J. S. Sandhu
J. L. Reuter

Arsenic Source Vapor Pressure Kinetics and Capsule Diffusion

Abstract: After diffusion temperature and time, the most important parameters in capsule diffusion source behavior are the dopant vapor pressure characteristics in the capsule. The vapor pressure behavior is a function of the degree of homogenization of the Si-dopant system and hence of the source preparation technology. Various methods of preparing Si-As source material are discussed. Homogenized-source preparation is described as it relates to reproducibility and controlled capsule diffusion behavior. The measurement of the kinetics of arsenic vapor pressure development in a typical capsule system and the role of vapor pressure in determining capsule diffusion behavior are described. Finally, the dependence of arsenic vapor pressure characteristics, and hence of the diffusion, on source weight-to-capsule volume ratio is described.

Introduction

For tight control of the diffusion of an impurity into silicon in a capsule diffusion process, three boundary conditions are of major importance: temperature of diffusion, length of time of diffusion, and diffusion source behavior. Probably the most vital, and certainly most difficult variable to control, is the diffusion source behavior. Essentially, the relationship of source behavior to diffusion in a capsule may be expressed by the following illustration:

$$\text{Dopant source} \rightleftharpoons \text{Dopant vapors} \rightleftharpoons \text{Wafer surface concentration} \rightleftharpoons \text{Diffusion phenomenon}$$

The degree of equilibration in the expression above is a function of the dopant source $\rightleftharpoons$ dopant vapors. The dopant vapor behavior, in turn, depends largely on the dopant source composition and to some extent upon the temperature behavior. For a controlled diffusion phenomenon, the wafer surface concentration must be controlled and, hence, the dopant pressure behavior of the source.

It is inconvenient to control the impurity vapor pressure behavior by using an elemental impurity, even in capsule diffusion, since the weight involved would be extremely small and the vapor pressure would change with diffusion time. Accordingly, for the commonly used capsule dopant sources, the dopant impurity is incorporated into intrinsic silicon, which is then pulverized for use as a diffusion source. In semiconductor processing, the three different techniques described below have been used primarily for incorporating the dopant impurity into silicon.

• *Mixture of arsenic and silicon*

The simplest method for making an arsenic diffusion source would be a mechanical mixture of pulverized arsenic and intrinsic silicon. The major drawbacks in this case are inhomogeneity in mixing and the concentration change that occurs during diffusion into the silicon powder.

• *Freeze-out source*

Another commonly used method for preparing an arsenic-doped material as a diffusion source employs the addition of a weighed amount of arsenic into molten silicon. The dopant is allowed to dissolve and the solution is then frozen, powdered, and used for diffusion. During this process, the molten mixture continuously loses the dopant, because of extensive vaporization before the solution, represented by point A in the phase rule diagram[1] of Fig. 1, can be frozen. The freezing process as such is a nonequilibrium cooling phenomenon. Various phase boundary conditions are capable of generating, in addition to the substitutional solution of As, silicon alloy phases such as silicon monoarsenide and diarsenide, in varying relative proportions depending strongly and

strictly upon the amount of As dissolved in silicon and the cooling cycle. Precise control of the time and temperature in this technique is mandatory for the proper composition of this multiphase system and, hence, for the reproducibility of the freeze-out source.

• *Single-crystal sources*

Single-crystal sources are prepared by the Czochralski method of pulling crystals from a molten mixture of silicon and arsenic, followed by pulverization. This technique incorporates much better equilibrium control as compared with the freeze-out method. However, since the segregation coefficient between arsenic concentration in the melt and the crystal is low (0.3), the concentration of the melt near the liquid-solid interface increases to a value that allows some incorporation of the unstable phases in capillary cores in the growing crystal, especially in the high-concentration range. Good results would be expected with this technique only for concentrations of about 10^{19} cm^{-3}.

Sources prepared by these three techniques do suffer from limitations. Because of their multiphase nature, it is difficult to produce exactly the same composition from time to time. Thus each source would require a different set of diffusion conditions. Since we are interested in impurity diffusion concentration, but only within the maximum solid solubility limit[2] as shown in Fig. 2, and also in the equilibrium conditions during the diffusion process in a capsule, the diffusion source must represent a homogeneous substitutional solution of the desired concentration of the impurity into silicon. The diffusion results from such a source would then be consistent and reproducible.

The technique[2] described below in the experimental section involves the preparation methodology for the one-phase substitutional solution of As in Si, the results of which are described here as "homogeneous diffusion sources."

Experimental

• *Homogeneous diffusion source preparation*[2]

A two-step preparation process is employed: 1) Prepare a master source of 20 atomic percent arsenic concentration. 2) Dilute the master source with intrinsic Si powder to a suitable concentration; follow with thermal homogenization.

