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Release of Arsenic from Semiconductor Wafers

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The production of integrated circuits and other semiconductor devices requires the introduction of impurities or dopants into the crystal lattice of a silicon substrate. This "doping" or junction formation is achieved through one of two processes: thermal diffusion or ion implantation. Ion implantation, the more contemporary and more accurate of the two processes, accomplishes junction formation by bombarding selected areas of the silicon wafer with a beam of dopant ions. Inorganic arsenic, which is regulated by the Occupational Health and Safety Administration (OSHA) as a carcinogen, is frequently used as dopant material. Silicon wafers are found to emit inorganic arsenic following ion implantation. Data collected during this experiment demonstrate that arsenic is released over a 3.5-hour period following implantation and that the total amount of arsenic emitted may approach 6.0 μg per 100 wafers processed within 4 hours after implantation. The discovery and quantification of this phenomenon suggest that newly implanted silicon wafers are a potential source of arsenic contamination—a source that may impact both the quality of the work environment and the integrated circuit product.

Introduction

Integrated circuits and other semiconductor devices are produced by selectively introducing controlled amounts of impurities into the atomic lattice of a silicon substrate. These impurities, called dopants, dislodge and replace individual silicon atoms within the larger crystal structure. Once properly introduced, the impurities alter the electrical characteristics of localized regions of the silicon substrate. Silicon "doped" with Group IIIA elements of the periodic table (*e.g.*, boron) produces regions of positive (p) carriers, whereas silicon doped with Group VA elements (*e.g.*, arsenic) produces regions of negative (n) carriers. These localized areas of doped silicon are used for the electrical definition of functional units called pn junctions. One or more pn junctions are defined in the substrate to form diodes, transistors and other active elements of an integrated circuit.

Doping is most frequently achieved through one of two processes: thermal diffusion or ion implantation.[1,2] Thermal diffusion, which historically has been used for the dop-

