

13. W. G. Spitzer and J. R. Ligenza, *ibid.*, **17**, 196 (1961).
14. J. R. Ligenza, *J. Phys. Chem.*, **65**, 2011 (1961).
15. J. R. Ligenza, *This Journal*, **109**, 73 (1962).
16. C. T. Sah, H. Sello, and D. A. Tremere, *J. Phys. Chem. Solids*, **11**, 288 (1959).
17. J. L. Sprague, J. A. Minahan, and O. J. Wied, *This Journal*, **109**, 94 (1962).
18. M. O. Thurston, J. C. C. Tsai, and K. D. Kang, "Diffusion of Impurities into Silicon Through an Oxide Layer," Report 896-Final, Ohio State University Research Foundation, U. S. Army Signal Supply Agency Contract DA-36-039-SC-83874, March 1961.
19. B. McDonald and A. Goetzberger, *This Journal*, **109**, 141 (1962).
20. V. R. Evans, "The Corrosion and Oxidation of Metals," pp. 819-859, Edward Arnold Ltd., London (1960).

Gettering of Metallic Impurities from Planar Silicon Diodes

S. W. Ing, Jr.,¹ R. E. Morrison, L. L. Alt, and R. W. Aldrich¹

Semiconductor Department, General Electric Company, Electronics Park, Syracuse, New York

ABSTRACT

Experimental studies are presented in which reverse leakage currents in diffused silicon planar diodes are reduced by orders of magnitude via an intermediate temperature (800°-1000°C) gettering of metallic impurities which presumably cause excess leakage. Inorganic oxides having melting points below the gettering process temperature have been employed as the getters. Life test data on gettered diodes are also presented. The effectiveness of such gettering processes is further demonstrated by experiments in which radioactive copper is utilized as the diffused contaminant.

In the modern day manufacturing of diffused silicon devices, one or more gettering steps are usually incorporated in the process to prevent introduction of undesirable metal impurities into the junction region or to remove any metal impurities that may be already there. Goetzberger and Shockley (1) have shown that a number of fast diffusing metals, such as Cu, Fe, Mn, and Au, when introduced into silicon diodes can cause excess reverse leakage current below avalanche breakdown. This current varies directly with reverse voltage raised to the n th power where " n " was between 4 and 7. They attribute the cause of this rise to localized high field points which cause Zener tunneling current to flow. They have further demonstrated that the excess reverse current can be reduced considerably by gettering with phosphorus or boron silicate at temperatures of 1000°C and higher. In their case, the lower limit on the gettering temperature was governed mainly by the liquidus temperature of their gettering glasses as it was found that the formation of a low viscosity oxide mixture was essential for the process to be effective.

The purpose of our work was to investigate the possibility of effecting gettering at temperatures lower than those which have been reported, which would be of great practical interest, by using suitable inorganic oxide compositions that have lower liquidus points. Furthermore, this process would be applied to the planar type of diodes in which the

junctions terminate at the interface between the silicon and the thermally grown silicon dioxide.

The metal oxides and oxide mixtures used in this investigation as the gettering agents are listed along with their melting points, if known, in Table I. When one of these oxides is applied to the silicon wafer surface at elevated temperatures, one would expect some chemical reaction to occur which would incorporate silicon into the oxide, thus altering its liquidus point. Since the gettering treatments are carried out in an air ambient, the reaction products could therefore be considered as binary oxide mixtures of the silicon and the metal oxides. Only a few of these systems have been investigated in regard to their phase relationships. For example, in the lead oxide and silicon dioxide system, Geller and his co-workers (2) have found liquid-solid eutectics at 8, 15, and 30% silicon dioxide concentrations, all occurring within the temperature range of approximately 720°-740°C. For the boron trioxide and crystalline silicon dioxide system, Giellise and his co-workers (3) have presented a tentative phase diagram showing a continuous liquidus curve starting from pure silicon dioxide to pure boron oxide. It is therefore possible within a certain period of time from the start of the gettering process, to have the applied glass remain in its liquidus state, at or slightly above its initial melting point, while the concentration of the silicon in the glass is still low. A gettering temperature range of 800°-1000°C was then chosen. The metal impurities that diffuse via an interstitial mechanism should have sufficiently high

¹ Present address: Electronics Laboratory, General Electric Company, Electronics Park, Syracuse, New York.

