

Metal Precipitates in Silicon p - n Junctions*

A. GOETZBERGER AND W. SHOCKLEY

Shockley Transistor Unit of Clevite Transistor, Mountain View, California

(Received May 24, 1960)

Metal precipitates in junctions were found to cause excess reverse current below avalanche breakdown, which is conjectured to be due to Zener tunneling at localized high-field points. This current varies as V^n where n is between 4 and 7. By a potential plotting method, it was shown that this excess current is not caused by a surface effect. Metal precipitates can be removed or prevented by "gettering" from surface layers. Metallic coatings and certain glassy oxide layers were investigated. Results indicate that layers of Ni and Zn have a limited gettering effect. Glassy layers, especially those of boron and phosphorus, have the greatest gettering effect.

A NUMBER of metals, such as Cu, Au, and Fe, have a strongly temperature-dependent solid solubility in silicon which causes supersaturation and formation of precipitates during the cooling cycle. Dash¹ observed precipitation of Cu preferentially on dislocations. The first part of this paper reports effects of precipitates on p - n junctions; the second part is concerned with methods of improving junctions by removing these precipitates by means of gettering.

EXPERIMENTS ON JUNCTIONS CONTAINING PRECIPITATES

Goetzberger and Shockley² found a localized current path through junctions that had been treated in a manner expected to produce metal precipitates. Phosphorus was diffused into p -type silicon slices of 0.04 ohm cm resistivity to a depth of approximately 6 μ . They were treated for 5 min in hydrofluoric acid, then nitrates of different metals were applied in aqueous solution to one of the pair of slices that were used for each experiment, the untreated slice serving as a control. After drying, both slices were heated for 60 min in H_2 at 1000°C, then cooled within 6 min to room temperature. Wax dots were placed on both slices and dice were etched by spraying with CP8 (5 parts concentrated HNO_3 , 3 parts concentrated HF) to produce diode chips.

The avalanche breakdown voltage was about 12 v. A large percentage of the treated diodes had a rounded or "soft" reverse characteristic caused by excess current below avalanche breakdown voltage. The control diodes that were made from a slice subjected to the same heat treatment were predominantly hard. Figure 1 shows a statistical evaluation of softness and hardness after treatment with different metals, each run consisting of at least 50 diodes. Diodes with more than 10 μ a reverse current at breakdown were defined as soft.

Evidence that the reverse current flowed at a localized spot was obtained by using a potential plotting method applied to one diode that had been softened by diffusion

of iron (Fig. 2). A constant reverse current was fed into the diode through a small wire contact. A second probe at fixed location was used as a voltage reference, and the voltage between it and a third movable probe was measured for an array of points spaced typically at 0.05 mm on the surface. (The potential probes were formed by passing a current pulse to obtain low impedance contacts.) From the sheet conductance of 1.0 mhos and the potential profile, it follows that all the reverse current of 200 μ a can be accounted for within experimental error at the localized point.

The reverse characteristic of this diode is given in Fig. 3. The -70° line shows a current that varies as $V^{5.5}$ where V is the reverse voltage. Since this soft current obeys the $V^{5.5}$ law to voltages as low as 0.8 v, it cannot be due to avalanche, and is conjectured to be due to Zener tunneling at localized high-field points caused by precipitates.

In general, diodes softened by processes expected to produce metal precipitates have soft currents which vary as V^n with n lying between 3 and 7. These characteristics are readily distinguishable from junctions having points of low voltage avalanche breakdown, which show a sharp upward bend on a plot like Fig. 3.²

Soft currents, which followed a power law of voltage,

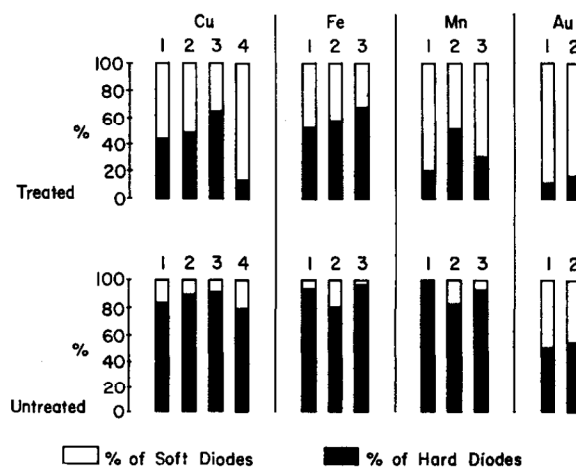


FIG. 1. Percentage of hard and soft diodes after treatment with different metals. (The number above each bar is the number of the test run.)

