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DIFFUSION OF IMPURITIES INTO SILICON FROM GASEOUS SOURCES

by R. M. McLouski

Prepared by

WESTINGHOUSE DEFENSE AND SPACE CENTER

Baltimore, Md.

for Goddard Space Flight Center



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION . WASHINGTON, D. C. . NOVEMBER 1966



INASA CR-524

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Prepared under Contract No. NAS 5-2755 by WESTINGHOUSE DEFENSE AND SPACE CENTER Aerospace Division Baltimore, Md.

for Goddard Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

This report describes a number of diffusion experiments performed during a development program whose purpose is to obtain additional insight into the effects of gaseous dopants on silicon and, thereby, better control of the resulting surface conditions and resistivity profiles. Experiments performed with diborane, phosphine, and arsine gases as the source of impurities for diffusion in silicon demonstrated their superiority to the conventional solid or liquid diffusion sources. Several means of controlling the deposition sheet resistivity were found to be available, with the time of deposition being the simplest controlling parameter for a given deposition temperature and concentration of oxygen and dopant in the furnace feed gas. The data gathered from the experiments are presented in both tabular and graphical form, and the diffusion systems employed are described. Analyses of the data and of the diffusion systems indicate that many problems associated with solid and liquid source methods are avoided by the use of the gaseous system. It was found possible to control the sheet resistivity over a wide range of doping levels.

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by R. M. McLouski

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Aerospace Division

INTRODUCTION

The formation of p-n junctions in silicon by solid state diffusion of impurities can be accomplished by a variety of methods. Earlier methods of junction formation, such as vacuum and sealed tube diffusions, have given way to open tube diffusions employing solid or liquid impurity sources, which are widely used in the manufacture of today's devices.

The advent of functional electronic blocks demanded improved control of such diffusion parameters as surface concentration of impurity atoms, impurity concentration profiles, penetration and planarity of junctions, and the preservation of near-perfect silicon surfaces. Some of these demands were partially met using the conventional methods of diffusion, i.e., solid and liquid impurity sources. However, it was apparent that these diffusion processes must be developed to a higher degree of accuracy and reproducibility. This was not deemed possible with the solid and liquid dopant systems because of inherent disadvantages in these diffusion systems. Therefore, a development program was undertaken to obtain additional insight into the effects of gaseous dopants on silicon, and, thereby, better control of the resulting surface conditions and resistivity profiles. A number of diffusion experiments were performed on three gaseous impurities: B_2H_6 (diborane) for the acceptor impurity; PH_3 (phosphine) and AsH_3 (arsine) for the donor impurities. This report summarizes the results of these experiments.

EXPERIMENTAL PROCEDURES

Diffusion Sample Preparation

The silicon wafers used for the arsine and phosphine diffusion experiments were 7/8 inch diameter, 1.25 ohm-cm, P-type; those used for the diborane diffusion experiments were 7/8 inch diameter, 1.25 ohm-cm, N-type. The wafers were lapped from a thickness of 0.017 inch to 0.013 inch using 12 micron Al_2O_3 grit. They were then lapped to 0.011 inch using 3 micron Al_2O_3 grit

^{*}Prepared under Contract NAS 5-2755.

and polished to approximately 0.010 inch using 1 micron Al_2O_3 grit. Immediately prior to the diffusion experiments, the silicon wafers were cleaned as follows:

- 1. Immersion in H_2SO_4 (100%) maintained at 220 ± 5°C for 20 minutes.
- 2. Rinse in running deionized H₂O for 10 minutes.
- 3. Immersion in HNO $_3$ (65%) maintained at 90 ± 5°C for 20 minutes.
- 4. Rinse in running deionized H₂O for 10 minutes.
- 5. Immersion in $90 \pm 10^{\circ}$ C deionized H₂O.
- 6. Removal from H₂O above and blown dry with N₂.

The wafers were then stored in clean dry glass containers until used. If the wafers were not used within a period of 6 hours after cleaning, steps 5 and 6 were repeated.

Gas Dilution System

Standard diffusion furnaces furnished with a gas control system illustrated schematically in Figure 1 were used to control the concentration of dopants in the furnace feed gas. These systems

were capable of varying the mixing and dilution of dopant carrier gas with a known concentration of impurity atoms over a wide range. With this system, concentrations from 0.01 ppm to 10,000 ppm of impurity were readily controllable. By using different concentrations of dopant in the carrier gas, the range of dopant concentration could be extended to 0.001 ppm. The arsine, phosphine and diborane gases used in the diffusion study were a mixture of 1% impurity in argon.

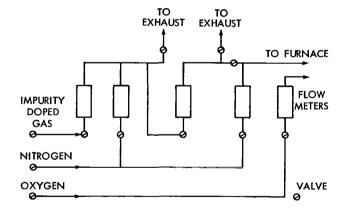


Figure 1-Schematic of gas dilution system.

Diffusion Tube Design

It was found necessary to use specially fabricated diffusion tubes in conjunction with the

metal hydride doping gases fed to the furnace. Reasons for the particular design are found in the discussion section. The tube design used in conjunction with the AsH_3 and Ph_3 experiments is illustrated in Figure 2. The spout, or inner tube, fed the doping gas to a zone in the furnace where the temperature was at least $300^{\circ}C$.

The diffusion tube used for the diborane experiments is illustrated in Figure 3. The inner feed tube in this case fed the doping gas to a zone in the furnace where the temperature was approximately 900°C.

Arsine Diffusion Procedure

Following the cleaning procedure described above, a silicon wafer was laid in the center of a 6" x 1" x 1/4" quartz diffusion boat. This boat rested in a quartz cradle which would incline it at an angle of approximately 10° to the direction of the gas flow when inserted into the tube. The diffusion boat was then placed into a deposition furnace maintained at 1100 ± 1°C equipped with the gas control system and diffusion tube described above. The total flow of gas down the tube was 3.5 1/min. The composition of the gas was 99.5% nitrogen and 0.5% oxygen. Immediately after the insertion of the wafer into the furnace, a flow of AsH, gas sufficient to bring the percentage of AsH, to 0.20% was metered into the diffusion tube.

After a deposition time of 15 minutes, the flow of ${\rm AsH_3}$ to the deposition furnace was turned off and the wafer allowed to remain at

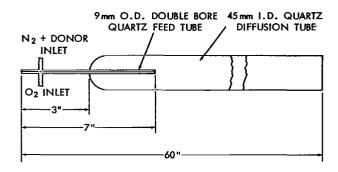


Figure 2—Donor diffusion tube design.

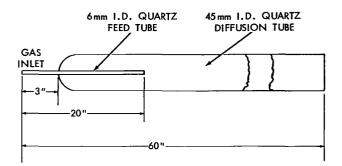


Figure 3-Acceptor diffusion tube design.

temperature for an additional two minutes. It was then removed from the furnace and the arsenic glass formed during the deposition removed by a 30 second dip in 10% HF. The sheet resistance and junction depth were measured by a four-point probe (Reference 1) and interference microscope techniques (Reference 2). At least four four-point probe readings were taken on the slice, with the average value being used to compute the sheet resistance. The stain used to delineate the junction was a 6 to 1 mixture of 85% $\rm H_3$ $\rm PO_4$ - 48% HF.

