Magnetic moments of substitutional gold in silicon

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Abstract. The magnetic susceptibility of silicon samples containing isolated gold impurities on substitutional sites in different charge states has been measured using a sensitive Faraday balance. A paramagnetic moment, which could not be detected by electron paramagnetic resonance measurements, was found for the neutral gold impurity Au^0. There is no evidence for a paramagnetic moment of the charged impurities Au^- and Au^+. These results are in agreement with a model given by Anderson and Watkins, and with recent measurements of the Zeeman effect and of the magnetic circular dichroism of the absorption.

1. Introduction

Considerable effort has been expended in trying to understand the electronic structure of substitutional gold in silicon. One of the principal difficulties is that no electron paramagnetic resonance (EPR) signals have been found for this centre, although they are expected from a simple and widely accepted model according to which Au^0 has the same structure as the substitutional platinum acceptor Pt^- [1, 3–5].

Recently, Anderson has given a new explanation for the absence of an EPR signal [7]. He argues that rapid tunnelling of the defect between two equivalent trigonal distortions associated with a given tetragonal distortion would render $g_\perp$ nearly zero and EPR signals unobservable if the level splitting due to tunnelling is of the order of a few cm^{-1}. This model has been supported in the meantime by an experimental investigation by Watkins *et al* [6] who investigated the Zeeman effect of optical transitions at the Au^0 centre, and characterized its ground state as paramagnetic with $S = \frac{1}{2}$, $g_\parallel = 2.8$, and $g_\perp \approx 0$. With these parameters, Greulich-Weber *et al* [2] were able to interpret their measurements of the magnetic circular dichroism of the absorption.

Furthermore, Watkins *et al* observed rapid reorientation of the tetragonal distortion between the equivalent $\langle 100 \rangle$ directions, from which they concluded that the defect is associated with a single gold atom, and not with a gold-correlated complex. This could be an important point in the further discussion of the topic, because more recently Son *et al* [11] claimed to have found an EPR signal of the isolated gold atom for the first time. The authors investigated silver-doped specimens which contained a very small amount of gold (0.1% of the silver concentration). Besides the expected silver-correlated defects, they found an EPR centre of orthorhombic symmetry with spin $S = \frac{1}{2}$ which they attributed to Au^0. They suggested that gold has a strong tendency toward pair formation, and hence that isolated gold impurities are only found if all possible partners are scavenged by a high silver concentration. This would imply that all previous investigations, including those mentioned

above, have actually been dealing with gold-correlated complexes rather than with single gold atoms.

The objective of our investigation was to look for a paramagnetic moment of the isolated gold atom in its different charge states by a method which depends only on the ground state of the centre and is independent of the effects that can prevent the observation of EPR signals. One such possibility is given by measurements of the magnetic susceptibility using a sensitive Faraday balance. Admittedly this method is not very accurate, but it allows for a decision as to whether a magnetic moment exists or not, and also for a rough estimate of its magnitude.

2. Specimen preparation

Our starting materials were samples of floating-zone silicon doped with 2.5×10^{13} P cm^{-3} (referred to as 'nearly intrinsic' in the following), 8×10^{16} P cm^{-3}, and 8×10^{16} B cm^{-3} respectively. The specimen dimensions were typically about $2 \times 4 \times 6$ mm^3.

In order to remove surface impurities, the samples were etched in CP6 (45.50 vol% HNO$_3$ (65%), 27.25 vol% CH$_3$COOH (96%), 27.25 vol% HF (40%)), and subsequently passivated by a HF dip.

Gold of 99.99% purity was deposited on the surface from a AuCl$_4$ solution, and diffused into the silicon at 1170 °C in a helium atmosphere. After a diffusion time of at least 72 hours the samples were quenched to room temperature in a mixture of oil and water. The diffusion time was long enough to make sure that the gold concentration in the middle of each specimen was at least 80% of the concentration at the surface [8].

Elemental gold that had remained at the surface was etched away in a 3HCl + HNO$_3$ mixture.

