C.P.D. MEASUREMENTS ON OXIDIZED SILICON SURFACES

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Contact potential difference (C.P.D.) measurements against a platinum electrode were made on the surface of oxide layers of 2000 Å thickness covering the $p-n$ junction in silicon samples. The significant and not sufficiently reproducible inhomogeneity in C.P.D. has been attributed to the inhomogenous distribution of impurities on the surface and in the bulk of the oxide layer, built in during the preparation of the samples or to local charge accumulations due to external effects on the surface of the thick insulating oxide layer. By etching off the oxide in HF, the inhomogeneity gradually decreased and, after removing 1200 to 1400 Å of the oxide, became less than the error of measurements of $\pm 0,02$ V.

A new method of measurement, yielding well reproducible results, has been developed for investigating the silicon samples covered with thick oxide layer of great C.P.D. inhomogeneity. From the results it is concluded that the mobile positive and negative charges on the surface and in the bulk of the oxide layer separate and accumulate on the p and n-type sides of the samples due to the reverse voltage applied during the heat treatment at 180 °C.

The differences in charge accumulation found on the samples can be attributed to minor differences in the technological process.

Introduction

The presence of the inversion-layer channels of relatively good conductivity at the oxide-semiconductor interface of silicon samples covered with thermally grown oxide layers was observed by several authors [1—5], the conductivity of the channels depending on the voltage applied to the silicon slab, on the ambient atmosphere and on previous treatment of the samples.

A model for interpreting the phenomena in the inversion layer and for explaining its formation was suggested by ATALLA et al. [3]. According to this model, mobile positive and negative charges are present on the surface and probably also in the bulk of the oxide layer covering the silicon. The results of ATALLA's measurements of photovoltage and other electric characteristics on the surface of the oxidized silicon surfaces were in good agreement with the model suggested.

As shown by SHOCKLEY et al. [6], the mobile charges on the surface of oxidized silicon samples could be detected by measuring the contact potential difference (C.P.D.). Their results supported the validity of ATALLA's model. For the C.P.D. measurements, they used p-type silicon samples of 1 Ωcm resistivity with diffused p—n junction,

Fig. 1. Schematic diagram of SHOCKLEY's samples.

covered with a thermally grown oxide layer of 300 to 1000 Å thickness. A schematic diagram of the samples is shown in Fig. 1, the results of SHOCK-LEY's measurements are presented in Fig. 2. The curves *a* and *b* were obtained in laboratory atmosphere of 35 % relative humidity, with and without 20 V reverse bias voltage, respectively; curve *c* was measured in an atmosphere of 100 % humidity with 20 V reverse bias voltage, then, after switching off the bias voltage, curve *d* was obtained. The results represented in curve *d* were interpreted by the supposition that the mobile charges on the surface and also probably in the bulk of the oxide layer separated due to the bias voltage, the positive and negative charges accumulating at the *p*-type side and on the *n*-type side of the sample, respectilvey. After removing the applied field, the original equilibrium was restored by redistribution of the charges (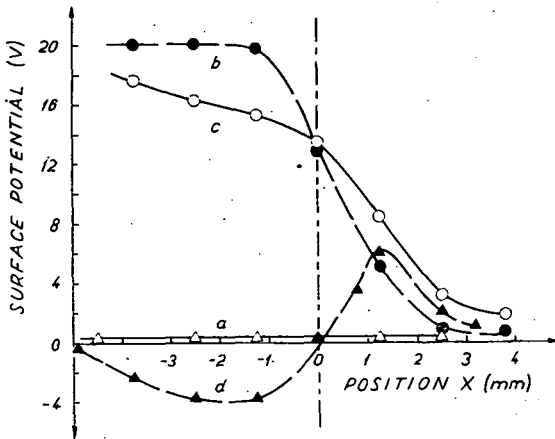curve *a*). The time constant of the redistribution of the charges in wet atmosphere was of the order of some minutes, whereas in a dry ambient it was higher by several orders of magnitude.

Fig. 2. Results of C.P.D. measurements of SHOCKLEY [6] on oxidized silicon samples.

SHOCKLEY interpreted the charges as mobile slow states on the surface and probably in the bulk of the oxide layer. According to his opinion, these charges are responsible for the formation of the inversion channel on the oxide-silicon interface.