The above diffusion procedure was repeated twice so that for a given time, temperature, and concentration of oxygen three specimens were run. This procedure was performed for the following conditions: times - 15, 30, 45 and 60 minutes; temperatures - 1100, 1200, and 1250 \pm 1°C; O_2 concentrations - 0.5, 2 and 15%. The values obtained for the above deposition conditions are found in Table 1.

Following the deposition and the removal of the arsenic glass, four wafers representing a spread of deposition resistivities were selected and placed into a drive-in furnace maintained at $1200 \pm 1^{\circ}\text{C}$ for a period of 4 hours. The atmosphere flowing through the furnace tube was 1 l/min. of oxygen. After this redistribution diffusion, the sheet resistance and junction depth were determined as above. This procedure was performed for the following conditions: temperature — 1200 and 1250 \pm 1°C; times — 4, 8 and 16 hours. The results of this redistribution diffusion are found in Table 2.

Table 1

Arsine Depositions.

Run	Wafer	Temp (°C)	% Oxygen	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg ρ_s (ohms/sq)	Xo (fringes*)
1	1	1100	0.5	15	216		< 1
2	2	1100	0.5	15	240	238	< 1
3	3	1100	0.5	15	258		< 1
4	4	1100	0.5	30	187		< 1
5	5	1100	0.5	30	190	196	< 1
6	6	1100	0.5	30	210		< 1
7	7	1100	0.5	45	167		< 1
8	8	1100	0.5	45	187	180	< 1
9	9	1100	0.5	45	165		< 1
10	10	1100	0.5	60	110		1
11	11	1100	0.5	60	103	110	1
12	12	1100	0.5	60	118		1
13	13	1100	2	15	140		< 1
14	14	1100	2	15	130	136	< 1
15	15	1100	2	15	138		< 1
16	16	1100	2	30	178		< 1
17	17	1100	2	30	178	178	< 1
18	18	1100	2	30	178		i -
19	19	1100	2	45	227		< 1
20	20	1100	2	45	208	216	< 1
21	21	1100	2	45	198		< 1
22	22	1100	2	60	240		1
23	23	1100	2	60	242	253	1
24	24	1100	2	60	277		1
25	25	1200	0.5	15	142		2
26	26	1200	0.5	15	150	146	2
27	27	1200	0.5	15	145		2 2
28	28	1200	0.5	30	136		3
29	29	1200	0.5	30	128	132	3
30	30	1200	0.5	30	130		3
31	31	1200	0.5	45	114		4
32	32	1200	0.5	45	109	112	4
33	33	1200	0.5	45	112		4
34	34	1200	0.5	60	92.6		4
35	35	1200	0.5	60	92.6	90.9	4
36	36	1200	0.5	60	87.6		4
37	37	1200	2	15	228	İ	1
38	38	1200	2	15	235	230	1
39	39	1200	2	15	238		1
40	40	1200	2	30	190	J	2
41	41	1200	2	30	202	199	2
42	42	1200	2	30	207		2
43	43	1200	2	45	126	ļ	3
44	44	1200	2	45	135	133	3
45	45	1200	2	45	140	Í	3
46	46	1200	2	60	130		4
47	47	1200	2	60	108	120	4

*One fringe = 0.273 microns

Table 1 (Continued)

Run	Wafer	Temp (°C)	% Oxygen	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg $ ho_{_{\mathbf{S}}}$ (ohms/sq)	Xo (fringes
49	49	1200	15	15	211		1
50	50	1200	15	15	230	228	1
51	51	1200	15	15	242		1
52	52	1200	15	30	200		2
53	53	1200	15	30	208	204	2
54	54	1200	15	30	205		2
55	55	1200	15	45	170		3
56	56	1200	15	45	180	177	3
57 ·	57	1200	15	45	182		3
58	58	1200	15	60	159		4
59	59	1200	15	60	158	158	4
60	60	1200	15	60	158		4
61	61	1250	0.5	15	91.3		5
62	62	1250	0.5	15	80.4	85.3	5
63	63	1250	0.5	15	84.4		5
64	64	1250	0.5	30	74.2		6
65	65	1250	0.5	30	75.5	75.6	6
66	66	1250	0.5	30	77.0		6
67	67	1250	0.5	45	70.0		7
68	68	1250	0.5	45	70.0	70.3	7
69	69	1250	0.5	45	71.0		7
70	70	1250	0.5	60	64.8		8
71	71	1250	0.5	60	63.5	63.3	8
72	72	1250	0.5	60	61.5		8
73	73	1250	2	15	175		3
74	74	1250	2	15	180	178	3
75	75	1250	2	15	180		3
76	76	1250	2	30	142		4
77	77	1250	2	30	150	142	4
78	78	1250	2	30	133		4
79	79	1250	2	45	84.5		6
80	80	1250	2	45	88.8	87.8	6
81	81	1250	2	45	90.1		6
82	82	1250	2	60	84.0		7
83	83	1250	2	60	79.0	81.3	7
84	84	1250	2	. 60	80.9		7
85	85	1250	15	15	214		2
86	86	1250	15	15	215	216	2
87	87	1250	15	15	218		2
88	88	1250	15	30	159		3
89	89	1250	15	30	178	166	3
90	90	1250	15	30	163		3
91	91	1250	15	45	144		5
92	92	1250	15	45	147	145	5
93	93	1250	15	45	144		5
94	94	1250	15	60	122		6
95	95	1250	15	60	119	120	6
96	96	1250	15	60	122		6

Table 2
Arsine Redistribution Diffusion.

Run	Wafer	Temp (°C)	Time (hr) Steam - O ₂	Initial Resistivity, $ ho_s$ (ohms/sq)	Final Resistivity, $ ho_{_{_{\mathbf{S}}}}$ (ohms/sq)	Initial Xo (fringes)	Final Xo
1	83	1200	0 - 4	79.0	67.8	7	9
2	31	1200	0 - 4	1 44	81.0	4	9
3	76	1200	0 - 4	142	101	4	9
4	38	1200	0 - 4	235	126	1	8
5	84	1200	0 - 8	80.9	61.4	7	14
6	33	1200	0 - 8	112	57.1(?)	4	26
7	77	1200	0 - 8	150	90.0	4	12
8	50	1200	0 - 8	230	120	1	12
9	65	1200	0 - 16	75 . 5	45.0	6	19
10	32	1200	0 - 16	109	56.4	4	19
11	78	1200	0 - 16	133	65.8	4	17
12	39	1200	0 - 16	238	113	1	15
13	66	1200	1 - 3	77.0	74.5	6	9
14	95	1200	1 - 3	119	105	6	9
15	90	1200	1-3	163	125	3	8
16	51	1200	1 - 3	242	166	1	8
17	68	1200	1 - 7	70.0	51.2	7	14
18	94	1200	1 - 7	122	100	6	13
19	89	1200	1 - 7	178	115	3	11
20	49	1200	1 - 7	211	124	1	11
21	67	1200	1 - 15	70.0	43.7	7	
22	47	1200	1 - 15	108	65.5	4	19 17
23	88	1200	1 - 15	159	89.1		
24	41	1200	1 - 15	202	91.6	3	16
25	71	1250	0 - 4	63.5		2	16
26	48	1250	0 - 4	124	44.5	8	16
27	25	1250	0 - 4	142	67.0	4	15
28	42	1250 1250	0 - 4	207	68.4	2	15
29	62	1250 1250	0 - 8		98.5	2	14
30	10	1250 1250	0 - 8	80.4	39.6	5	23
31			0 - 8	110	49.2	1	22
32	68	1250		157	71.0	3	20
	40	1250	0 - 8	190	83.7	2	22
33 34	70	1250	0 - 16	64.8	24.5	8	30
34 35	11 26	1250	0 - 16	103	37.4	1	30
36		1250	0 - 16	150	51.0	2	30
37	85	1250	0 - 16	214	78.3	2	27
1	72	1250	1 - 3	61.5	44.5	8	17
38	12	1250	1 - 3	118	85.7	1	13
39	60	1250	1 - 3	158	97.4	3	13
40	65	1250	1 - 3	215	110	1	13
41	79	1250	1 - 7	84.5	49.3	6	22
42	28	1250	1 - 7	136	57.8	3	21
43	75	1250	1 - 7	180	82.0	3	21
44	87	1250	1 - 7	218	92.2	1	18
45	64	1250	1 - 15	74.2	33.5	6	31
46	30	1250	1 - 15	130	46.4	3	30
47	73	1250	1 - 15	175	. 68.5	_3	26
48	52	1250	1 - 15	200	82.5	2	26

