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STUDY OF DEFECTS IN p-TYPE SILICON IMPLANTED WITH CHANNELED LOW ENERGY PHOSPHOROUS IONS

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Abstract: Phosphorous ions with energy of 40 keV were implanted in p-type silicon at the room temperature in the (111) direction. Low fluences of 10^{12} and 10^{13} ions/cm^2 were used. The temperature dependence of the Hall coefficient and sheet resistivity measurements, together with layer removal technique, were made on van der Pauw geometry of »mesa« structure samples after annealing at higher temperatures starting from 250°C.

A shallow phosphorous donor level (E_c — 0.044 eV) has been found in the highly compensated samples annealed at 450°C. At the higher temperatures (550°C, 650°C) two deeper localized energy levels: E_c — 0.21 eV and E_c — 0.42 eV were determined and associated with multiple vacancy-phosphorous complexes.

It has been found that degeneracy in the samples does not occur for the above experimental conditions.

1. Introduction

It is well known that heavy ion bombardment introduces a severe damage in the crystalline material. The incoming ions spend a part of their energy displacing target atoms from their original positions in the lattice. Initially, the resultant ion implantation damage has a strongly localized character and is centered around the track of the incident ion. At high doses the damage regions overlap to form an amorphous layer.

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The main purpose of our investigation was to detect by electrical measurements deep localized energy levels in the bandgap of silicon, associated with point type defects and introduced by low energy phosphorous ions implanted under channeling conditions. Furthermore, we wanted to check the possibility of the occurrence of degenerate semiconducting layer near the maximum of the implanted ion profile even in the case of relatively low implanted ion doses. It was shown previously[1] that such a layer had a strong influence on the shape of the experimental carrier concentration vs temperature curves and might have introduced substantial errors in the determination of the positions of localized energy levels in the bandgap.

In order to solve this problem we used Hall-effect and sheet resistivity measurements as a function of temperature in conjunction with the sequential layer removal technique. The results of such combined measurements are presented in the subsequent Sections and discussed in view of the validity of the degeneracy model.

2. *Experimental procedure*

The investigation was carried out on 100 ohm cm floating-zone p-type silicon single crystals (»Wacker«). Wafers of diameter of about 20 mm and (111) orientation were implanted over an area of 15 mm in diameter at room temperature*). We used 40 KeV phosphorous ions and low fluences such as 10^{12} and 10^{13} ions/cm^2. Ions were implanted under $\langle 111 \rangle$ channeling direction into substrates of opposite conductivity type to form p-n junctions, which provided the electrical insulation necessary for investigations of the electrical properties of the implanted layer.

Hall measurements were made using the van der Pauw configuration. The van der Pauw pattern was delineated by meshing and »mesa« etching of the implanted surface of the wafers.

The implanted samples were annealed at successively higher temperatures in a quartz tube. The annealing times were thirty minutes for all temperatures and implants.

The anodic stripping technique was utilized in order to remove uniform silicon layers, i.e. silicon dioxide layer was anodically grown and then removed by etching in the concentrated hydrofluoric acid. The anodization was carried out with the constant current density of 5 mA/cm^2 in a presence of high intensity »white« light.

The Hall-effect and sheet resistivity measurements were performed in the temperature range from 77—350 K after each annealing step (up to 850°C) and after subsequent removals of surface implanted layers (up to the thickness of 2200 Å).

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*) The implantation was performed with the mass isotope separator at the University of Rome.

