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FURNACE-TUBE CONTAMINATION

NASA Grant NGR 05-010-041

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University of California, Santa Barbara

As a result of improper use, the furnaces in the Solid-State Laboratory became drastically contaminated. People had neglected to use gloves in handling glassware, cleaning of wafers had not been thorough, wafers with photoresist had been inserted into the furnaces, and a bottle of welding-grade N_2 had accidentally been connected to the "house" nitrogen line. This report covers the effort to identify and eliminate the contamination.

In order to check the progress of furnace cleaning, diodes were fabricated and the diode reverse characteristics were examined. Since the diodes were probed and characterized prior to metallization, the measured characteristics include the effect of the point contacts formed by the probe-silicon interface.

A point contact with n-type material will be forward biased if a positive potential is applied to the probe with respect to the semiconductor. For p-type material the contact will be forward biased if the probe is negative with respect to the semiconductor. These bias conditions are illustrated in Fig. 1.

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*Most of the work reported in this document was performed by Mr. David L. Heald, NASA Trainee, Department of Electrical Engineering, University of California, Santa Barbara.

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In an attempt to calibrate the effect of the probe-silicon contacts, two probes were applied to a p-type silicon wafer and to an n-type wafer. Wafers of both high and low resistivity were used for each type. The resulting curves are shown in Figs. 2 through 5. If the point contacts had been identical, the curves would have been symmetrical and similar to that expected for two diodes back to back. The reverse breakdown voltage for low-resistivity material (0.05-0.1Ω-cm) is relatively small and that for high-resistivity material (1-2 Ω-cm) is relatively large.

The characteristic observed while probing a p-n junction diode is a result of three junctions in series. Masking the forward characteristics of the silicon p-n junction are two reverse-biased point contacts. For reverse bias across the silicon p-n junction the point contacts are forward biased and therefore do not materially affect the characteristics. Thus the reverse characteristics presented in the following photographs are essentially the reverse characteristics of the silicon p-n junctions.

As an interesting tangent, Figs. 6 and 7 show the characteristics of a n^{+}-n (ohmic) junction. The characteristics were measured by means of probing prior to metallization. The shapes of the characteristics are fixed almost entirely by the nature of the probe-silicon point contact.

As previously stated, the degree of furnace contamination is measured in a qualitative manner by the amount of reverse leakage current in a diode fabricated by use of the furnace. As an arbitrary standard, leakage currents were measured at a reverse bias of about twenty volts. An arbitrary diode geometry was used as a standard. Diodes were judged to be acceptable if the leakage current without illumination was 0.5 na or less and in normal room illumination was 0.5 μa or less. The cross-section area of the standard diode was about 1×10^{-4} sq. cm.

Prior to the fabrication of the diodes, all furnace tubes and glassware were (a) rinsed in trichloroethylene, acetone, and DI water, (b) washed in concentrated HF (48%) diluted with water (1:1) for five to ten minutes, and (c) given a final DI-water rinse. The glassware and tubes were then dried as quickly as possible.

During the first part of the project, wafer cleaning after photoresist was limited to J-100 stripper (fresh), methyl alcohol rinse, DI water rinse, ten-second dip in 10:1 HF followed by another rinse in DI water, and blow dry in N_2. (Using buffered HF for the dip left a residue on the wafer.) After the above procedure was carried out, dark spots remained on the wafer. In an effort to eliminate the spots, aqua regia was tried with little effect on the appearance of the wafer; however, the resulting diode characteristics were noticeably worse!

Late in the project the following cleaning procedure adapted from F. Cocca, et al,[1] was used.

J-100 stripper (fresh)

Methyl alcohol rinse

DI rinse

Blow dry in N_2

Boil in trichloroethylene - 5 minutes

Ultrasonically clean in trichloroethylene - 2 minutes

Boil in acetone - 5 minutes

Ultrasonically clean in acetone - 2 minutes

DI rinse

Boil in conc. HNO_3 - 15 minutes

DI rinse

10:1 HF dip using plastic or Teflon tweezers

(not Teflon-coated metal tweezers)

DI rinse

Blow dry in N_2

The foregoing procedure resulted in a cleaner-looking wafer and in good diode characteristics.

At the beginning of the project, the five furnaces with suspected contamination were shut down and the tubes removed. The furnaces involved in this procedure were those for BCl_3 predeposition, boron drive, phosphorous drive, $POCl_3$ predeposition, and oxidation. The boron and phosphorous drive tubes and the BCl_3 predeposition tube were replaced with new tubes. The $POCl_3$ predeposition and oxidation tubes were cleaned and reused.

In order to isolate the contamination, groups of diodes were fabricated by the use of different combinations of furnaces. The procedure will be described in the following paragraphs.

Two sets of diodes were fabricated using the oxidation furnace for oxide growth and the $POCl_3$ predeposition furnace for the predeposition and drive. One set was gettered. The results are shown in Figs. 8 through 10. The gettering improved the characteristics slightly. Figure 10 shows one of the worst devices. At this point it was not known if the contamination was from the N_2 line or the old furnace tubes.

Next, three more sets of diodes were made using the same substrate wafer and the same $POCl_3$ predeposition furnace for predeposition and drive. Two groups had the oxide grown in the oxidation furnace, one with wet O_2 (Fig. 11) and one with dry O_2 (Fig. 12). The oxide for the third group was grown in the boron drive furance, which was expected to be clean (Fig. 13). Since all three groups had channel currents,it was concluded that the $POCl_3$ predeposition furnace was contaminated.