Experimental

The C.P.D. measurements were performed with the apparatus described in [7] (with Kelvin's method). The reference electrode, vibrating with 120 cps perpendicularly to the surface of the sample, was a platinum slab of quadratic form and approximately 1 mm² surface area, stabilized in room atmosphere.

The schematic diagram of our samples is shown in Fig. 3. The samples were covered by a thermally grown oxide layer of 2000 Å thickness and provided with two aluminium contacts (denoted by *C* in Fig. 3) alloyed to the *p*- and *n*-type sides of the samples.

The measurements were performed under dry, pure nitrogen of atmospheric pressure. The sample holder, the sample and the reference electrode were placed in a vacuum system and evacuated to 10^{-2} torr. Then dry nitrogen was slowly introduced into the
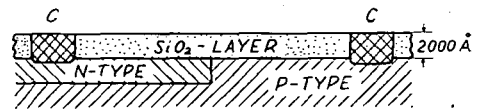

Fig. 3. Schematic diagram of our samples used for the measurements. The alloyed aluminium contacts are denoted by C.

system. The moisture was removed by freezing, using a glass spiral cooled by liquid air. The measurements were performed after rinsing the apparatus with dry nitrogen several times. The samples were displaced under the reference elec-trode with the aid of an electromagnetic apparatus in steps of 0.5 mm, within an error of 0.05 mm.

The mobility of the charges on the surface and in the bulk of the oxide was increased by heating to 180°C under 18 V reverse bias voltage. The heating was made by a tube furnace placed on the vacuum chamber. Two series, consisting of five samples each, prepared with the same apparatus and the same technology, but with a time difference of some weeks were examined.
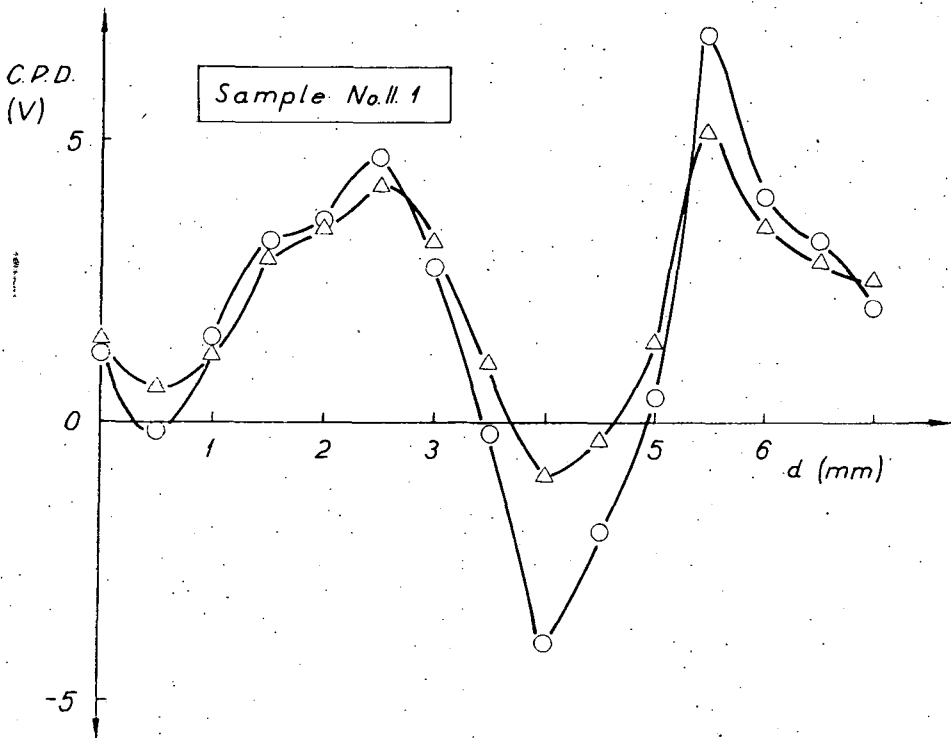

Fig. 4. C.P.D *vs.* distance along the middle line of the sample II. 1.

