-500 was approximately 20 seconds/wafer. This allowed us to run 600 wafer-starts/day/PE-500 without stressing the system. Rework was held to 1.5% and the photo limited yield (KLA) was 97%.

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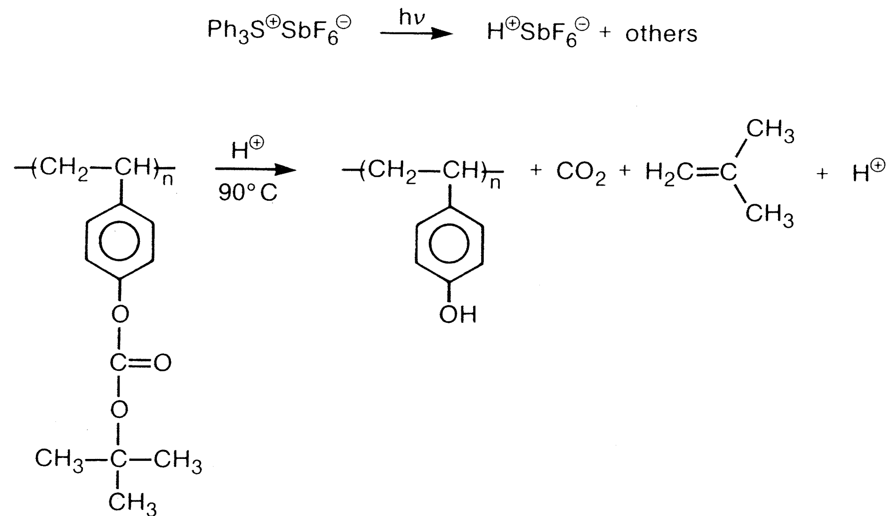

Figure 1. Chemistry of the t-BOC/Ph_3S-SbF_6 resist system.

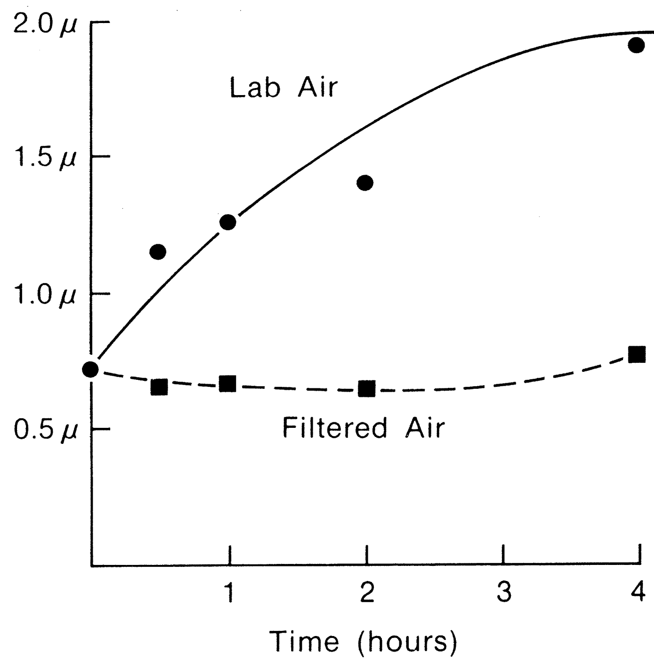

Figure 2. Negative tone linewidth change for coated t-BOC wafers that stood in two environments. (●) Laboratory air. (■) Carbon filtered air.