Following the drive-in procedure described above, additional redistribution diffusions in wet/dry atmospheres were performed. The procedure followed in this case was as follows: Four wafers representing a spread of deposition resistivities were selected and placed into a drive-in furnace maintained at $1200^{\circ} \pm 1^{\circ}$ C for a period of 4 hours. The atmosphere used for the first hour of the diffusion was 50 ml/min of O_2 which had been passed through H_2O maintained at 100° C. The final 3 hours of drive-in were performed in an atmosphere of dry O_2 metered to the furnace at the rate of 1 l/min. This procedure was repeated for the following conditions: temperatures — 1200 and $1250 \pm 1^{\circ}$ C; atmosphere — 1 hr steam, 3 hr dry O_2 ; 1 hr steam, 7 hr dry O_2 ; and 1 hr steam, 15 hr dry O_2 . The results of these procedures are also found in Table 2.

Phosphine Diffusion Procedure

Following the cleaning procedure described above, a silicon wafer was laid in the center of a 6" x 1" x 1/4" quartz diffusion boat. This boat rested in a quartz cradle which would incline it at an angle of approximately 10° to the direction of the gas flow when inserted into the tube. The diffusion boat was then placed into a deposition furnace maintained at $900 \pm 1^{\circ}$ C and equipped with the gas control system and diffusion tube described above. The total flow of gas down the tube was 3.5 l/min. The composition of the gas was 99% nitrogen and 1% oxygen. Following a preheat time of 5 minutes, a flow of Ph_3 gas sufficient to bring the percentage of Ph_3 to 0.057% was metered into the diffusion tube. After a deposition time of 5 minutes, the flow of Ph_3 to the deposition furnace was turned off and the wafer allowed to remain at temperature for an additional two minutes. It was then removed from the furnace and the phosphorus glass formed during the deposition removed by a 30 second dip in 10% HF. The sheet resistance and junction depth were measured as noted previously. At least four four-point probe readings were taken on the slice, with the average value being used to compute the sheet resistance. The stain used to delineate the junction was a 6 to 1 mixture of 85% H $_3PO_4$ - 48% HF.

The above diffusion procedure was repeated twice so that for a given time, temperature, and concentration of oxygen three deposition runs were made. This procedure was performed for the following conditions: times -5, 15, 30, 45 and 60 minutes; temperatures -900, 1000 and $1100 \pm 1^{\circ}\text{C}$; O_2 concentrations -1, 35 and 50%. The values obtained for the above deposition conditions are found in Table 3.

Following the deposition and the removal of the phosphorus glass, five wafers representing a spread of deposition resistivities were selected and placed into a drive-in furnace maintained at $1000 \pm 1^{\circ}\text{C}$ for a period of 60 minutes. The atmosphere flowing through the furnace tube was 50 ml/min of oxygen which had been passed through H_2O maintained at 100°C . After this redistribution diffusion, the sheet resistance and junction depth were determined as above. This procedure was performed for the following additional conditions: temperatures — $1000 \text{ and } 1200 \pm 1^{\circ}\text{C}$; times — 1, 2 and 4 hours. The results of this redistribution diffusion are found in Table 4.

 $\begin{tabular}{ll} Table 3 \\ \hline \end{tabular}$ Phosphine Depositions.

Run	Wafer	Temp (°C)	% Oxygen	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg $ ho_{ extsf{s}}$ (ohms/sq)	Xo (fringes)
1	1	900	1	5	46.0		1
2	2	900	1	5	47.8	46.6	1
3	3	900	1	5	45.9		1
4	4	900	1	15	25.5		1
5	5	900	1	15	22.0	23.6	1
6	6	900	1	15	23.2		1
7	7	900	1	30	15.6		1
8	8	900	1	30	15.0	15.2	1
9	9	900	1	30	14.9		1
10	10	900	1	45	12.0		2
11	11	900	1	45	12.2	12.1	2
12	12	900	1	45	12.1	•	2
13	13	900	1	60	10.6		2
14	14	900	1	60	10.1	10.2	2
15	15	900	1	60	10.0		2
16	16	900	35	30	165		1
17	17	900	35	30	1.64	159	1
18	18	900	35	30	150	200	1
19	19	900	35	45	215		1
20	20	900	35	45	212	209	1
21	21	900	35	45	200	200	1
22	22	900	35	60	284		1
23	23	900	35	60	249	259	1
24	24	900	35	60	245	203	1
25	25	1000	1	5	20.1		1
26	26	1000	1	5	19.0	19.7	1
27	27	1000	1	5	20.0	10.1	1
28	28	1000	1	15	10.8		2
29	29	1000	1	15	11.1	10.8	2
30	30	1000	1	15	10.7	10.0	2
31	31	1000	1 1	30	7.70		3
32	32	1000	1	30	7.60	7.70	3
33	33	1000	1 1	30	7.82	1.10	3
34	34	1000	1	45	I)
35	35	1000	1 1	45 45	4.60 5.10	4.0	4
36	36	1000	1 1	45 45	5.10	4.9	4
37	37	1000	1 1	60	4.30		4 5
38	38	1000	1 1	60		4.4	
39	39	1000	1	60	4.30 4.50	4.4	5
40	40	1000	35	5	83.3		5
41	41	1000	35	5	80.2	82.0	1
42	42	1000	35	5	84.5	83.0	1
43	43	1000	35	5 15			1
44	44	1000	35		44.0	. 49.9	1
45	45	1000	35 35	15	44.5	43.3	1
45 46	46	1000		15	41.5	ļ	1
46	46		35	30	25.0	04.4	3
48	48	1000 1000	35	30	24.9	24.4	3
40	40	1000	35	30	32.2		3

Table 3 (Continued)