The cleanliness of the N_2 line was next investigated by comparing diodes from the BCl_3 predeposition furnace with a set from a new and clean BBr_3 predeposition furnace. Oxides were grown in the boron drive furnace (new tube and no N_2). A separate N_2 bottle was connected to the BCl_3 furnace (new tube). The BBr_3 furnace also had a new tube but previously had "house" nitrogen flowing through it. The results are shown in Figs. 14 and 15 and were nearly identical. According to Grove[2],Fig. 6.28, a one-sided step junction with a substrate resistivity of 1.0 Ω-cm or 5×10^{15} impurities/cm^3 should have a breakdown of about 100 volts. Considering junction curvature, Fig. 6.31,[2] the breakdown should be between 50 and 70 volts for a junction depth of 2-3 μ. (After predeposition for BBr_3, V/I≈2; for BCl_3, V/I≈8; predeposition was followed by one-hour oxidation in dry O_2 at 1150°C.) If the junction is not one-sided, the breakdown will be slightly higher. Since the observed breakdown is in the expected range, it was felt that the "house" nitrogen line was clean.

The condition of the oxidation furnace was next determined. Figures 17 through 21 show the characteristics of junctions made on the same substrate wafer and using the same BCl_3 predeposition cycle. Figure 17 represents the control group using the boron drive furnace for oxide growth. Oxides on the other two sets were grown in the oxidation furnace with wet O_2. One group (Figs. 20 and 21) was placed in the $POCl_3$ predeposition furnace and gettered in the contaminated tube. These could not be distinguished electrically from their counter group which had not been gettered (Figs. 18 and 19). In both of these groups, about half of the diodes had "soft" characteristics and about half had "hard" characteristics. The contamination evidently results from use of the oxidation furnace.

At this point in the project, the boron drive, BCl_3 and BBr_3 furnaces were known to be clean, and the $POCl_3$ and oxidation furnaces known to be contaminated. The phosphorous drive furnace was expected to be clean, but had not been tested.

During the following two weeks, new tubes were placed in the $POCl_3$ predeposition and oxidation furnaces and good diodes were fabricated using the $POCl_3$ predeposition furnace. Use of the oxidation furnace resulted in poor diodes. By the end of the following month, both BCl_3 and $POCl_3$ predeposition furnaces were giving poor results again.

It was found that jungling on the $POCl_3$ predeposition furnace allowed pressure to build up and force liquid $POCl_3$ into the valves and flow meters. This was felt to be responsible for the degraded results when using the $POCl_3$ predeposition furnace. Solenoid valves were eliminated and the jungling simplified and correct. A leaky valve was probably responsible for the poor results from the BCl_3 furnace. Additional checks on the BBr_3 and the two drive furnaces indicated that they were still clean.

In an attempt to eliminate the contamination in the oxide furnace, a new tube was installed. Figure 22 shows the results from a BBr_3 predeposition and oxide grown with wet O_2 in the oxidation furnace. Since the oxidation furnace was running at 950°C, the junctions remained shallow. The resulting sharp curvature of the junction probably is responsible for the low breakdown voltage. However, the soft breakdown does indicate contamination. In an effort to eliminate the contamination, all glassware was recleaned and the solenoid valves bypassed with Teflon tubing. The result of this process is shown in Fig. 23. The leakage current at 20-volts reverse bias was 60 nanoamps. While this level of reverse leakage current is considered to be satisfactory, some improvement is possible by the use of higher-resistivity water for the wet-O_2 oxidation.

In summary, great care and large blocks of time are required to isolate and eliminate contamination of the furnaces in the diffusion room. As outlined in the foregoing paragraphs, the fabrication of diodes by use of various combinations of furnaces may be used to isolate the contamination.

REFERENCES

1. F. Cocca, R. Cohen, S. Simonne, "A Simple Method of Preparing 'Sodium-Free' Thermally Grown Silicon Dioxide on Silicon," Proc. IEEE 55, p. 2193, December 1967.
2. A. S. Grove, Physics and Technology of Semiconductor Devices, John Wiley, 1967.

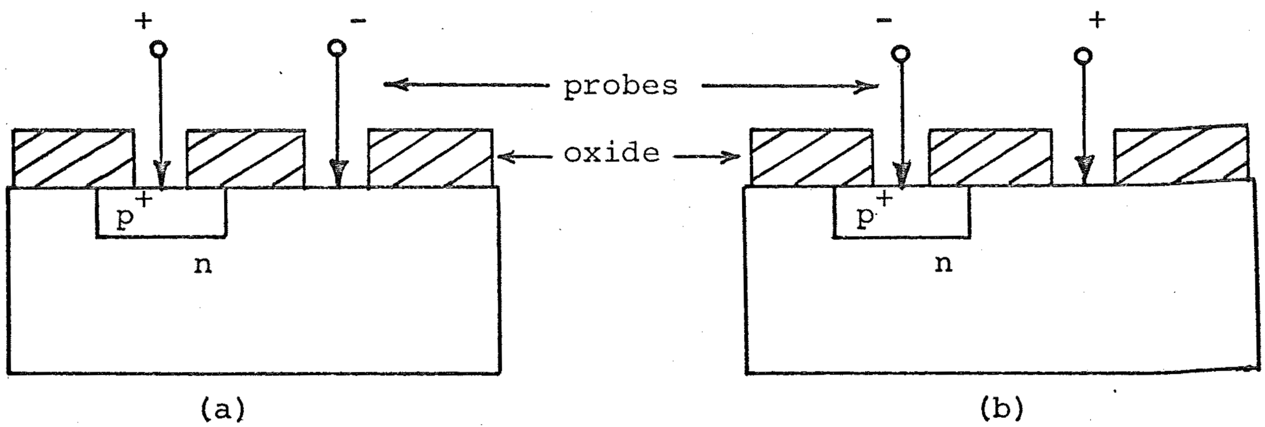

Figure 1 - (a) Left-hand probe-silicon junction is reverse biased. Right-hand probe-silicon junction is reverse biased. The p^+-n junction is forward biased.