Preparation of master source

1) Intrinsic polycrystalline silicon of 99.999% purity (Dow Corning) is ground to less than 150 μm (100-mesh size).
2) Weighed amounts of the silicon powder and arsenic of 99.999% purity (Gallard & Schlesinger Co.) are loaded into a capsule with cavities at each end (Fig. 3). The tube is then evacuated to a pressure of $<5 \times 10^{-6}$ mm Hg while the silicon cavity is maintained at 475° C and the arsenic cavity at 200° C for 60 min to eliminate adsorbed gases. The tube is then sealed under vacuum.

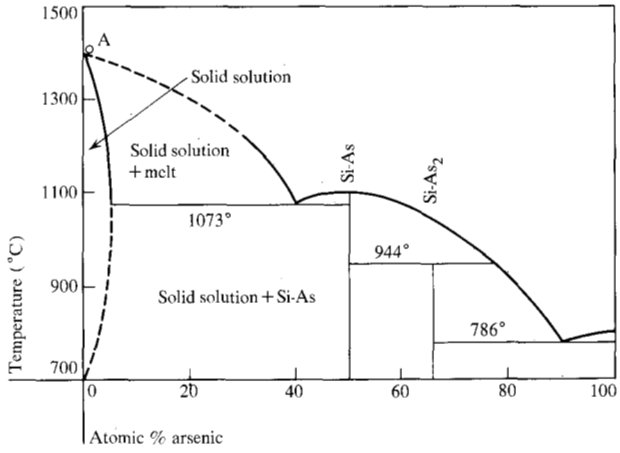
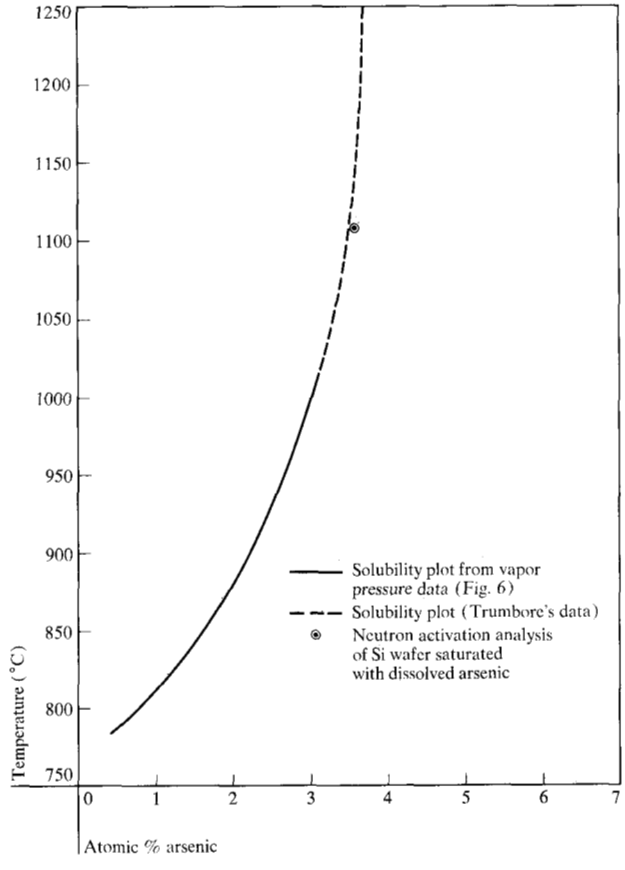


Figure 1 Phase diagram for Si-As system.

Figure 2 Solid solubility of As in Si, vs temperature.