Table 3 (Continued)									
	6	Temp	%	Time	Resistivity, ρ_s	Avg ρ_s	Xo		
Run	Wafer	(°C)	Oxygen	(min)	(ohms/sq)	(ohms/sq)	(fringes)		
	-	1 .		·					
49	49	1000	35	45	17.5		4		
50	50	1000	35	45	17.5	17.6	4		
51	51	1000	35	45	17.9		4		
52	52	1000	35	60	14.5		5		
53	53	1000	35	60	14.3	1 4. 3	5		
54	54	1000	35	60	14.1		5		
55	55	1000	50	30	135		1		
56	56	1000	50	30	155	144	1		
57	57	1000	50	30	143		1		
58	58	1000	50	45	215		1		
59	59	1000	50	45	225	218	1		
60	60	1000	50	45	210		1		
61	61	1000	50	60	230		1		
62	62	1000	50	60	225	227	1		
63	63	1000	50	60	227		1		
64	64	1100	1	5	7.94		2		
65	65	1100	1	5	8.04	7.94	2		
66	66 .	1100	1	5	7.92		2		
67	67	1100	1	15	4.12		6		
68	68	1100	1	15	4.32	4.26	6		
69	69	1100	1	15	4.34	1	6		
70	70	1100	ī	30	2.85		8		
71	71	1100	1	30	2.84	2.83	8		
72	72	1100	1	30	2.80		8		
73	73	1100	1	45	2.20]	10		
74	74	1100	i	45	2.25	2.22	10		
75	75	1100	1	45	2.20		10		
76	76	1100	1	60	1.93		11		
77	77	1100	1	60	1.93	1.93	11		
78	78	1100	1	60	1.94	1.00	11		
79	79	1100	35	5	19.6		1		
80	80	1100	35	5	19.8	19.6	1		
81	81	1100	35	5	19.7	10.0	1		
82	82	1100	35	15	14.5		3		
83	83	1100	35	15	15.8	14.8	3		
84	84	1100	35	15	14.8	14.0	3		
85	85	1100	35	30	6.02		7		
85 86	86	1100	35	30	6.52	6.29	7		
				30	6.33	0.29	7		
87	87	1100	35	1			8		
88	88	1100	35	45 45	5.23 4.77	5.08	8		
89	89	1100	35			9.00			
90	90	1100	35	45	5.26		8		
91	91	1100	35	60	5.26	4 00	9		
92	92	1100	35	60	4.28	4.88	9		
93	93	1100	35	60	5.10		9		
94	94	1100	50	5	50.2	65.0	1		
95	95	1100	50	5	70.5	65.3	1		
96	96	1100	50	5	65.3		1		
97	97	1100	50	15	27.0	05.0	3		
98	98	1100	50	15	23.2	25.0	3		
99	99	1100	50	15	25.2		3		

Table 3 (Continued)

Run	Wafer	Temp (°C)	% Oxygen	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg ρ_s (ohms/sq)	Xo (fringes)
100	100	1100	50	30	9.3		6
101	101	1100	50	30	10.1	9.60	6
102	102	1100	50	30	9.6	ļ	6
103	103	1100	50	45	8.10		8
104	104	1100	50	45	6.00	7.43	8
105	105	1100	50	45	8.20		8
106	106	1100	50	60	6.56		8
107	107	1100	50	60	7.63	7.23	8
108	108	1100	50	60	7.52		8

 $\begin{tabular}{ll} Table 4 \\ Phosphine Redistribution Diffusion. \end{tabular}$

Run	Wafer	Temp (°C)	Time (hr)	Initial Resistivity, $ ho_s$ (ohms/sq)	Final Resistivity, ρ_s (ohms/sq)	Initial Xo (fringes)	Final Xo (fringes)
1	61	1000	1	230	234	1	1
2	17	1000	1	165	325	1	1
3	1	1000	1	46.0	34.0	1	2
4	6	1000	1	23.2	11.6	1	3
5	76	1000	1	1.93	1.93	11	11
6	23	1000	2	249	308	1	1
7	19	1000	2	215	293	1	1
8	55	1000	2	135	152	1	4
9	4	1000	2	25.5	11,4	1	6
10	72	1000	2	2.80	2.52	8	8
11	24	1000	4	245	259	1	1
12	17	1000	4	164	183	1	1
13	95	1000	4	70.5	76	1	4
14	5	1000	4	22.0	9.93	1	7
15	73	1000	4	2.20	2.04	10	10
16	58	1200	1	215	141	1	9
17	56	1200	1	155	135	1	9
18	40	1200	1	83.3	80.0	1	10
19	32	1200	1	7.60	4.33	3	18
20	77	1200	1	1.93	1.32	11	24
21	63	1200	· . 2	227	99.3	1	11
22	55	1200	2	135	94.3	1	12
23	97	1200	2	27.0	21.4	3	16
24	108	1200	2	7.63	6.62	8	21
25	78	1200	2 ·	1.94	1.18	11	30
26	59	1200	4	225	98.3	1	15
27	16	1200	4	165	90.6	1	16
28	43	1200	4	44.0	26.3	1	22
29	46	1200	4	25.0	6.93	1	30
30	38	1200	4	4.30	1.84	5	37

Diborane Diffusion Procedure

Following the cleaning procedure described above, a silicon wafer was laid in the center of a 6" x 1" x 1/4" quartz diffusion boat. This boat rested in a quartz cradle which would incline it at an angle of approximately 10° to the direction of the gas flow when inserted into the tube. The diffusion boat was then placed into a deposition furnace maintained at $950 \pm 1^{\circ}$ C equipped with the gas control system and diffusion tube described above. The total flow of gas down the tube was 4.5 $1/\min$. The composition of the gas was 96.7% nitrogen and 3.3% oxygen. Following a preheat time of 2 minutes, a flow of B_2H_6 gas sufficient to bring the percentage of B_2H_6 to 0.004% was metered into the diffusion tube. After a deposition time of 5 minutes, the flow of B_2H_6 to the deposition furnace was turned off and the wafer allowed to remain at temperature for an additional two minutes. The wafer was then removed from the furnace and the borate glass formed during the deposition removed by a 30 second dip in 10% HF. The sheet resistance and junction depth were measured as noted above. At least four four-point probe readings were taken on the slice, with the average value being used to compute the sheet resistance. The stain used to delineate the junction was a 6 to 1 mixture of 85% H_3 PO $_4$ - 48% HF.

The above diffusion procedure was repeated twice so that for a given time and temperature three specimens were run. This procedure was performed for the following times and temperatures: times -5, 10, 20, 40 and 60 minutes; temperatures -950, 1000, 1050, 1100 and 1150 \pm 1°C. The values obtained for the above deposition conditions are found in Table 5.

Following the deposition and the removal of the borate glass, six wafers representing a spread of deposition resistivities were selected and placed into a drive-in furnace maintained at $1150 \pm 1^{\circ}$ C for a period of 30 minutes. The atmosphere flowing through the furnace tube was 50 ml/min of oxygen which had been passed through H_2O maintained at 100° C. After this redistribution diffusion, the sheet resistance and junction depth were determined as above. This procedure was performed for the following additional conditions: temperatures — 1150 and 1200 \pm 1°C; times — 0.5, 1 and 2 hours. The results of this redistribution diffusion are found in Table 6.

Table 5
Diborane Depositions.