(b) Left-hand probe-silicon junction is forward biased. Right-hand probe-silicon junction is forward biased. The p^+-n junction is reverse biased.

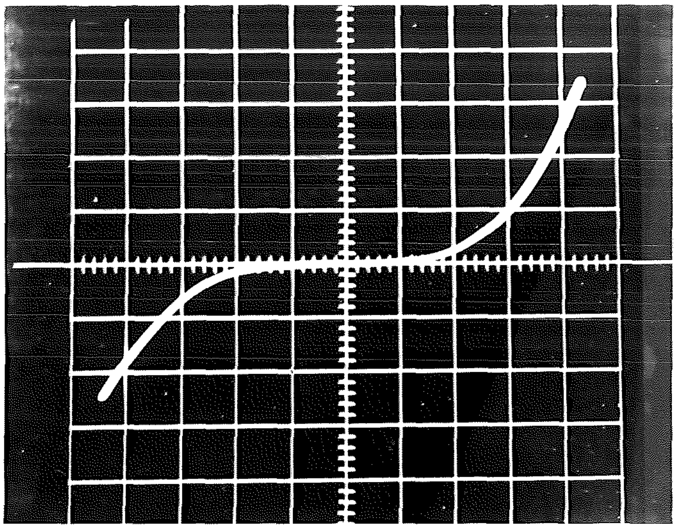

Fig. 2 Probes contacting high-resistivity p region (1-2 Ω - cm)

Vertical: 1 ma/div.
Horizontal: 5 v/div.

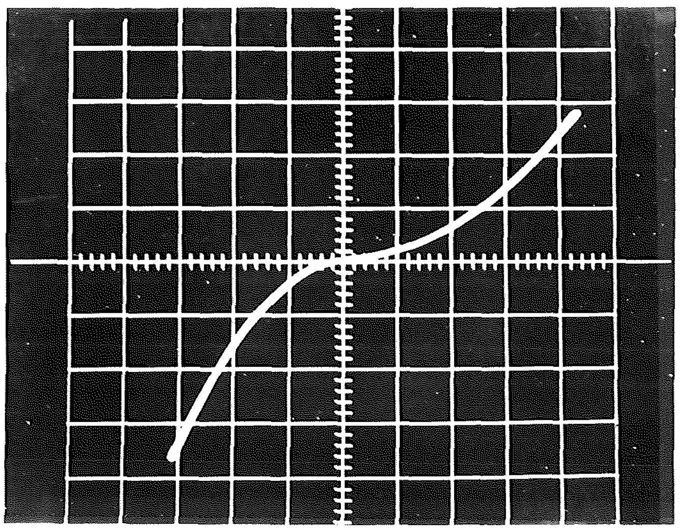

Fig. 3 Probes contacting low-resistivity p^+ region (0.05 - 0.1 Ω - cm)

Vertical: 0.05 ma/div.
Horizontal: 0.2 v/div.

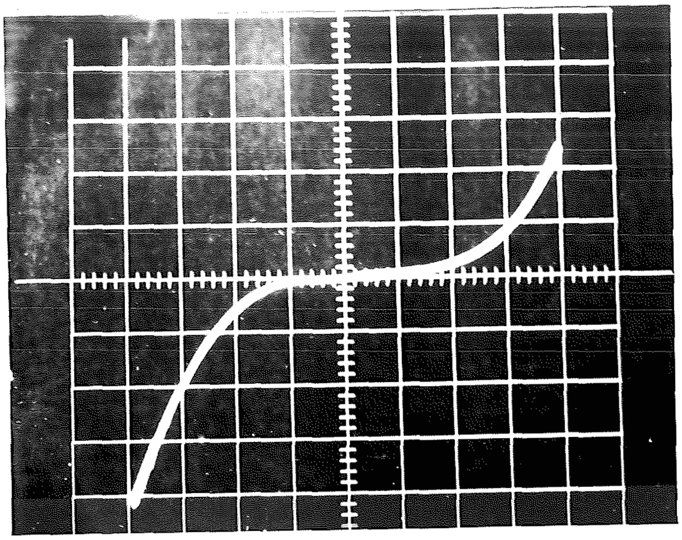

Fig. 4 Probes contacting high-resistivity n region (1-2 Ω - cm)

Vertical: 0.05 ma/div.
Horizontal: 5.0 v/div.