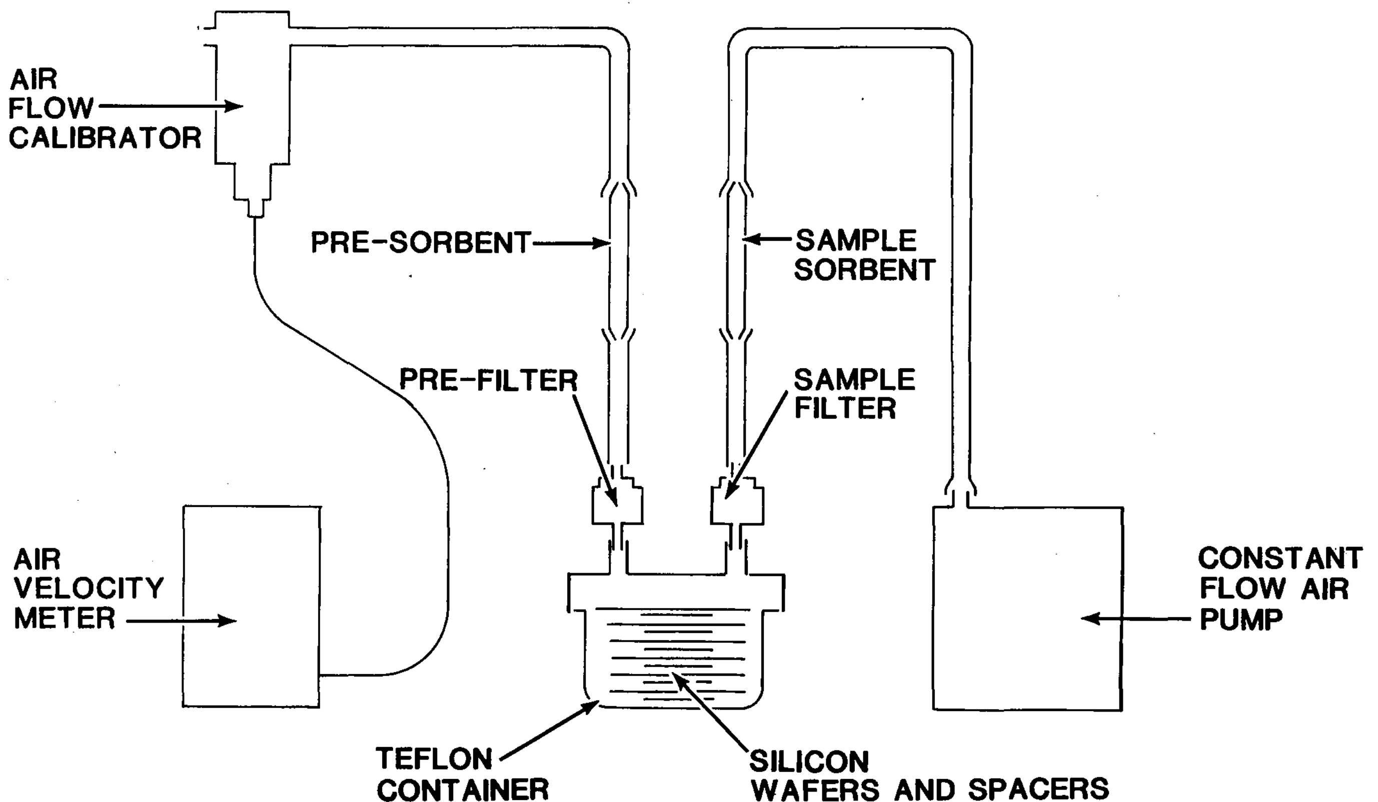

Figure 1 — Sampling apparatus.

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TABLE I

Ion Implanter Test Conditions

Test conditions	First test run	Second test run
Energy setting, keV[A]	50	50
Beam current, milliamperes	7	7
Implantation angle, degrees	7	7
Penetration, angstroms	500-1000	500-1000
Dopant dose level, ions/cm^2	6×10^{18}	6×10^{15}
Duration of implant, min	20	10

[A]Measured as effective voltage at the wafer surface.

ing of silicon wafers, increasingly is being replaced by ion implantation as the process of choice for many applications. Thermal diffusion of a dopant is achieved by heating silicon wafers to temperatures in excess of 1000°C. This allows atoms of the dopant to come in contact with the wafers and to diffuse slowly into the crystal lattice. The diffusion process is effective but slow; also, for many applications, it is too crude a process to achieve a high degree of control over the location of dopant atoms in the substrate.

Ion implantation is accomplished under high-vacuum conditions (10^{-6} torr). Impurities are introduced by creating a beam of dopant ions and accelerating the beam toward a silicon target. The ions bombard the wafer and plow their way into the crystal lattice. The ion implantation method permits greater control and accuracy during the formation of pn junctions.

Both thermal diffusion and ion implantation processes alter the electrical properties of the silicon by allowing dopant atoms to occupy positions in the crystal lattice previously held by atoms of silicon. In both processes, however, more atoms of the dopant are presented to the wafer than are fixed within the crystal lattice structure. Dopant atoms may accumulate at the wafer surface or in masking material used to define the pattern for the doping process. Although much is known about the conduct of dopant atoms in the crystal lattice of the substrate, no information is available in the literature on the fate of atoms associated with this superficial deposition. One hypothesis is that these atoms diffuse out of the wafer and are released into the surrounding environment. This idea has gained support from worker complaints of "odor problems" associated with wafer handling operations near the end station of ion implanters. Although this phenomenon (misnomered and frequently referred to as "out-gassing") has been discussed within the health and safety community of the integrated circuit industry, the open literature contains no information documenting its existence.

The objective of this investigation was to design and conduct an experiment capable of detecting the presence and measuring the magnitude of dopant released from semiconductor wafers. Arsenic was selected as the dopant of interest because of its extensive use and known health effects, and because reasonably sensitive methods of sampling and analysis are available for its detection. Ion implantation was chosen as the process of major interest because of its preeminence and future in the processing of integrated circuits.

Ideally, the experiment would answer three questions concerning the hypothesis: 1) whether arsenic is released from newly implanted semiconductor wafers, 2) whether this is a persistent problem, and 3) whether estimates can be made of the total amount of arsenic likely to be released into the workplace.

Experimental Design

Meeting the experimental objectives required the use of a sampling apparatus that allowed for the containment, collection and eventual analysis of arsenic emissions from implanted silicon wafers. The apparatus had to be designed in a manner that would prevent contamination of the sample media from non-wafer sources of arsenic and discourage the escape of emitted dopant.