Run	Wafer	Temp (°C)	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg $ ho_s$ (ohms/sq)	Xo (fringes)
1	1	950	5	108		< 1
2	2	950	5	100	105	<1
3	3	950	5	106		< 1
4	4	950	10	69.5		< 1
5	5	950	10	67.2	68.1	< 1
6	6	950	10	67.7		<1
7	7	950	20	53.4		<1
8	8	950	20	52.5	52.2	< 1
9	9	950	20	50.7	1	<1
10	10	950	40	40.5		1
11	11	950	40	40.7	40.9	1
12	12	950	40	41.6		1

Table 5 (Continued)

Run	Wafer	Temp (°C)	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg ρ_s (ohms/sq)	Xo (fringes)
13	13	950	60	37.2		1
14	14	950	60	36.1	36.3	1
15	15	950	60	35.7		1
16	16	1000	5	57.2	<u> </u>	<1
17	17	1000	5	53.6	55.7	<1
18	18	1000	5	56.3		<1
19	19	1000	10	41.9		<1
20	20	1000	10	39.6	40.3	<1
21	21	1000	10	40.4	20.0	<1
22	22	1000	20	29.4		<1
23	23	1000	20	29.2	30.6	<1
24	24	1000	20	31.9	30.0	<1
25	25	1000	40	26.0		1
26	26	1000	40	22.7	24.3	1
27	27	1000	40	24.2	24.0	1
28	28	1000	60	20.5		2
29	29	1000	60	18.5	20.7	2 2
30	30	1000	60	22.4	20.7	
31	31	1050	5	29.3		2
32	32	1050	5		90.7	2
33	33	1050		24.4	26.7	2
34	34	1050	5	26.4		2
35	35		10	22.3	24.4	2 2
36		1050	10	22.3	21.9	2
	36	1050	10	21.1		2
37	37	1050	20	15.8		3
38	38	1050	20	15.7	15.2	3
39	39	1050	20	14.3		3
40	40	1050	40	11.4		4
41	41	1050	40	11.8	11.3	4
42	42	1050	40	10.8		4
43	43	1050	60	10.5		4
44	44	1050	60	10.1	10.0	4
45	45	1050	60	9.5		4
46	46	1100	5	16.4		1
47	47	1100	5	16.3	16.1	1
48	48	1100	5	15.8		1
49	49	1100	10	11.8]	2
50	50	1100	10	11.7	11.7	2
51	51	1100	10	11.5]	2
52	52	1100	20	8.26	1	4
53	53	1100	20	8.06	8.19	$\overline{4}$
54	54	1100	20	8.24		4
55	55	1100	40	5.79		6
56	56	1100	40	5.79	5 . 78	6
57	57	1100	40	5.80		6
58	58	1100	60	4.62		7
59	59	1100	60	4.66	4.66	7
60	60	1100	60	4.70	1.50	7
61	61	1150	5	8.43		
62	62	1150	5	7.90	8.11	3
63	63	1150	5	8.02	0.11	3
64	64	1150	10			3
65	65	1150	10	5.78 5.60	5.66	5 5
		1 1 1 1 1 1	10 1	2 00	2 66	h

Table 5 (Continued)

Run	Wafer	Temp (°C)	Time (min)	Resistivity, ρ_s (ohms/sq)	Avg ρ_s (ohms/sq)	Xo (fringes)
67	67	1150	20	4.00		8
68	68	1150	20	3.92	3 . 95	8
69	69	1150	20	3.94		8
70	70	1150	40	2.60		12
71	71	1150	40	2.71	2.66	12
72	72	1150	40	2.67		12
73	73	1150	60	2.40		14
74	74	1150	60	2.20	2.35	14
75	75	1150	60	2.10		14

Table 6
Diborane Redistribution Diffusion.

Run	Sample	Temp (°C)	Time (hr)	Initial Resistivity, ρ_s (ohms/sq)	Final Resistivity, $ ho_{\rm s}$ (ohms/sq)	Initial Xo (fringes)	Final Xo (fringes)
1	4	1150	0.5	69.5	358	<1	3
2	10	1150	0.5	40.5	172	1	4
3	22	1150	0.5	29.4	111	<1	6
4	37	1150	0.5	15.8	47.0	3	6
5	43	1150	0.5	10.5	27.0	4	7
6	67	1150	0.5	4.0	6.6	8	11
7	7	1150	1	53.4	284	<1	6
8	11	1150	1	40.7	197	1	6
9	23	1150	1	29.2	128	<1	6
10	38	1150	1	15.7	59.5	3	8
11	44	1150	1	10.1	29.0	4	10
12	68	1150	1	3.92	8.0	8	13
13	5	1150	2	67.2	494	<1	7
14	12	1150	2	41.6	225	1	9
15	24	1150	2	31.9	160	<1	9
16	39	1150	2	14.3	57.4	3	11
17	45	1150	2	9.5	33.0	4	12
18	69	1150	2	3.94	9.5	8	16
19	8	1200	0.5	52.5	189	<1	8
20	13	1200	0.5	37.2	124	1	9
21	42	1200	0.5	10.8	26.5	4	12
22	40	1200	0.5	11.4	28.4	4	12
23	52	1200	0.5	8,26	19.6	4	12
24	74	1200	0.5	2.20	3.17	14	20
25	6	1200	1	6.77	300	<1	10
26	14	1200	1	36.1	200	1	10
27	35	1200	1	22.3	78.5	2	13
28	41	1200	1	11.8	33.8	2	15
29	53	1200	1	8.06	21.9	4	16
30		1200	1	2.71	4.70	12	22
31	9	1200	2	50,7	220	<1	14
32	15	1200	2	35,7	132	1	15
33	36	1200	2	21,1	76.3	2	20
34	34	1200	2	22,3	82.0	2	18
35	54	1200	2	8.24	2.48	4	19
36	72	1200	2	2.67	5.40	12	21

RESULTS

After each diffusion run, the sheet resistance was measured by the four-point probe technique, with at least four readings being taken on each slice. The variation of resistivity on each wafer after deposition was approximately $\pm 5\%$. After the redistribution diffusion, this variation in most cases was reduced to approximately $\pm 2\%$. The sheet resistances and junction depths obtained under the varying deposition conditions are tabulated in Tables 1, 2, and 5. The values for sheet resistances and junction depths obtained for the redistribution diffusion are tabulated in Tables 2, 4 and 6.

Figures 4, 5 and 6 illustrate the variation in arsine deposition resistivities vs. time at temperatures of 1100, 1200 and 1250°C, using O_2 concentrations of 0.5, 2 and 15%. The variation in resistivities obtained when the arsenic deposition diffusion is redistributed at temperatures of 1200 and 1250°C in an atmosphere of dry O_2 and steam is illustrated in Figures 7 through 10.

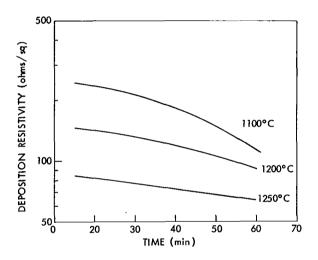


Figure 4—Arsine deposition resistivities vs. time with O₂ concentration of 0.5%.

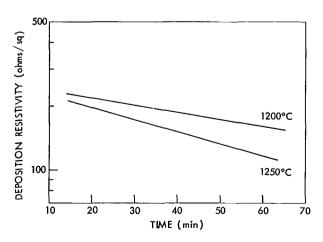


Figure 6—Arsine deposition resistivities vs. time with O₂ concentration of 15%.

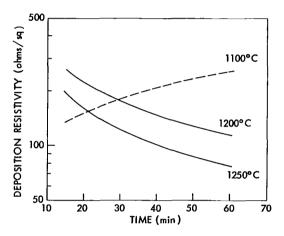


Figure 5—Arsine deposition resistivities vs. time with O_2 concentration of 2%.

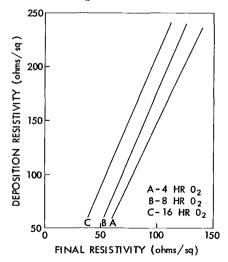


Figure 7—Arsine redistribution diffusion at 1200°C in O₂. Diffusion time for curve A was 4 hours, B, 8 hours and C, 16 hours.

