Electron Paramagnetic Resonance on Divacancies in Phosphorus-Implanted Silicon

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Abstract

Electron paramagnetic resonance has been used to study radiation damage after implantation of 50 keV phosphorus ions into high resistivity p-type silicon. Doses of $2 \cdot 10^{14}$ - 10^{16}P/cm^2 are found to produce small numbers ($\sim 10^{13}$/cm^2) of the Si-G7 spectrum, which arises from the single negative charge state of the divacancy. The observed introduction rate is an order of magnitude lower than the production as observed by infraredabsorption. This indicates, that nearly all of the divacancies are in the neutral charge state. Consequently the Fermi level must be positioned near the middle of the energy gap.

Annealing studies show annihilation of divacancies around 200 $^{\circ}$C. From this result a trap concentration of $9 \cdot 10^{20}$/cm^3 is calculated. Details in the resonance spectra, such as linewidth and relaxation time, point in the direction of a high concentration of defects or distortions of the crystal lattice.

Introduction

When crystalline material is bombarded with heavy charged particles severe damage is the result. The incoming ions spend part of their energy in displacing substrate atoms from their original positions. The radiation damage, which is brought about by ion implantation, has a strongly localized character and is centered around the track of the incident ion. At high doses these damage regions overlap to form an amorphous layer.

Ion implantation can be used as a technique for doping semiconductor material. It turns out, however, that the electrical properties of the implanted layer after irradiation at room temperature are governed completely by the amount of damage. Only after anneal at elevated temperatures a substantial fraction of the implanted ions becomes electrically active.

In this paper we present electron paramagnetic resonance (EPR) measurements on the radiation damage in phosphorus-implanted silicon. The great advantage of using EPR is the wealth of information, that is available on defects produced by electron and neutron irradiations in silicon [1]. At least 30 paramagnetic defects have been discovered. A number of them has been identified as single or multiple vacancies and vacancy-impurity complexes. Applied to ion implantation the advantage of EPR over other techniques is its sensitivity (10^{12}-10^{13} defects/cm^2 are enough for identification) and its resolution: even different charge states of the same defect can be recognized and studied separately although they are present in the same sample.

In our measurements we observed the negative divacancy (Si-G7) to be the dominant anisotropic paramagnetic defect after implantation of 50 keV phosphorus ions in high resistivity p-type silicon. Divacancy production and annealing has been studied. Results indicate a high defect concentration in the vicinity of the divacancies.

Experimental

The silicon samples were approximately 25 mm · 10 mm · 0.08 mm in size, oriented in such a way, that the surface is a (110) plane. All samples were cut from the same ingot of Czochralski-grown, 1000 Ωcm p-type silicon and were supplied by Philips Research Laboratories in Amsterdam. Implantations were performed in a 100 keV mass separator at the Institute for Nuclear Physics Research, Amsterdam [2]. Phosphorus ions with an energy of 50 keV were implanted in a nonchanneling direction at a dose rate of 10 μA/cm^2. After implantation the sample was cut in three parts. These parts were then placed on top of each other in the microwave cavity.

The resonance measurements were carried out at 4.2 K with a 23 GHz superheterodyne microwave spectrometer, tuned to detect dispersion. Power incident on the cavity was ~1 mW.

Phase sensitive detection at 19 Hz was employed to enhance the signal-to-noise ratio. Calibration of the spectrometer for determination of g-values and total number of spins was achieved using the known g-value of conduction electrons in heavily doped silicon, $g = 1{,}99875 \pm 0.0001$ [3].

Results

In all our samples we identified the Si-G7 spectrum, arising from the single negative charge state of the divacancy, as the dominant anisotropic paramagnetic defect. We also observed in each sample the isotropic resonance line at $g = 2.0055$, which has been related to dangling bonds present in amorphous silicon [4].

The divacancy is one of the best understood defects in silicon, largely because of the work of Watkins and Corbett [5]. The microscopic model they proposed to explain their results accounts for the observed hyperfine interactions and motional effects and the results of uniaxial stress experiments and production studies. The connection with electrical and optical work has been well established [6, 7].

EPR spectra

Fig.1 shows two divacancy spectra we observed in the same sample after implantation of $2 \cdot 10^{15} P/cm^2$. These two spectra belong to two different sets of divacancies with different spin-lattice relaxation times. 1a is recorded in phase with

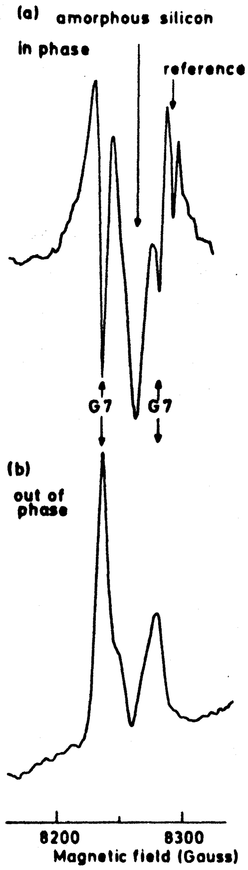

Fig.1. EPR spectra in dispersion at 23.190 GHz for H//[111]; a) in phase with magnetic field modulation; b) 90° out of phase. Temperature is 4.2 K.

magnetic field modulation and shows resonance lines for which slow passage conditions hold, including the reference line and the amorphous silicon resonance.

