

on the heating curve. This is exceedingly difficult to explain. One is therefore forced to look for less obvious reasons such as possible phase changes in the system or the excitation of an impurity in the material. A brief review of the literature given below may be of interest at this point.

1. An anomalous vapor pressure curve has been reported for cuprous oxide (7, 8), because of the formation of a eutectic with cupric oxide. The vapor pressure of oxygen in equilibrium with liquid Cu_2O at 1230°C (mp of Cu_2O) is 0.6 Torr. This vapor pressure increases to 402 Torr in cooling to 1080°C ($\text{CuO-Cu}_2\text{O}$ eutectic). Since the observed emission of L_2 is in the range of $1125^\circ\text{-}975^\circ\text{C}$, this emission may in some cases be related to the $\text{CuO-Cu}_2\text{O}$ eutectic at 1080°C , since it is known that CuO is present at least on the surface of the melt.

2. A rapid cooling rate of over 100°C per min is certainly a nonequilibrium condition, which may under these circumstances allow electronic transitions to occur which might otherwise be forbidden (9, 10).

3. Differential thermal analysis is indicated to explore the region $400^\circ\text{-}1300^\circ\text{C}$ to correlate light emission with perhaps extremely minute changes in the localized rate of cooling. No high-temperature phase changes have been reported for Cu_2O . However, crystallographic changes between 25° and 400°C have been reported (11) for cuprous oxide and similar changes for cuprous chloride (12).

4. The photoconductivity of Cu_2O is very complex (13), a maximum occurring at 0.57μ but complicated by "steps" in the absorption edge due to multiple level transitions, particularly in the yellow and green series of exciton absorption spectra (14) at 77.3°K . It is not known how this might affect the results observed.

In conclusion, it may be said that more precise measurements of the radiation observed will be required

to resolve the exact nature of this luminescence. This may be rather difficult, in view of the transient as well as high-temperature nature of the phenomena.

Acknowledgments

The author is pleased to acknowledge the technical discussions of Dr. P. N. Russell and Dr. R. H. McFee. Interpretations of the cinespectrograms by Mr. Carleton W. Clench are greatly appreciated.

Manuscript received Oct. 13, 1964.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1965 JOURNAL.

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Poisoning and Gettering Effects in Silicon Junctions

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ABSTRACT

A study was made to obtain an understanding of the factors involved in the "poisoning" phenomena which are responsible for high reverse currents in silicon junctions. A tentative model has been proposed which describes the conditions by which fast diffusing metal impurities can precipitate within junction regions under certain high-temperature ambients and yet not under others. Oxygen appears to be a significant factor which can control the degree and location of such metal precipitation. The role of oxygen was investigated in its relation to impurities and defects in silicon. Its importance was demonstrated by copper-oxygen reactions, oxygen tie up complexing to form SiO_4^{+} donor states, and by the effect of induced dislocations.

Considerable effort has been applied to the study of soft reverse characteristics of p-n junctions as indicated by excess reverse current below their normal avalanche breakdown voltage. The origin of this high leakage current is believed to be localized high electric fields caused by precipitated metal particles within the junction region. Goetzberger and Shockley (1,2) have shown that metals with temperature dependent solubilities in silicon, such as Cu and Fe, can form precipitates through which current flows by Zener tunneling as a result of the high fields. However, certain diffusion processes do yield devices which have good electrical characteristics whereas other high-temperature processes cause degradation of junctions. Prior to this work no explanation as to why and how these precipitates occur in the bulk and junction regions of Si has been offered. As these undesired impurities are introduced into silicon to some degree by all such processes, there must be some controlling factors which reduce or prevent these impurities from collecting in

junction regions in some cases but not in others. It is the purpose of this study to investigate those conditions which lead to the poisoning phenomenon and to establish a tentative model by which such precipitates locate in bulk silicon.

Previous observations.—It has been observed that diffused p-n-p structures as formed by Ga sealed-tube techniques yield "hard" breakdown (i.e., devices which show negligible poisoning effects but exhibit avalanche breakdown characteristics). Subsequent oxidation procedures cause these reverse characteristics to become "soft" or poisoned. Typical characteristics are shown in Fig. 1.¹ Later phosphorus diffusion generally causes a poisoned unit to return to its original characteristics. The following discussion of the effects of each of these

¹ All devices were surface contoured to confine the avalanche regions to the body rather than the surface of the device. Further information concerning this technique can be found in a paper by R. L. Davies and F. E. Gentry entitled, "Control of Electric Fields at the Surface of p-n Junctions," *IEEE Transactions on Electron Devices*, July, 1964.