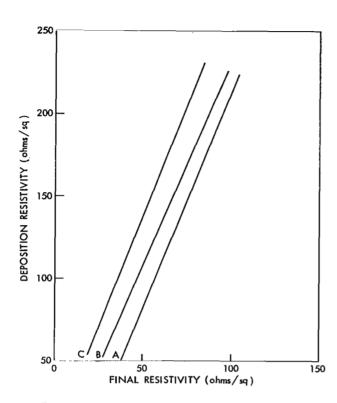


Figure 8—Arsine redistribution diffusion at 1250°C in O₂. Diffusion time for curve A was 4 hours, B, 8 hours and C, 16 hours.

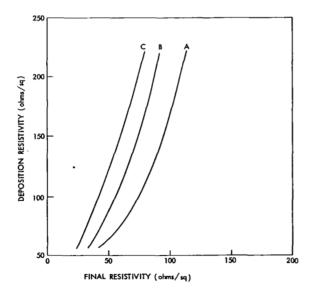


Figure 10—Arsine redistribution diffusion at 1250°C in steam and dry O_2 . Diffusion time for curve A was 1 hour in steam and 7 hours in O_2 ; for curve B, 1 hour in steam and 7 hours in O_2 ; and for curve C, 1 hour in steam and 15 hours in O_2 .

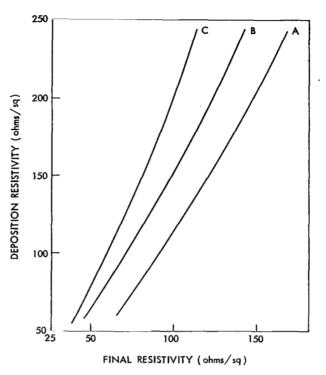


Figure 9—Arsine redistribution diffusion at 1200° C in steam and dry O_2 . Diffusion time for curve A was 1 hour in steam and 3 hours in O_2 ; for curve B, 1 hour in steam and 7 hours in O_2 ; and for curve C, 1 hour in steam and 15 hours in O_2 .

The overall effect of varying temperature, percentage of O_2 in the deposition gas steam, and deposition time upon the deposition resistivities achieved with phosphine are shown in Figures 11, 12 and 13. Figures 14, 15 and 16 illustrate the overall variation in resistivities obtained when the phosphorus deposition diffusion is redistributed at temperatures of 1000 and 1200°C for time intervals of 1, 2, and 4 hours.

For the diborane diffusion experiments, the overall variation in deposition resistivity with deposition temperature and time is shown in Figure 17. Figures 18 and 19 illustrate the variation in resistivities obtained when the boron deposition diffusion is redistributed at temperatures of 1150 and 1200°C for time intervals of 0.5, 1 and 2 hours.

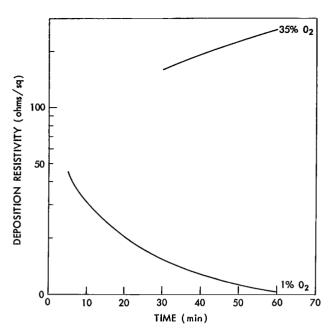


Figure 11—Phosphine deposition resistivities vs. time at 900°C.

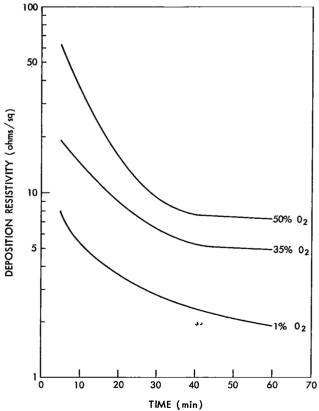


Figure 13—Phosphine deposition resistivities vs. time at 1100°C.

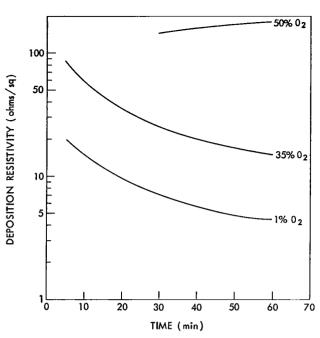


Figure 12—Phosphine deposition resistivities vs. time at 1000°C.

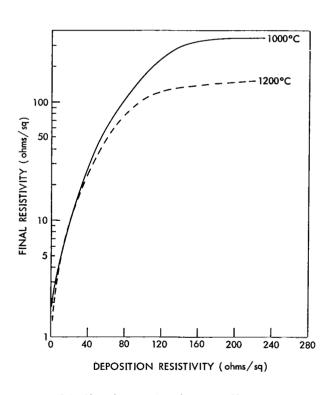


Figure 14—Phosphine redistribution diffusion at 1000 and 1200°C for 1 hour in steam (O_2 flow rate 50 ml/min).

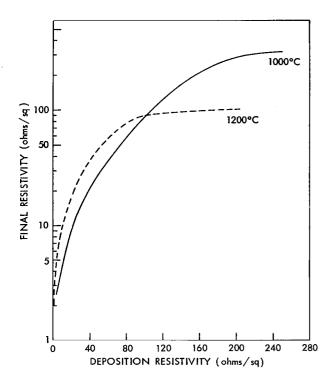


Figure 15—Phosphine redistribution diffusion at 1000 and 1200°C for 2 hours in steam (O_2 flow rate 50 ml/min).

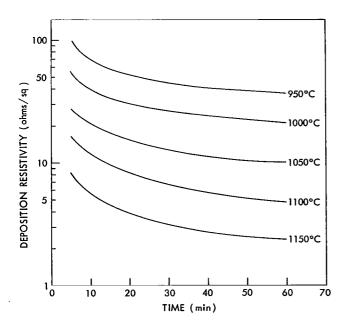


Figure 17—Diborane deposition resistivities vs. time $(B_2H_6 - 0.0046\%; O_2 - 3.3\%)$.

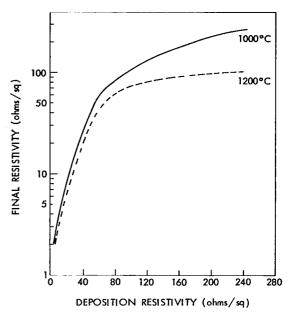


Figure 16—Phosphine redistribution diffusion at 1000 and 1200° C for 4 hours in steam (O₂ flow rate 50 ml/min).

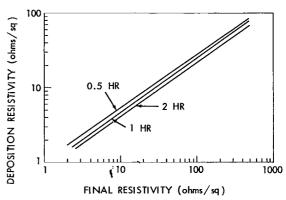


Figure 18—Diborane redistribution diffusion at 1150°C in steam (O_2 flow rate 50 ml/min).

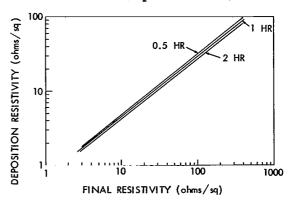


Figure 19—Diborane redistribution diffusion at 1200° C in steam (O₂ flow rate 50 ml/min).

It can be seen, then, from an examination of the tables and figures, that a wide range of sheet resistivities and junction depths for arsenic, phosphorus, and boron were achieved by a combination of deposition and redistribution conditions.