Figure 1 presents a schematic diagram of the sampling apparatus constructed for this experiment. The apparatus is designed to provide a continuous flow of clean air to a vacuum-tested container of implanted silicon wafers, allow the wafers to emit dopant into the airflow, and then allow the container exhaust to be sampled for trace amounts of the dopant.

The airflow through the apparatus is monitored by a Kurz® Series 1041 digital air velocity meter and an airflow calibrator. Supply air enters the sampling apparatus through the airflow calibrator and Tygon® tubing to an in-line pre-sorbent and pre-filter. The pre-sorbent is a standard 100/50-mg charcoal tube (SKC or equivalent). The pre-filter consists of a 13-mm cellulose ester filter (Millipore AAWP 01300 or equivalent) and backup pad in a stainless steel Swinney® holder. The purpose of the pre-filter and pre-sorbent is to remove any particulate or gaseous arsenicals from the supply air. The contaminant-free air then enters a Savillex® Teflon® container equipped with an airtight, pressure-tested threaded lid. The Teflon container has an approximate volume of 400 mL and holds 25 implanted test wafers. Uniform airflow across the surface of the wafers is promoted through the use of silicon spacers. The exhaust air from the Teflon container is drawn through a sampling train consisting of a 13-mm cellulose ester filter in a stainless steel holder followed by a standard 100/50-mg charcoal tube. The container, stainless steel holder and charcoal tube are interconnected with Teflon tubing. During the actual sampling, an airflow rate of 190 mL/min ± 15 mL/min is maintained by a DuPont P-4000 constant-flow air pump. Given the volume of the Teflon container and the sampling airflow rate, one container air change occurs approximately every 30 seconds.

Two sets of 25 silicon wafers, 100 mm in diameter with a 1,0,0 crystal orientation, were used during the experiment. These wafers were free of photoresist and any applied oxide layers. The wafers were implanted with arsenic ions in a

Varian/Extrion Series 8010 high-current ion implanter using an arsine source gas under the conditions shown in Table I. The values in Table I represent implanter settings typical of actual operating conditions. After each test implantation, the wafers were transferred immediately to the Teflon container. The container lid was screwed in place and the ports for supply and exhaust air were sealed. Then the container was transported from the fabrication area to a clean office work area, where it was connected to the remainder of the sampling apparatus. Within five minutes after completion of the implantation, the first air samples were being drawn. A total of five 40-minute samples were collected during each of the two test runs.

Methods of Analysis

The collection and analysis of arsenic emissions from silicon wafers were accomplished using a method proposed for the measurement of multiple inorganic arsenic species.[3] A 13-mm cellulose ester filter with a 0.45-μm pore diameter was treated with 0.1 mL of a 9:1 solution of 1M Na_2CO_3 and glycerol. The filter and backup pad were mounted in a Swinney stainless steel filter holder. The filter holder was then attached to a standard 100/50-mg charcoal tube via Teflon tubing. Sample air was drawn through the filter and charcoal tube at a rate of approximately 200 mL/min. Upon completion of the sample run, the Swinney holder was disassembled and the filter was transferred to a 37-mm diameter plastic petri dish for shipment. The charcoal tube was capped and shipped with blue ice in a styrofoam container.

Arsenic samples collected on the cellulose ester filter were analyzed by the NIOSH Method for Arsenic, P&CAM 346.[4] The filters were digested with nitric acid and analyzed by graphite furnace atomic absorption spectrophotometry. Detection limits of 18 and 20 ng were achieved during the analyses of the first and second test results. The analytical results were corrected for a collection efficiency of 0.98.[3]

Arsenic samples collected on the charcoal were analyzed by the NIOSH Method for Arsine, S229.[4] The analyte was desorbed with nitric acid and analyzed by graphite furnace atomic absorption. A detection limit of 5 ng was achieved during these analyses. The analytical results were corrected for a collection/desorption efficiency of 0.90.[4]

Results

The test results provided an immediate answer to the first question posed at the outset of the experiment—whether arsenic is released from implanted silicon wafers and emitted into the surrounding air. Table II presents the results of the two tests. The results of the first test identified the existence of arsenic releases and suggested a trend or pattern in the emission data. The results of the second test verified both the presence and pattern of arsenic emissions; however, a discrepancy arose in the amount of arsenic collected on treated filters. The success of detecting particulate arsenic on treated filters during the first test was not