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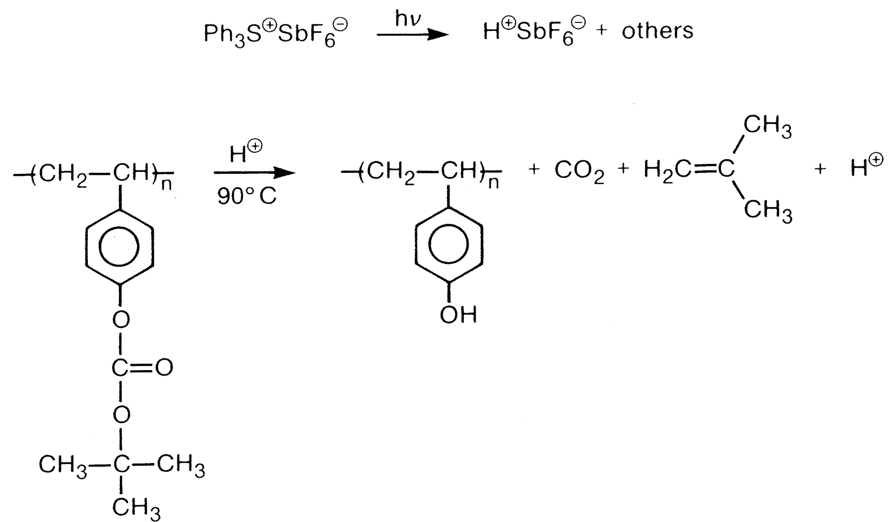


Figure 1. Chemistry of the t-BOC/Ph_3S-SbF_6 resist system.

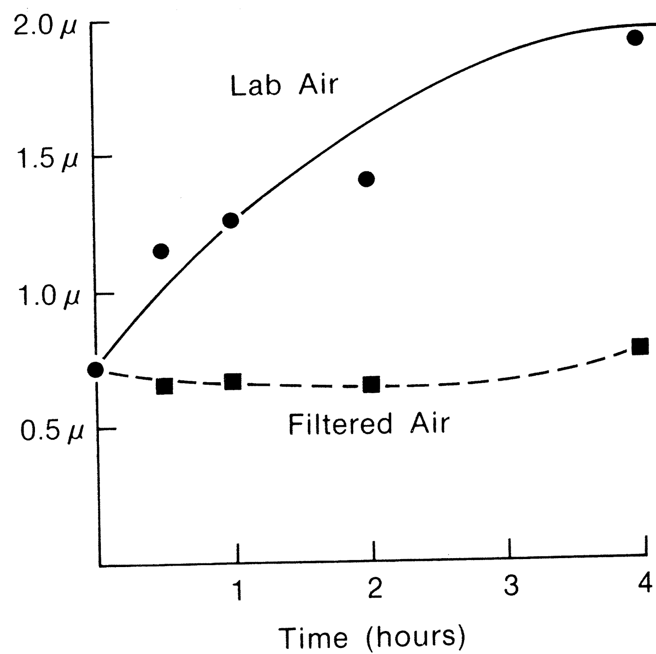


Figure 2. Negative tone linewidth change for coated t-BOC wafers that stood in two environme
(●) Laboratory air. (■) Carbon filtered air.

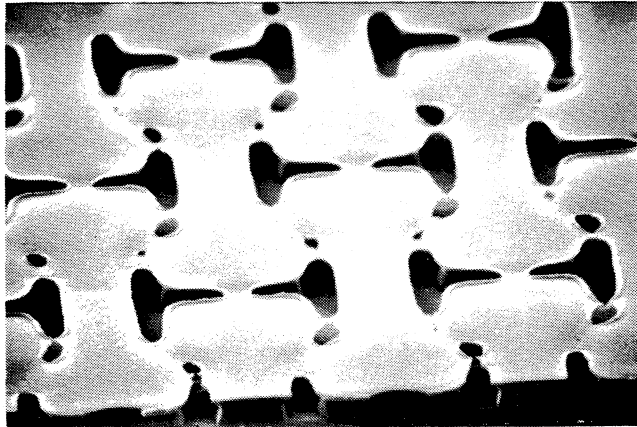


Figure 3. Effect of delay time on image when processed in the positive tone.

