Electron trapping in neutron transmutation doped silicon

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(Received 11 December 1978; accepted for publication 8 March 1979)

The isochronal anneal of phosphorus in neutron transmutation doped silicon has been studied with electron paramagnetic resonance. It was found that the fraction of phosphorus atoms occupying a substitutional lattice site increases almost linearly in the range of anneal temperatures from 250 to 700°C. Recovery of the Fermi level to the normal *n*-type position is observed to occur between 500 and 700°C. It is proposed that phosphorus atoms are constitutent parts of the electron trapping centers, capable of trapping two electrons.

PACS numbers: 72.80.Cw, 61.70.Tm, 76.30.Mi

The technology of high-voltage power devices, such as thyristors and power transistors, requires high-purity dislocation-free silicon with very tight tolerances in resistivity variations both on a macroscopic and microscopic scale. The nuclear transmutation doping, first proposed by Lark-Horovitz,[1] in which the homogeneity of the dopant distribution is determined only by the neutron flux homogeneity, has, in principle, these particular properties. A flux of thermal neutrons alters the ^{30}Si isotope, which is assumed to be randomly distributed in the natural concentration of 3.09%, in the stable phosphorus isotope ^{31}P. At present, there is sufficient experimental evidence from resistivity measurements to confirm the homogeneity in phosphorus donor distribution.[2]

During the transmutation doping process, consisting of a prolonged irradiation with nominally thermal neutrons, it is unavoidable that the silicon crystal is seriously damaged. A high-temperature anneal is therefore required to restore the host lattice and to force the phosphorus atoms to occupy the substitutional sites. We have undertaken a study to obtain a better understanding of the annealing process, with emphasis on a determination of the fraction of phosphorus

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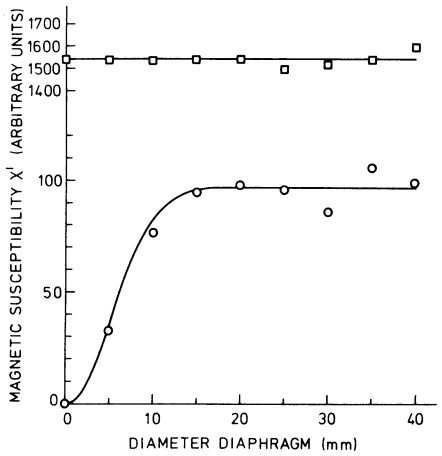

FIG. 1. Phosphorus EPR signal X' as function of the intensity of illumination with silicon-filtered penetrating light (○). The reference sample signal is also shown (□).

atoms that act as normal donors. The isochronal annealing procedure consisted of heat treatments of 1 h at successively higher temperatures, in steps of 100 up to 500 °C, and steps of 50 °C thereafter up to 700 °C.

The starting material was float-zone dislocation-free p-type silicon with a resistivity of 2000 Ω cm. Hall measurements as a function of temperature indicated that the degree of compensation was less than 0.1. Therefore, the initial phosphorus concentration was lower than 10^{12} atoms per cm^3. Part of this ingot was irradiated with a fluence of 1.3×10^{18} neutrons per cm^2 to give a resistivity of about 10 Ω cm. The irradiation was done in the Industrial Research Reactor of AERA, Harwell, U.K. The ratio of thermal to fast neutrons at the position of the sample holder was typically 800 : 1. In this particular run the sample temperature reached 220–250 °C.

Electron paramagnetic resonance (EPR) measurements are a powerful tool for the present study because unionized phosphorus donors on substitutional lattice sites can be detected unambiguously by means of the associated ERP spectrum. The spectrum is characterized by the g value of 1.9985 and an isotropic hyperfine splitting of 42.0 G.[3] Measurements were performed in a superheterodyne K-band spectrometer, microwave frequency 23 GHz, tuned to observe the dispersive part of the susceptibility. The sample temperature was about 8 K. Phosphorus concentrations in the neutron transmutation doped sample under investigation were determined as accurately as possible by comparing the resonance amplitudes with those of a reference sample. The reference sample was used to eliminate possible drift and irreproducibilities in the spectrometer tuning. It consisted of a piece of heavily P-doped silicon as described by Gere.[4] The reference sample was first calibrated against a conventionally-phosphorus-doped sample of 8.2 Ω cm. The neutron n-doped sample was cut to the same dimensions as the calibration sample. In EPR only the paramagnetic neutral donors are observed. It was found that by illumination of the sample with light of an appropriate wavelength the phosphorous donors are converted to the EPR-observable state. For that purpose the sample in the microwave cavity could be illuminated during the EPR measurements. The steady-state population under illumination is reached instantaneously compared to the time necessary to do the measurement. During the experiments the light intensity was kept constant. Figure 1 illustrates how the steady-state occupation of the phosphorous atoms increases as a function of light intensity. The saturation of the light reaching the sample is sufficient to convert all substitutional phosphorous into the paramagnetic state. While Fig. 1 presents results for the unannealed sample, a similar saturation effect was observed after each anneal step.

The phosphorus EPR signal was measured after each anneal step, first in the dark and after that under illumination. Results of the experiment are presented in Fig. 2, where the un-ionized substitutional phosphorus concentration is plotted as a function of the temperature in the isochronal annealing procedure. The open circles correspond to measurements of n_s obtained under saturation illumination with white light through a silicon filter at room temperature. The lower curve labeled n_d corresponds to the same measurements performed in the dark.