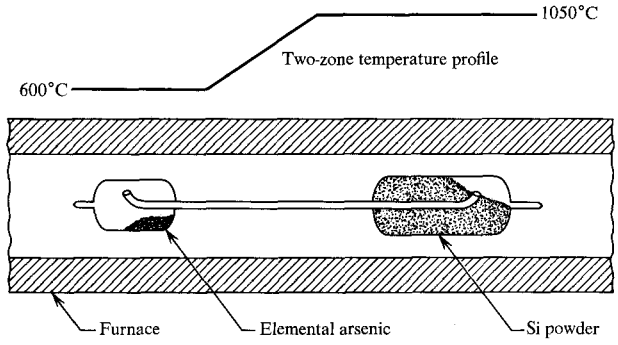
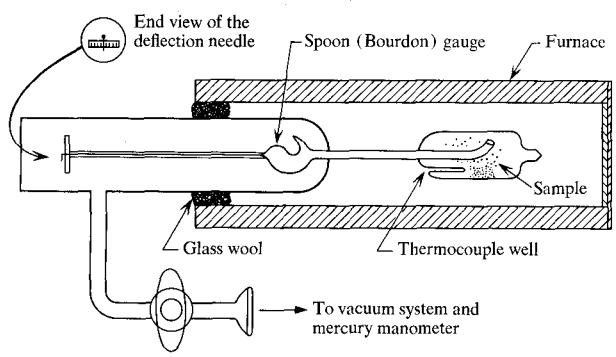
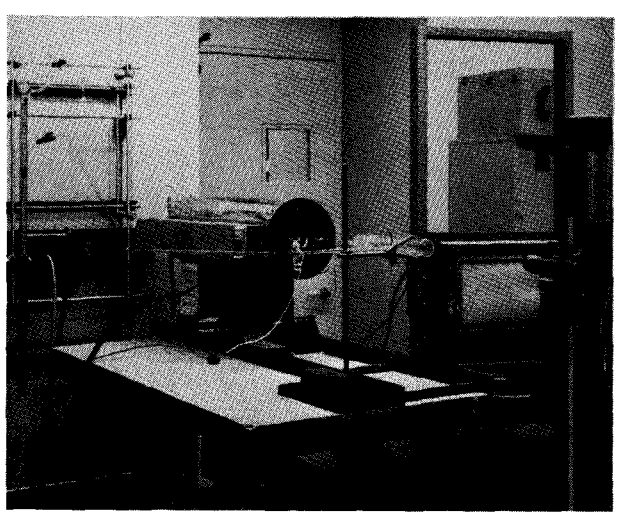


Figure 3 Schematic of preparation method for the thermally homogenized Si-As solid solution (master source).

Figure 4 Apparatus used for vapor pressure measurements. (a) Schematic; (b) laboratory arrangement.



(a)



(b)

3) To allow As diffusion into Si under controlled As pressure, the capsule is then placed in a two-zone furnace with the arsenic cavity at <625° C and the silicon cavity at 1050° C (Fig. 3) until all the arsenic transfers into the silicon cavity.
4) The entire capsule is placed in the 1050° C zone for 1 hour and is then removed, silicon cavity-end first.
5) The resultant multiphase Si-As alloy mixture contains conglomerates formed during the initial transfer of arsenic to silicon. The material is therefore repulverized to 150 μm (100 mesh).

Use of this master source for preparing sources of lower concentrations allows a controlled vapor pressure of arsenic that is less than 2 atm at temperatures up to 1050°C for any concentration of arsenic[1]. Preparation steps can then be carried out in a single zone when the master source is used.

Dilution of master source and homogenization

To prepare sources of various concentrations, the master source is added to 100-mesh intrinsic silicon powder in predetermined amounts. This mixture is then evacuated to 5×10^{-6} mm Hg and heated to 425°C under vacuum for 60 min and sealed.

The capsule is placed in a furnace at 1050° C for 50 hours to ensure thermal homogenization. The resultant mixture is then sieved through a 100-mesh screen and used for diffusion.

The resultant Si-As composition is then characterized by the radio-tracer technique. The source behavior for capsule diffusion can subsequently be characterized by the techniques described below.

- *Diffusion source characterization by vapor pressure kinetics*

Since the capsule diffusion control is a function of the dopant source $\rightleftharpoons$ dopant vapor pressure $\rightleftharpoons$ wafer diffusion, the kinetics of dopant pressure development in a capsule were studied as a function of source concentration and temperature. For a controlled diffusion in the capsule, the dopant vapor pressure should quickly approach the equilibrium value so that a constant impurity-vapor environment is maintained during the diffusion process.

Studies of vapor pressure kinetics were performed on source materials prepared by all the techniques described above. Use was made of a quartz manifold, Fig. 4(a), consisting of a Bourdon gauge[3], which is highly sensitive to pressure differentials of 0.5 Torr. The gauge is surrounded by a transparent quartz jacket, which is further connected to a mercury manometer through a side arm. The gauge is connected on one end to a long deflection needle, which further magnifies the response of the gauge, and on the other, to the sample cell provided with a thermocouple well.

The sample cell was filled with 0.033 g of doped material per cubic centimeter of the free volume. The "jacket" and the "cell" were then simultaneously evac-

uated to a pressure of $<5 \times 10^{-6}$ mm Hg. The source and Bourdon gauge were then baked at 425° C for one hour and sealed under vacuum. After the stopcock on the side arm of the jacket was closed, the manifold was demounted from the high vacuum and mounted and aligned in front of a movable furnace maintained at a desired temperature. The jacket side arm was then connected to a mercury manometer, Fig. 4(b), with provision made for regulating the gas pressure in the jacket to null the deflection of the Bourdon needle. The needle deflection was monitored through a cathetometer and calibrated against known pressure differentials. The furnace temperature was controlled within 0.5° C of the desired temperature. The furnace and material temperatures were monitored and recorded by a two-channel Leeds and Northrup recorder. The validity of the source temperature measurements was verified by measuring the vapor pressure of elemental arsenic during heating.