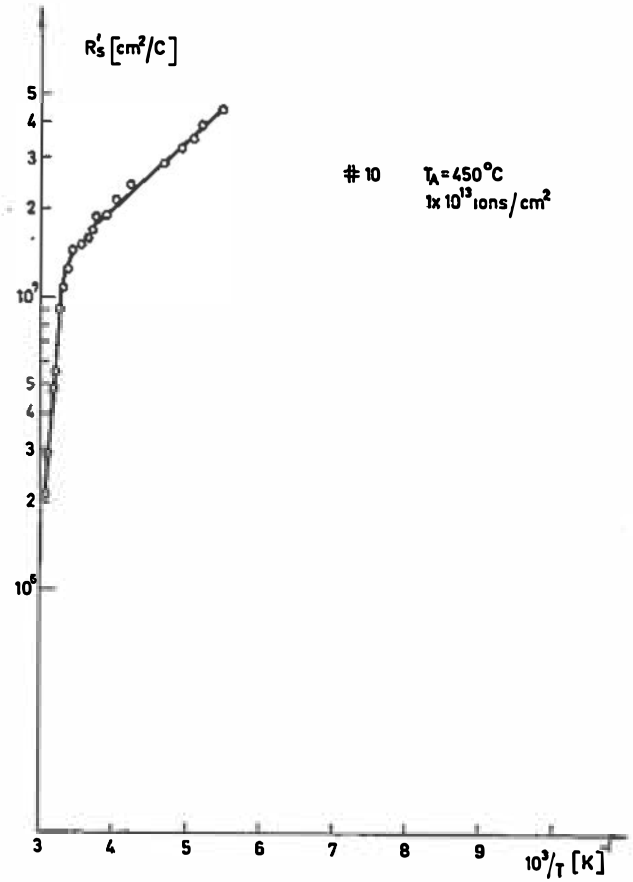

Fig. 1. The Hall coefficient as a function of temperature after annealing at 450°C.

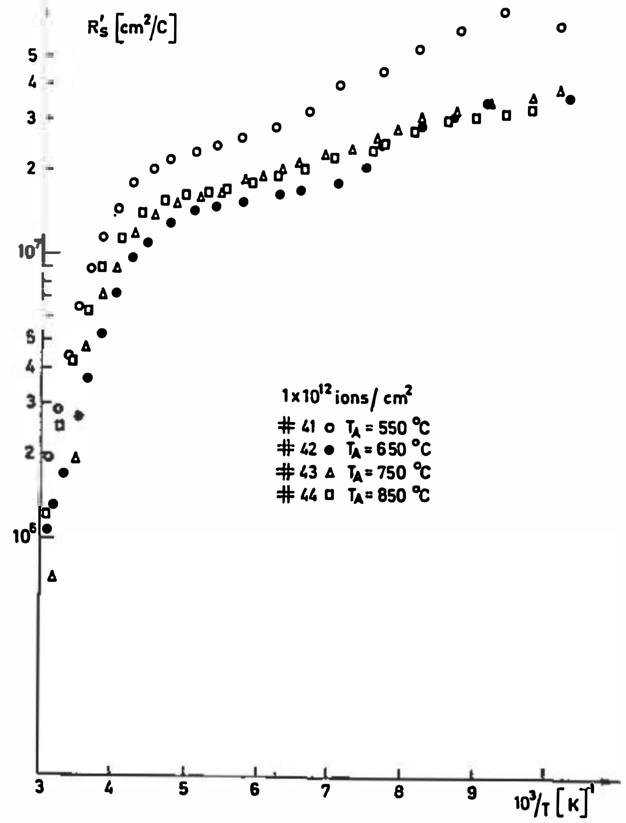

Fig. 2. The temperature dependence of the Hall coefficient as a function of annealing temperature of samples implanted with 10^{12} ions per cm^2.

The effective surface carrier concentration $(N_s)_{\text{eff}}$ and the effective mobility μ_{eff} have been calculated from the sheet resistivity ϱ_s and the sheet Hall coefficient R_s using the relations

$$(N_s)_{\text{eff}} = \frac{1}{R_s e}, \tag{1}$$

$$\mu_{\text{eff}} = \frac{R_s}{\varrho_s}, \tag{2}$$

where e is the electronic charge.

The depth distribution of the volume carrier concentration n and the mobility μ were calculated according to the formulas

$$n_i = \frac{\Delta\,(1/\varrho_s)_i}{e d_i\, \mu_i} \tag{3}$$

and

$$\mu_i = \frac{\Delta\left(\frac{R_s}{\varrho^2{}_s}\right)_i}{\Delta\,(1/\varrho_s)_i}, \tag{4}$$

where μ_i, n_i and d_i are the mobility, carrier concentration and thickness of the i-th layer and $\Delta\,(\quad)_i$ are changes associated with the removal of this layer.