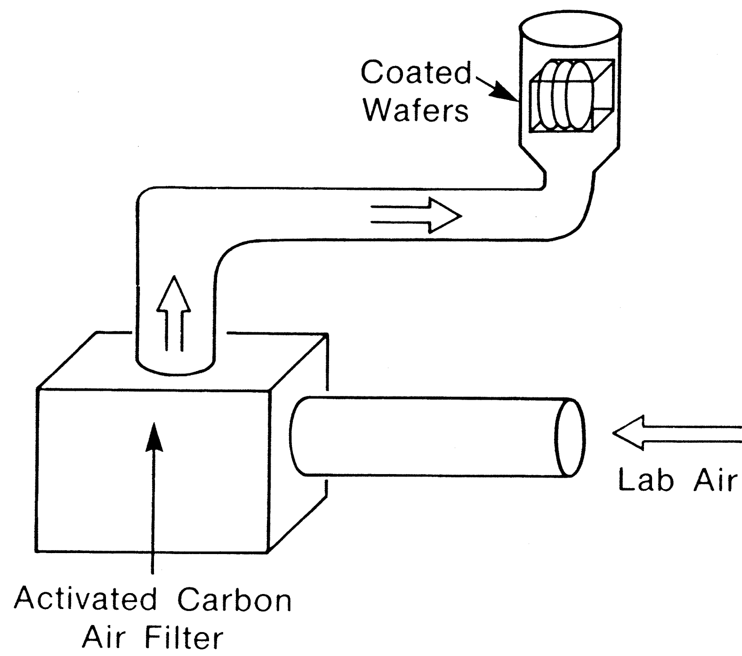


Figure 4. Schematic of carbon filtration unit.