TABLE II

Arsenic Emissions From Semiconductor Wafers

Time, min[A]	Arsenic found on treated filter, ng[B]	Arsenic found on charcoal, ng[C]	Total arsenic collected, ng[D]
First test			
45	0	421	421
85	76	70	146
125	82	123	205
165	0	166	166
205	1	102	103
		Total arsenic emitted	1041
Second test			
49	0	127	127
91	0	83	83
136	0	62	62
177	0	40	40
218	0	30	30
		Total arsenic emitted	342

[A]Time in minutes from completion of arsenic implantation to completion of sample collection.
[B]Values determined as (sample - blank)/collection efficiency. A minimum detection limit of 18 ng was achieved during the analysis of the first test results, and a 20 ng detection was achieved during analysis of the second test results. A collection efficiency of 0.98 was used for the treated filter method.[3]
[C]Value determined as (sample - blank)/desorption efficiency. A minimum detection limit of 5 ng was achieved during the analysis of the test results. A desorption efficiency of 0.90 was used for the charcoal tube method.[4]
[D]No arsenic was detected on either the pre-sorbent tubes or pre-filters.

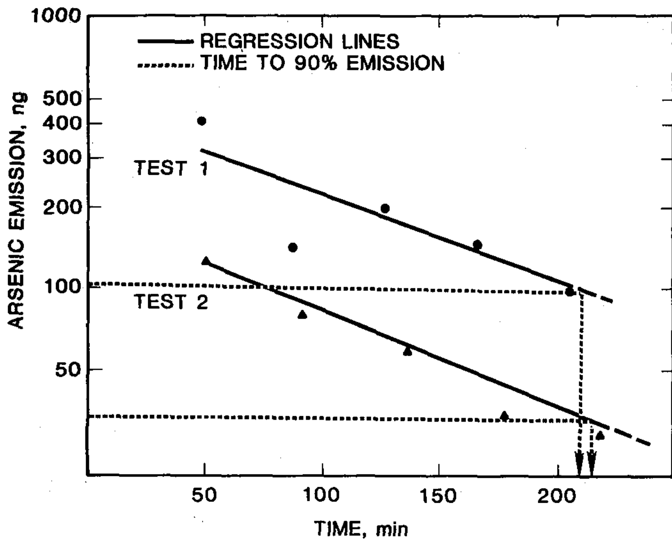

Figure 2—Emission-time profile of arsenic releases from semiconductor wafers.

repeated. The reason for this discrepancy is not believed to be attributable to changes in the ion implanter test conditions; however, no specific explanation for the difference can be advanced at this time.

The second question concerns the persistency of the problem of arsenic emissions from implanted wafers. The experimental results were plotted to form an emission-time profile of each test. The curvilinear relationship found between time and the amount of arsenic dopant emitted was then simplified through a logarithmic transformation of the data. This adjustment to a common logarithm also provided for a better fit of the emission data. The log-linear, emission-time profiles of the test data are presented in Figure 2.

Based on the data plotted in the emission-time profiles, a least squares linear regression technique was used to fit two lines to the data. These regression lines (solid) were then used to predict the time at which 90 percent of the implanted arsenic available for emission would be released (dotted). Because the predicted relationship between the amount of dopant emitted and the time since implantation is log-linear, arsenic release rates approach zero asymptotically near the end of each test. To provide a usable estimate of the time required for nearly complete emission, we assumed that essentially all of available arsenic was emitted during the course of the experiment. Thus, an estimate of the length of time to 90 percent emission of the dopant was predicted from the regression lines at the point where it is assumed 10 percent of the arsenic remains to be released. Based on the total arsenic collected during the experiment, values of 104 and 34 ng represent the 10 percent values for Tests 1 and 2, respectively. Based on the regression lines in Figure 2, emissions of these magnitudes would be expected to occur after approximately 210 minutes into Test 1 and 215 minutes in Test 2. It is therefore reasonable to propose that 90 percent of the arsenic available for emission will have been released approximately 3.5 hours (212 minutes) following implantation.

The final question of concern was whether a good estimate could be made of the total amount of arsenic likely to be released into the workplace. Toward this end, a cumulative curve was plotted for data from each of the tests. Again, the arsenic emissions are presented on a logarithmic scale. Figure 3 presents the cumulative emission-time profile for each test. The results in Table II present the actual amount of arsenic emitted from 25 implanted wafers. The objective of constructing the cumulative emission-time curves was to provide an upper and lower boundary on the estimate of the amount of arsenic likely to have been emitted.