* Work sponsored by Air Force Cambridge Research Center.

¹ W. C. Dash, J. Appl. Phys. 27, 10, 1193 (1959).

² A. Goetzberger and W. Shockley, *Structure and Properties of Thin Films* (John Wiley & Sons, Inc., New York, 1959), pp. 298-301; Bull. Am. Phys. Soc. Ser. II, 4, 409 (1959).

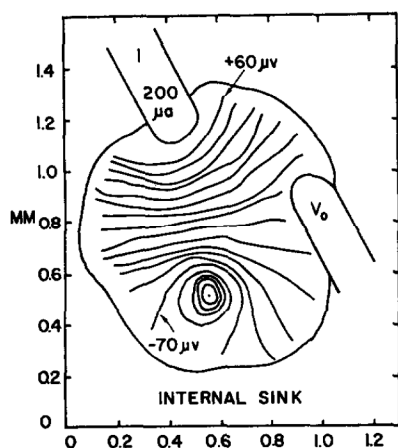


FIG. 2. Equipotential plot of iron diffused junction.

were also observed by Pell³ in germanium and Plummer⁴ in silicon. Both associated this current with a volume effect rather than a surface effect.

REMOVAL OF PRECIPITATES BY GETTERING

Because soft characteristics are undesirable in most devices, there is considerable interest in techniques which avoid formation of precipitates during the diffusion process.

One way of obtaining good junctions consists in excluding every trace of softening metals from the silicon. However, this is extremely difficult since in some cases a fraction of an atomic layer on a slice of silicon is sufficient to achieve saturation.

A more practical procedure is one which allows removal of metal precipitates during or after diffusion

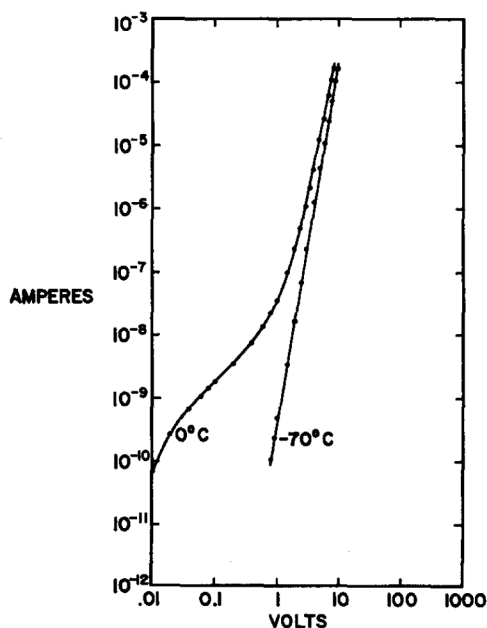


FIG. 3. Current-voltage characteristic of iron diffused junction.

³ E. M. Pell, J. Appl. Phys. **28**, 4, 459 (1956).

⁴ A. R. Plummer, J. Electronics and Control **V**, 5, 405 (1958).

by means of gettering.⁵ Two possible methods of gettering were investigated. One consisted of gettering by a thin layer of Zn or Ni on the surface; the other was gettering by a glassy layer of oxides. Only the second method proved satisfactory.