After the calibration procedure was completed, the furnace was moved over the apparatus as shown and the needle deflection and manometer reading were periodically noted. The gas pressure in the jacket as determined by the manometer reading was periodically adjusted as desired. The measurements were continued for up to 36 hours after the equilibrium was established.

To determine the dependence of effective source concentration on source weight-to-capsule volume ratio, the vapor pressure kinetics measurements were repeated for various amounts of the source material of each original dopant concentration. The new rate of vapor pressure development and the new equilibrium vapor pressure representing the effective source concentration were thus determined.

• *Diffusion procedures and characterization*

To evaluate the diffusion characteristics of the doping sources, capsule diffusions were performed for various concentrations of arsenic in the powdered source and for various diffusion temperatures and times. Identical diffusion procedures were used in each case. Our conventional quartz capsules[4] were acid-cleaned, rinsed with deionized water, and baked at a temperature higher than that used for diffusion. P-type silicon wafers (1 Ω-cm resistivity, 1.25 in. dia. and ⟨100⟩ orientation) were used as a vehicle for the experiment. The source weight-to-capsule volume ratio was determined and kept constant for a comparison study of vapor pressure kinetics and diffusion characteristics. The starting furnace temperature rise time was the same for both the vapor pressure kinetics study and the diffusion experiments. A calculated amount of the source was loaded into a diffusion boat. Wafers were cleaned with buffer etch, rinsed with deionized water, and dried before being loaded into the diffusion boat. Two wafers were used for each experiment. The diffusion capsule containing the loaded boat was evacuated to 5×10^{-6} mm Hg pressure, baked at 500° C for 30 min to eliminate adsorbed gases, and sealed off. The capsule was then placed into the flat zone of a diffusion furnace, which was profiled and maintained at a desired temperature. On completion of the desired diffusion cycle, the capsule was quenched in cold water. The wafers were then removed, rinsed, and dried.

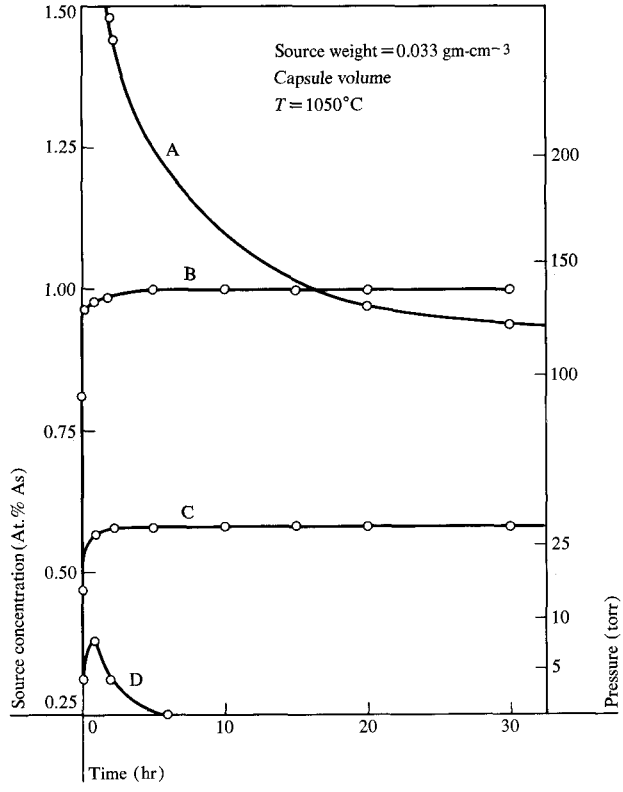


Figure 5 Vapor pressure and source concentration vs time for four diffusion sources. Source A: 1.0% As, freeze-out preparation; source B: 1.0% As, thermally homogenized; source C: 0.58% As, thermally homogenized; source D: 0.25% As, pulverized doped single crystal.

The wafer diffusion was characterized by determining the surface concentrations of arsenic. Incremental sheet resistance, plasma resonance, and neutron activation techniques were used.