The conclusions that can be drawn from this experiment can be summarized as follows. Already before any intentional anneal the concentration of phosphorus on substitutional sites amounts to 6×10^{13} atoms per cm^3, which is equal to about 25% of the total phosphorus created. The large magnitude of this fraction is probably a result of the inadvertent temperature rise during the reactor irradiation. Upon anneal the substitutional phosphorus content increases, quite gradually in the broad temperature range from 250 to 700 °C. In this temperature range the phosphorus atoms are apparently released by the annealing of a variety of radiation defects of which they were constituent parts. The information at present available about this process is insufficient to allow definite statements to be made about the identity of the centers involved. However, in other EPR studies a number of radiation defects have been observed for which a relation with phosphorus was established. The best known of

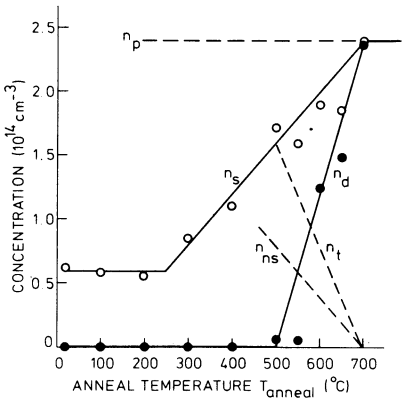

FIG. 2. Concentration n_s and n_d of neutral substitutional phosphorus in neutron transmutation doped silicon after isochronal anneal of 1 h at T_{anneal}. Measurements made in the dark ●, and under illumination ○; derived results for n_p, n_{ns}, and n_t are represented by dashed lines.

these, the phosphorus-vacancy complex, is immobile only below 150 °C [5] and will have escaped from our samples because of the high irradiation temperature. Other phosphorous-related defects to be considered are the Si-A_1 center[6] and the Si-ML_1, to ML_6 centers.[7] Complicated spectra arising from radiation damage were observed, in general agreement with the results of Corbett *et al.*[8] after neutron irradiation and of Stetter *et al.*[9] after thermal neutron irradiation. As yet, no attempts were made to identify the corresponding centers by orientation-dependent studies.

Only after anneal at 500 °C and above the phosphorus EPR spectrum is also visible when the sample is kept in the dark. Between 500 and 700 °C the last electron traps disappear and the Fermi level recovers to the normal n-type position. This is consistent with results obtained by deep-level transient spectroscopy.[10] Guldberg[11] observed seven bulk electron traps which disappear upon anneal betwen 425 and 725 °C. In an EPR study similar to the present one, Kaufman *et al.*,[12] using a lower neutron fluence, found higher temperatures for the onset of the recovery. In addition, Young *et al.*[13] made a careful study of all the electrical parameters associated with annealing effects in neutron-irradiated material. An analysis of the EPR signal both of the substitutional phosphorous as observed in the dark as well as those associated with radiation damage was given.

Both processes, that is the occupation of the regular lattice sites by the phosphorus atoms and the anneal of the electron traps, reach completion at the same temperature, 700 °C. This suggests that the nonsubstitutional phosphorus participates in the formation of complexes capable of electron trapping. A further analysis also yields the multiplicity of the trapped charge of the complex involved. The procedure is illustrated by the dashed lines in Fig. 2.

The total concentration of phosphorus n_p (2.4×10^{14} cm^{-3}) present in the sample consists of a substitutional fraction, concentration $n_s(T)$, which depends on the annealing temperature and a nonsubstitutional fraction concentration

$$n_{ns}(T) = n_P - n_s(T)$$

illustrated by the dashed line in Fig. 2. In the temperature range 500–700 °C the EPR signal in the dark, corresponding to the occupied substitutional phosphorus, concentration n_d, is determined by the fraction of substitutional phosphorus, concentration n_s, of which we have to substract the total negative charge $n_t(T)$ stored in the complexes:

$$n_d(T) = n_s(T) - n_t(T).$$

The total electrical charge $n_t(T)$ stored in the complexes is proportional to the concentration of nonsubstitutional phosphorus atoms, n_{ns}, since they are part of the complex and also proportional to the number of electrons that can be stored in one complex β,

$$n_t(T) = \beta\,[n_t(T) - n_s(T)].$$

Therefore,

$$n_d(T) = n_s(T) - \beta\,[n_P - n_s(T)].$$

At the point where the annealing process has reached 500 °C, the stored charge trapped in the complexes just equals the number of substitutional phosphorus atoms according to Fig. 2:

$$n_d(500) = n_s(500) - \beta\,[n_P - n_s(500)] = 0,$$

resulting in

$$\beta = n_s(500)[n_P - n_s(500)]^{-1} = \frac{1.6\times10^{14}}{2.4\times10^{14} - 1.6\times10^{14}} = 2.$$

Note that the validity of the derivation does not depend on the shape of $n_s(T)$ and $n_d(T)$ although a nearly linear behavior is observed. This linear behavior, also observed by other investigators,[12] excludes a single activation energy for both the annealing process of the defects as well as the process of occupying regular lattice sites of the phosphorus atoms.

On the basis of the earlier assumption that the only trapping centers present above 500 °C are identifiable with the nonsubstitutional phosphorus centers, we conclude that each of these centers can trap two electrons.

We thank Dr. J. Shannon, Philips Res. Labs., Salford, U.K. for arranging the irradiation.

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