On the basis of the results of Stolwijk *et al* [8–10] we expect that the Au concentration is about 10^{17} Au cm^{-3}, and so the shallow acceptors in the boron-doped samples and the shallow donors in the phosphorus-doped samples are almost fully compensated. Consequently, at low temperature virtually all gold atoms should be negative, neutral, and positive, respectively, for the three different types of doping.

For the doped specimens, this can be checked by conductivity measurements. For this purpose the expressions for n, N_{Au^-}, N_{B^-}, p, N_{Au^+}, and N_{P^+} in terms of the Fermi level and temperature, using the entropy factors of Catania *et al* [12], were inserted in the charge-balance equation

$$n + N_{Au^-} + N_{B^-} = p + N_{Au^+} + N_{P^+} \tag{1}$$

with $N_{Au^-} + N_{Au^+} + N_{Au^0} = c_{Au}$, to calculate the Fermi level and, eventually, n and p. The result was combined with Conwell's evaluation [13] of the mobility μ as a function of the charged impurity concentration to obtain a theoretical curve for the conductivity $\sigma(c_{Au})$ at room temperature. Comparing this with the experimental values of σ, we obtained $N_{Au^-} \approx 8 \times 10^{16}$ cm$^{-3} \pm 20\%$ for the n-doped specimens, and $N_{Au^+} \approx 8 \times 10^{16}$ cm$^{-3} \pm 20\%$ for the p-doped specimens.

Unfortunately the dependence of σ on c_{Au} becomes quite flat when the Au concentration is larger than the original doping concentration. This not only limits the accuracy of our approach for the doped specimens to an estimated 20%, but also precludes a determination of c_{Au} for the nearly intrinsic specimen altogether. However, we have no reason to expect a significant difference in the solubility of Au between the nearly intrinsic and the doped specimens, because the doping concentration of *all* specimens is less than 1% of the intrinsic

density at the diffusion temperature. Therefore it is justified to use the same value of c_{Au} and $N_{Au^0} \approx 8 \times 10^{16}$ cm^{-3} $\pm$ 20% for the nearly intrinsic specimens.

We notice in passing that this value is somewhat lower than the maximum solubility of Au at the diffusion temperature [8], which must be expected because pairs and clusters which are not electrically active are included in the total concentration.

3. Experimental methods

The force on the specimen from a gradient of the magnetic field in vacuum is given by

$$F_{Vac} = \chi H V \frac{dB}{dx} \tag{2}$$

where χ is the susceptibility and V the volume of the sample, H and B are the magnetic field and flux density, respectively. To obtain F_{Vac}, the force F'_{Vac} on the specimen holder, a thin quartz hook, has to be subtracted from the measured force. In our magnetic balance the force is compensated automatically, so the specimen position always remains constant. The compensating currents I and I' which are proportional to the forces with and without the specimen, respectively, are the primary experimental data. For details, see [14].

The absolute value of χ at room temperature was obtained from a comparison of the values in vacuum and in an oxygen atmosphere in which the force is

$$F_{Ox} = (\chi - \chi_{Ox}) H V \frac{dB}{dx}. \tag{3}$$

The susceptibility of the specimen is obtained from

$$\chi = \chi_{Ox} \frac{F_{Vac}}{F_{Vac} - F_{Ox}}$$

or, in terms of the compensating currents,

$$\chi = \chi_{Ox}^0 \frac{p}{p_0} \left(\frac{T_0}{T} \right)^2 \frac{I_{Vac} - I'_{Vac}}{(I_{Vac} - I'_{Vac}) - (I_{Ox} - I'_{Ox})} \tag{4}$$

where I_{Vac} and I_{Ox} are the currents in vacuum and in an oxygen atmosphere at the pressure p and the actual temperature T, respectively. χ_{Ox}^0 is the susceptibility of O_2 under normal conditions (at $T_0 = 293$ K and $p_0 = 101\,325$ Pa). In this equation the ideal-gas law has been assumed for the oxygen atmosphere, and the Curie law for the temperature dependence of its susceptibility.

We notice that the above expression for the susceptibility is independent of the specimen volume. This is an advantage over more conventional methods of calibration in which a solid specimen of known magnetic moment is used. Furthermore, we can do the calibration for each sample without opening the cryostat and remounting the specimen.