Results and discussion

• *Vapor pressure kinetics*

Figure 5 shows the vapor pressure kinetics of four different diffusion sources at 1050° C. The corresponding time-dependence of the effective source concentration, as derived from the dopant concentration-to-equilibrium vapor pressure relationships of Fig. 6[2], is also shown in Fig. 5. Curves A and B of Fig. 5 represent two sources with the same arsenic concentration (1.0 atomic %) but

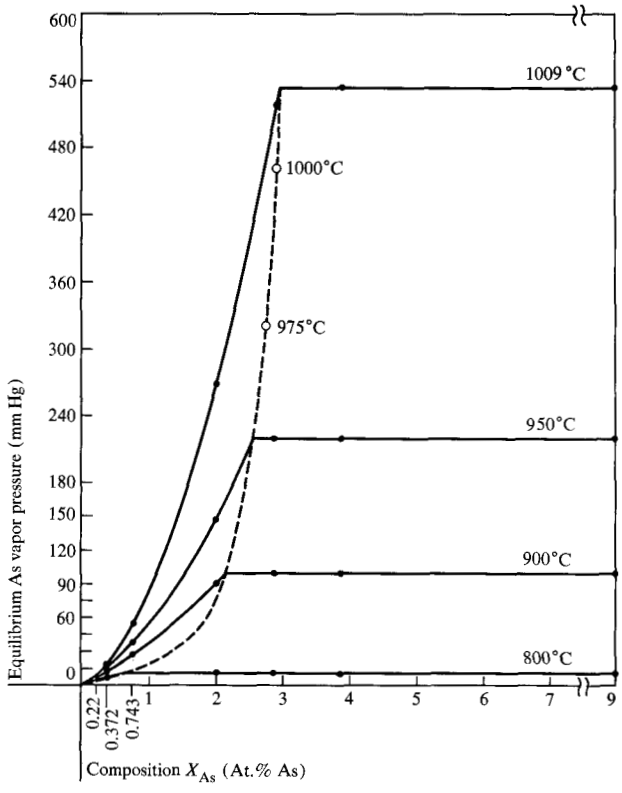


Figure 6 Equilibrium arsenic pressure vs Si-As alloy composition (X_{As}) determined[2] by radiotracer and chemical techniques.

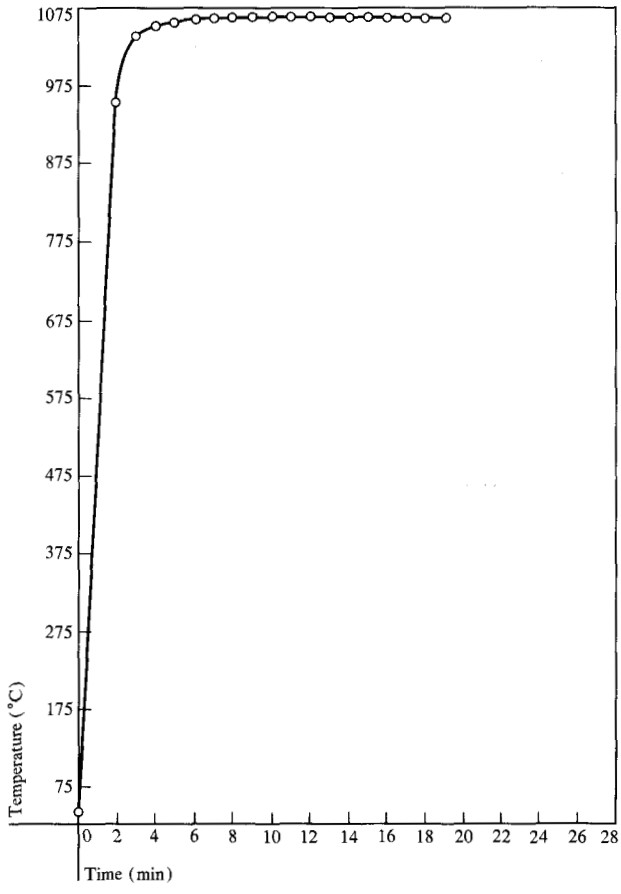


Figure 7 Sample temperature vs time.

prepared by two different techniques. Source A was prepared by the freeze-out method described in the introduction. Source B, on the other hand, represents a one-phase chemically homogenized diffusion source prepared by the technique described in the experimental section. Curve C represents another homogenized solution of 0.58 atomic percent arsenic concentration. Curve D represents a 0.25 atomic percent arsenic source obtained by pulverizing a doped single crystal as described in the introduction.

It is evident from Curves A and D that the doping materials prepared by the second and third techniques (freeze-out mixture, and doped single crystal) show a significant transient behavior for the first 20 hours, after which they behave like homogenized sources, of a concentration representative of the arsenic concentration in the source.

