

## ELECTRON PARAMAGNETIC RESONANCE OF TITANIUM IN SILICON

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### Abstract

After a 10 day anneal at  $T=1380^\circ\text{C}$  of p-type silicon in an ampoule of natural quartz a new isotropic electron paramagnetic resonance at  $g = 1.99806 \pm 0.00004$  was observed. An identification of the defect as titanium was obtained from the hyperfine structure and verified by intentionally doping silicon with isotopically enriched Ti. Stress measurements indicate an effective spin  $S=3/2$  of the center, strongly suggesting an interstitial  $T_i$ -position of Ti in its positive charge state on the basis of the Ludwig and Woodbury model.

### Introduction

Transition metal impurities in silicon have received a great deal of attention since the pioneering work of Ludwig and Woodbury (1). To date a number of 40 EPR-spectra have been related to the presence of metals of the first transition series in silicon, some 20 of which are associated with isolated ions on substitutional or interstitial sites in the silicon lattice in a number of charge states. Spectra of 6 out of the 10 3d-transition metal species have been observed, viz. V, Cr, Mn, Fe, Ni and Zn. To our knowledge there has never been an EPR-observation of Sc, Ti, Co or Cu in silicon, isolated, clustered or associated with another impurity, though (with the exception of Sc) observations of these elements in silicon by other techniques, like DLTS or luminescence, have been made. This paper reports measurements on a new EPR-spectrum, which we ascribe to titanium; therefore, we will reproduce some data, relevant to titanium, from Weber's review paper (2).

Titanium introduces 2 donor levels in the gap, near  $E_v+0.25$  eV and  $E_c-0.28$  eV; additionally an acceptor level at  $E_c-0.08$  eV has been found. In spite of the low diffusion coefficient of Ti (four to five orders of magnitude smaller than the other transition metals) Weber assumes interstitial solution of Ti and identifies these levels with  $3d^2/3d^3$ ,  $3d^3/3d^4$  and  $3d^4/3d^5$ , respectively, on the basis of the Ludwig and Woodbury model. A microscopic observation of Ti, as possible with EPR could substantiate or disqualify this identification and possibly shed some light on the diffusion mechanism of Ti.

In the next section we will give an outline of the experimental procedure, followed by a presentation of our results. The last section contains a discussion on the interpretation of these observations.

### Experimental procedure

Float-zoned p-type silicon samples ( $20 \times 2 \times 2 \text{ mm}^3$ ), containing boron (resistivity  $0.9 \text{ } \Omega\text{cm}$ ;  $2 \times 10^{16} \text{ B/cm}^3$ ), aluminium ( $0.8 \text{ } \Omega\text{cm}$ ;  $2 \times 10^{16} \text{ Al/cm}^3$ ), gallium ( $1.5 \text{ } \Omega\text{cm}$ ;  $1.5 \times 10^{16} \text{ Ga/cm}^3$ ) or indium ( $10 \text{ } \Omega\text{cm}$ ;  $0.12 \times 10^{16} \text{ In/cm}^3$ ) were annealed for 10 days at  $1380^\circ\text{C}$  under argon atmosphere in a closed quartz ampoule. Samples were allowed to cool from  $1380^\circ\text{C}$  to just below red heat at the entrance of the oven, followed by a quench to room temperature in water. In the following we will distinguish 4 types of treatment:

- a. anneal in an ampoule of natural quartz (titanium content 63 ppm)
- b. anneal in an ampoule of synthetic quartz (titanium content  $< 0.1 \text{ ppm}$ )
- c. as b, with  $\text{TiO}_2$ -powder rubbed onto the samples
- d. as c, with  $\text{TiO}_2$ -powder, enriched in the  $^{47}\text{Ti}$  isotope to  $68.5 \pm 0.2\%$

Sample resistivity was monitored by conventional four-point-probe technique. EPR-measurements were performed with a superheterodyne spectrometer operating at  $23 \text{ GHz}$ . The magnetic field could be rotated in the  $(011)$ -plane of the silicon samples. We used phase sensitive detection at  $83 \text{ Hz}$  magnetic field modulation. Uniaxial stress could be applied in situ along the  $[011]$ -direction. Most measurements were performed at  $4.2 \text{ K}$ . The g-value of titanium could be obtained to an accuracy of  $\pm 0.00004$  by comparison to the g-value of phosphorus  $g=1.9985$  (postulated to be  $1.99850$  exactly), hyperfine splitting  $A=117.53 \text{ MHz}$  (3), which was present in minute amounts in our samples.