Significant C.P.D. inhomogeneities were found on all samples. A typical result can be seen in Fig. 4, which shows the curves of two subsequent measurements. The true C.P.D. inhomogeneity of the specimen is obviously greater than the values obtained, because the measurements yielded the mean values of the C.P.D. on the area under the reference electrode. The poor reproducibility of the measurements is to be explained by significant C.P.D. inhomogeneities in the oxide layer and by errors in adjusting the position of the reference electrode above the sample. This seems to be supported by the fact that deviations in the C.P.D. values obtained by repeated measurements in a fixed position of the reference electrode within

the range of 6 to 8 hours were all less than the error of measurements, but a very slight displacement of the electrode along the sample produced considerable changes in the measured C.P.D.

C.P.D. inhomogeneities, similar to those shown on Fig. 4 were also observed by V. G. LITOVCHENKO [8]; these could be removed by washing the sample with carbon tetrachloride. In our case, we found only a scarcely measurable reduction of the C.P.D. deviations with this method. The considerable inhomogeneities observed could only be removed by etching off about 1200 to 1400 Å, of the oxide layer. In [7] the error of measurement was found to be $\pm 2\,mV$; in the present investigations it was higher by a factor of about ten. This may be due partly to the smaller area of the reference electrode, and partly to greater inhomogeneities in the sample itself. It is to be remarked that the C.P.D. inhomogeneities after gradual etching off the oxide were always observably higher on the p-type side of the sample than on the n-type side.
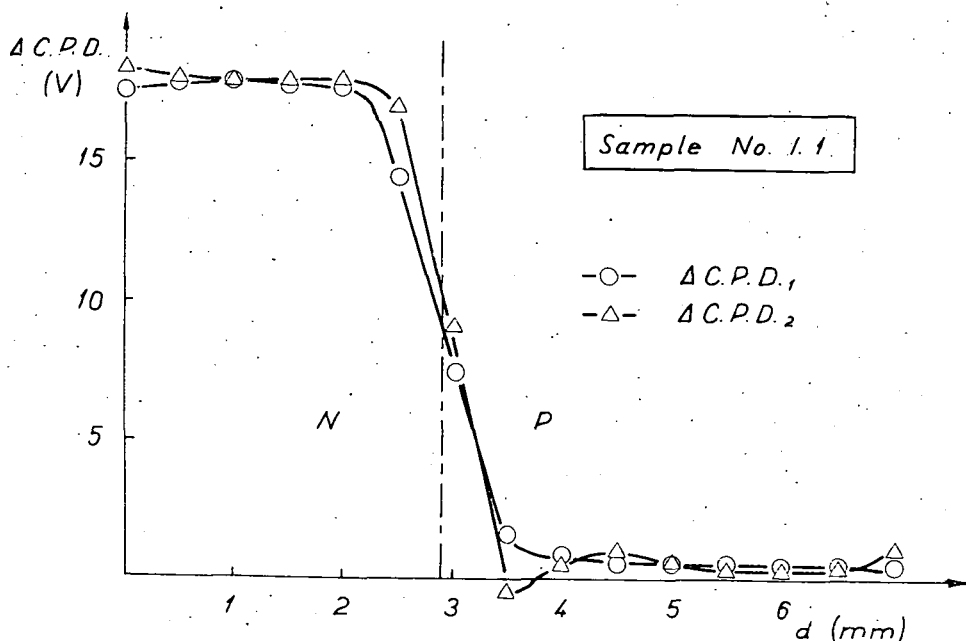

Fig. 5. Results of Δ C.P.D.$_1$ and Δ C.P.D.$_2$ measurements *vs.* distance along the middle line of sample I. 1. Both curves were obtained at room temperature before and after the heat treatment of 180 °C, respectively. The position of the $p-n$ junction is marked by a broken line.

Because of the great inhomogeneities observed on the samples with 2000 Å oxide layer and the poor reproducibility of the measurements, the investigations could not be performed in the way suggested by SHOCKLEY; practically only potential curves corresponding to differences between curves a and b, and c and d of Fig. 2, respectively, could be obtained. Analysis of the curves in Fig. 2 showed that the inversion effects caused by the charges on the surface or in the bulk of the oxide could be inferred from the deviations of the curves ΔC.P.D.$_1$, and ΔC.P.D.$_2$, ob-

tained from the measurements (see below). These deviations should be only slight according to SHOCKLEY's results. Based on the analysis of the curves, we found that intersections of the curves ΔC.P.D.$_1$ and ΔC.P.D.$_2$ should be expected in several points, with maximum differences of about ± 2 V between the two curves.