3. *Results*

Samples implanted with 10^{13} phosphorous ions per cm^2 were annealed at 250°, 350°, 450°, 550°, and 650°C for thirty minutes. The 250° and 350°C annealing steps were not efficient to activate electrically the implanted phosphorous ions to a greater extent, and the measurement of the Hall coefficient as a function of temperature was not possible before annealing at 450°C. Fig. 1 shows such a curve and its low temperature slope gives the energy level 0.044 eV below the conduction band corresponding to the localized phosphorous donor levels.

Fig 2 shows the temperature dependence of the Hall coefficient as a function of annealing temperature of samples implanted with 10^{12} ions per cm^2. The maximal concentration of free carriers has been already achieved after the 650°C annealing. It amounts to about 48 percent of implanted ions for the dose of 10^{12} ions/cm^2, and 60 percent for 10^{13} ions/cm^2.

The dependence of Hall coefficient on reciprocal temperature and the thickness of removed layers is shown in Fig. 3 (for the annealing temperature of 550°C) and in Fig. 4 (T_A = 650°C). A remarkable increase in the Hall coefficient can be seen after removal of the first layer (1000 Å). In addition, there are several steps in the curves indicating the existence of deeper localized levels in the upper half of the forbidden energy gap. From the positions of plateaus between slopes in the curves we may conclude that several defects are present in comparable concentrations. In such a case we applied a method for correction of experimental slopes

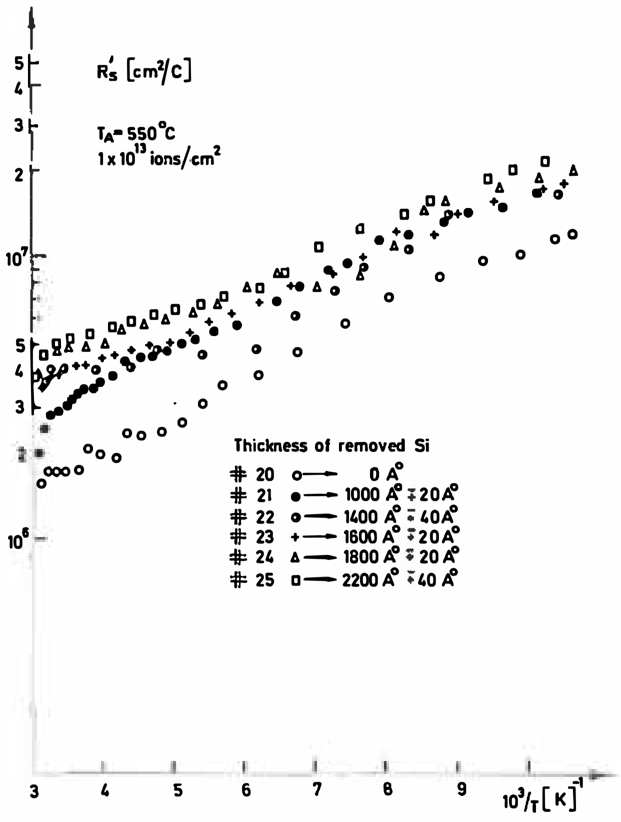

Fig. 3. The dependence of Hall coefficent on reciprocal temperature and the thickness of removed layers for the annealing temperature of 550°C.

