

INVESTIGATION OF THE Si-NL52/ P_b DEFECT IN BULK SILICON

Peter Stallinga*, T. Gregorkiewicz, and C.A.J. Ammerlaan

Van der Waals-Zeeman Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

* Present address: Dept. of Materials Science, University of California at Berkeley, CA 94720. e-mail: pjotr@phys.uva.nl

ABSTRACT

The most prominent defect in Si/SiO₂ interfaces is the P_b defect, originally ascribed to a silicon dangling bond stabilized at the interface by the presence of oxygen. Recently, in oxygen-lean, hydrogen-implanted bulk silicon a similar spectrum (Si-NL52) was detected. The features of the spectrum led to the conclusion that a model of a paramagnetic interstitial hydrogen molecule (at a hexagonal site) is a more likely candidate. The current work studies in more detail the possible cause for the varying of intensity ratio of the hyperfine and Zeeman lines. A model is made in which a conversion can take place between the ortho- and para species of H₂. Upon application of microwave power the ratio changes conform the experimental data.

Introduction

The success of silicon as starting material for micro electronics is largely due to the features of its oxide, which is an ideal insulator [1]. On the other hand, the increasing number of devices on an IC is made possible by the continuing scaling down of the structures. The ever decreasing dimensions make the two-dimensional structures relatively more important with regard to the three-dimensional ones. This explains the escalating interest in the physics of surfaces and interfaces of semiconductors.

Defects in the oxide and at the Si/SiO₂ interface cause trapping of charges and thus formation of unwanted electrical fields, thereby influencing the carrier transport properties and degrading the overall performance of the device. This defect formation may eventually lead to a spontaneous occurrence of short-circuit in the insulating oxide and a breakdown of the device. Evidently, it is of utmost importance to know the exact nature of these defects, such as their formation kinetics and microscopic structure.

The most familiar intrinsic defect at the interface is the P_b center, which accounts for up to 100% of all electrical trapping [2]. Its electron paramagnetic resonance (EPR) spectrum was first detected by Nishi [3] and subsequently attributed by Poindexter *et al.* [4] to a silicon dangling bond stabilized normal to the <111> Si/SiO₂ interface. Later, the same spectrum was found in oxygen-implanted silicon (SIMOX), where a layer of silicon oxide is created below the surface [5]. Also in the novel material porous silicon (po-Si) the same spectrum was revealed [6]. This

brought new interest to the P_b center as part of the quest for the explanation of the luminescence in po-Si.

In previous experiments an EPR spectrum with similar features as the P_b spectrum is described [7]. This spectrum was observed in an entirely different type of silicon. The spectrum, labeled Si-NL52, was detected in high-purity (FZ), undoped, bulk silicon, after a high-dose hydrogen implantation, followed by a short (20 min.), low-temperature heat treatment (250 °C). A comparison of the two spectra revealed that they must originate from basically the same microscopic structure [8]. What is more, it is shown that the spectroscopic features of Si-NL52/ P_b point to the involvement of hydrogen:

- Varying of the ratio of HF and Zeeman line intensities.
- Observation of hydrogen originated HF interactions in EPR and ENDOR (Si-NL52).

Furthermore, the field-scanned ENDOR (FSE) spectrum revealed that the exact symmetry within the trigonal spectral class is D_{3d} and not C_{3v} as is often mentioned in the literature. On the basis of these spectroscopic data a new model for Si-NL52/ P_b was proposed. Instead of the silicon dangling bond a model of a paramagnetic hydrogen molecule at the hexagonal (D_{3d}) interstitial lattice site was presented.

In this work a closer look is taken at the origin of the varying of the intensity ratios.