For all practical parameters of diffusion these materials would exhibit time-dependent source concentrations, exhibiting as much as twice the final concentration during a good first portion of the diffusion cycle. Homogenized sources, as represented by B and C on the other hand, approach the steady state condition at a rate closely resembling that of the source temperature, Fig. 7, and accordingly will exhibit the time-independent source concentration behavior. Also, on examination of the basic shapes of the kinetic profiles A and D, it is apparent that it would be extremely difficult to reproduce such profiles with sample-to-sample preparation by the same technique. The homogenized sources, however, representing the nontransient behavior as in B and C, would be expected to be easily reproducible.

The source behavior as presented in Fig. 5 takes into account the depletion of the dopant due to vaporization, which depends upon the source weight-to-capsule volume ratio and the rate and uniformity of depletion. The higher the temperature, time of diffusion, or source concentration, the greater is the degree of depletion, and thus the greater is the deviation of the effective source concentration from that of the true concentration.

From the examination of kinetic profiles in Figs. 8(a) and (b) at 1050° C and for various source weight-to-capsule volume ratios for homogenized sources, it is observed that the deviation from the true source concentration due merely to depletion can be as high as 35% for a source weight-to-capsule volume ratio of 0.033 gm-cm^{-3}. However, a more important observation from these

kinetic curves discloses that even under the most severe depletion conditions, such as noticed in Figs. 8(a) and (b), the depletion observed in each case is approximately the same as would be expected from the equation described below in Eq. (8), which assumes a fast and homogeneous depletion throughout the bulk of the source material. The homogeneous depletion implies that the arsenic from the bulk of a crystallite diffuses out to compensate for the arsenic leaving from the surface in such a way as to maintain uniform concentration throughout the crystallite.

This phenomenon is quite interesting. Although the inward diffusion of arsenic into silicon powder is quite rapid, due to the polycrystalline nature of the source particles with the crystallite size being quite small, the subsequent out-diffusion rate of arsenic observed here is almost instantaneous. Possibly the high concentration diffusion causes significant lattice degradation of the silicon material. The dependence of arsenic diffusivity upon its doping concentration in silicon[6] could be related to the same phenomenon.

Under the fast and homogeneous depletion conditions,

$$\text{effective concentration (at.\%)} = \text{true concentration (at.\%)} - \text{depletion (at.\%)}; \quad (1)$$

where

$$\text{depletion (at.\%)} = \frac{N_{As}\ \text{(vapor)}}{N_{Si} + \text{original } N_{As}\ \text{(solid)} - N_{As}\ \text{(vapor)}} \times 100 \quad (2)$$

and

$$N_{As}\ \text{(vapor)} = 4N_{As_4} + 2N_{As_2},$$

since N_{As} (monatomic) is negligible in vapor. Also, since

$$N_{As}\ \text{(solid)} - N_{As}\ \text{(vapor)} \ll N_{Si},$$

Eq. (2) can be approximated to

$$\text{depletion (at.\%)} = \frac{N_{As}\ \text{(vapor)}}{N_{Si}} \times 100. \quad (3)$$

Assuming ideal gas law behavior, we have

$$\frac{P_1V_1}{N_1T_1} = \frac{P_2V_2}{N_2T_2}.$$

Using Avogadro's law,

$$\frac{1 \times 22400}{1 \times 273} = \frac{P_{As}\ \text{(Torr)}}{760} \times \frac{V\ \text{(ml)}}{N_{As}\ \text{(vapor)} \times T\text{(K)}}. \quad (4)$$

From (3) and (4),

$$\text{depletion (at.\%)} = \frac{273}{T\ \text{(K)}} \times \frac{V\ \text{(ml)}}{N_{Si}} \times \frac{4P_{As_4} + 2P_{As_2}}{760} \times \frac{100}{22400}. \quad (5)$$