DISCUSSION

Physical and Chemical Properties of Arsine

The properties of arsine as reported in the literature (References 3 through 6) can be summarized as follows:

1. Synonyms: arsine, arsenic hydride

2. Description: colorless gas; unpleasant garliclike smell

3. Formula: AsH₃

4. Constants:

Molecular wt. - 77.93Melting point - 113.5 °C Boiling point - -55 °C Density - 2.69 g/l at 0°C.

The gas used in the diffusion study was a 1% mixture of AsH, in argon.

The decomposition reactions which were investigated in the course of the arsine diffusion study are described by the following equations:

$$2AsH_3 \longrightarrow 2As + 3H_2 \tag{1}$$

$$4AsH_3 + 3O_2 \longrightarrow 2As_2O_3 + 6H_2.$$
 (2)

Equation 1 occurs in the absence of oxygen; Equation 2 occurs when an excess of oxygen is available. The method of using arsine for a diffusion source as shown in Equation 1 above with nitrogen as a carrier gas was tried but found unsatisfactory. Without the presence of oxygen, "pitting" of the silicon surface occurred. Closer examination revealed the formation of a silicon-arsenic alloy on the surface of the silicon. For this reason, oxygen must be used during the diffusion. The decomposition reaction used to provide an arsenic diffusion source is then described by Equation 2 above. This method was used throughout the arsine diffusion study.

Arsine Diffusion Process

In general, the process of using AsH_3 as the source for the diffusion of arsenic into silicon was found to be superior to the conventional solid and liquid diffusion sources from the standpoint of handling ease and the control of diffusion resistivities. Using Equation 2 above, many diffusion runs were made to determine the parameters which affected the diffusion. From experimental results, it was found that, in addition to temperature and time, parameters such as percentage of

oxygen and arsine in the furnace feed gas, flow rates of gases, and diffusion tube design influenced the deposition resistivity. The effect of such parameters on diffusion together with the experimental results are stated separately as follows:

1. Percentage of oxygen in the doping gas

Variation of the percentage of oxygen present in the doping gas may be used to vary the sheet resistivity of the deposition. This is readily apparent from an examination of Figures 4, 5 and 6. The $\rm O_2$ concentrations of 0.5, 2 and 15% were selected to give the widest possible deposition resistivities consistent with other control parameters for the arsenic diffusion experiments. At temperatures of 1100°C, sporadic conversion occurred for oxygen concentrations of 8%; for $\rm O_2$ concentrations greater than 10%, conversion did not occur.

2. Percentages of AsH_3 in the doping gas

The percentages of AsH_3 in the furnace feed gas could be used to vary the sheet resistivity of the deposition. This method was found to be reproducible for AsH_3 concentrations greater than 0.05%. The 0.2% arsine concentration used in the diffusion experiment was found to be the near maximum percentage that could be used without causing a brownish stain on the wafers for deposition periods of one hour and oxygen concentration of 0.5%.

3. Flow rates

The flow rate of gas in conjunction with the furnace profile determine the uniformity of the deposition. It was found experimentally that for a furnace profile that was flat within 1° C for a distance of 6 inches the deposition would vary $\pm 5\%$ for silicon wafers that were laid flat on a quartz boat, when a total flow rate of 3.5 l/min. of gas were used. The I.D. of the quartz deposition tube was 45 mm. The flow rate of 3.5 l/min. was, therefore, used throughout the arsine diffusion experiment.

4. Diffusion tube design

The decomposition reaction described in Equation 2 above occurs at approximately 300° C. If a standard deposition tube is used, the As_2O_3 formed condenses on the walls of the diffusion tube and the deposition results are erratic. For this reason, the design illustrated in Figure 2 was used throughout the diffusion experiments. The feed gas remains sufficiently cool to curtail decomposition until fed directly into a zone of the furnace where the temperature was approximately 300° C. Reaction of the AsH_3 to As_2O_3 then occurs and the As_2O_3 formed is carried back over the silicon wafers, giving a uniform, reproducible, deposition.

Physical and Chemical Properties of Phosphine

The properties of phosphine as reported in the literature (References 3 through 6) can be summarized as follows:

- a. Synonyms: phosphine, hydrogen phosphide
- b. Description: colorless gas, garliclike smell

c. Formula: PH₃

d. Constants:

Molecular wt. - 34.04Melting point - -132.5 °C Boiling point - -87.5 °C Density - 1.529 g/l at 0°C.

The gas used in the diffusion study was a 1% mixture of PH, in argon.

The decomposition reactions which were investigated in the course of the diffusion study are described by the following equations:

$$2PH_{3} \longrightarrow 2P + 3H_{2} \tag{3}$$

$$2PH_3 + 3O_2 \longrightarrow P_2O_3 + 3H_2O$$
 (4)

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$
 (5)

$$2P_2O_5 + 5Si \longrightarrow 5SiO_2 + 4P.$$
 (6)

Equation 3 occurs in the absence of oxygen; Equation 4 occurs when a limited amount of oxygen is present; and Equations 5 and 6 describe the reactions when an excess of oxygen is available. The methods of using phosphine for a diffusion source as shown in Equations 3 and 4 above were tried but found unsatisfactory. Without an excess of oxygen, damage to the silicon surface occurred. For this reason, an excess of oxygen must be used during the diffusion. The decomposition reaction used to provide a phosphorus diffusion source is then described by Equations 3 and 4 above. This method was used throughout the phosphine diffusion study.

Phosphine Diffusion Process

In general, the process of using PH_3 as the source for the diffusion of phosphorus into silicon was also found to be superior to the present methods of liquid and solid source. Process capability in regard to the control of resistivity was initially determined to be +5% for the 2 to 50 ohms/sq range, and $\pm 10\%$ for the 50 to 250 ohms/sq range. A sufficient amount of data is not available, as yet, to indicate exact process control capability. This capability could be improved when employed in a strictly manufacturing organization. The present system, however, can be used to achieve a wide range of surface concentrations. Resistivities in excess of 250 ohms/sq can be achieved by using a deposition temperature of 1100% and an oxygen concentration in excess of 50%.

During the period of investigation, many diffusion runs were made to determine other parameters which affected the diffusion. From experimental results, it was found that in addition to temperature, time, and percentage of oxygen in the doping gas, parameters such as percentage of phosphine in the doping gas, flow rates, and diffusion tube design influenced the deposition

resistivity. The effect of such parameters on diffusion together with the experimental results are stated separately as follows:

a. Percentage of PH2 in the doping gas

The percentage of PH_3 in the doping gas could be used to vary the sheet resistivity of the deposition; however, this method was not found to be reproducible. The background doping of the deposition tube and diffusion boat affected the reproducibility of the deposition. To eliminate this variable, 0.057% PH_3 in the doping gas was found to be the near minimum percentage that could be used to achieve reproducible deposition resistivities. This percentage may be increased to achieve lower sheet resistivities in a minimum amount of time, as, e.g., in an emitter diffusion.

b. Flow rates

The flow rate of gas in conjunction with the furnace profile determine the uniformity of the deposition. It was found experimentally that for a furnace profile that was flat within 1° C for a distance of six inches (maximum furnace capability), the deposition would vary $\pm 5\%$ for silicon wafers that were laid flat on a quartz boat, when a total flow rate of 3.5 l/min of gas were used. The I.D. of the quartz diffusion tube was 45 mm. The flow rate of 3.5 l/min was, therefore, used throughout the phosphine diffusion experiments.