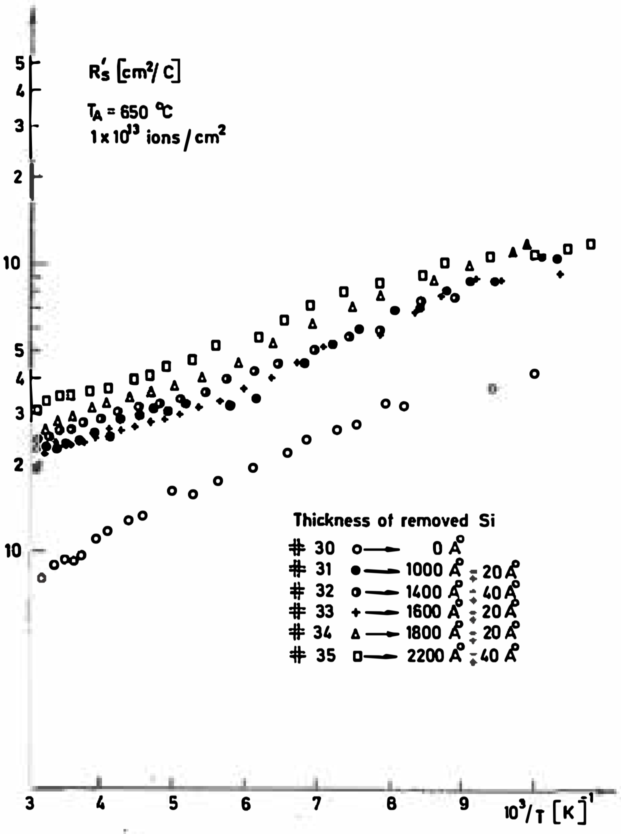

Fig. 4. The dependence of Hall coefficient on reciprocal temperature and the thickness of removed layers for the annealing temperature of 650°C.

suggested by Vitovskii et al.[2] in order to get the correct positions of localized energy levels. The data from Figs. 2,3, and 4 were taken to calculate the energy levels. The results are presented in Fig. 5. Two energy levels were placed at (0.21 ± ± 0.01) eV and (0.42 ± 0.01) eV below the conduction band.

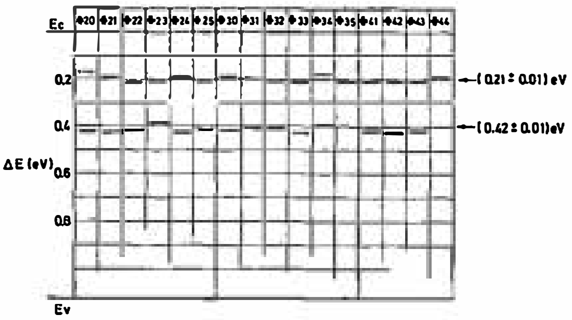

Fig. 5. The positions of localized energy levels calculated with data from Figs. 2, 3 and 4.

The ratio of the Hall coefficient and sheet resistivity gives the Hall mobility. Such data are shown in Fig. 6 for two annealing temperatures. The most important feature is that curves are typical for a non-degenerate silicon ($T^{3/2}$ dependence for impurity scattering and $T^{-5/2}$ dependence for lattice scattering).

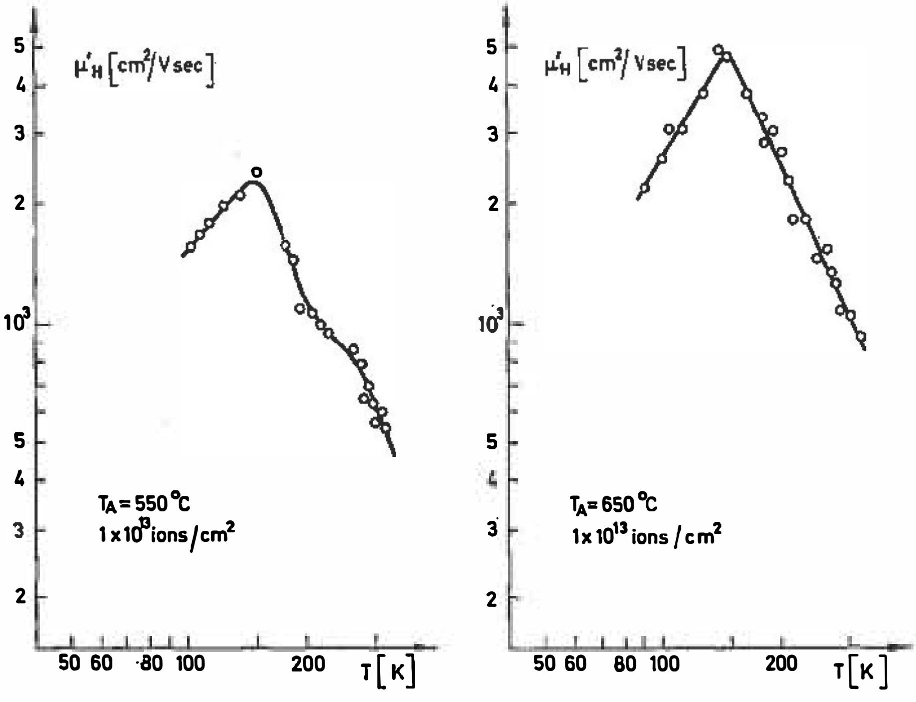

Fig. 6. The Hall mobility for two annealing temperatures.