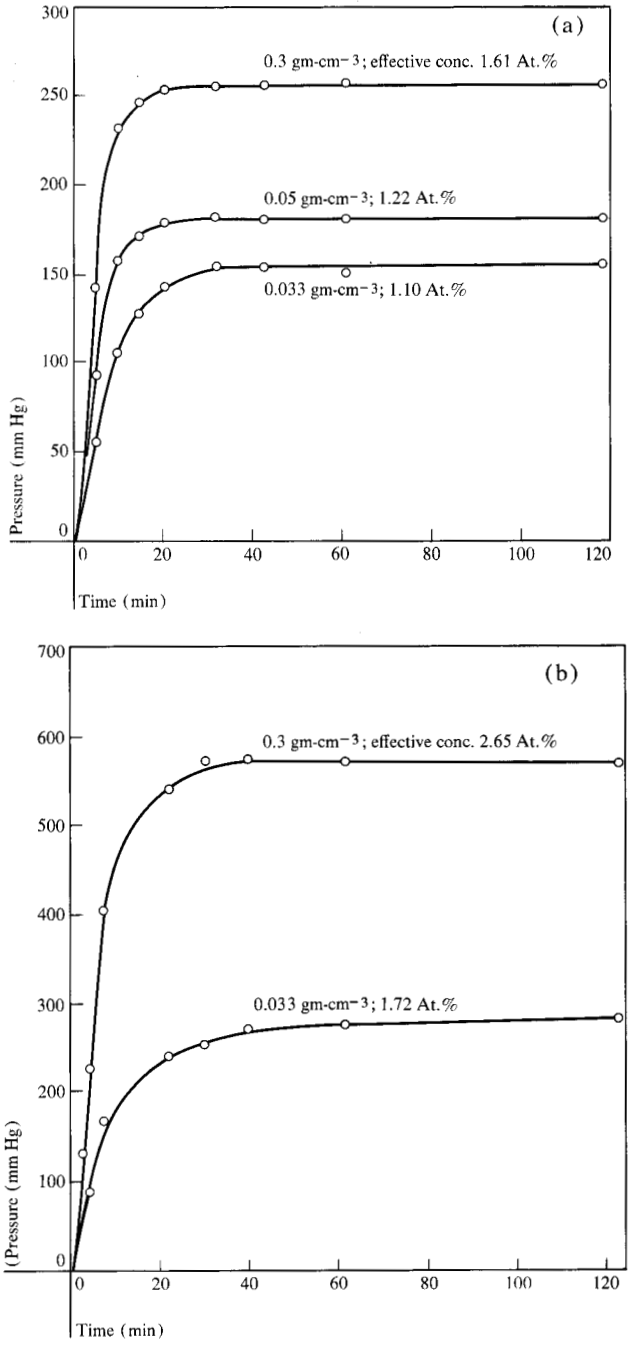


Figure 8 Effect of depletion on concentration at a diffusion temperature of 1050°C. True source concentration (a) 1.72 at. %; (b) 2.9 at. %.

Now using the equilibrium relationship[5]

$$As_4 \overset{K}{\rightleftharpoons} 2\ As_2,$$

we have

$$4P_{As_4} + 2P_{As_2} = 4P + K \pm \sqrt{K^2 + 4PK}, \quad (6)$$

Table 1 Effect of depletion on concentration.

Ratio of source wt. to capsule vol. (gm-cm^{-3})	*True[a] Conc. (at.%)*	*Effective concentration (at.%)*					
		1050° C		*1000° C*		*950° C*	
		Exp.[a]	*Calc.*	*Exp.[a]*	*Calc.*	*Exp.[a]*	*Calc.*
0.033	0.55	0.5	0.5	0.5	0.5	0.5	0.51
0.033	1.2					1.0	1.02
0.033	1.35			1.0	1.03		
0.3	1.72	1.61	1.60				
0.05	1.72	1.22	1.22				
0.033	1.72	1.10	1.11				
0.3	2.9	2.65	2.64				
0.033	2.9	1.72	1.72				
0.033	4.0	2.24	2.2				

[a]Determined by equilibrium vapor pressure measurements using 2 gm-cm^{-3} sample so that the arsenic depletion was negligible. The vapor pressures were converted to concentration using Fig. 6.

where P is the total arsenic pressure in Torr. From Eqs. (5) and (6),

$$\text{depletion (at.\%)} = \frac{273}{T} \times \frac{V}{N_{Si}} \times \frac{(4P + K \pm \sqrt{K^2 + 4PK})}{760} \times \frac{1}{224}$$

$$= \frac{273}{T} \times \frac{M_{Si}}{R} \times \frac{(4P + K \pm \sqrt{K^2 + 4PK})}{760} \times \frac{1}{224}, \quad (7)$$

where M_{Si} is the atomic weight of Si (=28) and R is the source weight-to-capsule volume ratio in gm-cm^{-3}. Substituting Eq. (7) in Eq. (1) gives

$$\text{effective concentration (at.\%)} = \text{true concentration (at.\%)} - \frac{273}{T} \times \frac{M_{Si}}{R} \times \frac{(4P + K \pm \sqrt{K^2 + 4PK})}{760} \times \frac{1}{224}. \quad (8)$$

Table 1 compares the experimental values of the true and effective source concentrations with the corresponding values calculated using Eq. (8) for various temperatures and source weight-to-capsule volume ratios. The experimental data are derived from vapor pressure measurements such as described in Figs. 6[2] and 8. The close agreement between the calculated and the measured values also indicates that the SiO_2 surface of the capsule must also be relatively passive and does not substantially contribute to the depletion of the source. This agreement demonstrates the significance of Eq. (8) in applications to capsule diffusion operations. For example, a specific alloy composition can be used to attain new compositions through variations in the value of R, assuming, of course, a knowledge of the equilibrium vapor pressure of arsenic over the new composition.