Table I. Oxides and oxide mixtures used for gettering

Compound	B ₂ O ₃	B ₂ O ₃ -P ₂ O ₅	P ₂ O ₅	V ₂ O ₅	V ₂ O ₅ -BaO	Pb ₂ P ₂ O ₇	PbO
Melting point, °C	577	—	563	690	—	824	888

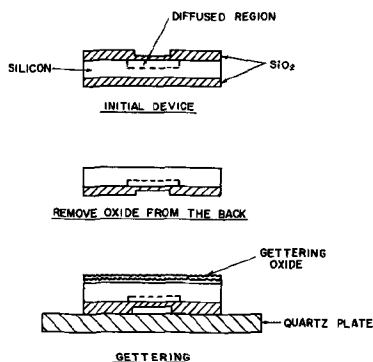


Fig. 1. Schematics of the procedure

diffusion rates at these temperatures to allow capture by the liquid oxides.

Experimental Procedure

In our experiments, 0.9 ohm-cm n-type silicon wafers approximately 9 mils thick, were used as the starting material. These wafers went through a standard process of steam oxidation, window cutting, boron predeposition, and final diffusion under oxidizing ambient. The oxide thicknesses were about 10,000Å and the junction depths were 7-8 μ . After diffusion, the wafer was cut into quarters, each quarter containing a number of diodes of 2-4 mm² area. One piece was retained as a control sample, and the other pieces were used for gettering.

All the oxides except V₂O₅ were applied by a paint-on technique using the oxides in a saturated solution, or slurry, in ethylene glycol monoethyl ether. The boron and phosphorus oxide mixture was prepared by mixing equal volumes of the saturated solutions of the individual oxides in ethylene glycol monoethyl ether at room temperature. The experimental procedure is depicted in Fig. 1. The thermal oxide which covered the junction area was not touched. The oxide on the back side of the wafer was removed, the gettering agent was applied, and the wafer was inserted into the furnace under an air ambient. Following the gettering period, which usually lasted around 30-60 min, the wafer was withdrawn from the furnace and air quenched. In the case of V₂O₅ gettering, the wafer was simply floated on top of the melt in a quartz crucible, with only the back side of the wafer contacting the melt. In a few runs BaO was added (in a ratio of 3-8, BaO-V₂O₅) to the V₂O₅ for the purpose of reducing creeping of the V₂O₅ onto the top surface of the wafer. In all cases, excepting those with P₂O₅ and Pb₂P₂O₇, the glasses formed could be easily removed by using suitable chemical etches. P₂O₅ and Pb₂P₂O₇ glasses were relatively difficult to etch chemically, so these were lapped off. Reverse bias and current measurements and life tests were then performed on the diodes.

Results and Discussion

The results, in general, showed considerable improvement in the reverse characteristics of the diodes gettered with the above mentioned oxides. The reverse leakage currents decreased by orders of magnitude and became much less voltage dependent.

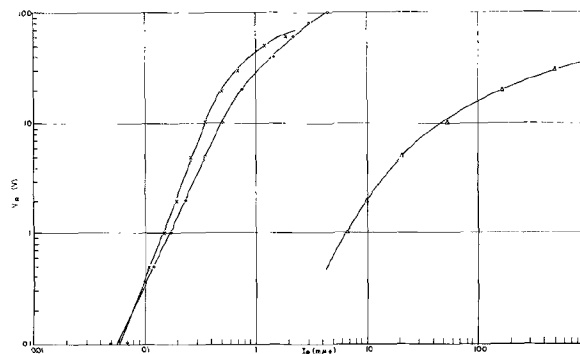


Fig. 2. Reverse bias characteristics of diodes gettered with boron oxide and boron-phosphorus oxide mixture. x, B₂O₃ 30 min, 900°C; o, B₂O₃-P₂O₅ 30 min, 900°C; Δ, ungettered.

I_R, the reverse current, became proportional to V_R, the reverse bias, raised to a power of 0.5 or less prior to the onset of avalanche multiplication condition. This reverse current and bias relationship is typical of space charge layer carrier generation phenomena (4). As a check on the possibility that the observed gettering might be independent of the presence of the oxides, some wafers were subjected to the entire process except no oxide was applied to the back side. No improvement in diode characteristics was observed.