### Experimental results

All samples showed a marked increase of the resistivity after anneal; resistivity of samples b increased by  $50\%$ , while samples c had converted to n-type. Variation of resistivity, measured on the four faces of the samples a could be as large as a factor 10 (in some cases conversion to n-type occurred) and may be indicative for the presence of a slow diffusing donor.

In EPR we observed in all samples an isotropic spectrum with g-value  $g=1.99806 \pm 0.00004$ , which was labelled Si-NL29. The intensity of the spectrum substantially increased by irradiation of the samples with infra-red light of wavelengths shorter than  $1.65 \mu\text{m}$ . In the samples, prepared according to treatments a, b and c, two series of 6 and 8 weaker equally spaced lines, symmetrically located around the central line, were found (fig. 1A, 1B). Due to the intensity of the central line the two inner resonances of both series are not observed, while the high field resonance coincides with a phosphorus resonance. Hyperfine splitting is isotropic and equal for both sets:  $|A|=15.66 \pm 0.03 \text{ MHz}$ . From the isotropy it is concluded that the element responsible for these resonances is at a high-symmetry site: undistorted substitutional or interstitial. The hyperfine structure reveals the presence of two isotopes of nuclear spin  $5/2$  and  $7/2$ , with natural abundances about 8 and 6%, respectively. These isotopes must have nearly equal nuclear g-values  $g_N$ , since the linespacing of both sets is equal. The only element meeting these requirements is titanium, having 5 isotopes:  $^{46}\text{Ti}$ ,  $^{48}\text{Ti}$ ,  $^{50}\text{Ti}$  (nuclear spin  $I=0$ ),  $^{47}\text{Ti}$  ( $I=5/2$ ,  $7.28\%$ ,  $g_N=-0.3153$ ) and  $^{49}\text{Ti}$  ( $I=7/2$ ,  $5.51\%$ ,  $g_N=-0.3154$ ) (4). This identification is further substantiated by the following results:

1. Samples annealed under conditions c showed a ten times stronger EPR signal than samples annealed under conditions a. Samples treated according to procedure b showed ten times less resonance intensity than samples a. The intensity of the EPR-signal is thus seen to be correlated to the amount of Ti present during anneal.

2. Samples d yield a marked increase in the  $^{47}\text{Ti}$ -resonance, as expected when Ti is the element responsible for NL29. From the given enrichment in  $^{47}\text{Ti}$  ( $68.5 \pm 0.2\%$ ) the calculated intensity ratio of a  $^{47}\text{Ti}$ -resonance over the central line is  $0.39 \pm 0.01$ ; experimentally we find this ratio to be  $0.39 \pm 0.02$  (fig. 1C). We conclude that NL29 has to be identified with a single Ti-atom at a site of tetrahedral symmetry.