At low temperatures, a helium atmosphere of approximately 10^4 Pa was used for thermal contact to the temperature control unit of the cryostat. The small diamagnetism of the helium gas is negligible. $\chi(T)$ is now obtained from the ratio of the compensating current at temperature T to that at room temperature:

$$\chi(T) = \chi_{RT} \frac{I_T - I'_T}{I_{RT} - I'_{RT}} \tag{5}$$

where again I and I' are the compensating currents with and without the specimen, respectively.

$\chi(T)$ was measured between 4.6 K and 30 K. Usually the average of two measurements in an applied field of 660 mT and in a reversed field of the same strength was taken for χ,

but in some cases we also measured the field dependence of χ to exclude the presence of permanent ferromagnetic moments.

Furthermore, to make sure that no other paramagnetic or ferromagnetic impurities were introduced into the specimens during the diffusion process, we performed EPR measurements. These show only one very weak and broad feature which can be attributed to precipitations of gold silicide or to conductive artifacts.

4. Experimental results

4.1. Au^0

The change in susceptibility due to paramagnetic centres of density N_{Au^0} is

$$\Delta \chi = \frac{C}{T} \qquad (6)$$

with $C = N_{Au^0} g_{eff}^2 \mu_B^2 S(S+1) \mu_0 / 3 k_B$.

g_{eff}^2 is the mean square gyromagnetic ratio, averaged over the equivalent centre orientations. For $g_\perp = 0$, we obtain $g_{eff}^2 = g_\parallel^2 / 3$. The other parameters are μ_B = the Bohr magneton, S = the spin, μ_0 = the magnetic permeability, k_B = the Boltzmann constant.
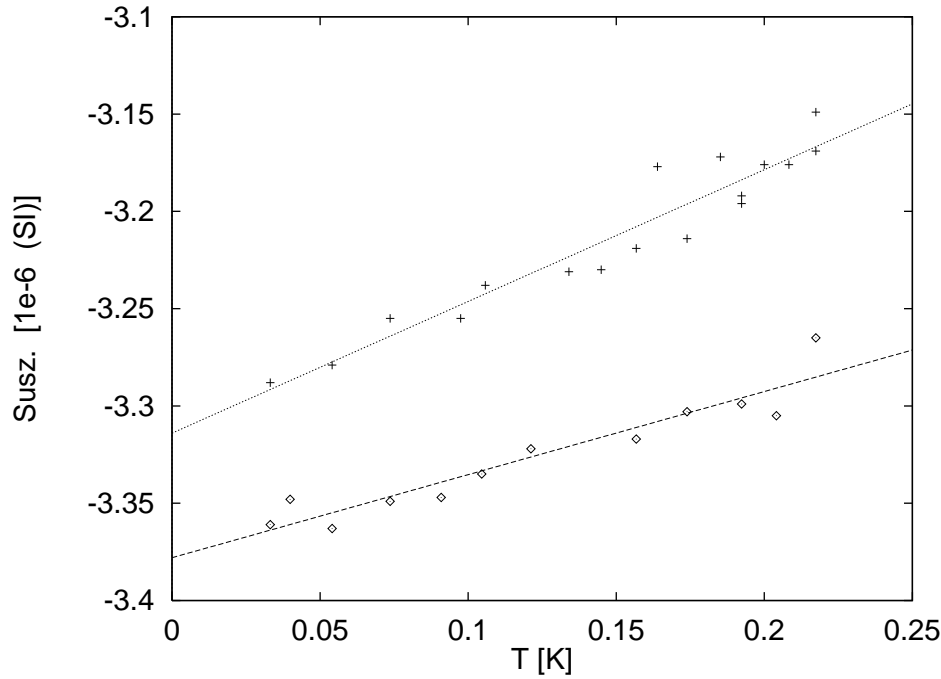

Figure 1. The susceptibility in SI units of nearly intrinsic Si after Au diffusion (+). The reference specimen ($\diamond$) underwent the same heat treatment but was not doped with Au.

In figure 1 we have plotted the susceptibility of a nearly intrinsic specimen after Au diffusion, and of another one that had undergone the same heat treatment but without Au doping, versus $1/T$.