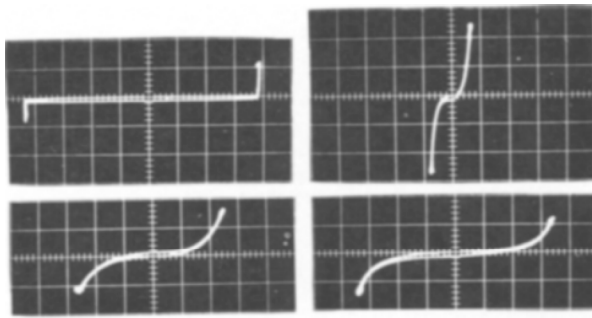


Fig. 1. Typical reverse characteristics of Ga diffused p-n-p junctions showing relative effect of cooling rate exposure to oxygen ambient at 1200°C: Vertical axis 5 ma/div; Horizontal axis 200 v/div. (a) (top left) as diffused; (b) (top right) furnace cool, 250°C/hr; (c) (bottom left) slow cool, 15°C/hr; (d) (bottom right) quenched.

three high-temperature operations results in a model which describes mechanisms that affect precipitation of these impurities in junction regions.

The formation of p-n-p structures by the normal sealed tube technique employs a Ga source along with silicon wafers which are sealed in a quartz capsule and back filled with argon through a liquid nitrogen trap. Avalanche-type electrical characteristics are ascribed to three possible effects. (A) The system is clean, free of poisoning impurities; (B) simple, glassy phase gettering occurs on the silicon surface; (C) fast diffusing impurities are removed by surface reactions which occur due to a lower partial pressure of oxygen in the sealed tube. In practice the first two are not probable. Deliberately poisoned Ga p-n-p structures, sealed in argon and heat-treated without a Ga source, are brought back to their original sharp characteristics with a significant increase in minority carrier lifetime. As no liquid phase is present, some other mechanism than glassy phase gettering must take place. This is probably the same means by which good p-n-p structures are originally formed. At the diffusion temperature (1250°C), metallic impurities are considered to be present from the source, quartz, gas ambient and on or in the silicon. The solid solubility of these impurities in silicon will be in equilibrium with phases present (such as oxides or gas) and dependent on temperature. On cooling, precipitation of these metallic impurities can occur because of decreasing solubility. A driving force to the surface is necessary to prevent precipitation in the vicinity of the junction. Such surface reactions can take place under a low partial pressure of oxygen by forming stable compounds of an oxygen complex. It has been shown by Schwuttke (3) that impurities such as copper will locate preferentially at regions of high oxygen concentration. This migration of residual oxygen in the silicon toward the surface would be a sufficient driving force for the removal of these fast diffusing impurities.

Under conditions of open-tube oxidation, silicon is exposed to temperatures 1100°-1250°C under wet or dry oxygen ambient to form an oxide phase on the silicon surface. Simultaneously, oxygen diffuses into the silicon along with undesired impurities. On cooling, precipitation of these impurities will occur at structural defects in the bulk with the size and location of the precipitates governed to some degree by the cooling rate. Sites of high oxygen concentrations can be formed in the bulk, thus preventing the mechanism of transport of fast diffusing impurities to the surface.

In fabricating p-n-p-n devices, phosphorus diffusion of the n-type emitter junctions often will restore p-n-p units which have been previously poisoned by the oxidation-mask step. In this two-step phosphorus diffusion process, first a phosphorus-silicate glass is formed under nitrogen or oxygen. Here an apparent liquid phase gettering effect (1) takes place. Normally, after this

first predeposition step, the glass formed is removed prior to a higher temperature diffusion anneal under oxygen. It can be assumed that under these conditions liquid phase gettering is not present but rather some other mechanism is responsible for the prevention of downgrading. This might be explained by high surface doping concentrations which strain the lattice and thereby form dislocations at the surface. Prussin (4) and Quisser (5) have shown that the stress introduced by solute contraction of phosphorus and boron in silicon is sufficient to generate dislocations. With these dislocations present, a "sink" can be formed, trapping fast diffusing impurities as "atmospheres" of the dislocations or by complexing with oxygen in these regions.

A poisoning model.—The model suggests that a controlling relationship exists between the gas ambient (particularly oxygen) and the type of diffused donor or acceptor impurity in silicon. It appears that the degree and location of such precipitation of fast diffusing metal impurities is influenced by the oxygen movement in the silicon. Clustering or precipitation of these impurities will occur at sites of high oxygen concentration, forming oxygen complexes and thus reducing the metal impurity level in other regions of the silicon. Oxygen will form atmospheres around diffusion induced dislocations thus depleting adjacent areas of oxygen and metallic impurities. Considerable evidence has been obtained to support this concept. These experiments have been based on copper-oxygen reactions, oxygen complexing to form SiO_4^{+} donor states and surface induced dislocations.