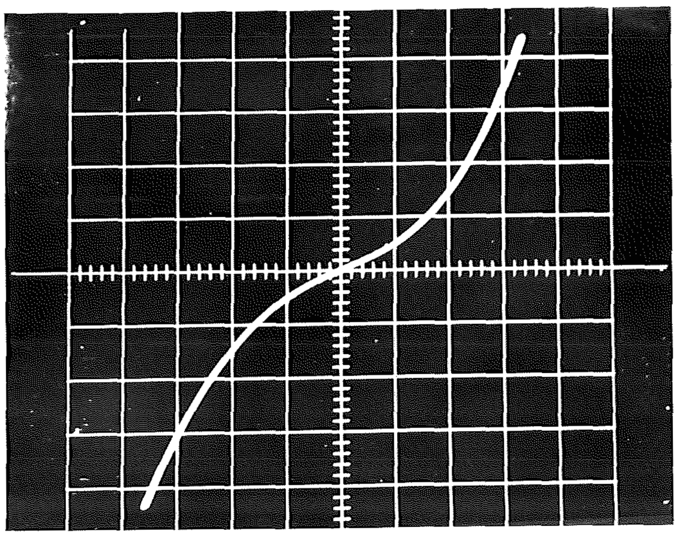

Fig. 5 Probes contacting low-resistivity n^+ region (0.05 - 0.1 Ω - cm)

Vertical: 0.05 ma/div.
Horizontal: 0.1 v/div.

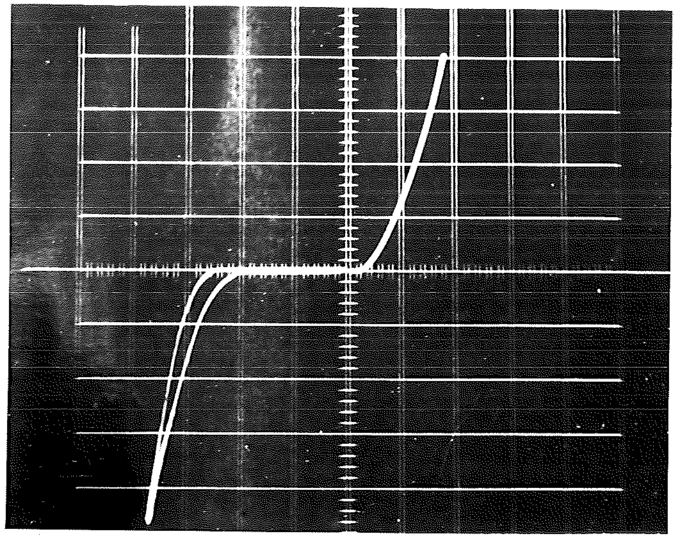

Fig. 6 n^+-n junction (Oxide grown in boron drive furnace) Leakage current, 40na. @20v.

Vertical: 0.02 ma/div.
Horizontal: 2 v/div. (fwd.)
Horizontal: 10 v/div. (rev.)

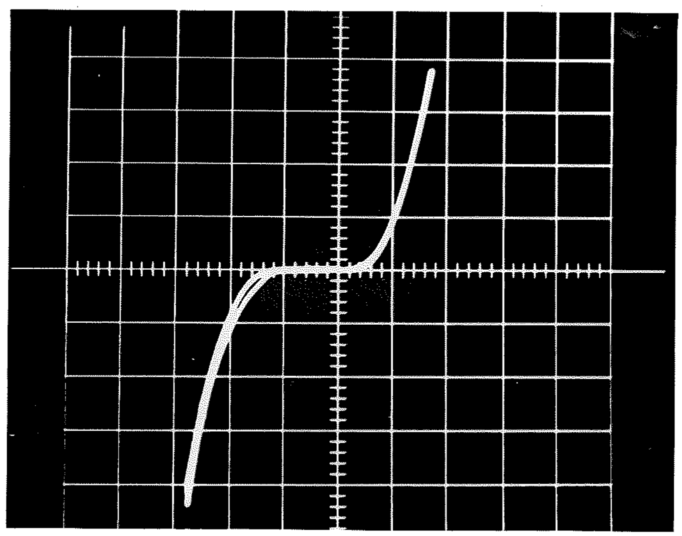

Fig. 7 n^+-n junction (Oxide grown in boron drive furnace)

Vertical: 0.02 ma/div.
Horizontal: 1.0 v/div. (fwd.)
Horizontal: 10. v/div. (rev.)

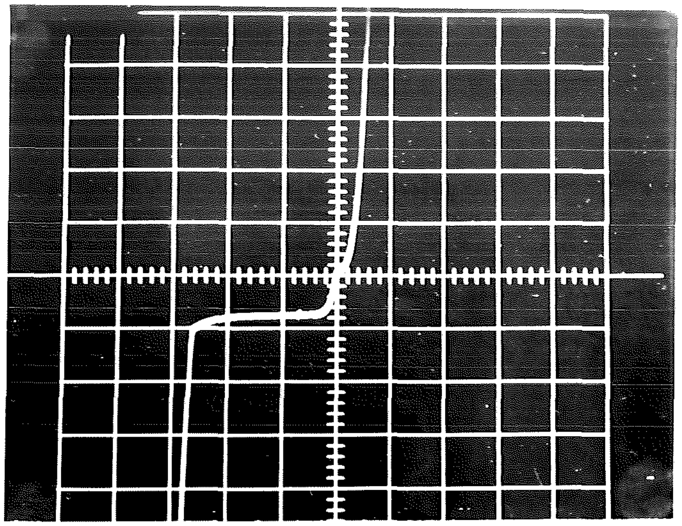

Fig. 8 n^+-p (Phosphorous predeposition furnace, oxide grown in oxidation furnace.)