Possible sources of error that can be responsible for the scatter of the data are

(i) the actual specimen temperature which cannot be determined directly without disturbing the balance;

(ii) traces of oxygen in the helium atmosphere; and

(iii) small displacements of the specimen which is held by a quartz hook but not cemented in its position.

Opening the cryostat and mounting a new specimen almost inevitably introduces small changes of the specimen position and makes it necessary to readjust the balance. As a consequence, the reproducibility of the absolute magnetic moment and susceptibility is only of the order of 3 to 5%, while the accuracy is much better within one set of data obtained without remounting the specimen. Therefore the change of the absolute value of χ due to Au doping should not be considered as significant but, on the other hand, the effect on the slope of $\chi(1/T)$ is clearly distinguishable, and an accuracy of about $\pm 10\%$ for the slope is obtained from the statistical scatter of the data. This allows us to determine the value of the Curie constant C and, eventually, g_{eff} for the neutral Au atom with some confidence. Assuming that $S = 1/2$, we obtain $g_{eff} = 1.7$. Considering the experimental uncertainties, this value is in good agreement with the results of Watkins *et al* which would yield $g_{eff} = 1.62$.

4.2. Au⁻

The doping concentration of the starting material (8×10^{16} P cm^{-3}) was nearly compensated by the Au acceptors (indicated by a high room temperature resistivity). If, as expected, Au⁻ has no magnetic moment, the change in χ at low temperatures due to Au doping should
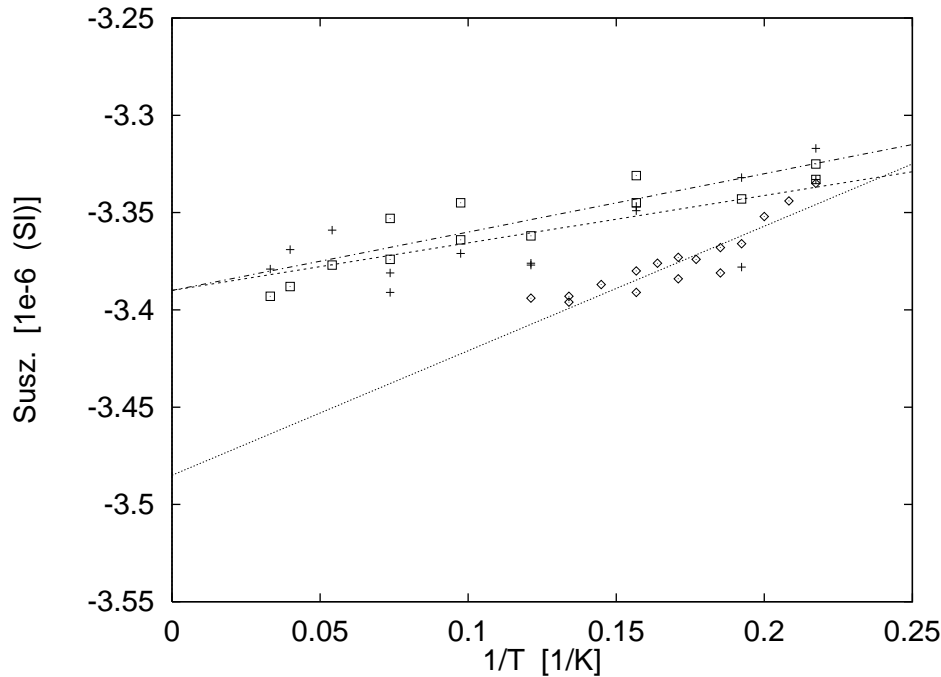

Figure 2. The susceptibility of n-Si before and after Au diffusion; ◇: starting material with 8×10^{16} P cm^{-3}; +: after Au diffusion; — · —: the nearly intrinsic reference sample.

correspond to a removal of occupied phosphorus donors, i.e. χ should approach the value of the undoped reference specimen.