Experimental

In an effort to determine the source of contamination, various parameters of the open tube systems were evaluated. Ga-diffused p-n-p wafers were chosen for this initial study. These structures offered good initial reverse avalanche-type characteristics which are sensitive to the poisoning phenomena.

Gallium diffused p-n-p structures, which were formed in chemically polished 20-22 ohm-cm n-type Si, generally had a junction depth of 3 mils and a base region of 3 mils so that avalanche voltages of 700-900v were obtained. Wafers were pelletized to a diameter of 0.640 in. and subsequently edge beveled to a 6° angle to eliminate surface effects. In all tests only avalanche type p-n-p wafers were selected for evaluation. Cleaning prior to heat-treatments were kept the same for all tests, except when specifically altered to study the effect of different cleaning cycles. This standard cleaning consisted of hot solvents, hot alkaline cleaning; $\text{HF}:\text{HNO}_3$ etch modified with iodine, and HNO_3 boil. Each step was followed by a large number of deionized water rinses.

From these initial experiments it was established that poisoning of the reverse characteristics of Ga p-n-p's could be accomplished at temperatures greater than 700°C under an oxygen ambient. With increasing temperatures, up 1250°C, there appears to be no significant correlation between temperature and the degree of electrical characteristic softening. This effect is observed regardless of prior pellet cleaning treatments and special care observed to prevent contamination by the furnace and the quartz tube, the latter being coated with a sodium-silicate glass to form a gettering sink on the surface. The use of an ultra-pure ambient oxygen did indicate some improvement in reverse currents.

Under a given set of experimental conditions, cooling rate of the p-n-p structures from 1250°C in oxygen did show pronounced effects in the degree of softening observed. Typically, a quenching rate such as 500°C/min in an oxygen ambient causes the least degree of poisoning whereas a furnace cool of 250°C/hr from 1250° to 900°C resulted in the highest degree of poisoning. By approaching equilibrium conditions with a cooling rate of 3-7°C/hr from 1250° to 900°C, harder avalanche breakdowns resulted than the furnace cool.

These typical reverse characteristics are shown in Fig. 1. Interrupted cooling was carried out by furnace cooling from 1250° to 1000°C and holding for 15 hr, then moderately quenched to room temperature by pulling the pellets out of the furnace slowly. The purpose of this experiment was to form SiO_2 precipitates as described by Kaiser (6); these precipitates should serve as complexing sites for metallic impurities. This process did result in considerable improvement over the normal furnace cool with reverse characteristics similar to that obtained by rapid quenching.

The most significant parameter was that effect observed by different gas ambients. No downgrading resulted at any temperature up to 1200°C when exposed to an argon ambient and allowed to furnace cool. On quenching some small degree of softening occurred. From these results it was felt that downgraded units could be "gettered" back under these conditions. Such p-n-p units obtained from various conditions of heat-treatment were sealed in a quartz ampoule under argon, heated at 1200°C for 1 hr, and allowed to furnace cool. In every case avalanche type characteristics were obtained with voltage 10-20% less than the original values. Lifetime values were increased by a factor of two to four above the initial values immediately following diffusion (hereafter defined as "as diffused"). Poisoning was also prevented by exposure of the p-n-p's in a hydrogen ambient at 1000-1100°C. However, electrical characteristics previously softened by oxidation treatments were severely poisoned on exposure to hydrogen. Under nitrogen at temperatures above 800°C, significant softening occurred.

Effect of Oxygen with Impurities and Defects in Silicon

The results from preliminary experiments indicated the oxide phase and/or oxygen ambient have some influence in the transport mechanism of impurities in Si. Motivated by these results, further investigations were made to determine the role of oxygen and its relation to impurities and defects in Si. In these experiments the behavior of oxygen was evaluated by converting the dissolved oxygen into SiO_4^{+} donor states. The effects of diffused Cu and surface induced dislocations during oxygen diffusion and the subsequent effect on this oxygen-formed donor level was the basis of evaluation.

Oxygen complex (SiO_4^{+}).—Oxygen when diffused into Si can form donor states under suitable time and temperature conditions (7). These donor states, SiO_4^{+} , appear to form by association of groups of four oxygen atoms with one Si atom at a temperature of 450°C and reach a maximum level in about seventy hours. The degree to which the donor level will form is dependent on the dissolved oxygen. Logan and Peters (8) report the maximum solubility of oxygen in Si at 1250°C to be 3×10^{17} at./cm³, which offers a maximum donor level of 1×10^{15} /cm³ (8).