A. Gettering with Zn and Ni

This procedure was tried because it was found by Bemski and co-workers⁶ that coating silicon with Ni and heating it to temperatures of 1000°C or more was very effective in improving minority carrier lifetimes in the silicon. The reason for this effect is believed to be the gettering action of a liquid Ni-Si phase on the surface, due to a very low distribution coefficient of certain recombination centers. Since some of the metals which reduce lifetime in silicon also cause softness of characteristics, it was thought that this treatment might reduce softness. In addition to Ni, Zn was tried in our experiments because it had been found previously that Zn

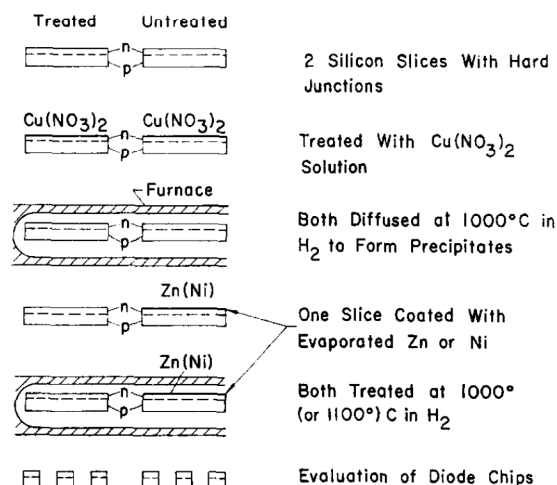


FIG. 4. Gettering experiment with Zn and Ni.

seemed to improve characteristics. The procedure is shown in Fig. 4.

Four identical silicon slices which contained originally hard junctions were used for each experiment. (Only two of them are represented in Fig. 4.) One of them was evaluated before treatment, the remaining three were coated with $\text{Cu}(\text{NO}_3)_2$ solution and subjected to heat treatment in order to form precipitates. One of these was coated with a layer of evaporated Ni and another with Zn, followed by 60 min heat treatment at 1000°C in hydrogen. Diode chips were then etched from each slice and the hardness evaluated. Again, characteristics with more than 10 μa reverse current at breakdown were defined as soft. The results of six experiments, shown in Fig. 5, indicate that both the Ni and the Zn treatments improve the junctions somewhat, but fail to restore the hardness present before treatment.

⁵ A. Goetzberger, Bull. Am. Phys. Soc. Ser. II, **5**, 160 (1960).

⁶ G. Bemski, Phys. Rev. **103**, 567 (1956).

Since there was some doubt whether the gettering temperature of 1000°C was high enough, the same test was repeated at 1100°C . Results were similar to those obtained at 1000°C .

B. Gettering with Oxide Layers

1. Predeposition Treatment

The second method of gettering studied was one which used oxide layers on the surface. It had been observed that junctions which were measured after predeposition with P_2O_5 or B_2O_3 vapors without further diffusion were predominantly hard. Therefore, it was concluded that the layer formed on the surface of the silicon and consisting of a glassy mixture of these oxides with SiO_2 might have gettering properties. A possible mechanism is shown in Fig. 6. Metal atoms diffuse from the precipitate within the space charge region to the surface where they react with the getter material by

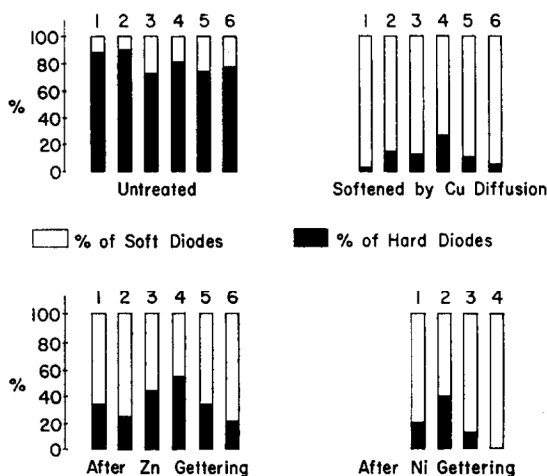


FIG. 5. Results of gettering with Zn and Ni (numbers again indicate number of test run).

formation of chemical compounds, such as phosphates or borates. Concentration of free metal on the surface will be extremely low, a condition favorable for gettering. Simultaneously with the diffusion of the metal atom, a vacancy has to diffuse from the precipitate to the surface in order to keep the volume constant. This process, which involves self-diffusion of silicon, may be of importance in limiting the rate and controlling the temperature dependence of the gettering effect.