The differences in the carrier concentration of the samples before and after removal of the implanted layers are shown in Fig. 7. It is seen from the figure that the maximum of the carrier concentration is within the first 1000 Å of the implanted layer, i. e. for 10^{13} ions/cm^2, and $T_A = 650°C$ it is equal to $4.5 \cdot 10^{17}$ electrons/cm^3. Such a number is much lower than the limiting carrier concentration for degeneration in silicon (which is around 10^{19} cm^{-3}).

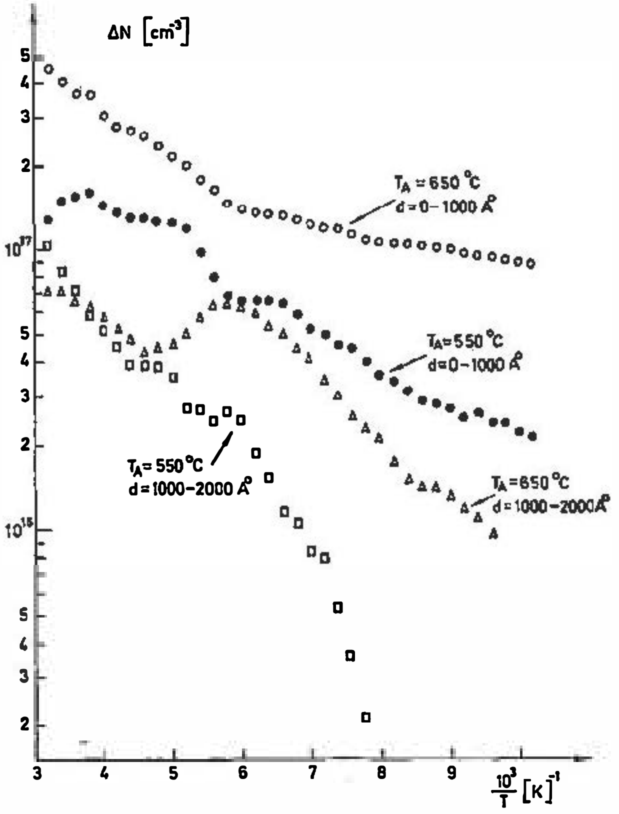

Fig. 7. The differences in the carrier concentration of the samples before and after removal of the implanted layers.

The distribution of defects in the implanted layer is given in Fig. 8. The concentration of both defects decreases with depth. However, their behaviour is different in respect to the thermal treatment. The higher annealing temperature increases the concentration of defects with the energy level at E_c — 0.21 eV, and the opposite is true for the E_c — 0.42 eV level.

Both defects have a tendency for out-diffusion towards the surface with the increase in the annealing temperature.

4. *Discussion and conclusion*

Three energy levels associated with lattice defects have been found by the Hall effect measurements in the phosphorous implanted layer:

— E_c — 0.044 eV, which corresponds to the well-known donor level of the phosphorous dopants in the substitutional sites of the silicon lattice,

— E_c — 0.21 eV, which was also found previosly after irradiation of silicon with fast neutrons, electrons and gamma-rays[3], as well as after low energy phosphorous implantation[4], and

— E_c — 0.42 eV, a level not yet obtained in the case of phosphorous implantation into silicon. This energy is close to that of the E-center or divacancy, but such an identification is not correct because of a much higher thermal stability of that defect in the implanted silicon (up to 750°C).

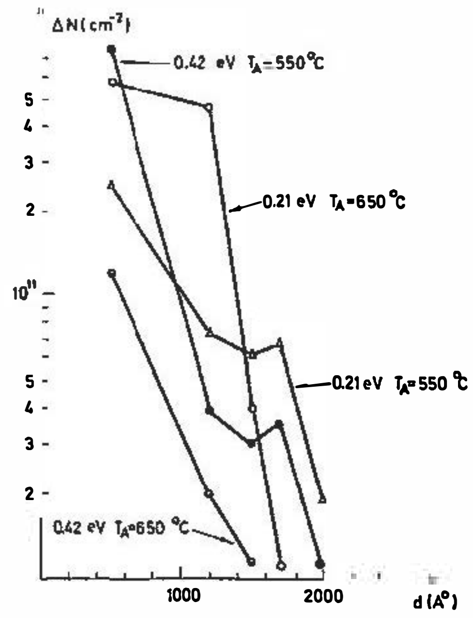

Fig. 8. The distribution of defects in the implanted layer as a function of distance from the sample surface.