Experimentally, oxygen was diffused into polished p-type Si slices of 30-100 ohm-cm resistivity (net impurity concentration less than 3×10^{14} at./cm³). One half of this lot was sealed in a quartz ampoule under argon, and the other half was used as a control lot. In the sealed tube, a portion of the slices had the oxide removed, and the other half the oxide was left intact. These were heat treated at 1250°C for the same periods of time as they were originally oxygen diffused, i.e., 30 min to 3 hr. After this heat-treatment they were annealed at 450°C for 72 hr along with control slices which were not heat treated previously in argon.

From microscopic examination of stained cross sections, n-type layers were observed on the control slices to depths up to 1.5 mils depending on resistivity of the starting material. Those slices which were argon heat-treated with the oxide removed did not show any conversion. Silicon with the oxide left on converted, but to a lesser degree.

This effect was also observed when cooling rates that approached equilibrium conditions were used

following open tube oxidation. In an earlier investigation, we had found that cooling rates of 3-15°C/hr, from 1250° to 900°C, prevented the formation of SiO_4^{+} complexes. From these results it was postulated that this cooling rate would permit oxygen to form stable precipitates (SiO_2) or possibly diffuse to the surface of the slice. Under these conditions, therefore, the oxygen is tied up or reduced to level below which the conversion to donors is detectable.

Role of copper and oxygen.—The relationship between oxygen and the poisoning impurity should be determined. It appears that some residual oxygen is required to form favorable sites for nucleation and precipitation of such impurities away from the junction region but near or at the surface. The presence of an oxide phase on Si (always prevalent under an oxidizing ambient) would allow such precipitation to occur internally within the Si at many possible structural defect sites. The size of such precipitates would be governed by the precipitation kinetics of the species involved.

Some idea of these kinetics may be gleaned by examining the effects of Cu and oxygen such as offered by the investigations of Schwuttke (3). Results from that study show Cu to precipitate at regions of high oxygen concentrations with the possible formation of copper-oxygen complexes. It was also shown that dissolved oxygen will form atmospheres around dislocations thereby depleting adjacent areas of oxygen. Therefore, the presence of high concentrations of diffused oxygen should be a favorable location for the precipitation of impurities such as Cu during cooling.

As the normal impurity level of a species such as Cu is too low to be resolved by infrared examination, Cu was diffused into Si to decorate dislocation (9) sites with and without diffused oxygen. By observing the degree of decoration, as to size and shape, and to the level at which it occurs, a correlation with diffused oxygen appeared possible.

Chemically polished 20 ohm-cm n-type Si was oxygen diffused at 1250°C with a maximum surface concentration of 3×10^{17} at./cm³. The time of diffusion was adjusted so that complementary error function gradient of probable oxygen would result in a level $\sim 1 \times 10^{14}$ at./cm³ at a distance of three mils from the surface. A shallower diffusion was also made to the same level one mil from the surface. Along with controls containing only residual oxygen, Cu was diffused at 900°C for 10 min and rapidly quenched to room temperature.

By polishing in 0.2 mil increments from the surface and examining the slices with infrared, Cu was found to be precipitated in the high oxygen concentration regions near the surface. Unlike the control slices which showed fine dispersion of decorated dislocation tails, the samples containing oxygen were decorated by copper in the form of star-like clusters. This is similar to that observed by Schwuttke.

Effect of dislocation traps.—Realizing the effect of dislocations as trapping sites for oxygen and impurities such as copper, it was felt that such a site, if it can be introduced at the surface during diffusion, would offer a sink for fast diffusing impurities. The effect of cold working, introducing a stress, and subsequent heat-treatment to elevated temperatures would result in the formation of dislocations. Such line defects must be terminated, either by a surface, a grain boundary, or they may form closed loops. We could expect that in single crystals they would either propagate through the crystal, or form a loop with one surface. If such terminated loops could be produced at the surface, trapping at elevated temperatures of these impurities with an affinity for forming "atmospheres" with dislocations would appear possible.

It is known that a certain amount of damage is introduced into the surface of Si by impact loading, resulting in a stressed surface condition. On heating to some specific temperature, this stress will be re-

lied with some resultant plastic deformation and subsequent formation of dislocations. Beveled Ga-diffused p-n-p pellets were stressed in this manner by sandblasting the surfaces lightly with a fine grit of 10μ size. Alternate surfaces and both surfaces of beveled pellets were sandblasted to evaluate directional effects of gettering. These units, along with control pellets were exposed to the standard oxidizing conditions of 1200°C for 30 min and furnace cooled. Etching the pellets first in HF to remove the oxide followed by 20 sec in CP-6 modified with iodine was sufficient to obtain the original avalanche characteristics on all the sandblasted units, regardless of the side on which the dislocations were introduced. Control pellets were badly downgraded.