Vertical: 0.1 ma/div.
Horizontal: 20 v/div. (fwd. & rev.)

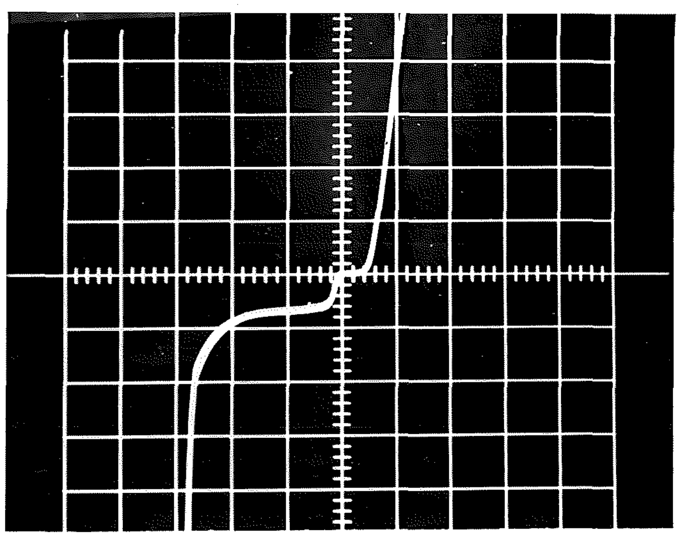

Fig. 9 n^+-p Gettered junction (Otherwise, same as Fig. 8)

Vertical: 0.05 ma/div.
Horizontal: 20 v/div. (fwd. & rev.)

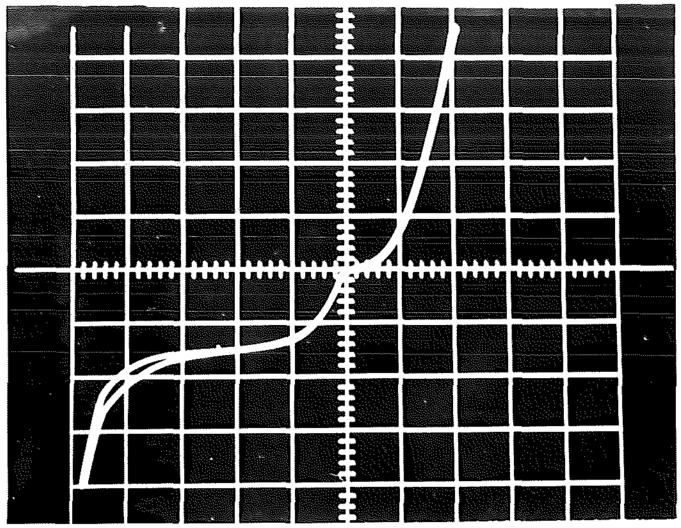

Fig. 10 n^+-p (Phosphorous predeposition, oxide grown in oxidation furnace)

Vertical: 0.5 ma/div.
Horizontal: 10 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

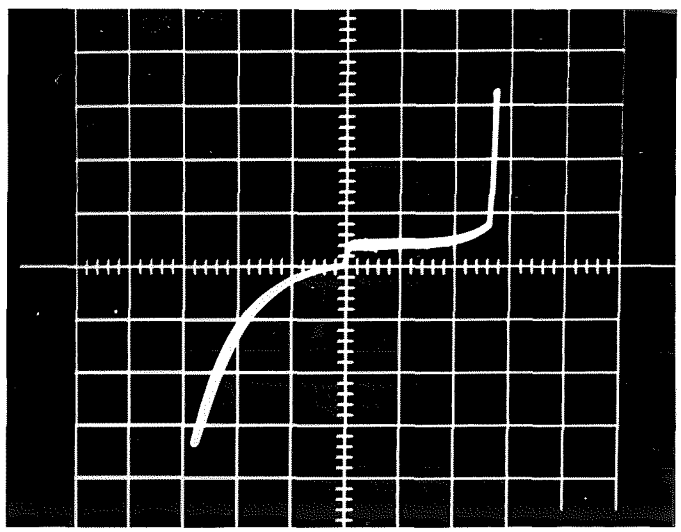

Fig. 11 n^+-p junction (Wet-0_2, oxidation furnace)

Vertical: 0.05 ma/div.
Horizontal: 5 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

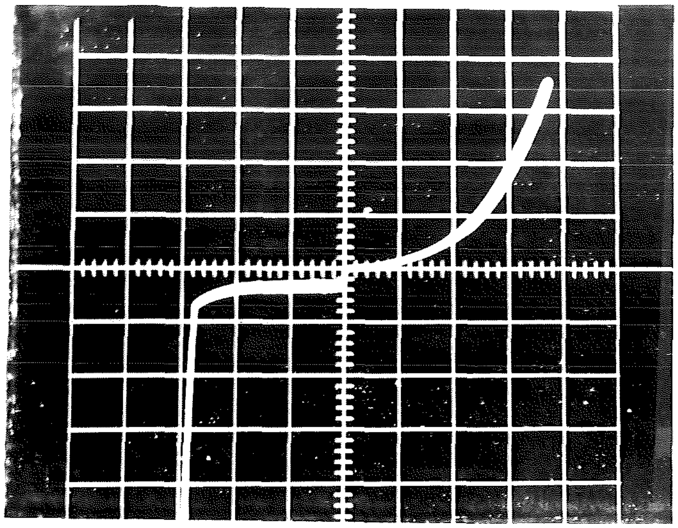

Fig. 12 n^+-p junction (Dry O_2, oxidation furnace)
(same substrate wafer and phosphorous pre-deposition furnace as for Fig. 11.)