Results

In Ref. [7] the varying of the Zeeman:HF intensity ratio ($Z:HF$) is ascribed to a changing of the relative abundances of the ortho- and para species of charged H_2 , i.e., a conversion between ortho- H_2 and para- H_2 , and *vice versa*. In Figure 1 the level diagram of such systems is drawn. In this model, the relaxations that are taken into account include electronic (λ_E) and nuclear (λ_N). Apart from this, relaxations paths (indicated with λ_C and λ_X) between the two forms of H_2 are allowed. At thermal equilibrium the level occupancies follow the Boltzmann equations determined by the position of the energy levels which in turn is depending on the Zeeman splitting ($g\mu_B B$) and the ortho-para splitting (ΔE), see also Table 1 (NB: in this model the nuclear levels are considered degenerate). The systems can be brought outside thermal equilibrium by microwaves. The relaxations can be expressed in a set of differential equations. For instance, the time derivative of level 5, which is linked to level 2 (electronic), level 4 and 6 (nuclear) and level 8 (conversion) is written as

$$\begin{aligned} dN_5/dt = & \lambda_E(b_{5,2}N_2 - b_{2,5}N_5) + \lambda_N(b_{5,4}N_4 - b_{4,5}N_5) + \lambda_N(b_{5,6}N_6 - b_{6,5}N_5) + (1) \\ & + \lambda_C(b_{5,8}N_8 - b_{8,5}N_5), \end{aligned}$$

with $b_{i,j}$ the Boltzmann coefficients

$$b_{i,j} = 2/(1 + e^{-(E_j - E_i)/kT}). \quad (2)$$

Figure 1 Level diagram of a system of molecular hydrogen with para ($I=0$) and ortho ($I=1$) species. The electronic, nuclear and conversion relaxation paths are indicated with λ_E , λ_N and λ_C respectively, while λ_R indicates the resonant (EPR) transitions. The offset of the ortho-levels (ΔE) is larger than the Zeeman splitting ($g\mu_B B$) but smaller than the free-hydrogen value of 14.7 meV [9].

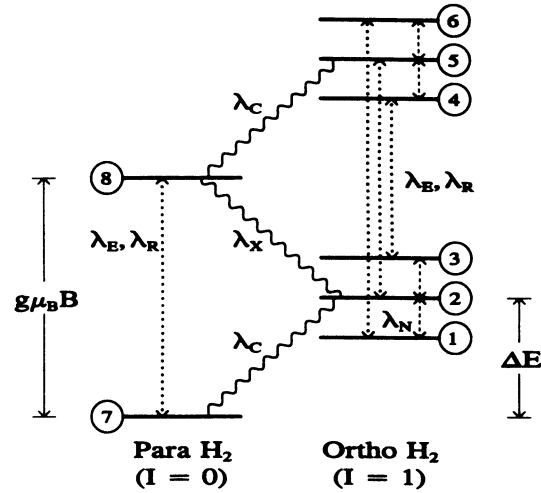


Table 1 Energy positions and quantum numbers of the 8 levels of H₂ and the way in which they are linked. The value of ΔE is obtained from the fit.

Level	Energy	m_s	I	m_I	connected to level							
					1	2	3	4	5	6	7	8
1	ΔE	-1/2	1	+1	-	λ_N	-	-	-	λ_E	-	-
2	ΔE	-1/2	1	0	λ_N	-	λ_N	-	λ_E	-	λ_C	λ_X
3	ΔE	-1/2	1	-1	-	λ_N	-	λ_E	-	-	-	-
4	$\Delta E + g\mu_B B$	+1/2	1	-1	-	-	λ_E	-	λ_N	-	-	-
5	$\Delta E + g\mu_B B$	+1/2	1	0	-	λ_E	-	λ_N	-	λ_N	-	λ_C
6	$\Delta E + g\mu_B B$	+1/2	1	+1	λ_E	-	-	-	λ_N	-	-	-
7	0	-1/2	0	0	-	λ_C	-	-	-	-	-	λ_E
8	$g\mu_B B$	+1/2	0	0	-	λ_X	-	-	λ_C	-	λ_E	-
ΔE is ortho-para splitting = 1.23 meV					λ_E : Electronic				λ_N : Nuclear			
$g\mu_B B$ is Zeeman splitting = 96 μ eV					λ_C : Conversion				λ_X : Cross-C			