This is in fact seen in figure 2 where we have plotted the susceptibility of the sample before and after Au diffusion as a function of temperature and, in addition, the susceptibility of a nearly intrinsic sample as a reference. We notice that the slope of $\chi(1/T)$ before Au diffusion corresponds to the expected value for 8×10^{16} P cm^{-3}.
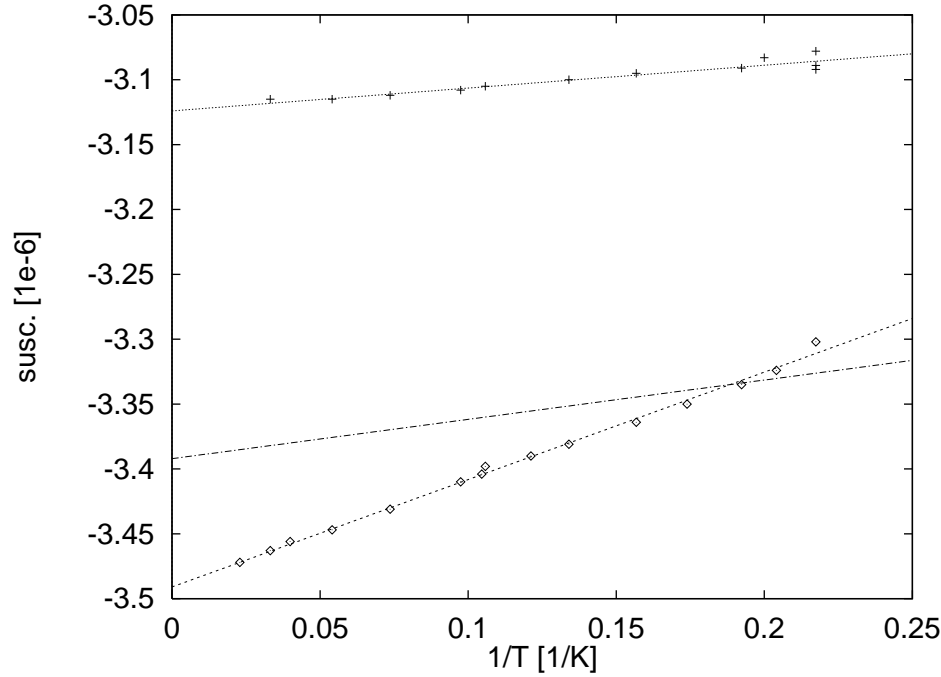

Figure 3. The susceptibility of p-Si before and after Au diffusion; ◇: starting material with 8×10^{16} B cm^{-3}; +: after Au diffusion; — · —: the nearly intrinsic sample, without heat treatment.

4.3. Au$^+$

The starting material was doped with 8×10^{16} B cm^{-3}. Again the resistivity measurements at room temperature indicated nearly full compensation of the shallow acceptors by Au donors. A comparison of the measurements before and after the Au diffusion process in figure 3 clearly shows a decrease of paramagnetism from a value that corresponds to 8×10^{16} B cm^{-3}, to the behaviour of a nearly intrinsic specimen. There is no evidence for a paramagnetic moment associated with Au$^+$.

5. Conclusions

From our experiments we have for the first time obtained direct evidence for a magnetic moment of Au^0 in silicon. On the other hand, our results indicate that no moments are associated with Au$^+$ and Au$^-$. These results as well as the magnitude of the moment of Au^0 are in agreement with the model given by Anderson and Watkins. From the susceptibility

alone, i.e. without additional knowledge about the magnitude of g_{eff}, we would not be able to distinguish between $S = \frac{1}{2}$ and $S = \frac{3}{2}$, but $S = \frac{1}{2}$ appears more likely if we believe in the analogy to the vacancy.

If the hypothesis of Son *et al* [11] should prove to be correct, all of our results would remain valid, but the species that we and many other authors have investigated would be some Au-correlated complex instead of substitutional Au. This cannot be rigorously excluded, but we consider it as unlikely because of the defect concentration which fits quite well to the solubility of Au and to the Au concentration obtained from our own conductivity measurements. In our starting material the concentrations of all of the other defects including oxygen are too low for the formation of 8×10^{16} cm^{-3} pairs, and we are confident that a contamination of this order of magnitude has not been introduced by our diffusion treatment.

Acknowledgments

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