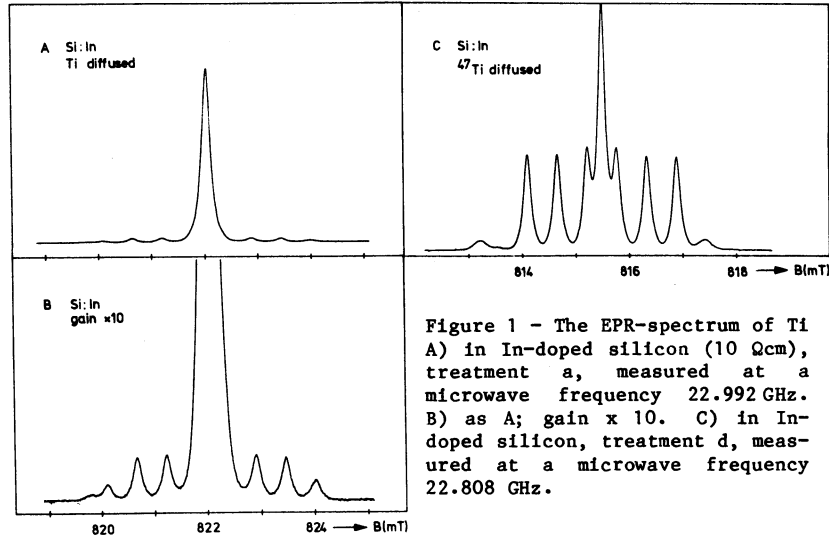


Figure 1 - The EPR-spectrum of Ti  
A) in In-doped silicon (10  $\Omega$ cm),  
treatment a, measured at a  
microwave frequency 22.992 GHz.  
B) as A; gain x 10. C) in In-  
doped silicon, treatment d, meas-  
ured at a microwave frequency  
22.808 GHz.

In order to determine the effective spin of the center we applied uniaxial stress along a  $[0\bar{1}1]$ -direction of a Si:B-sample treated according to a. We observed a fine structure splitting into three components, indicating effective spin  $S=3/2$ . A systematic study was not (yet) performed, but some preliminary results can be given here. The  $M_S=-3/2 \leftrightarrow -1/2$  and  $M_S=1/2 \leftrightarrow 3/2$  resonances are considerably broadened by random crystal strains, possibly induced by iron clusters that are inevitably present after such a long high temperature treatment and relatively slow cooling, whereas the  $M_S=-1/2 \leftrightarrow 1/2$  is not. This is in accord with Berke's (5) formula for the energy  $\Delta E$  of the  $M_S \leftrightarrow M_S-1$  transition:

$$\Delta E = g\mu_B B + (2M_S-1)K = h\nu \quad (1)$$

in which  $K$  is a function of magnitude and direction of stress  $P$  on the crystal.  $B$  is the magnetic field,  $\mu_B$  is the Bohr magneton and  $\nu$  is the microwave frequency. Without stress the position of the lines would be given by :

$$B_0 = \frac{h\nu}{g\mu_B} \quad (2)$$

Applying uniaxial stress along  $[0\bar{1}1]$  introduces stress components  $X_{yy}=X_{zz}=-P/2$  and  $X_{yz}=P/2$ , yielding a fine structure splitting  $\Delta B = B-B_0$ :

$$\Delta B = \frac{3P}{4g\mu_B} [-C_{11} + (3/2 C_{11} - C_{44}) \sin^2 \theta] (2M_S-1) \quad (3)$$

with  $B$  in the  $(0\bar{1}1)$ -plane, making an angle  $\theta$  with  $[100]$ .  $C_{11}$  and  $C_{44}$  are the two independent spin-lattice coefficients in cubic symmetry.

Experimentally there were some indications of anisotropy of the high- and low-field stress splitting, but these were hardly resolved (anisotropy  $< 0.3$  mT). In order to obtain an estimate for the spin-lattice coefficients we will assume  $C_{44} \approx 3/2 C_{11}$ . From the slopes of the straight lines  $\Delta B$  versus  $P$ , shown in figure 2, and the variation of  $\Delta B$  with  $\theta$  we obtain :

$$|C_{11}| = 1.8 \pm 0.3 \times 10^{-34} \text{ J/Pa} \quad (4)$$

and  $C_{44}/C_{11} = 1.5 \pm 0.2$ .