Further experiments were made under longer oxidizing conditions up to 5 hr at 1250°C , always resulting in unpoisoned units. If the sandblasted pellets were quenched very rapidly from any of the oxidizing conditions, downgraded characteristics were obtained. However, reheating at 1200°C in oxygen for 30 min and furnace cooling restored the original electrical characteristics.

To evaluate trapping ability of the introduced dislocation "sponge" at the surface, Ga diffused p-n-p wafers were Cu diffused at temperatures of 900°C - 1200°C under oxygen and furnace cooled. No poisoning occurred with those pellets having surfaces in a lapped or sandblasted condition. By infrared examination, Cu precipitation effects could not be observed whereas the control slices always showed a large degree of either finely dispersed or gross precipitates in the crystal. Quenching of Cu diffused p-n-p wafers from 900°C - 1200°C under oxygen always resulted in severely poisoned units. Fine dispersed decorated dislocations were always present in the crystal and subsequent removal of this precipitation was accomplished to a large degree by reheat-treating at 1200°C followed by a furnace cool.

The rapid mobility of copper was first demonstrated by the following experiment: One side of a p-n-p wafer was chemically polished and the other side was finely sandblasted. Then drops of CuNO_3 solution were placed on the polished side with care being exercised to keep the sandblasted side free of copper. Next the slice was heat treated in oxygen at 1000°C for 30 min and quenched at a rate of $500^\circ\text{C}/\text{min}$. No downgrading of the reverse characteristics resulted. Moreover, after chemically polishing the sandblasted side, no copper precipitation was observable by infrared examination. However, p-n-p slices that were chemically polished on both sides and subjected to the same process had electrical characteristics which were badly softened and also showed heavy copper precipitation throughout the slices.

Surface induced dislocations on copper and oxygen.—It has been shown in this study that surface induced dislocations have a definite effect in preventing the downgrading phenomena, both in the formation and oxidation of p-n-p units. Copper decoration and infrared examination showed that impurities such as Cu are removed to a very significant degree by dislocation effects. However, it is possible that oxygen also contributes to this mechanism by forming atmospheres around these dislocations sites at the surface.

Oxygen was diffused into p-type Si having chemically polished, sandblasted and lapped surfaces with resistivities of 30, 54, 63, and 100 ohm-cm for 3 hr at 1250°C under wet O_2 . One lot was allowed to furnace cool ($250^\circ\text{C}/\text{hr}$) and the second lot was quenched to room temperature. After removing the oxide, both lots were annealed at 450°C for 84 hr. These were cross sectioned and stained to reveal any n-type conversion caused by oxygen-silicon interaction to form SiO_4^+ . These results are illustrated in Fig. 2. Typically, n-layers were formed in the polished wafers, in some cases with a thin p-layer at the surface. In the lapped and sandblasted wafers, a thin 0.1-0.2 mil but nonuni-



Fig. 2. Typical effect of various surface treatments on the formation of the SiO_4^+ complex from oxygen diffused into 54 ohm-cm p-type Si at 1250°C for 3 hr, $250^\circ\text{C}/\text{hr}$ cooling rate; after 72 hr anneal at 450°C ; beveled X-section depth magnified 10X. Microscope 60X.(a) Chemically polished surface.