The measurements were performed as follows: the reference electrode was adjusted above a certain position of the sample and the C.P.D.$_1$ was measured first with a reverse bias voltage of 18 V, then after switching off the bias voltage. The difference of both measurements gave a value of ΔC.P.D.$_1$ The measurements were
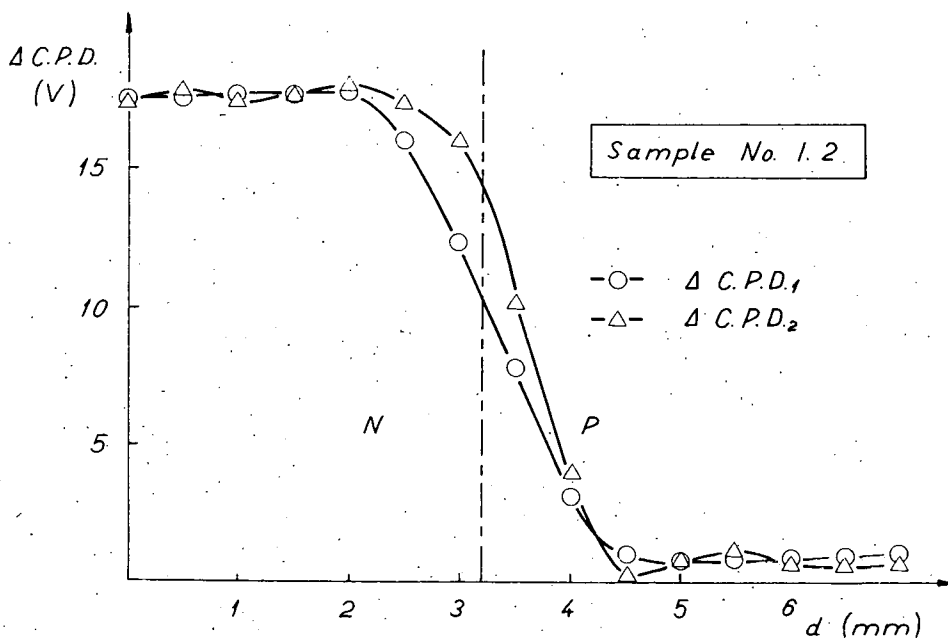

Fig. 6. Results of Δ C.P.D.$_1$ and Δ C.P.D.$_2$ measurements obtained at room temperature on sample I. 2., before and after the heat treatment of 180 °C, respectively.

repeated after displacing the reference electrode along the middle line of the sample by 0,5 mm, perpendicularly to the p-n junction. From the values of ΔC.P.D.$_1$ measured as different points of the sample the curves ΔC.P.D.$_1$ were plotted. In this way it was possible to eliminate the potential due to the inhomogeneities from the difference of both potentials. It was important for the results to make both measurements on the same area of the samples, the differences resulting from the errors of adjustment being eliminated in this way.

The samples were then heated to 180°C in dry nitrogen atmosphere for 30 to 40 minutes, applying a reverse bias of 18 V, and cooled to room temperature; the C.P.D. was measured again with and without bias voltage in the way described above. The difference of both measurements gave the values of ΔC.P.D.$_2$.

The results obtained from the measurements on samples I.1 and I.2 are shown in Figs. 5 and 6. The place of the p-n junction is marked by a broken line. It

can be seen, as expected, that after the heat treatment the potential curve of the
p-n junction became steeper and the values of the two curves were different.
The differences can be attributed to the redistribution of the charges on the surface
and in the bulk of the oxide layer, resulting from the bias voltage applied during
the heat treatment. This is supported by the fact that after keeping the samples in
dry nitrogen at room temperature for 24 hours without bias voltage, repeated
measurements reproduced the data of the original ΔC.P.D.$_1$ curves within the
arror of measurement of about $\pm 0,02$ V. By repeating these cycles (measurement
in dry nitrogen — heat treatment — repeated measurement) practically the same
results as shown in Fig. 5 and 6 were obtained. It is to be mentioned that, while
the deviations of the ΔC.P.D.$_1$ values obtained for the same point of the sample
did not exceed $\pm 0,02$ V *i.e.* the values were well reproducible, the deviations of
the ΔC.P.D.$_2$ values were much greater in some cases. Differences between the
two curves could, however, be unquestionably demonstrated in all cases. Results
very similar to those shown in Figs. 5 and 6 were obtained with the other samples
of series I.