In order to test the hypothesis that the glassy layers getter the softening impurities, silicon slices containing hard junctions like those in the preceding experiment were doped with Cu. Then they were subjected to another predeposition with P_2O_5 in dry nitrogen at 1050°C for 30 min. The results [Fig. 7(a)] show a strong gettering effect.

Soft diodes are not only obtained by metal doping, but also by a long diffusion at high temperatures, if the furnace chamber is not exceptionally clean. A 2-hr

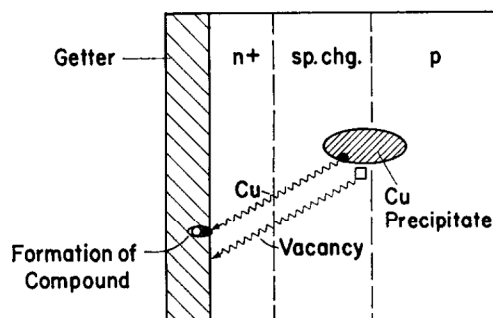


FIG. 6. Mechanism of oxide gettering.

diffusion at 1300°C usually yields 100% soft diodes. This type of softness, which is conjectured to result from ever-present metal impurities in the diffusion furnace, responds to the same gettering treatment, as can be seen in Fig. 7(b).

Figure 8 gives some information about time and temperature dependence of the gettering efficiency of P_2O_5 and B_2O_3 predeposits. In both cases, silicon slices which had been diffused for 2 hrs at 1300°C , and which contained 100% soft junctions, were used. The phosphorus oxide treatment was carried out in a two-temperature-zone furnace with a source temperature of 210°C . For the boron predeposit the silicon slices were enclosed in a platinum box together with a pure B_2O_3 source. (No gettering effect could be observed with a diluted source of 25% B_2O_3 and 75% SiO_2 .) Figure 8 shows that the phosphorus pentoxide seems to be effective at a slightly lower temperature than the boron oxide. The transition between hard and soft in the case of the phosphorus predeposit is not so abrupt as it appears, due to the arbitrary value of $10\ \mu\text{a}$, which was chosen as the definition of softness. The results of Fig. 8 are representative of only one set of experiments. Slight variations can be observed under different diffusion conditions.

2. Paint-on Treatment

Phosphorus and boron oxides can be applied to the silicon surface not only from the vapor phase, but also by the so-called "paint-on" technique.⁷ This procedure

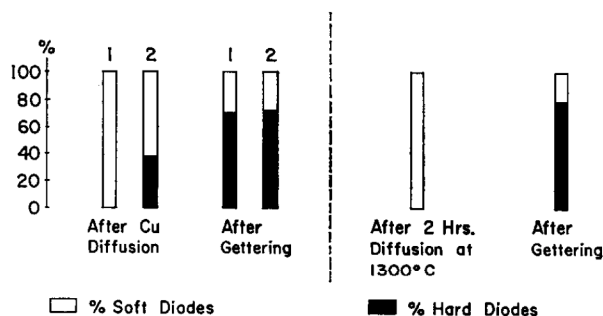


FIG. 7. (Left) P_2O_5 gettering on copper diffused junction. (Right) P_2O_5 gettering on junction softened by 1300°C diffusion.

⁷ H. E. Hughes, J. H. Wiley, and P. Zuk, *IRE Wescon Convention Record*, 1957; Part 3, Electron Devices; p. 80.

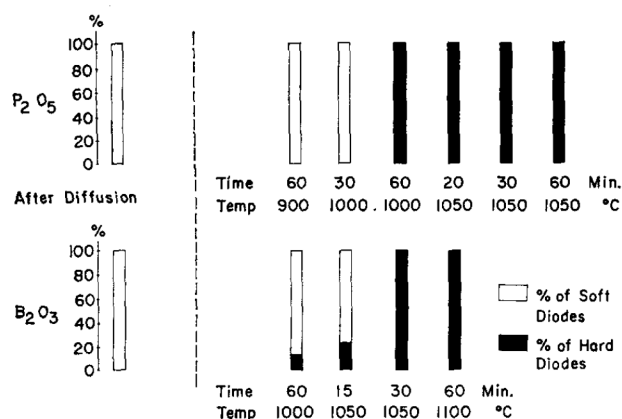


FIG. 8. Temperature and time dependence of P_2O_5 and B_2O_3 gettering.

has the advantage of using only one side of the slice for the gettering treatment, which leaves a highly doped layer on the silicon. It was tried on silicon slices of $150\ \mu$ thickness and also found effective. It works, however, only for a limited time at a high temperature (such as 1300°C) because the oxides tend to evaporate.