The defect associated with the E_c — 0.21 eV level exhibits even higher stability and anneals out at 850°C. It is possible to make some speculations upon the nature of that defect. Based on the finding of Cembali et al.[5] that, in the case of channeled phosphorous implantation, the damage peak is somewhat deeper inside the crystal than the implanted ion distribution peak, the higher annealing temperatures may induce enhanced diffusion and pairing of phosphorous ions and implantation-induced vacancy clusters in the intermediate zone. An indication of such a process is shown in Fig. 8.

As it is well known that simple vacancy- or divacancy-impurity complexes anneal out at temperatures below 600 K, such defects are excluded in our case. However, we know that some multiple vacancy-oxygen complexes are stable up to 800 K$^{6)}$. Therefore, it seems plausible that the two energy levels, $E_c - 0.42$ eV and $E_c - 0.21$ eV belong to the three-vacancy- or multiple vacancy-phosphorous defects. Of course, such identifications should be confirmed by the ESR measurements.

Finally, we have shown that the ordinary way of calculating the energy levels from the slopes of the Hall coefficient vs. temperature curves is permissible in the case of silicon implanted with channeled low energy phosphorous ions up to fluences of 10^{14} ions/cm^2, since neither degeneracy nor the so-called »current-flow switches« occur in the implanted layer.

References

1) C. Mac Donald and G. Galster, Rad. Effects **6** (1970) 223;

2) N. A. Vitovskii, T. V. Mashovets and S. M. Ryvkin, Fiz. tverd. tela **4** (1962) 2849, Soviet Physics Solid State **4** (1969) 2088;

3) J. H. Crawford, Jr., The Interaction of Radiation with Solids, ed. by R. Strumane, J. Nihoul, R. Gevers and S. Amelinckx, North-Holland Pub.shing Co., Amsterdam 1964, p. 449;

4) N. B. Urli and R. Gibson, Proc. II Inter. Conf. on Ion Implantation in Semiconductors, Germisch-Parten-Kirchen 1971. ed. by I. Ruge, J. Graul, Springer-Verlag Berlin (1971), p. 466;

5) F. Cembali, R. Galloni, F. Mousty, R. Rosa and F. Zignani, Rad. Effects **21** (1974) 245;

6) J. W. Corbett, J. C. Bourgoin, L. J. Cheng, J. C. Corelli, Y. H. Lee, P. M. Mooney, and C. Weigel, Proc. Inter. Conf. on Radiation Effects in Semiconudstors, Dubrovnik, Sept. 6—9, 1976.

STUDIJ DEFEKATA UVEDENIH IMPLANTACIJOM NISKOENERGETSKIH KANALIZIRANIH IONA p^{31} U p-TIP SILICIJA

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Sadržaj

U silicij p-tipa, vodljivosti 100 Ohm-cm, implantirani su ioni fosfora p^{31} na sobnoj temperaturi s energijom 40 keV. Smjer implantacije je bio (111). Upotrebljene su doze od 10^{12} i 10^{13} iona po cm^2. Izvršena su mjerenja zavisnosti temperature Hallovog koeficijenta o vodljivosti slojeva na uzorcima nakon napuštanja na višim temperaturama, počevši od 250°C, uz postepeno skidanje slojeva metodom anodne oksidacije. Nakon napuštanja dobiven je donorski nivo fosfora ($E_c - 0.044$

eV), te nivoi E_c — 0.21 eV i E_c — 0.42 eV koji pripadaju kompleksima višestrukih praznina i iona fosfora unutar implantiranog sloja.

Diskutirana je nehomogenost u raspodjeli tih defekata u ovisnosti o dubini unutar implantiranog sloja, te ovisnost koncentracije defekata o temperaturi napuštanja. Pokazano je da kod gore navedenih uvjeta implantacije ne dolazi do stvaranja degeneriranog sloja unutar silicija.