• Relationship of diffusion surface concentration to vapor pressure characteristics

Table 2 presents the vapor pressure-determined source concentrations and the diffused-surface concentrations as determined by neutron activation, plasma resonance, and incremental sheet resistance techniques.

As observed, the diffusion concentrations determined by neutron activation and the effective source concentrations determined by vapor pressures are in good agreement.

Each one of these techniques accounts for the total amount of arsenic present in the alloy form. This observation demonstrates the capsule equilibrium phenomenon. The incremental sheet resistance, and, to a larger extent, the plasma resonance technique, on the other hand, determine the concentration of electrically active dopant concentrations only. Accordingly, for true diffusion concentration values above 3×10^{20} cm^{-3}, the dopant concentration values determined by these techniques are relatively much lower.

Summary and conclusions

Homogenized diffusion source technology can provide a controlled and predictable vehicle for capsule diffusion because of equilibrium conditions. Characterization, by vapor pressure kinetics, of the homogenized sources provides a sensitive and realistic method for predicting diffusion behavior. With polycrystalline source particles in a homogenized diffusion source, there is homogeneous and fast depletion of the dopant from the source to vapor; hence, the effective source concentration is predictably related to the source weight-to-capsule volume ratio for a given temperature.

Table 2 Relationship of diffusion surface concentration to vapor pressure characteristics.

Temperature (° C)	*Effective source conc. from vapor pressure measurements* (cm^{-3})	*Diffusion concentration* (cm^{-3})		
		Neutron activation[a]	*Incremental sheet resistance*	*Plasma resonance*
1050	2.5×10^{20}	2.3×10^{20}	1.2×10^{20}	2.3×10^{20}
1050	5.0×10^{20}	5.0×10^{20}	2.5×10^{20}	3.1×10^{20}
1050	1.12×10^{21}	1.07×10^{21}	1.8×10^{20}	2.1×10^{20}
1000	2.5×10^{20}	2.3×10^{20}	3.7×10^{20}[b]	2.3×10^{20}
1000	5.0×10^{20}	5.0×10^{20}	2.5×10^{20}	4.0×10^{20}
1000	1.12×10^{21}	1.07×10^{21}		3.5×10^{20}
950	2.5×10^{20}	2.3×10^{20}	6.4×10^{20}[b]	2.35×10^{20}
950	5.0×10^{20}	5.0×10^{20}	4.6×10^{20}	4.6×10^{20}
950	1.12×10^{21}	1.07×10^{21}	9×19^{20}	

[a]Neutron activation surface concentrations were determined for 1050° C diffusions and were assumed to be the same at other temperatures, since they are the same as the effective source concentrations.
[b]Because of extremely shallow junction depth, this result is somewhat inaccurate.

Acknowledgments

The authors are very grateful to H. S. Rupprecht and the IBM Corporation for encouragement and support during the course of this study. We thank R. Kastl and J. Makris for diffusion and characterization support, and V. J. Lyons for valuable discussions and advice.

References

1. V. W. Klemm and P. Pirscher, *Z. Anorg. Allg. Chem.* **247,** 211 (1941); F. A. Trumbore, *Bell System Tech. J.* **39,** 205 (1960).
2. V. J. Lyons and J. S. Sandhu, "Diffusion Source and Method of Producing the Same," German patent 2012459, issued to IBM Corporation, October 1970. J. S. Sandhu, "Solid-Vapor Equilibria in Si-As System," presented for the Northwestern University Material Science Colloquium series, April 1968.
3. V. J. Lyons and V. J. Silvestri, *J. Phys. Chem.* **64,** 266 (1960).
4. M. C. Duffy and R. P. Gnall, "A Survey of Diffusion Processes for Fabricating Integrated Circuits," *Solid State Technology* **9** (10), 27 (1966).
5. D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements*, American Chemical Society, Washington 1956, p. 233.
6. T. L. Chiu and H. N. Ghosh, *IBM J. Res. Develop.* 15, 472 (1971, this issue).

Received June 10, 1971

The authors are with the Cogar Corporation, Technology Division, Wappingers Falls, New York 12590. The work described in this paper was completed at the IBM Components Division Laboratory, E. Fishkill (Hopewell Junction), New York 12533.