If the phase sensitive detector is tuned to detect signals, which are 90° out of phase, all these lines have disappeared and another divacancy spectrum emerges. This spectrum has a much longer relaxation time, resulting in adiabatic fast passage conditions with a corresponding lineshape [8].

The divacancy spectra, that are observed after electron irradiation [5], have a still longer relaxation time; they are best studied at 20K. Below that temperature the relaxation time becomes so long that the signal strength diminishes an order of magnitude. We did not observe such effects upon cooling down to 1.5K. Consequently both groups of divacancies have a shortened relaxation time. Apart from this the linewidths have increased: they are 5 and 8 G respectively for in phase and out-of-phase resonances as compared to 3 G for resonance in electron irradiated silicon.

Production

The divacancy production rate we have measured was quite low: at our lowest dose of $2 \cdot 10^{14} P/cm^2$ it is 0.022 divacancies per ion. At higher doses this ratio decreases constantly, at $\Phi = 2 \cdot 10^{15} P/cm^2$ the production rate is 0.0073 divacancies/ion (approximately $\Phi^{-\frac{1}{2}}$ dependence). We have observed divacancies up to a dose of $10^{16} P/cm^2$; at these high fluences the scatter in the results was too large to draw reliable conclusions about production rates, except that saturation is important.

This introduction rate may be compared with the results of infraredabsorption experiments by Stein [9], who has measured production rates, which are two orders of magnitude larger. This discrepancy can be solved by assuming, that the majority of the divacancies are in the neutral charge state and therefore not detectable by EPR. This tells us something about the position of the Fermi level: nearly everywhere it will be less than 0.55 eV from the valence band, the level which is the separation between the negative and the neutral charge state. A lower

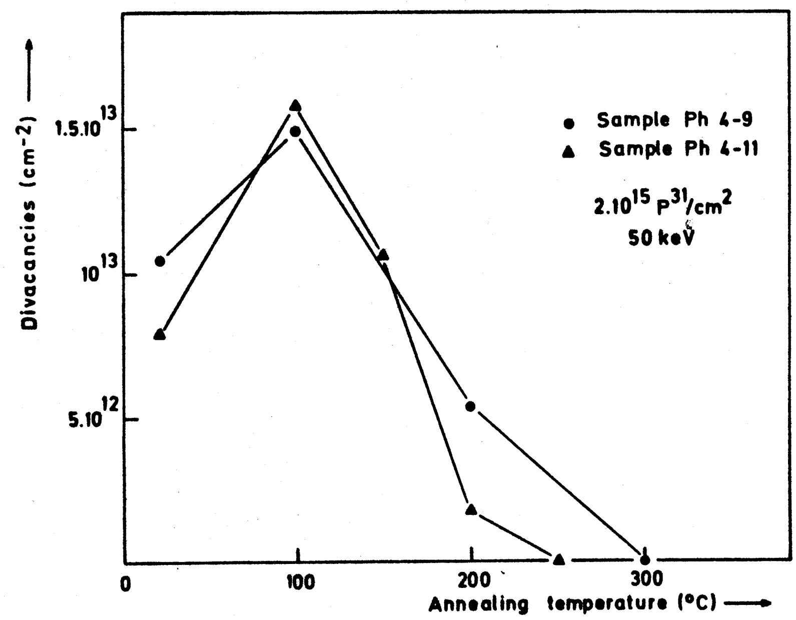

Fig.2. Isochronal annealing curve for divacancies, measured out of phase. Annealing time is 30 minutes.

limit of 0.25 eV results from the fact, that the Si-G6 spectrum, associated with the positive charge state, is not observed.

Annealing

Fig.2 shows the result of two isochronal annealing studies on samples which were implanted to the same ion dose. Sample Ph 4-9 was annealed at 100 ^{o}C temperature intervals, sample Ph 4-11 was annealed at 50 ^{o}C steps. Annealing time at each temperature was 30 minutes.

All divacancies have disappeared completely after heating to 250 ^{o}C. This temperature is substantially lower than the temperature region in which Watkins and Corbett [5] observed divacancy annealing in electron irradiated silicon. Their results for 15 minutes annealing time are compared with ours in Fig.3.