The results of cycles of measurements on sample II.1 can be seen in Fig. 7a
and 7b. In this case the values of ΔC.P.D.$_2$ were measured at 40 °C. The differences
between the curves ΔC.P.D.$_1$ and ΔC.P.D.$_2$ were much greater than expected in
the *p*-type part of the sample, whereas on the *n*-type part only slight difference
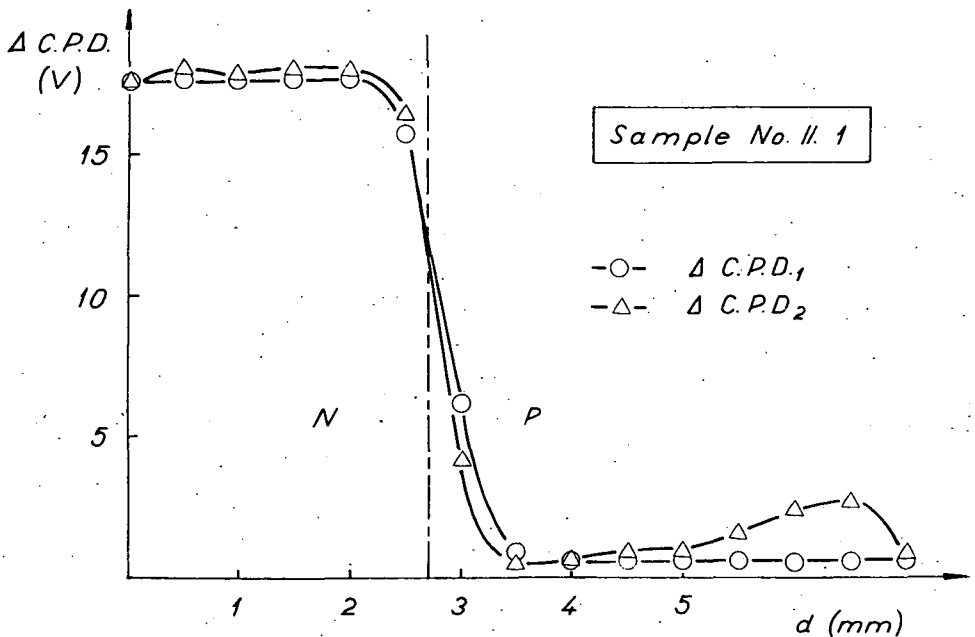were found. As the measurements were begun at a distance $d = 7$ mm from the

Fig. 7a. Results of Δ C.P.D.$_1$ and Δ C.P.D.$_2$ measurements on sample II. 1. The values of Δ C.P.D.$_1$
were obtained at room temperature before the heat treatment of 180 °C. The values of Δ C.P.D.$_2$
were measured at 40 °C after the heat treatment. The measurements of Δ C.P.D.$_2$ were begun at
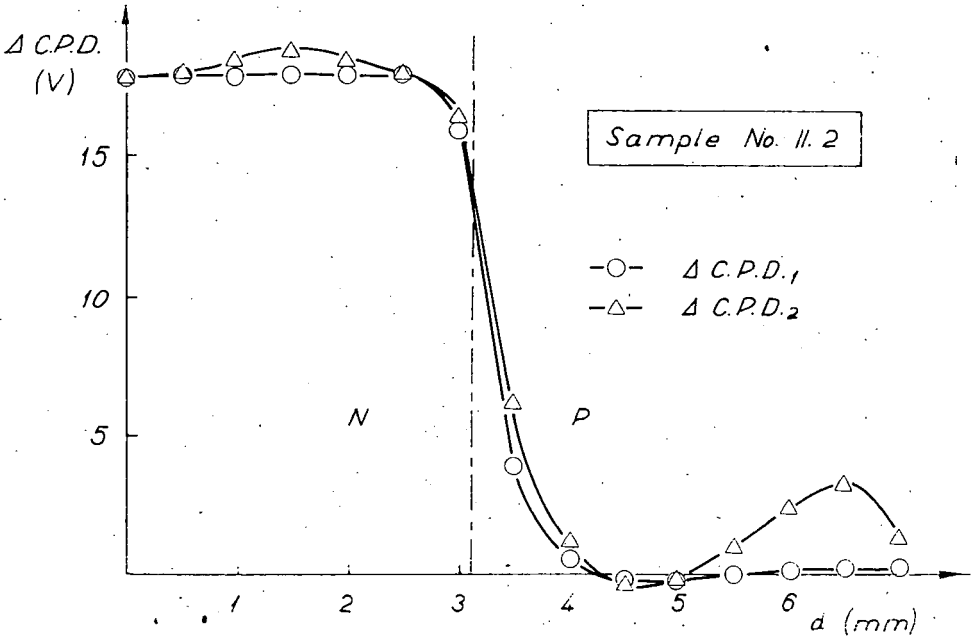the point $d = 7$ mm.