Following are a number of curves which show the extent of gettering under various process conditions as reflected in the electrical characteristics of the diodes. Each curve represents measurements taken on one of the ten or so diodes on a wafer that has undergone the same treatments. Generally about 80% of the diodes on one single wafer show similar breakdown voltages, and the variations in reverse currents are within a factor of two. The major difference of a few of the diodes from the majority is their lower breakdown voltages. In Fig. 2, the current is plotted vs. the reverse voltage for diodes gettered with boron-oxide and with a boron and phosphorus oxide mixture at 900°C for 30 min. The characteristic of an ungettered diode also is shown here for comparison. The gettered devices show vast improvement over the ungettered device. The reduction in the current is especially pronounced at high biases. However, there is no significant difference here, prior to life test, between the two diodes gettered with different oxides.

In Fig. 3 we compare phosphorus pentoxide with the boron and phosphorus oxide mixture as getter. Again, we initially observe no real difference between the two; both show considerable improvement over the ungettered material.

In Fig. 4 the characteristics of diodes gettered with the boron and phosphorus oxide mixture for 30 min at 800°, 900°, and 1000°C are presented. If we focus our attention at the higher bias region, which is the region of greater interest, we see considerable improvement in the leakage current by going from 800° to 900°C. However, no appreciable gain is observed by increasing the gettering temperature to 1000°C.

A series of runs also were made to see the effect of the gettering time duration of the diode reverse

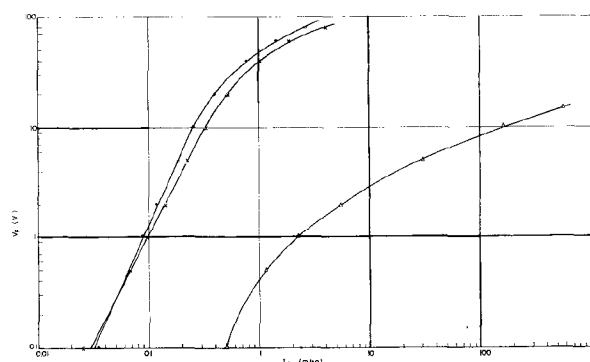


Fig. 3. Reverse bias characteristics of diodes gettered with phosphorus oxide and boron-phosphorus oxide mixture. x, P_2O_5 30 min, $900^\circ C$; o, $P_2O_5-B_2O_3$ 30 min, $900^\circ C$; Δ , ungettered.

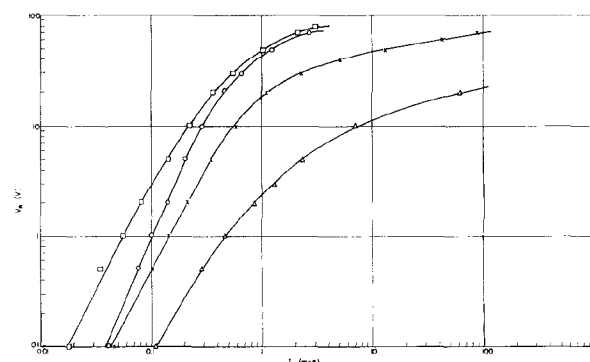


Fig. 4. Reverse bias characteristics of diodes gettered with boron-phosphorus oxide mixture at various temperatures. x, $B_2O_3-P_2O_5$ 30 min, $800^\circ C$; o, $B_2O_3-P_2O_5$ 30 min, $900^\circ C$; □, $B_2O_3-P_2O_5$ 30 min, $1000^\circ C$; Δ , ungettered.

current. Gettering was done at $800^\circ C$ for 60, 150, and 300 min using the boron, phosphorus oxide mixture. Figure 5 shows the reduction of the leakage current by increasing the period of gettering time from 60 to 150 min. However, a 300 min gettering period proves to be too long; all diodes showed soft characteristics and are not shown on this plot. Too long a heating time could cause extensive evaporation of the oxides which may seriously limit their gettering action and, in this case, apparently a reverse process took place after the gettering action had stopped during the latter half of the 300 min heating time.