In resonance (EPR) the populations of the accompanying levels are being equalized. This can be seen as a quasi relaxation. For instance, resonance between the levels 2 and 5 can be simulated in a time derivative

$$dN_5/dt = \lambda_R(N_2 - N_5). \quad (3)$$

In dynamic equilibrium the level populations are not changing and can be found as the solutions of the 8 equations $dN_i = 0$ with the (arbitrary) boundary condition $\sum N_i = 1$. The intensity of the EPR line can then be found as the number of resonant transitions of Equation 3. In Figure 2 the result of this is drawn as a function of the applied microwave amplitude λ_R for values $\lambda_C = \lambda_E$, $\lambda_X = 0$ and $\lambda_N = 0.23\lambda_E$. For low powers

the intensity ratio is determined by the splitting of the ortho and para hydrogen levels ($Z:HF \approx 3 \exp(\Delta E)$). For high powers the systems are pumped to ortho- H_2 and the ratio is close to 2:1. Comparison with the experimental data [8] reveals that the model with the here used parameters can well describe the ratio $Z:HF$, although the individual intensities deviate more from the experiment. One important reason is that in the model inhomogeneously broadened lines are (intrinsically) assumed. These saturate to a constant value, while the experimental, homogeneously broadened, lines dramatically drop in intensity upon saturation.

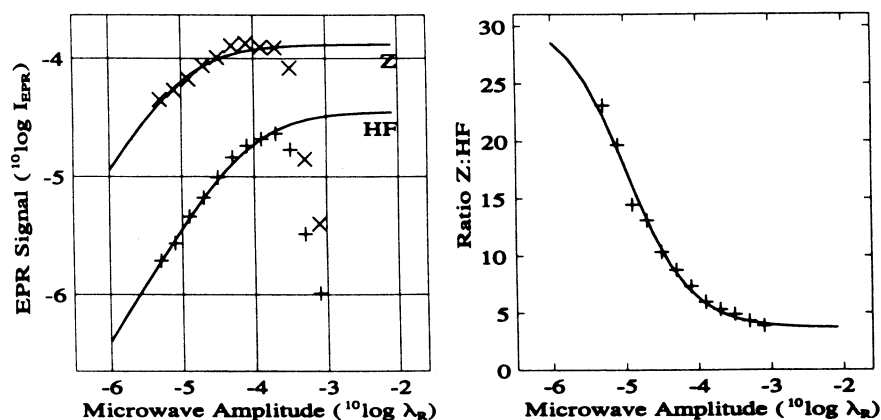


Figure 2 a) Simulation (solid lines) and experimental intensities of the Zeeman (x) and hyperfine (+) lines of the Si-NL52/ P_6 spectrum as a function of the microwave amplitude (λ_R). b) Ratio $Z:HF$.

References

- [1] W. Weber and M. Brox, MRS Bull. **18**, 36 (1993).
- [2] A. Stesmans and K. Vanheusden, Phys. Rev. B **44**, 11353 (1991).
- [3] Y. Nishi, Jpn. J. Appl. Phys. **10**, 52 (1971).
- [4] E.H. Poindexter, P.J. Caplan, B.E. Deal, and R.R. Razouk, J. Appl. Phys. **52**, 879 (1981).
- [5] R.C. Barklie, A. Hobbs, P.L.F. Hemment, and K. Reeson, J. Phys. C **19**, 6417 (1986).
- [6] M.S. Brandt and M. Stutzmann, Appl. Phys. Lett. **61**, 2569 (1992).
- [7] P. Stallinga, T. Gregorkiewicz, C.A.J. Ammerlaan, and Yu.V. Gorelkinskii, Phys. Rev. Lett. **71**, 117 (1993).
- [8] P. Stallinga, T. Gregorkiewicz, and C.A.J. Ammerlaan, MRS Fall Meeting, Boston (1993).
- [9] I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).