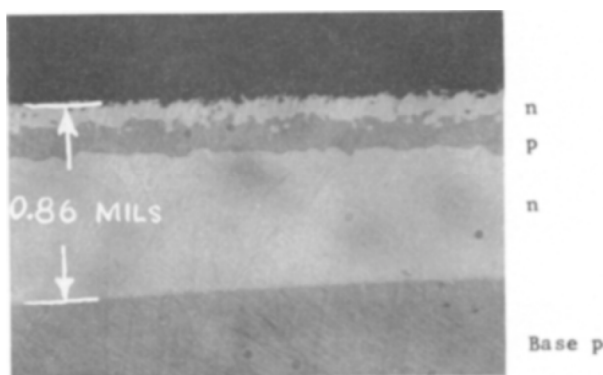


Fig. 2b. Lapped surface

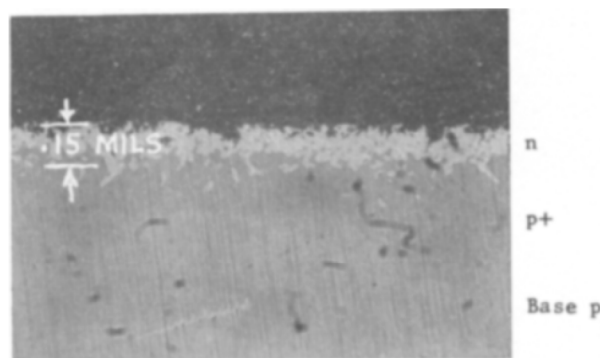


Fig. 2c. Sand blasted surface

form n-layer formed at the surface. This thin surface n-region was delineated by a p-type layer and another deeper n-region. Only a p-region more highly doped than the base was observed under the shallow n-surface layer in the sandblasted samples. In the resistivity range tested, no significant difference was observed between the type of structure formed by quenching or furnace cooling. By re-annealing at 575°C for 20 hr, the deep n-type conversion layers formed in the polished and lapped slices were removed. Under these conditions, the SiO_4^+ complex is disassociated. The thin n-surface layer on the lapped and sandblasted slices could not be annealed out at this temperature.

The previous experiments were repeated except that Cu was diffused into the oxidized Si prior to annealing at 450°C . The diffusion of Cu was carried out under two temperature conditions; one at 900°C for 15 min and another at 1200°C for 20 min, to obtain different copper solute levels in the Si. A sig-

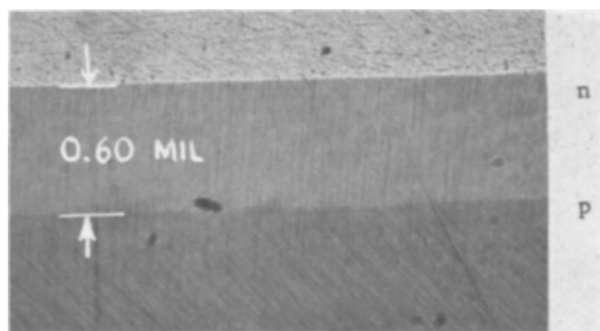


Fig. 3. Effect of Cu diffusion on the formation of the SiO_4^+ donor level in 54 ohm-cm p-type Si; beveled X-section depth magnified 10X; microscope 60X. (a) Typical n-layer formed by diffused oxygen.

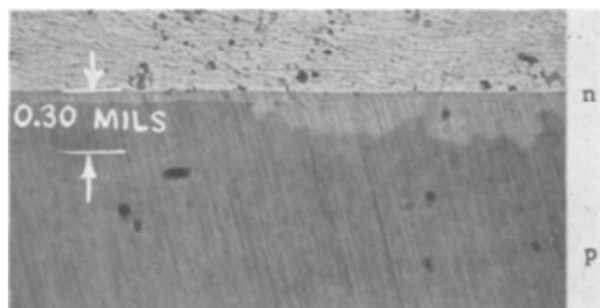


Fig. 3b. After Cu diffusion, 1200°C, furnace cool

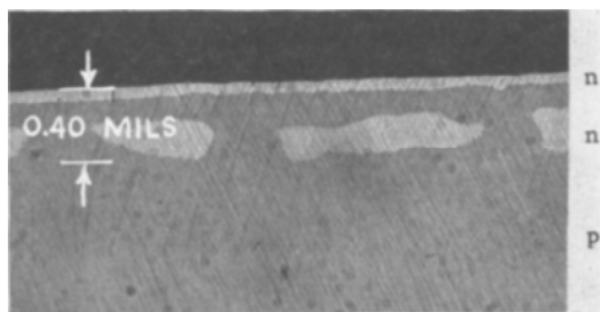


Fig. 3c. After Cu diffusion, 1200°C, quenched

nificant effect of Cu was observed in the donor formation after annealing at 450°C.

Typical results are shown in photomicrographs of Fig. 3. Directly after Cu diffusion from 1200°C, both quenched and furnace cooled polished slices showed an n-layer ~ 0.1 mil deep not observed on slices diffused with Cu at 900°C. After annealing at 450°C, n-layers formed on polished control slices (no Cu) and were partially eliminated on those which were Cu diffused. The effect was more pronounced when the Cu was quenched from diffusion temperatures. No significant effect of Cu on the oxygen formed donor level was found between sandblasted and lapped wafers as compared to polished control slices.