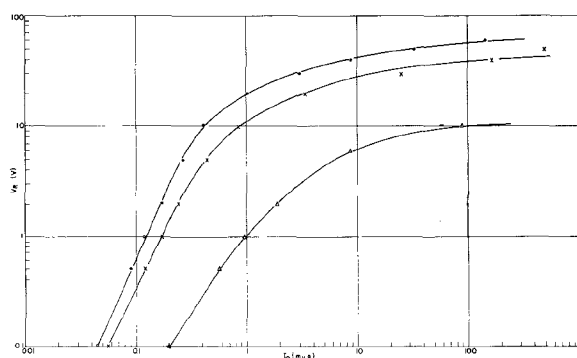


Fig. 5. Reverse bias characteristics of diodes gettered with boron-phosphorus oxide mixture for different periods. x, $B_2O_3-P_2O_5$ 60 min, $800^\circ C$; o, $B_2O_3-P_2O_5$ 150 min, $800^\circ C$; Δ , ungettered.

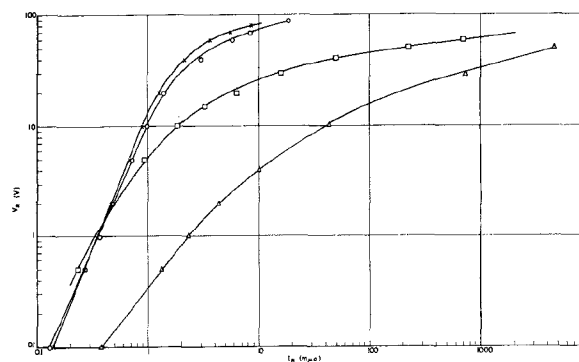


Fig. 6. Reverse bias characteristics of diodes gettered with various oxides. x, $Pb_2P_2O_7$ 30 min, $900^\circ C$; o, V_2O_5-BaO 30 min, $900^\circ C$; □, PbO 30 min, $900^\circ C$; Δ , ungettered.

Figure 6 shows the effect of gettering using $Pb_2P_2O_7$, V_2O_5-BaO mixture and PbO at $900^\circ C$. Again a vast decrease in leakage current is observed by gettering; however, PbO seems to be the least effective among all the oxides used.

We have seen so far the results prior to life testing. We can summarize the results by saying that all the oxides used in the experiment are effective and a gettering temperature of $900^\circ C$ and a time period of 30-60 min seems to be quite adequate. If conditions necessitate a lower temperature, $800^\circ C$ gettering can be used, although it is less effective. The limiting factors in using gettering temperatures lower than $800^\circ C$ can, perhaps, be itemized as follows: (a) higher oxide viscosity, (b) slower diffusion rate of the metal impurities, and (c) increased gettering time required, resulting in the depletion of oxide due to volatilization.

The gettered diodes were subjected to heat testing in room ambient at temperatures of 190° - $300^\circ C$ with or without reverse bias. All diodes showed good stability after many hundreds of hours of heating at $300^\circ C$, if no bias was applied. When a 50v reverse bias was applied during heat soaking at $190^\circ C$, with the exception of diodes gettered by P_2O_5 , and the $P_2O_5-B_2O_3$ mixture, all gettered diodes tend to fail after 50 or more hours. Some typical test results are shown in Table II. Each of the results shown represents a group of four to six diodes. At $300^\circ C$ the failure rate accelerated and became quite rapid. The reverse leakage current increase could be catastrophic. Heating to 200° - $300^\circ C$ for a few hours with the bias removed usually would restore these failed diodes, but they are subsequently even more susceptible to degradation. The failures are most probably due to some chemical interaction occurring in the thermal oxide and silicon interface region of the junction. The reversible nature of the failure strongly suggests ionic movements under the influence of a high electric field. These ionic species could have formed or introduced into the thermal oxide and silicon transition region during the gettering process. At the heat test temperature and high electric field ionic polarization could occur and gives rise to the formation of a silicon surface inversion layer. This proposed failure mechanism is just a conjecture. We have no direct evidence to substantiate it. However, diodes gettered with P_2O_5 seem to