c. Percentage of oxygen in the doping gas

The percentage of oxygen used during the deposition phase of the diffusion has a marked effect upon the deposition resistivities as illustrated in Figures 11, 12 and 13. This is accomplished as follows: The decomposition reaction used to provide a phosphorus diffusion source is, as stated above,

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$
 (7)

$$2P_2O_5 + 5Si \longrightarrow 5SiO_2 + 4P.$$
 (8)

Phosphorus is thus freed and diffuses into the silicon, a SiO_2 layer being simultaneously formed between the glass layer and the silicon. The further supply of P_2O_5 through the SiO_2 layer to the silicon boundary takes place relatively slowly since the diffusion of P_2O_5 in SiO_2 is small. According to D'Asaro (Reference 7), at 1250°C the diffusion constant $D = 10^{-14}$ cm²/sec, while for the diffusion of phosphorus into silicon $D = 7 \times 10^{-12}$ cm² sec. During the deposition, when an excess of oxygen is available,

$$O_2 + Si \longrightarrow SiO_2. \tag{9}$$

Equation 9 then acts to shift the equilibrium of Equation 8 to the left, which has as a consequence a decrease in phosphorus concentration and, therefore, a decrease in surface concentration.

For depositions performed at 900°C, which employed a 35% concentration of oxygen in the furnace feed gas, the minimum time required to achieve reproducible diffusions was 30 minutes. Where a 50% concentration of oxygen was used, conversion did not occur even for deposition times of one hour. Similarly, for depositions at 1000°C, the depositions less than 30 minutes varied and were not stable where oxygen concentrations of 50% were employed. For deposition times of 60 minutes, sporadic conversion occurred for oxygen concentrations of 60%; no conversion was observed for concentrations of 70%.

Physical and Chemical Properties of Diborane

The properties of diborane as reported in the literature (References 3 through 6) can be summarized as follows:

a. Synonyms: diborane, boroethane, boron hydride

b. Description: colorless gas, sickly sweet odor

c. Formula: B2H6

d. Constants:

Molecular wt. - 27.7 Melting point - -165.5°C Boiling point - -92.5°C

Density - 0.477 (liquid at -112°C)

0.577 (solid at -183°C)

Vapor pressure - 244 mm Hg at -112℃

The gas used in the diffusion study was a 1% mixture of B_2H_6 in argon.

The decomposition reactions taking place in the diffusion can be described by the following equations:

$$B_2H_6 \xrightarrow{} 2B + 3H_2 \tag{10}$$

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O.$$
 (11)

The method of using diborane for a diffusion source as shown in Equation 10 above was tried but not found satisfactory. As noted in the use of arsine and phosphine, oxygen must be used during the diffusion; otherwise, pitting of the silicon surface occurs. The decomposition reaction used to provide a boron diffusion source is then described by Equation 11 above. This method was used throughout the diborane diffusion study.

Diborane Diffusion Process

The process of using B_2H_6 as the source for the diffusion of boron into silicon was found to be superior to the present methods of liquid and solid sources. Functional electronic blocks

having NPN and PNP transistors, diodes, resistors, and four-layer PNPN switches have been fabricated using this process. No significant differences in device characteristics have been observed when the devices were compared with those fabricated by using a BBr_3 source. A significant increase in device uniformity and yield per wafer was noted because of an increase in uniformity of depositions attained with B_2H_6 . Process capability in regard to the control of resistivity was initially determined to be +5% for the 2 to 100 ohms/sq range, and +8% for the 100 to 400 ohms/sq range. A sufficient amount of data is not available, as yet, to indicate exact process control capability. This capability could be improved when employed in a strictly manufacturing organization. The present system, however, can be used to achieve a wide range of surface concentration.

During the period of investigation, many diffusion runs were made to determine other parameters which affected the diffusion. As noted in the case of phosphine and arsine, it was found that, in addition to temperature and time, parameters such as percentages of oxygen and diborane in the doping gas, flow rates of gases, and diffusion tube design influenced the deposition resistivity. The effect of such parameters on diffusion together with the experimental results are stated separately as follows:

a. Percentage of oxygen in the doping gas

The percentage of oxygen present in the doping gas may be used to vary the sheet resistivity of the deposition; however, this method of control was not found to be reproducible. Using a temperature of 1150° C, a deposition time of 30 minutes, a B_2H_6 concentration of 0.0046%, and a varying concentration of oxygen, the following results were obtained: $3\% O_2 - 3.2$ ohms/sq; $10\% O_2 - 3.4$ ohms/sq; $16\% O_2 - 3.2$ ohms/sq; $32\% O_2 - 33.4$ ohms/sq. Similar experiments were run at temperatures of 1000, 1050 and 1100° C. In all cases, the results were not reproducible, especially for concentrations of oxygen greater than 10%. For this reason, this variable was reduced to the minimum by using the minimum amount of oxygen necessary to attain reproducible diffusions. This figure for the diffusion experiment was chosen to be 3.3%, although percentages of oxygen from 3 to 10% could have been used. For percentages of oxygen much below 3%, a brownish stain would appear on the surface of the wafers for deposition times of 1 hour at temperatures of 1050, 1100 and 1150° C.

b. Percentage of B_2H_6 in the doping gas

The percentage of $\rm B_2H_6$ present in the doping gas could be used to vary the sheet resistivity of the deposition; however, as in the case of oxygen, this method was not found to be reproducible. The background doping of the deposition tube diffusion boat affects the reproducibility of the deposition. In eliminating this variable, 0.0046% $\rm B_2H_6$ in the doping gas was found to be the nearmaximum percentage that could be used without causing a brownish stain on the wafers for deposition periods of one hour. For this reason, this percentage was then used throughout the diborane diffusion study.

c. Flow rates

The flow rate of gas in conjunction with the furnace profile determine the uniformity of the deposition. It was found experimentally that for a furnace profile that was flat within 1° C for a

distance of 6 inches (maximum furnace capability) the deposition would vary 5% for silicon wafers that were laid flat on a quartz boat when a total flow rate of 4.5 l/min of gas was used. The I.D. of the quartz diffusion tube was 45 mm. The flow rate of 4.5 l/min was, therefore, used throughout the diffusion experiment.

d. Diffusion tube design

The decomposition reaction described in Equation 11 above was determined experimentally to occur at approximately 400°C. If a standard deposition tube is used, the B_2O_3 formed condenses on the walls of the diffusion tube and the deposition results are erratic. For this reason, the "tube within a tube" design illustrated in Figure 2 was used throughout the diborane diffusion experiment. The feed gas remains sufficiently cool to curtail decomposition until fed directly into a zone of the furnace where the temperature was approximately 900°C. Reaction of the B_2H_6 to B_2O_3 then occurs and instead of depositing and remaining on the walls of the diffusion tube the B_2O_3 formed is carried back over the silicon wafers, giving a uniform reproducible deposition.

CONCLUSIONS

An investigation into the use of the gaseous hydrides $(B_2H_6, PH_3 \text{ and AsH}_3)$ demonstrated their superiority to the conventional solid or liquid diffusion sources. The gases were used in the fabrication of functional electronic blocks having unipolar and bipolar transistors, resistors, diodes, capacitors, four-layer switches, and surface barrier devices. No significant differences in device characteristics were noted when these devices were compared with those made with conventional solid or liquid diffusion sources. A significant increase in device uniformity and yield per wafer was noted. This investigation has established a diffusion capability more than adequate for second or third generation functional electronic blocks.

(Manuscript received December 3, 1965)

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