Vertical: 0.05 ma/div.
Horizontal: 5 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

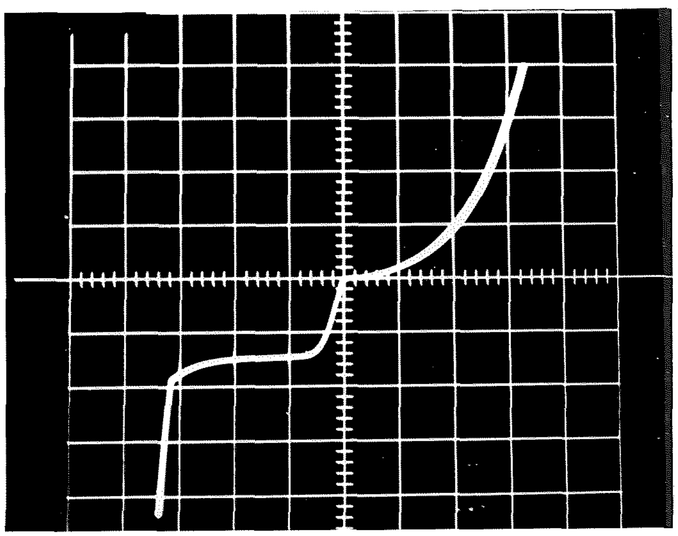

Fig. 13 n^+-p junction (Dry O_2, boron drive furnace)
(same substrate wafer and phosphorous predeposition furnace as for Fig. 11.

Vertical: 0.05 ma/div.
Horizontal: 5 v/div. (fwd.)

Vertical: 0.2 ma/div.
Horizontal: 20 v/div. (rev.)

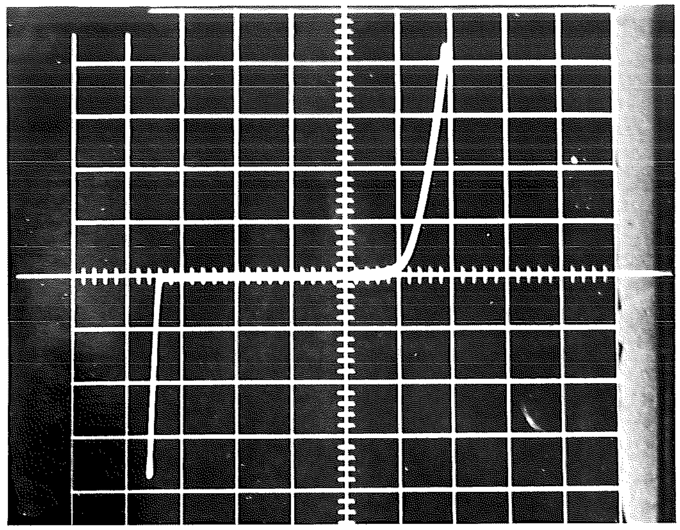

Fig. 14 p^{+}-n junction (BCl_3 predeposition furnace, oxide grown in boron drive furnace) 0.45 μa leakage current @ 20v.

Vertical: 0.05 ma/div.
Horizontal: 20 v/div. (fwd. & rev.)

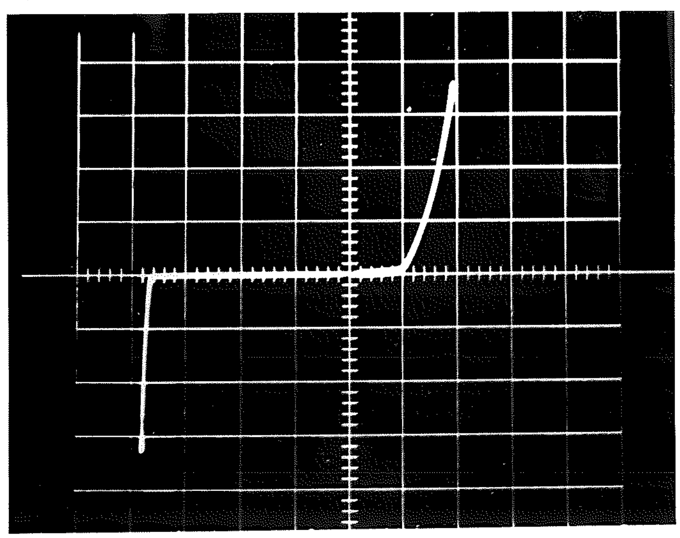

Fig. 15 p^{+}-n junction (BBr_3 predeposition furnace, oxide grown in boron drive furnace) 0.45 μa leakage @ 20v.

Vertical: 0.05 ma/div.
Horizontal: 20 v/div. (fwd. & rev.)