Table II. Typical life test results of gettered diodes

Gettered with	Life test temperature, °C	Life test bias, v		0	20	Time, hr 60	150	330
B ₂ O ₃	300	0	$\frac{I_R^*}{V_B^{**}}$	0.54 80			0.11 75	
B ₂ O ₃	190	50	$\frac{I_R}{V_B}$	0.3 80			300 80	
Pb ₂ P ₂ O ₇	300	50	$\frac{I_R}{V_B}$	0.85 95	1200 100			
P ₂ O ₅	190	0	$\frac{I_R}{V_B}$	0.38 85				0.1 90
P ₂ O ₅	300	50	$\frac{I_R}{V_B}$	0.59 85		0.79 85		
B ₂ O ₃ + P ₂ O ₅	190	0	$\frac{I_R}{V_B}$	0.44 85				0.15 88
B ₂ O ₃ + P ₂ O ₅	300	0	$\frac{I_R}{V_R}$	0.35 82				0.24 82
B ₂ O ₃ + P ₂ O ₅	190	50	$\frac{I_R}{V_B}$	0.27 95				0.28 92
B ₂ O ₃ + P ₂ O ₅	300	50	$\frac{I_R}{V_B}$	0.90 83			0.36	6.4 81

* I_R (mA amp) measured at $V_R = 10$ v.** V_B (v) diode breakdown voltage.

be more stable. As shown in Table II, for a P₂O₅ gettered diode, slight degradation is observed after, for example, life tested at 300°C and 50v bias for 60 hr. Even more stable devices resulted from using the boron-phosphorus oxide mixture as the gettering agent. Here we see no change in leakage current

after soaking at 190°C for over 300 hr with 50v reverse bias applied. The diodes also stood up well after 150 hr at 300°C and 50v bias but started to degrade after over 300 hr. This test condition of 300°C air ambient and 50v bias could be overly severe. The heat dissipation at the junction itself would amount to a tenth of a watt or more under these conditions. Hence, the temperature at the junction could well substantially exceed that of the environment.

The oxide gettering action we have shown so far yields no quantitative measurements on the actual metal impurities depleted. Therefore, a radio tracer technique was used to obtain such data. Radio Cu⁶⁴ was used as the metal impurity and was plated onto the back side of the diode wafer followed by indiffusion at 600°-700°C. After the diffusion, the excess copper was removed and the wafer subjected to gettering in the same manner as described previously. Following the gettering and removing of the gettering oxide, a radioautogram was taken of the wafer. Radioactivity counting was usually taken before and after gettering to give indications of change in copper concentration. In Fig. 7 we have two pairs of radioautograms showing the initial and final copper distribution after gettering at 900°C for 1 hr using boron oxide alone and the boron and phosphorus oxide mixture. As is evident, the copper tends to concentrate in the boron diffused region. This is probably due to, first, enhanced copper solubility in the heavier doped p-region (5) and second, more dislocations and hence, more copper precipitation in the diffusion induced stress region first demonstrated by Queisser (6) and then by Prussin (7). The effectiveness of gettering is obvious. The remaining copper appears as dots, probably clusters of precipitates scattered within the diffused region.

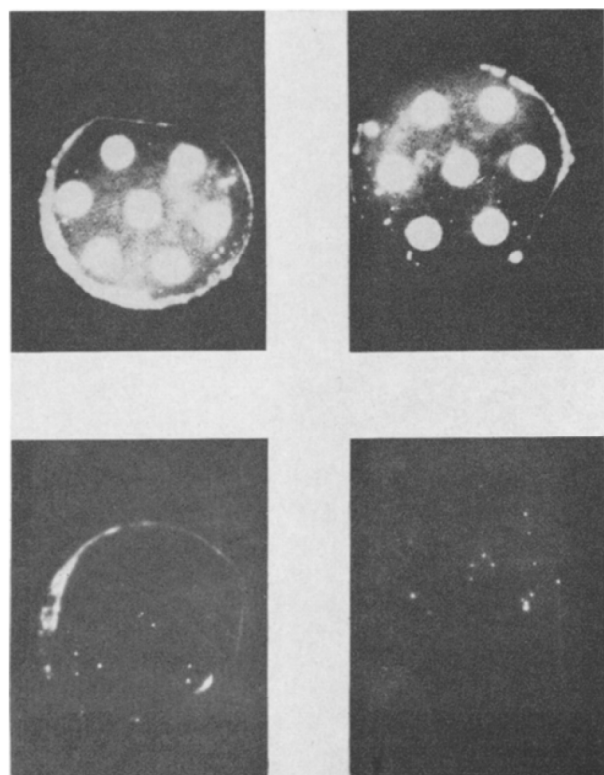


Fig. 7. (Upper and lower left) Before and after boron-phosphorus oxide mixture gettering of Cu⁶⁴ in silicon diodes. (Upper and lower right) Before and after boron oxide gettering of Cu⁶⁴ in silicon diodes.