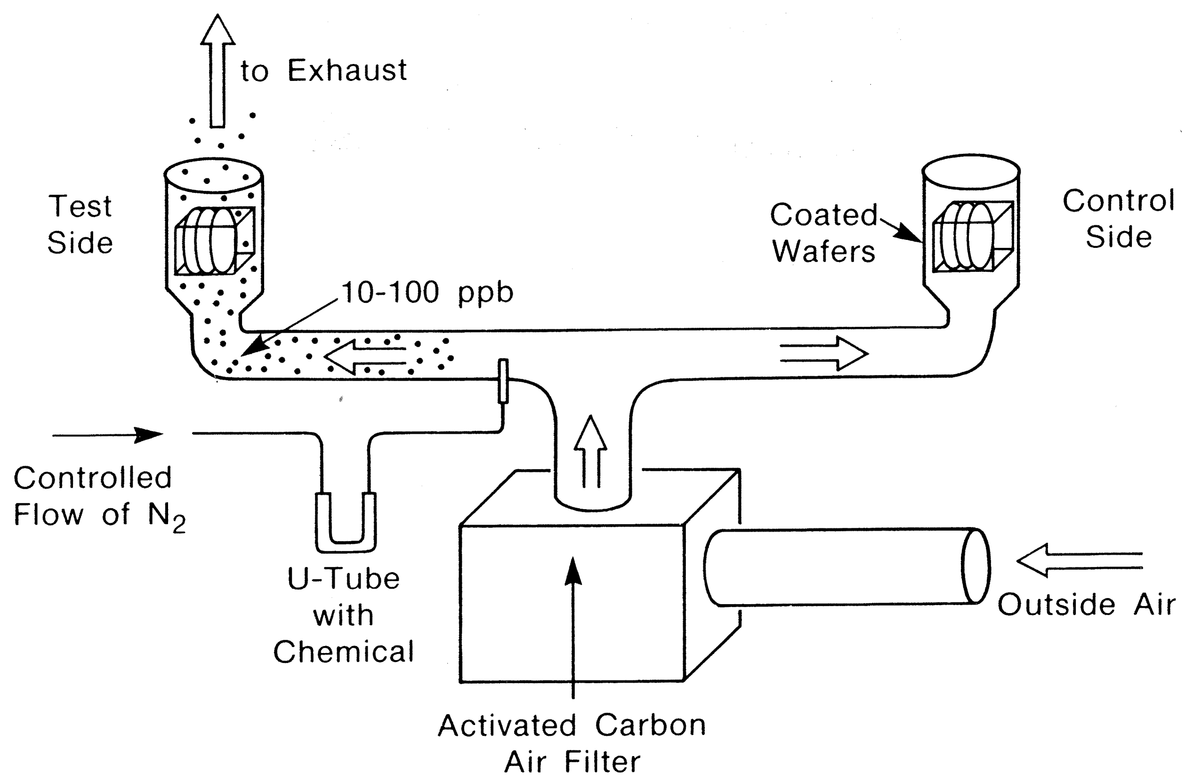


Figure 5. Dynamic flow system used to generate contaminated air.

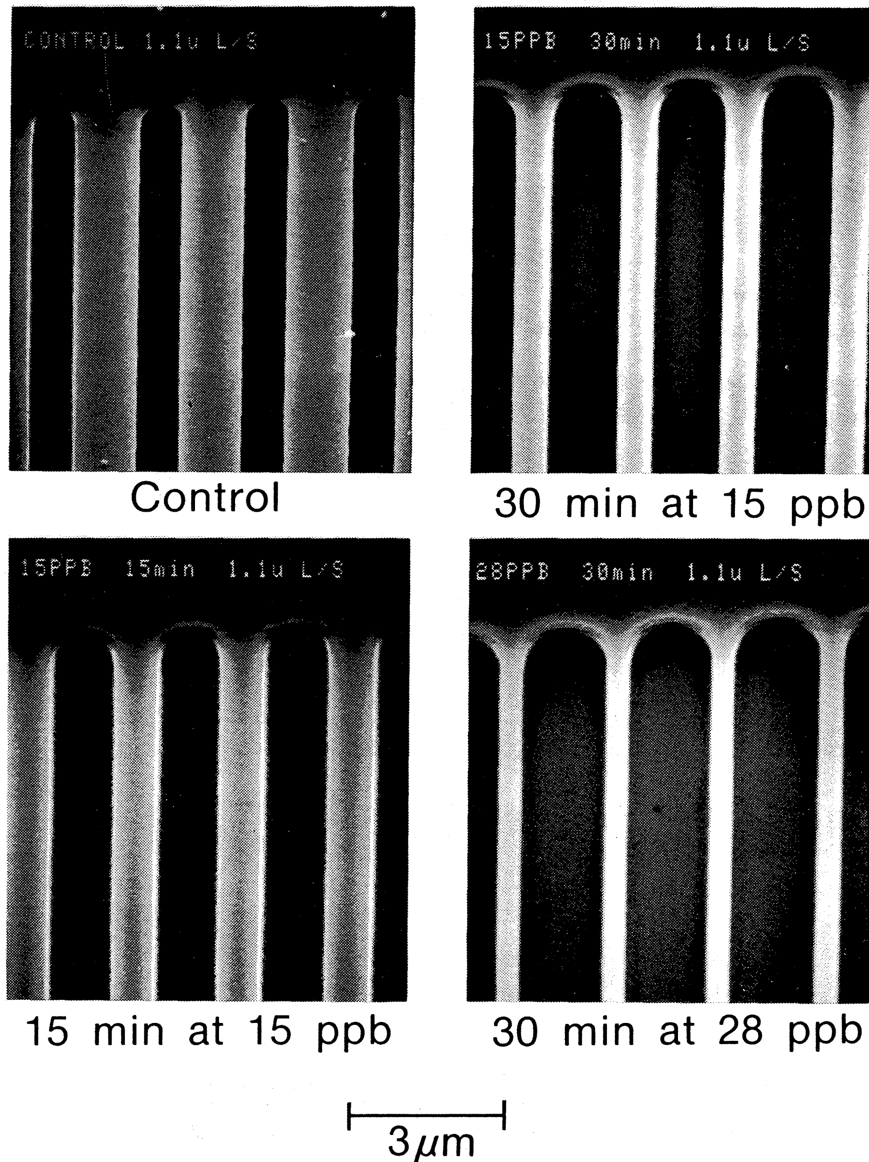
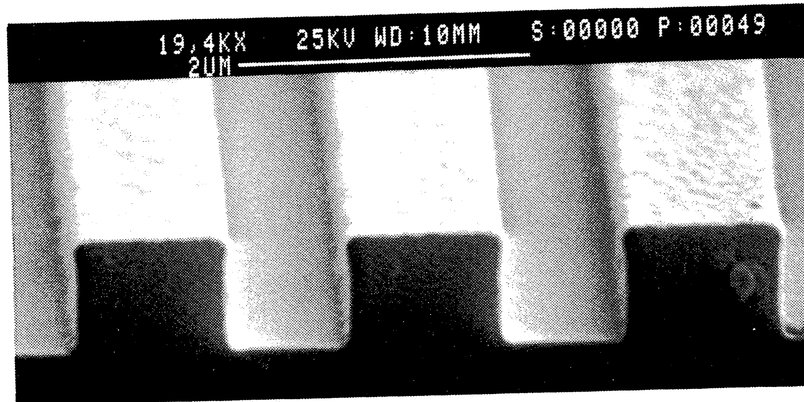
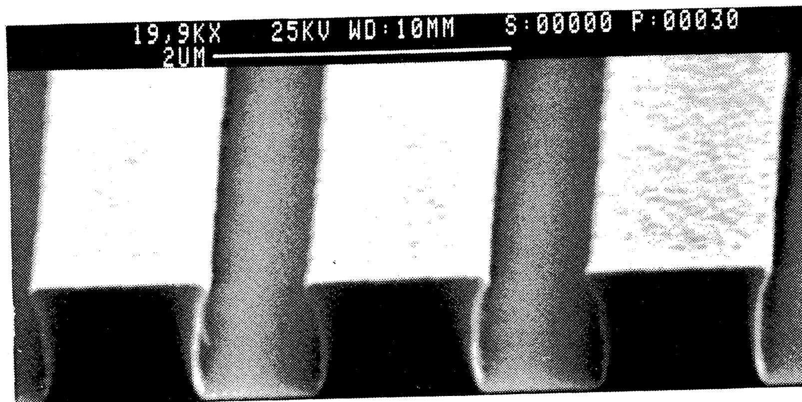