Oxygen-transport concept.—The concept of fast diffusing impurities locating at the silicon surface during nonoxidizing heat-treatments was further tested qualitatively. Wafers of 20 ohm-cm n-type silicon were prepared in three lots having chemically polished, lapped, and sandblasted surface finishes. These were oxidized in wet O_2 , forming 12,000Å of oxide on their surfaces. The oxide was removed from one half of each lot and, along with control wafers which were not previously oxidized, they were Ga diffused in the standard sealed tube process. Typically, p-n-p junctions formed through the oxide on the polished slices showed downgraded reverse characteristics. Those formed without an oxide present had hard break-

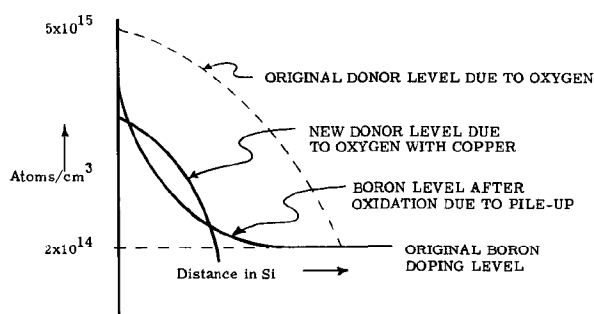


Fig. 4. Concentration profile diagram showing probable effect of Cu on the donor level (formed by oxygen).

downs, but the breakdown voltages were slightly less than the standard control slices. Sandblasted and lapped wafers with the oxide left on showed the same hard avalanche voltage breakdown as the control slices; whereas, those units with sandblasted surfaces from which the oxide had been removed, showed slightly higher voltages.

Discussion

The purpose of this investigation was to show that a relationship exists between oxygen, the oxide phase, and fast diffusing metal impurities in terms of both the degree and location of metallic precipitation in silicon. The effects of Cu used as an example in these experiments does not necessarily indicate that other fast diffusing metal impurities behave in the same manner. Dash (10) has shown that Au does not offer any observable precipitation. The precipitation kinetics of other metals such as Fe and Ni can be different than that of Cu. However, results have been obtained here which show that such precipitation in the bulk can be effectively prevented without glassy-phase surface gettering. The experiments with Cu and its effects in repressing the SiO_4^+ donor complex indicates ion-pairing as a possible mechanism. The SiO_4^+ donors formed as a result of diffused oxygen can be used as a sensitive measure of the oxygen level and can indicate effectively changes that take place within the silicon.

The effect of Cu on oxygen donor formation on chemically polished slices may be explained as follows. From photomicrographs of Fig. 2a and 3a, we can see the typical donor layer which is formed by oxygen conversion with no added Cu present. In some cases a p-layer has formed on the surface. This can be depicted by the concentration profile diagram of Fig. 4.

From the appearance of the layers formed, the p-type surface layer is assumed to be the result of boron pile-up during oxidation. If this pile-up at the surface exceeds the concentration of donors formed, a p-layer will predominate.

With Cu subsequently diffused into the Si, depending on its solubility level, and whether it was quenched or furnace cooled, the original donor level would be reduced by the tie-up of diffused oxygen and Cu. The p-layer which forms in the lapped wafers can be attributed to boron pile-up. The formation of the shallow n-type surface layer on both the lapped and sandblasted surfaces is probably due to the reaction of oxygen and dislocations. Thus an indication of the depth of damage and of the magnitude of dislocation formation was provided. Sheet resistance measurements indicate this level to be $\sim 5 \times 10^{15}/\text{cm}^3$. The absence of oxygen-formed donors in sandblasted specimens might be the result of greater boron pile-up to a level high enough to exceed the donor formation.

To examine more closely the effect of damage to the surface of Si, 2000 ohm-cm, p-type polished wafers were scribed with a diamond pencil leaving a number of scratches on the surface. These were oxidized and annealed at 450°C. As shown in Fig. 5, the depth of

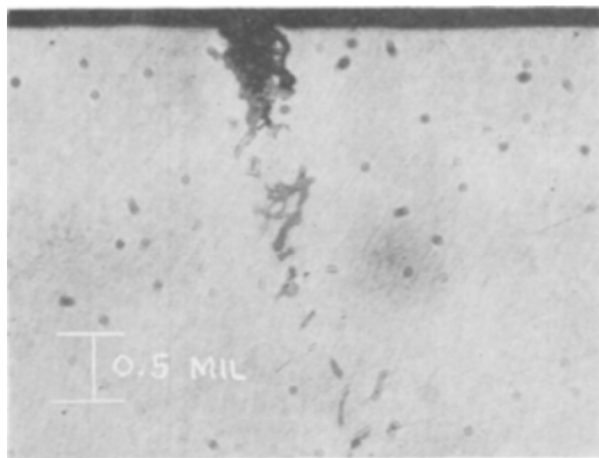


Fig. 5. Photomicrograph showing effect of damage due to scribe mark on polished 2000 ohm-cm p-type Si; after 1 hr oxidation at 1250°C and 450°C anneal for 72 hr; beveled X-section depth magnified 10X. a. Dark p-type regions within oxygen diffused and converted n-region. 75X.