Because of the visual similarity of the curves, an analysis of variance (ANOVA) was performed to determine whether the two groups of test data could be combined to construct a single curve. The results of the ANOVA suggested that the differential effects associated with the test conditions significantly influenced the results, which demonstrated that the variability between the test data groups was significantly greater ($p < 0.05$) than the variability within the groups. This outcome prevented the treatment of the test results as a single data set.

The difference in the magnitude of arsenic emissions between the two tests can be explained by the difference in ion implanter test conditions. The first test implant was conducted for a period of 20 minutes at a dopant dose level of 6×10^{18} ions/cm^2, whereas the second test implant was conducted for only 10 minutes at a dopant dose level of 6×10^{15} ions/cm^2.

The difference in variation between the test groups raises the question as to whether the same association between arsenic emission and time is demonstrated by the two sets of data. As a test for this similarity, a regression analysis of

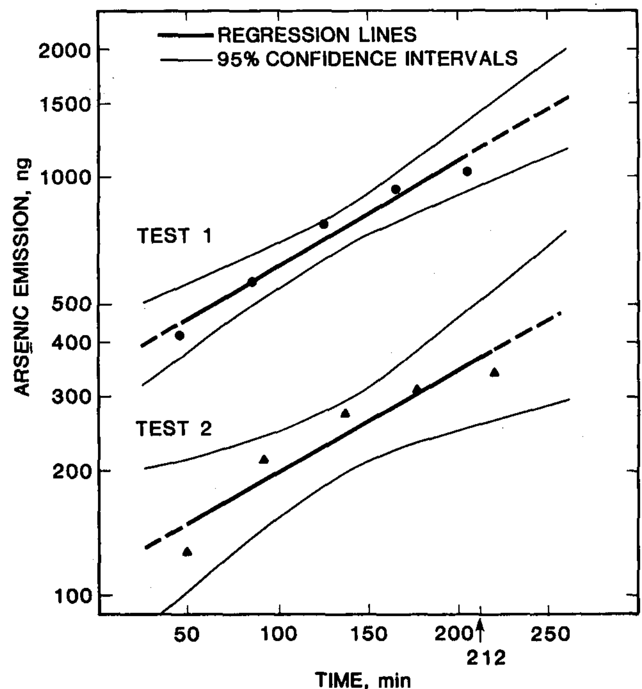

Figure 3—Cumulative emission-time profile of arsenic releases from semiconductor wafers.

the cumulative data was performed. The resulting regression coefficients were tested by use of a two-group comparison analysis of slope and the Student "t" test. Because the slopes of the regression lines were found not to differ significantly ($p > 0.10$), they are assumed to be demonstrating the same relationship or degree of dependency of arsenic emissions on time. The two regression coefficients were then tested for significance ($p < 0.05$), and 95 percent confidence intervals were constructed about the regression lines.

The two tests, although different in both magnitude and variation, represent emissions from the type of implanted wafers likely to be encountered in the integrated circuit workplace. The predicted mean arsenic emissions from 25 semiconductor wafers 3.5 hours (212 min) after implantation ranged between 370 ng (0.37 μg) and 1200 ng (1.2 μg). Based on the 95 percent confidence intervals, the total arsenic emissions from 25 wafers could be expected to reach 1500 ng (1.5 μg) within 4 hours after implantation.

Discussion

The experimental results provide evidence of the release of arsenic from semiconductor wafers. Specifically, these emissions are shown to occur following the implantation of arsenic into silicon wafers during the production of integrated circuits. This release of arsenic can be expected to occur over a period of at least 3.5 hours following implantation, and to result in a maximum potential arsenic emission of 1500 ng (1.5 μg) per 25 wafers or 6000 ng (6.0 μg) per 100 wafers processed. The significance of this finding is that integrated circuit and other semiconductor workers may be continually exposed to low levels of inorganic arsenic from the products they are handling. Although the test results indicate that the emitted quantities are quite small, the potential for more serious accumulations is present in any production facility where room ventilation around ion implantation units is restricted or nonexistent. As an added concern to production engineers and quality control specialists, newly implanted wafers represent a potential source of arsenic contamination that could adversely affect their integrated circuit products in other stages of production. Recognition and eventual abatement of this source of arsenic are likely to have the dual benefit of improving worker health and product quality.

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