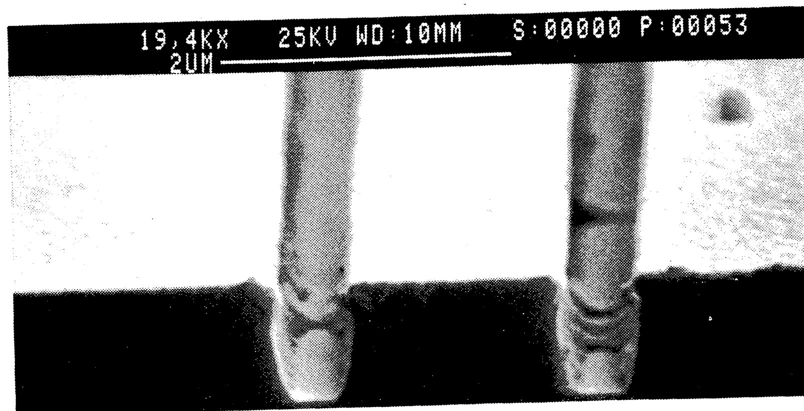
Figure 6. SEM photographs of negative tone image after a coated wafer stood in N,N-dimethylaniline contaminated air.



Control



Urethane
Floor Enamel



Urethane
Enamel

Figure 7. SEM photographs of positive tone image after standing for 15 minutes in desiccator containing paint fumes.