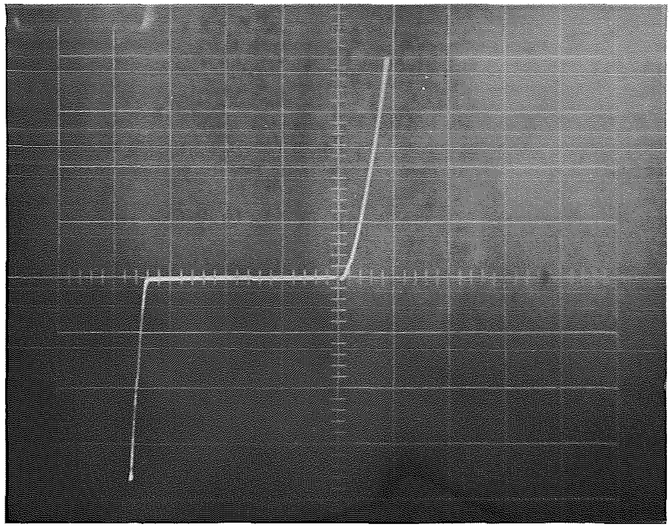

Fig. 16 p^+-n junction (BCl_3 predeposition furnace, same as for Fig. 14)

Vertical: 0.05 ma/div.
Horizontal: 20 v/div. (fwd. & rev.)

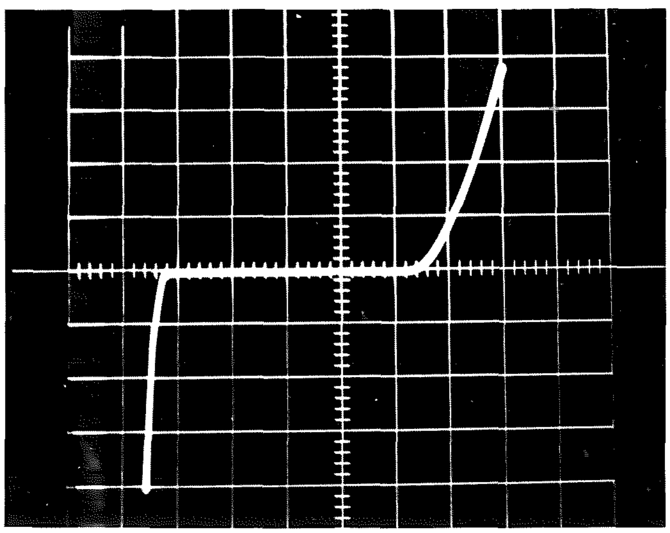

Fig. 17 p^+-n junction (BCl_3 predeposition furnace) (oxide grown in boron drive furnace) 0.43 μa leakage @ 20v.

Vertical: 0.05 ma/div.
Horizontal: 10 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

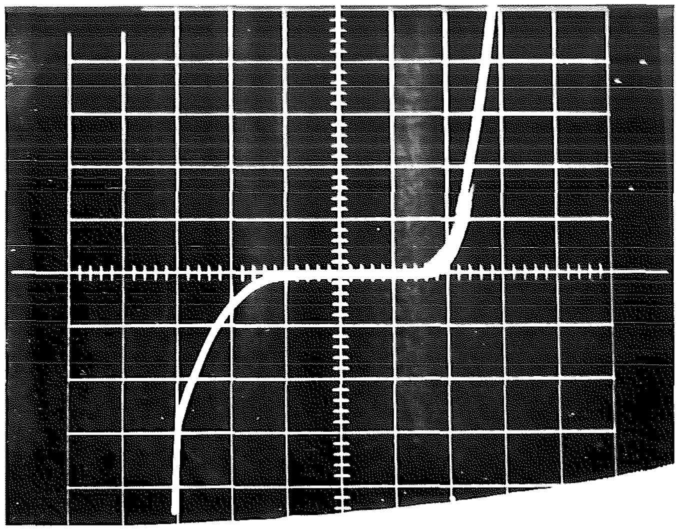

Fig. 18 p^+-n junction (BCl_3 predeposition furnace, Wet O_2, oxidation furnace) (same substrate wafer and predeposition as for Fig. 17)

Vertical: 0.05 ma/div.
Horizontal: 10 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