Sometimes it would be desirable to use a getter material that is not doping. Therefore a surface layer of PbO was tried for gettering. Results were promising, but the lead oxide glass could not be removed after gettering by any known etching treatment.

DISCUSSION OF RESULTS

The temperature dependence of gettering indicates that the diffusion of the precipitated metals to the surface is not the rate limiting factor, since the diffusion constant of all metals which were found to soften junctions is in the range of 10^{-6} to $10^{-5}\ \text{cm}^2/\text{sec}$, and varies little with temperature.⁸ Two other processes could cause the temperature threshold. One is the vacancy diffusion as already mentioned. The other is the temperature dependence of the chemical reactions on the surface, which lead to trapping of the metal atoms. The second possibility is suggested by the fact that the dependence of phosphorus oxide gettering on temperature is not the same as that of boron oxide gettering (Fig. 8).

Silicon dioxide itself has no effect on precipitates. This is plausible because of the strong bond between oxygen and silicon, which prevents formation of compounds with other elements. It was observed that gettering occurred only as long as the oxide glass on the surface was liquid. This can be understood by considering that there is always some oxidation of the silicon going on. As soon as the coating solidifies, a very thin

layer of silicon dioxide will grow on the surface of the silicon and prevent further gettering.

No detailed investigation has been made on the oxide gettering effect on lifetime. There should be, however, an improvement of lifetime. This was verified by a few experiments on transistors which showed a considerable increase in amplification after gettering treatment.

CONCLUSIONS

Softness of characteristics with current proportional to V^n was found to be a reversible phenomenon. It can be induced by diffusion and precipitation of certain metals in silicon. These metals can be removed or prevented by a surface layer of either boron oxide or phosphorus pentoxide on at least one side of a silicon slice. Figure 9 shows three different methods of producing

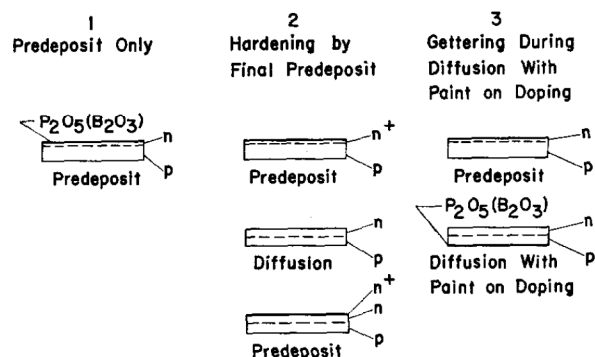


FIG. 9. Procedures for obtaining hard junctions.

hard junctions. Method 1 consists of a predeposit step only. Gettering and doping is done with the same surface layer. Method 2, which is important for deep junctions, consists of predeposition, diffusion and another predeposition. Finally, in method 3, a slice which has been predeposited on one side can be diffused while the other side is coated with paint-on doping.

Gettering is very easily achieved for all those devices which require a heavily doped surface layer. These can be degenerate layers on diodes for ohmic contacts or emitters of diffused transistors. The diffusion of this layer, which is usually the last step, can be designed to include the gettering effect.

ACKNOWLEDGMENTS

We would like to acknowledge the cooperation of Dr. Hans Wagner who designed some of the experimental apparatus, and Charles Stephens who made many of the electrical measurements. We also are indebted to B. McDonald, N. Zetterquist, and M. Lichtenstein for carrying out the diffusions.

⁸ F. M. Smits, *Ergeb. exak. Naturw.* **31**, 167 (1959).