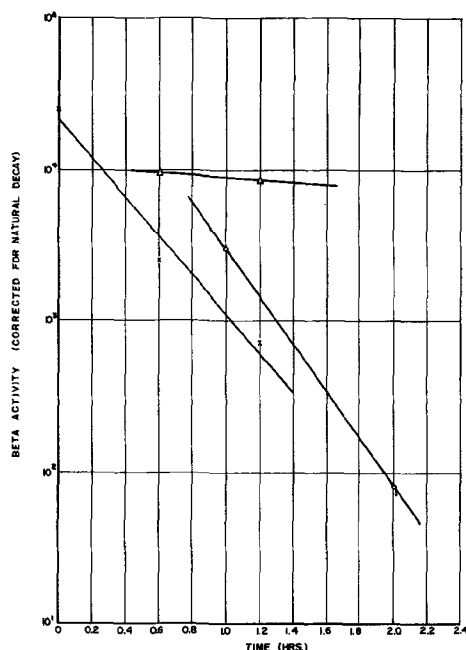


Fig. 8. Boron-phosphorus oxide mixture gettering rates of Cu^{64} in silicon diodes. x, Gettered with $\text{B}_2\text{O}_3\text{-P}_2\text{O}_5$ at 870°C ; o, gettered with $\text{B}_2\text{O}_3\text{-P}_2\text{O}_5$ at 1000°C ; Δ , ungettered, but heated in air at 870°C .

We have observed no significant difference in the results using the two different oxides. Some preliminary results on the gettering rate are shown in Fig. 8. Here we have plotted the log of the activity, which is proportional to the copper concentration, vs. gettering time duration at two different temperatures, 870° and 1000°C . The radioactivity plotted here refers to the β particle counting taken on the top surface where the planar diodes were located. For a first approximation we fit the points with straight lines, which is equivalent to assuming a first order depletion rate. A small positive temperature coefficient is apparent by comparing the slopes of these lines. We also have shown here the activities of the wafer before and after going through the heat cycle at

870°C without the gettering oxide applied. We see no significant change in the copper concentration level.

Conclusion

In conclusion, we have shown the feasibility of reducing the reverse leakage current of planar diodes by using suitable oxide gettering of metal impurities in the temperature range of $800^\circ\text{-}1000^\circ\text{C}$. The boron and phosphorus oxide mixture seems to be the outstanding gettering agent in that the gettered devices show good stability during life test. A radio tracer technique is shown to be a useful tool for studying the metal impurity distribution and the gettering kinetics.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1963 JOURNAL.

REFERENCES

1. A. Goetzberger and W. Shockley, *J. Appl. Phys.*, **31**, 1821 (1960).
2. R. F. Geller, A. S. Breamer, and E. N. Bunting, *J. Research Natl. Bur. Standards*, **13**, 243 (1934).
3. P. J. Gielisse, T. J. Rockett, T. S. Shevlin, and W. R. Foster, Ohio State University, Report No. 931-2, Contract No. AF33(616)-6509, Oct. 1959-Dec. 1959.
4. A complete treatment of this phenomena is given by C. T. Sah, R. N. Noyce, and W. Shockley, *Proc. IRE*, **45**, 1228, (1957), where further references to earlier work may also be found.
5. W. Shockley and J. L. Moll, *Phys. Rev.*, **119**, 1480, (1960).
6. H. J. Queisser, *Bull. Am. Phys. Soc.*, **6**, 106, (Mar. 1961); and H. J. Queisser, *J. Appl. Phys.*, **32**, 1776, (1961).
7. S. Prussin, *J. Appl. Phys.*, **32**, 1876 (1961).

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