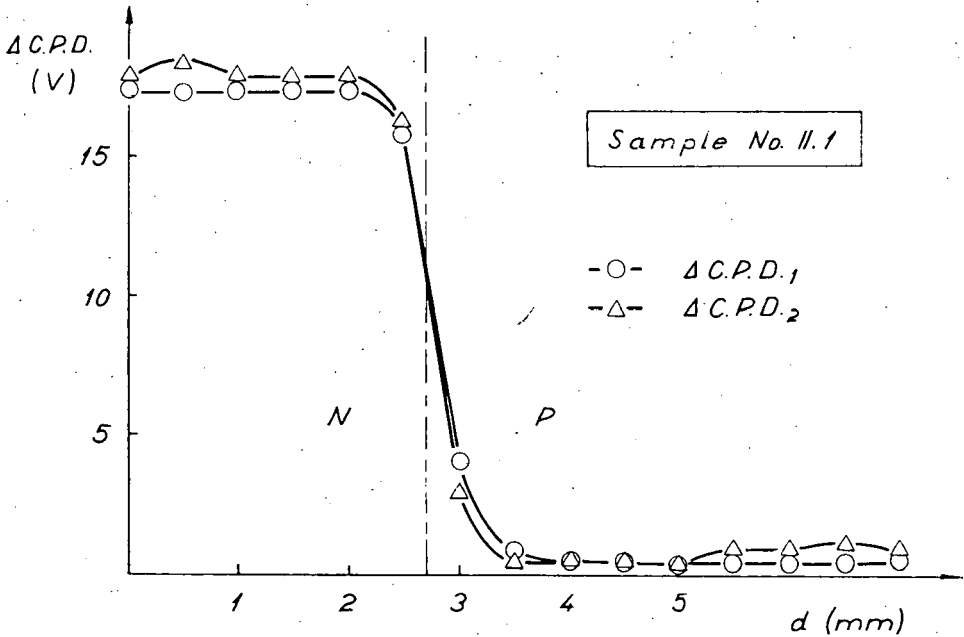Fig. 7b. Results of repeated measurements of Fig. 7a.

Fig. 7c. Results of repeated measurements of Fig. 7a and 7b. All conditions were unchanged, except that the measurement of Δ C.P.D.$_2$ were begun at the point $d=0$ mm.

Table I

Results of C.P.D. measurements on sample II. 1, shown also in Figs 7a, 7b and 7c.

d (mm)	Δ C.P.D.$_1$ (V)			Δ C.P.D.$_2$ (V)		
	a	b	c	a	b	c
0	17.42	17.43	17.45	17.41	17.85	17.98
0.5	17.41	17.42	17.44	17.85	18.02	18.49
1	17.42	17.42	17.41	17.82	17.48	18.03
1.5	17.41	17.43	17.44	18.03	17.83	17.92
2	17.40	17.39	17.41	17.84	17.78	17.83
2.5	15.64	15.65	15.62	16.47	17.98	16.61
3	5.68	4.98	3.87	4.42	6.25	3.04
3.5	0.92	0.72	0.77	0.53	1.03	0.21
4	0.63	0.52	0.43	0.60	0.21	0.42
4.5	0.42	0.40	0.38	0.82	−0.02	0.41
5	0.41	0.40	0.39	0.86	0.23	0.39
5.5	0.45	0.42	0.44	1.58	2.62	0.87
6	0.38	0.39	0.40	2.23	3.65	0.96
6.5	0.39	0.40	0.38	2.59	4.64	1.21
7	0.37	0.40	0.35	0.79	2.03	1.02