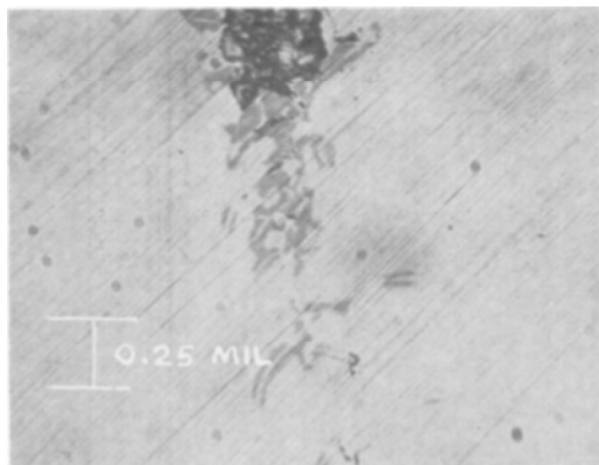


Fig. 5b. Enlarged view showing probable dislocation loops of high oxygen content within depleted dark stained regions. 150X.

the scribe mark was approximately 0.5 mil, but damage and subsequent dislocation formation extended to 2.5 mils. In this region of damage, darkly stained p-regions are present in the background of the n-type region where the latter is obtained because of oxygen conversion. These p-regions are assumed to be areas depleted of oxygen and are adjacent to dislocation loops containing atmospheres of oxygen removed from the depleted regions. From this observation, it is possible that the p-layer, assumed to be due to pile up, is also formed by the depletion of oxygen by reaction with surface induced dislocations.

The evidence indicates that oxygen can react with dislocations thereby forming shallow nonuniform n-type layers on the sandblasted and lapped surfaces. Further, there seems to be a reaction of Cu with oxygen as shown by their effects on the SiO_4^+ complex in polished wafers.

With the effect of a dislocation "sponge" at the surface, reheat-treating under oxygen of previously quenched wafers is of considerable interest. First it indicates that the introduced dislocations are not annealed out even with repetitive temperature cycles up to 1250°C. In addition the recovery of quenched and poisoned p-n-p units shows that fast diffusing impur-

ities are responsible for the downgrading phenomena. A period of time, slower than rapid quenching, is needed to permit the diffusion of these impurities to the dislocation "sponge." As oxygen cannot out-diffuse in the time of cooling evaluated and because the SiO_2 phase is always present on the Si surface, the introduced dislocations must be the major influence in the prevention and recovery of poisoned p-n-p structures.

It was also shown that a metal impurity such as copper can be transported from bulk Si, probably to some surface layer by heat-treatment under argon ambients. Such an ambient also resulted in depletion of the diffused oxygen level from the body of the silicon. The recovery of the reverse characteristics of Cu poisoned p-n-p junctions by this argon treatment would indicate that oxygen-copper complexing or tie-up occurs at or near the surface. Infrared examination of these structures support this view.

An explanation may be offered concerning the effect of cooling rate in an oxygen ambient. In quenching, impurities can precipitate at sites throughout the wafer in a more dispersed form. Under a moderate cooling rate such as a furnace cool, metal impurities can coalesce because of their rapid mobility; however, oxygen levels would not be significantly affected by precipitation or agglomeration. A cooling rate approaching equilibrium conditions affects the oxygen level either by outdiffusion or by precipitation as indicated by the absence of oxygen formed donors. Although the metal impurity level in the bulk Si can be assumed to be the same in all these cases, the resulting reverse leakage currents are not. The lower leakage observed with quenched samples indicates that the over-all effect of more finely dispersed precipitates is less than that of larger coalesced precipitates. If equilibrium cooling resulted in a depletion of oxygen levels by outdiffusion (because of precipitation as SiO_2 at the surface), a significant reduction in reverse currents should be achieved. Therefore, it appears that coalescence of oxygen occurs within the bulk during such a slow cool thus permitting oxygen-metal impurity complexing. Similar reverse currents are obtained to those of slow cooling by holding the slices at 1000°C for long periods of time. Precipitation of oxygen as SiO_2 here causes a reduction in oxygen level within the body of the silicon.

Under nitrogen ambients, downgrading is probably due to a nitride formation. No explanation is offered for the serious poisoning effect of hydrogen on p-n-p slices which have been exposed to oxygen.

Acknowledgments

The author wishes to acknowledge the effort of R. I. Jurgensen, who helped plan and carry out the many experiments in this study and to F. E. Gentry for many helpful discussions and for reviewing this work.

Manuscript received Oct. 22, 1964. This paper was presented at the Washington Meeting, Oct. 11-15, 1964.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1965 JOURNAL.

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