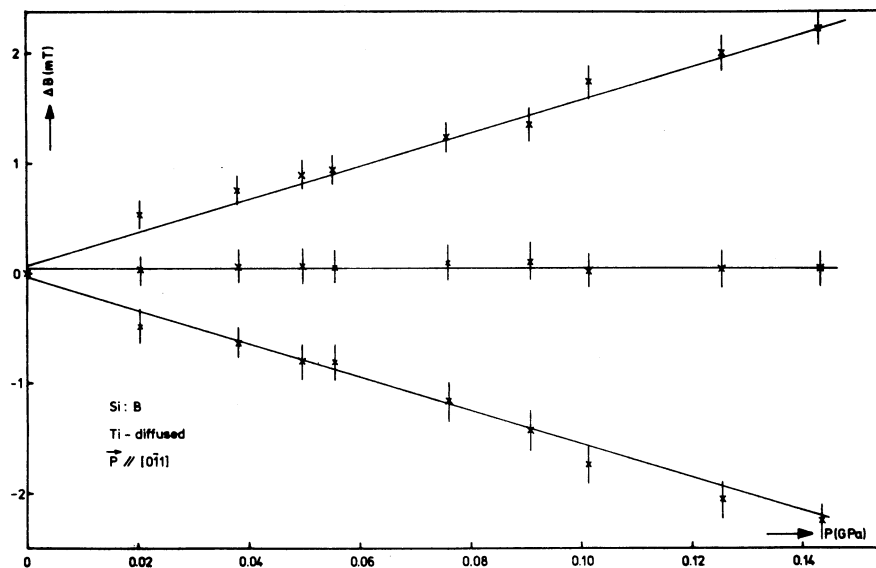


Figure 2 - Stress-dependence of the paramagnetic resonance Si-NL29 of the titanium center in Si:B.

Since the high-field stress-split resonance is lower in intensity than the low-field component we conclude this to be the  $M_s=1/2 \leftrightarrow 3/2$  transition, making  $C_{11}$  and  $C_{44}$  negative. Future measurements with the stress along [100] or [111] will allow a more accurate determination of  $C_{11}$  and  $C_{44}$ . For now, we conclude that the effective spin is  $3/2$ , a result that is also confirmed in Electron Nuclear Double Resonance (ENDOR) on  $^{47}\text{Ti}$  and  $^{29}\text{Si}$  nuclei (to be published).

#### Discussion

Neutral titanium as a free atom has a groundstate configuration  $3d^2 4s^2$ . When entered into the silicon lattice substitutionally, two  $3d$  electrons and one  $4s$  electron will be transferred to the  $4p$ -orbitals and, together with the other  $4s$  electron, form four  $sp^3$ -hybridized bonds with the four silicon neighbors, according to the Ludwig and Woodbury model. The four associated electron spins will pair off with those of the silicon neighbors, leaving a net spin zero on the Ti. In order to comply with the observed  $S=3/2$  three electrons would have to be released or trapped. Releasing three electrons would involve the breaking and reconstruction of three bonds, very probably leading to lower than tetrahedral symmetry, at variance with the experimental observation. Trapping of three electrons would lead to the presence of acceptor levels in the forbidden gap and a lowering of the resistivity in p-type material. From DLTS and our own resistivity measurements we know this not to be the case.

When entered interstitially in the lattice the two  $4s$  electrons will be transferred to the  $3d$ -shell and according to Hund's rule this will give rise to a spin 2. In order to be consistent with our EPR and resistivity measurements, one electron is to be released, leading to  $S=3/2$ , an increase of the resistivity in p-type materials and the introduction of a donor level in the gap; no symmetry lowering is to be expected. This is in agreement with all available data and we are led to the conclusion that Ti occupies an interstitial site of  $43m$  symmetry in the silicon lattice, observed in EPR

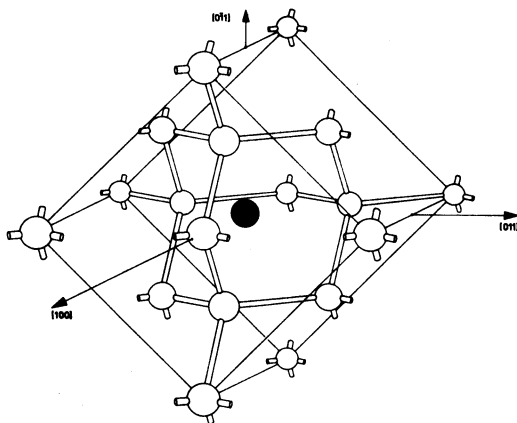


Figure 3 - The Ti-interstitial (black sphere), surrounded by Si-atoms.

in its singly positive charge state, confirming Weber's assignment of the electrical levels. This model is illustrated by figure 3.