contact on the n-type part, it could be supposed that the deviations on the n-type part might have decreased during the 15 minutes of the measurements, owing to the appreciable mobility of the charges at 40 °C. Therefore we repeated the measurements beginning from the point $d=0$ mm (Fig. 7c). It can be seen from the figure that the differences of the curves on the n-type part were somewhat greater, while those on the p-type part decreased, which seems to support the supposition of the charges being redistributed during the switching off the bias voltage in the measurements. The results shown in Figs. 7a, 7b and 7c are also listed in Table I. It can be seen also from this table that repeated measurements of ΔC.P.D.$_1$ were well reproducible. The deviations between the values of ΔC.P.D.$_2$ may be attributed to the redistribution of the charges during the measurements.

Fig. 8a and 8b shows the results of similar measurements on sample II.2. Here, however, all measurements were made at room temperature. The differences between curves ΔC.P.D.$_1$ and ΔC.P.D.$_2$ are rather high in both parts of the sample. The differences were attributed to the accumulation of the charges on the n and p-type parts of the sample during the heat treatment due to the bias voltage. It should be remarked that the maximum concentration of the negative and positive charges calculated from the curves of Fig. 8a and 8b resulted to be more than the double of those calculated on the basis of SHOCKLEY's measurements. Other samples of series II gave very similar results.

After the measurements described above the samples I.1 and II.1 were treated with HF; after etching off a layer of about 1200 to 1400 Å from the original oxide of 2000 Å thickness, the measurements were performed in the way suggested by SHOCKLEY. The curves obtained were very similar to those shown in Fig. 2. The values corresponding to the maxima and minima of curve d in Fig. 2 were, however, higher and deeper by about 15—20%, respectively.

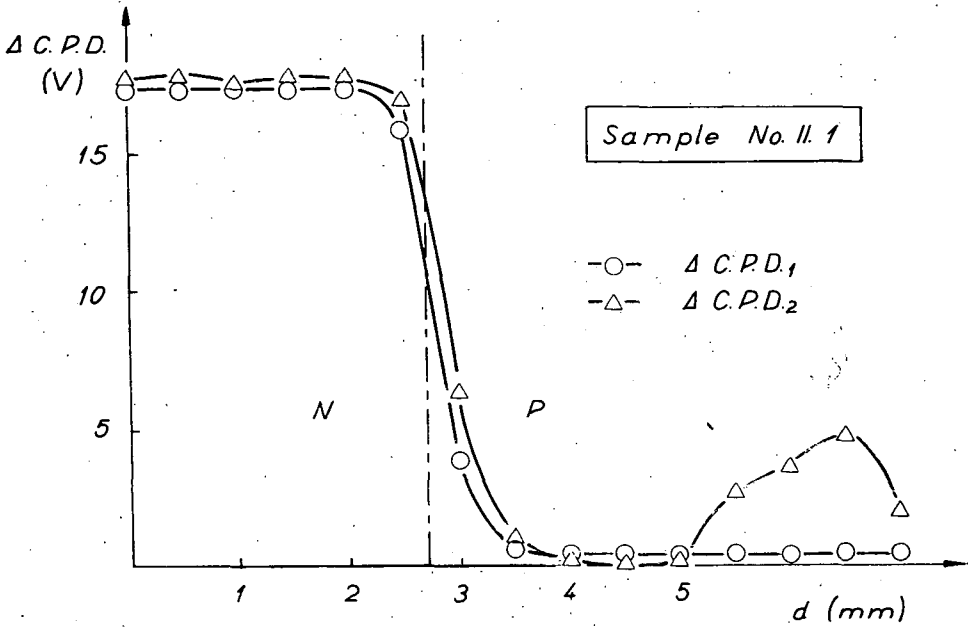*Fig. 8a.* Results of Δ C.P.D.₁ and Δ C.P.D.₂ measurements on sample II. 2 at room temperature, before and after heat treatment of 180 °C, respectively.
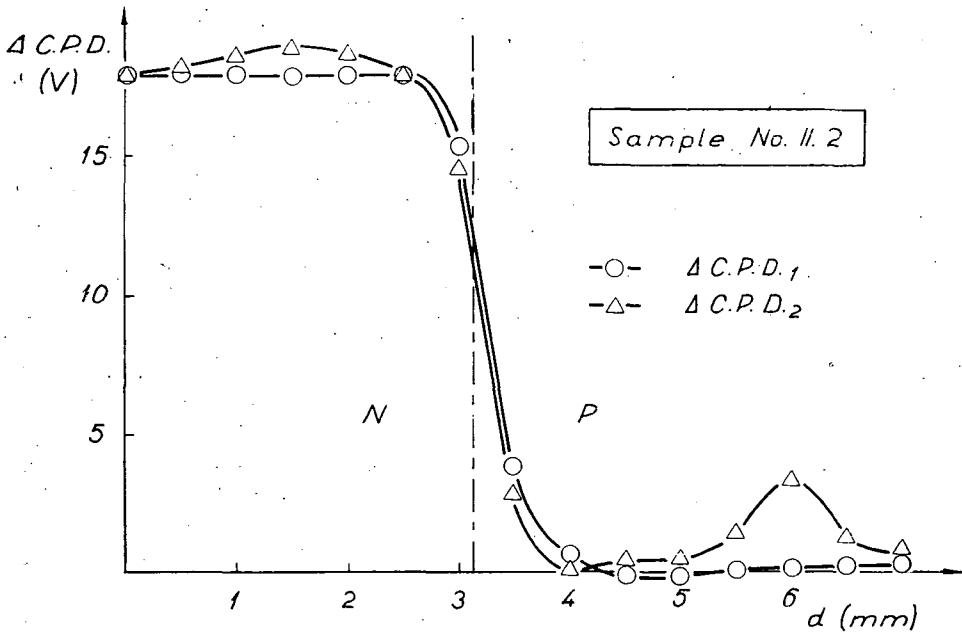