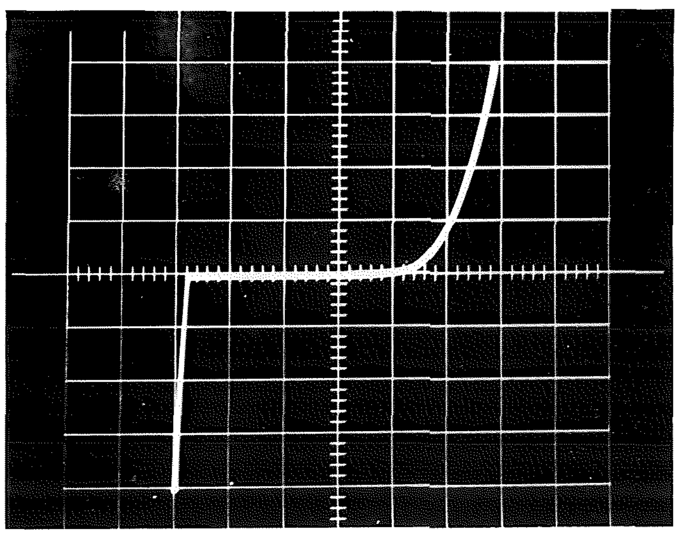

Fig. 19 Different junction on same wafer. Otherwise identical to Fig. 18

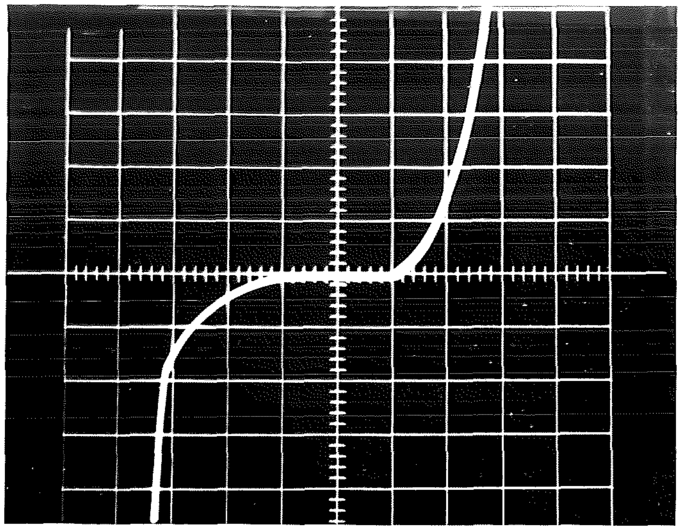

Fig. 20 p^{+}-n junction - "phosphorous gettered" (Otherwise identical to Fig. 18)

Vertical: 0.05 ma/div.
Horizontal: 10 v/div. (fwd.)
Horizontal: 20 v/div. (rev.)

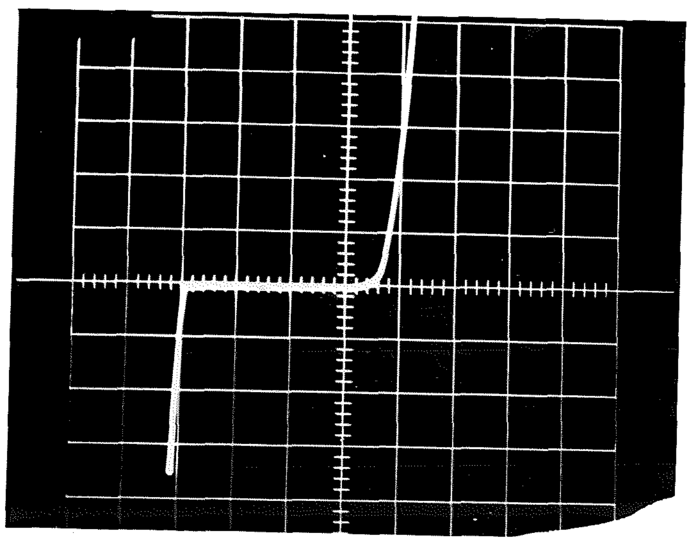

Fig. 21 Different junction on same wafer. Otherwise identical to Fig. 20.

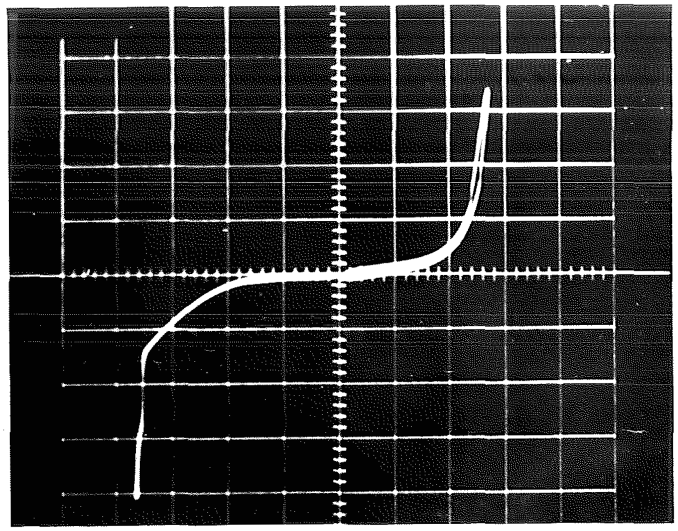

Fig. 22 p^+-n junction (oxide in oxidation furnace) leakage current @ 20 v. - 1μa.

Vertical: 0.02 ma/div.
Horizontal: 10 v./div. (fwd. & rev.)

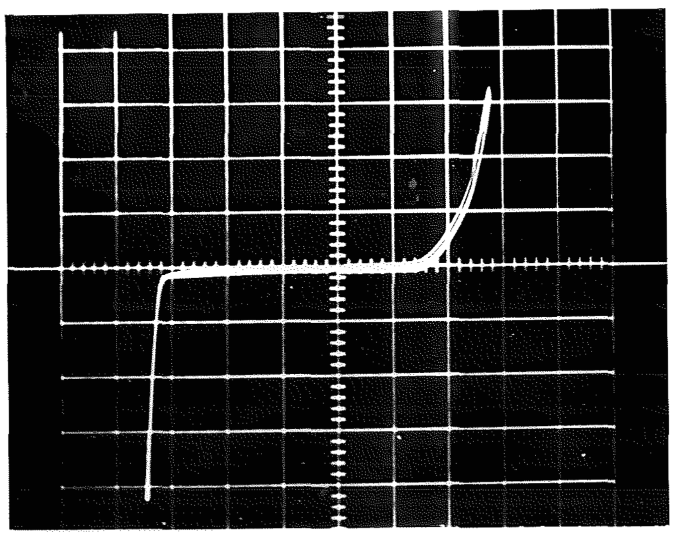

Fig. 23 p^+-n junction (solenoid valves of oxidation furnace by-passed) leakage current @ 20v. - 60 na.

Vertical: 0.02 ma/div.
Horizontal: 10 v./div. (fwd. & rev.)