In the Ludwig & Woodbury model the tenfold degenerate 3d-orbital will be split by the crystal field in a six-fold degenerate  $t_2$  and a fourfold degenerate  $e$  state, with the  $t_2$  state lowest for interstitial 3d-transition metals. This splitting is given by  $10Dq$ , with  $Dq$  the crystal field splitting parameter. The three electrons of the  $3d^3$ -configuration fill the six  $t_2$  levels according to Hund's rule, forming a  $^4A_2$  groundstate, with pure spin  $S=3/2$  and orbital momentum

$L=0$ . For this non-degenerate groundstate no Jahn-Teller instability is expected. From the observed g-shift  $\Delta g = (g-2.0023) = -0.0042$  and the relation

$$\Delta g = -\frac{8k\lambda_0}{10Dq} \quad (5)$$

valid for a system with a  $^4A_2$ -orbital groundstate, we can obtain the value  $k$ , which is a measure for the localization of the electron on the defect in ligand field theory ( $k=1$  for complete localization,  $k=0$  for complete delocalization) if the value of  $Dq$  were known from optical data ( $\lambda_0$  is the free ion spin-orbit coupling parameter). No optical data exist for Ti (or any other interstitial or substitutional transition metal) in silicon and we will have to content ourselves with an estimate for  $Dq$ . From the value of crystal field parameters of substitutional  $Co^{2+}$ , which also has an orbital singlet as its groundstate in II-VI compounds like ZnSe ( $Dq=350 \text{ cm}^{-1}$ ), ZnS ( $385 \text{ cm}^{-1}$ ) and III-V compounds GaAs ( $425 \text{ cm}^{-1}$ ), GaP ( $475 \text{ cm}^{-1}$ ), combined with the observed increase of  $Dq$  with increasing covalency (6,7), we estimate  $Dq$  for impurities in Si to be of the order  $500 - 600 \text{ cm}^{-1}$ . In our case this would lead to values for  $\lambda = k\lambda_0 \approx 3 \text{ cm}^{-1}$ , as compared to  $\lambda_0 = 30 \text{ cm}^{-1}$  for the free ion (8). Such large reductions of  $\lambda_0$  have also been invoked in the explanation of  $Cr^0$  and  $Mn^+$  EPR spectra (1) and seem to be characteristic for interstitial impurities in silicon.

Similarly, a reduction in the spin density on the Ti-nucleus is derived from the experimental value for the Fermi contact interaction :

$$A = \frac{2}{3}\mu_0 g_N \mu_N |\Psi(0)|^2 \quad (6)$$

in which  $g_N$  is the nuclear g-value,  $\mu_N$  the nuclear magneton and  $|\Psi(0)|^2$  the unpaired spin density on the nucleus. Adopting the Ludwig and Woodbury model, this interaction arises from core-polarization only. We compute  $|\Psi(0)|^2 = 0.42 \text{ \AA}^{-3}$  to be compared to the free ion value  $5.10 \text{ \AA}^{-3}$  (9). The reduction in  $A$  is seen to be of the same magnitude as the reduction in  $\lambda_0$ . These reductions of  $\lambda_0$  and  $A$  (by 90%) are comparable with those of interstitial  $V^{2+}$  in silicon (1), which is also a  $3d^3$ -system, where they amount to some 85% (assuming  $Dq=500 \text{ cm}^{-1}$  in both cases). Reductions in  $A$  have also been reported for interstitial iron in silicon (10), but without quantitative explanation offered. Qualitatively, reductions of  $A$  and  $\lambda_0$  are ascribed to

overlap and hybridization of 3d-orbitals with ligand orbitals, known to be more severe in increasingly covalent solids. These effects are certainly expected to play a significant role in the case of Ti in Si and to determine to a large extent the values of  $\lambda$  and A, since silicon is a strongly covalent solid. Although both  $\lambda_0$  and A are strongly reduced from their free ion values, we can not conclude, however, that most of the spin density has been transferred to the ligands, since this would induce sizable hyperfine interactions with  $^{29}\text{Si}$ -neighbors, that are absent in EPR. That covalency effects alone can be held responsible for these large reductions thus seems to be unlikely, but can not conclusively be decided against from the present data only. They should be supplemented by data for Dq, as can be obtained from optical measurements (absorption, luminescence), and ENDOR measurements, that map the wavefunction directly. A further discussion of these issues, that we feel to be very important to the understanding of interstitial transition metal ions in silicon, will therefore be deferred till subsequent publication of our ENDOR results.

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