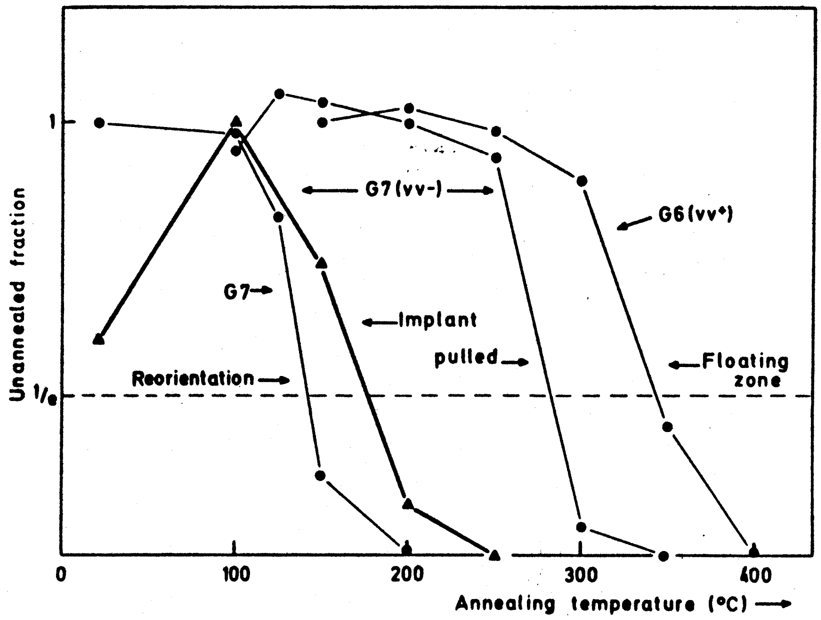

Fig.3. Comparison of the isochronal annealing curve for sample Ph 4-11 (heavy line) with the results of Watkins [5] for divacancy reorientation and annealing.

Watkins and Corbett observed the highest anneal temperature in high purity silicon. In oxygen containing material ($5 \cdot 10^{17}$ O/cm^{3}) the diffusing divacancies are trapped by the oxygen atoms and disappear at lower temperatures. Continuing this line of argument a lower anneal temperature indicates a higher trap concentration.

To estimate this concentration we have included in Fig.3 the disappearance of vacancy-vacancy axis polarization vs. anneal temperature [5]. This polarization is induced by applying uniaxial stress at 150 ^{o}C. At the temperature, where this polarization disappears, the jump frequency is just once per 15 minutes annealing time. From these data one obtains a jump frequency

$$\nu(T) = \nu_0 \exp(-E/kT) \qquad \nu_0 = 8 \cdot 10^{12}\ \mathrm{sec.}^{-1}, \quad E = 1.3\ \mathrm{eV}$$

To calculate the trap concentration from this jump frequency we use the formula [10]:

$$t = \frac{1}{4\pi NDR}$$

t : annealing time
N: trap concentration
R: capture radius

D is the diffusion constant:

$$D = \frac{1}{6}\nu(T)a^2$$

Using as a capture radius the silicon-silicon nearest neighbour distance a = 2.35Å one obtains:

$$N = \frac{6}{4\pi a^3 \nu(T)t} = \frac{3.7 \cdot 10^{22}}{J}$$

where J is the total number of jumps during the anneal period. For our case we calculate $J = 40$ and $N = 9 \cdot 10^{20}/\mathrm{cm}^3$.

A remarkable result from the annealing studies is the reverse annealing between room temperature and 100 °C. Other authors [11, 12] have concluded, that divacancies are not a primary defect but are formed by combining single vacancies, which are liberated from other defects which anneal below room temperature. Apparently this process continues up to 100 °C.

Discussion

Electron paramagnetic resonance is a valuable technique for obtaining information on a microscopic scale. It is an important result, that the observed divacancies are present in the original lattice, even at doses, which are high enough to produce an amorphous layer. The surrounding of the divacancies still has long range order [13]. In this normal crystalline environment there is a high density of defects, $\sim 10^{21}/\mathrm{cm}^3$. This concentration will probably be lower, since it was calculated assuming uncorrelated diffusion and the lowest possible capture radius.

It is this high concentration, which must be held responsible for the observed increase in linewidths and the shortening of the relaxation time. Perhaps additional relaxation takes place via the interaction with other spins, such as the spins, which give rise to the amorphous silicon resonance at $g = 2.0055$. The reported concentration [4] of these spins is comparable to our calculated trap density. Another detail in the resonance spectra must be mentioned here: the hyperfine interaction between the electron spin and the nuclear spin of the 4.7% abundant Si^{29} isotope could not be observed [14]. The expected satellite lines could have been smeared out by distortion of the lattice or by deformation of the wavefunction of the resonance electron. Of course such distortions would have its effect on the linewidth too.

Our annealing results compare very well with photoconductivity measurements by Stein [12] in neutron irradiated silicon. He observed the positive divacancy via the associated 3.9 μ band. His annealing curve after low temperature irradiation practically coincides with ours, as well above the maximum at 100 °C as below. Apparently implanted phosphorus ions produce comparable damage as, in the neutron experiment, the recoiling Si atoms, which have after all about the same mass.

Another important consideration is, that a similar annealing behaviour of positive (3.9 μ) and negative (EPR) divacancies provides a strong argument for ruling out changes in the Fermi level position as a rival explanation.

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13. See also K.L. Brower, W. Beezhold, this conference.

14. Noise would render the lines invisible if their intensity was diminished by a factor of three.