Fig. 8b. Results of repeated measurements of Fig. 8a showing the reproducibility of the measurements.

Conclusions

The inhomogeneities of C.P.D. found on the samples can be attributed to the following factors:

(a) contaminations of inhomogenous distribution on the oxide, getting to the surface during the manufacturing process and not removable by washing in distilled water or carbon tetrachloride,

(b) contaminations of inhomogenous distribution, getting into the bulk of the oxide during the manufacturing process, and their migration towards the surface layer of the oxide,

(c) inhomogeneities in the thickness and structure of the oxide layer,

(d) local charge accumulations on the surface of the thick, isolating oxide, due to external effects.

Sodium seems to play probably an important role among the contaminations [9]. It could not be determined by the measurements which of the factors mentioned above is dominant in producing the C.P.D. inhomogeneities observed.

The presence of mobile positive and negative charges on the surface and in the bulk of the oxide of 2000 Å thickness covering the silicon samples could be unquestionably verified by the measurements of $\Delta C.P.D._1$ and $\Delta C.P.D._2$, though the evaluation of these measurements is more complex and the extent of the accumulation of charges can only be determined with a greater error than by measuring the C.P.D. directly.

The differences of charge accumulation on the samples examined can be attributed to minor differences in the technological process.

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ИЗМЕРЕНИЯ C.P.D. НА ПОВЕРХНОСТИ ОКСИДИРОВАННОГО КРЕМНИЯ

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В работе выполненны измерения разницу контактного потенциала на поверхности образца кремния, имеюшего $p-n$ переходы и покрытого слоем с толшиной 2000 Å. Неоднородность полученного и слабо воспроизводимого C.P.D. приписана примеси встроенной и неоднородно распределонной в процессе производства на поверхности и внутри тольстого оксидированного слоя, или местному накоплению зарядов вследствие внешних воздействий на поверхности толстого и изоляционного оксидированного слоя. С постепенным травлением оксидированного слоя неоднородность уменьшалась и после удаления 1200—1400 Å толщины оксидированного слоя неоднородность была ниже 0.02 В, ошибки измерения.

Разработан новый метод для исследования образцов кремния с толстым оксидированым слоем и имеющих большой неоднородности C.P.D. Этим методом авторами получены воспроизводимые результаты.

На основе данных экспериментов сделан вывод о разделении мобильных положителных и отрицательных зарядов на поверхности и внутри оксидированного слоя под действием термообработки, и об аккумулировании зарядов на p и n местах образца.

Различное отклонение, полученное в аккумулировании зарядов на исследованных образцах приписано небольшим различиям в технологии изготовления образцов.