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METASTABILITY OF ZINC-RELATED CENTRES IN SILICON: PHOTO-EPR STUDY

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A photo-EPR study has been performed on silicon single crystals doped with natural zinc. In particular the spectral dependence of the intensity of the Si-NL34 EPR centre previously identified as a ZnCu pair of monoclinic symmetry has been investigated. Quenching of the signal by the impurity light has been observed. Two new EPR centres whose generation coincided with the quenching of the NL34 signal were investigated.

INTRODUCTION

Single shallow donor and acceptor centres in silicon are well studied. Much less is known about the centres with two ionisation levels, and especially double acceptors. Here the zinc impurity, whose diffusion procedure has recently been developed attracts much attention as electrical measurements [1)], DLTS [2)], and infrared absorption data [3)] become available. A variety of Zn-related energy levels has been found in the band gap of silicon indicating prolific affinity of this impurity to form complexes with shallow acceptors [4)] and transition metal elements [5)]. Consequently the EPR technique has also been applied yielding in several instances detailed identification of the observed defect centres [6,7)]. In the present study the Si-NL34 EPR spectrum previously identified with a zinc-copper pair has been investigated by the photo-EPR technique.

EXPERIMENTAL

The material for the study has been prepared by diffusing natural zinc into commercial, p-type, boron-doped, high resistivity FZ silicon (Wacker). The diffusion process has been conducted at 1200°C in a sealed, inert gas filled, quartz ampoule; different diffusion procedures and heat treatment sequences were used. The measurements were performed in an EPR spectrometer operating in X and K microwave bands, tuned to detect the dispersion part of the signal. The experimental set up permitted in situ illumination of the sample by means of a quartz lightguide. The light from the halogen source was dispersed by a monochromator and additionally passed through filters.

RESULTS AND DISCUSSION

In Figs. 1a and 1b the results of the photo-EPR experiment as obtained for two materials diffused in somewhat different procedures are presented. In both cases it has been found that the Si-NL34 spectrum

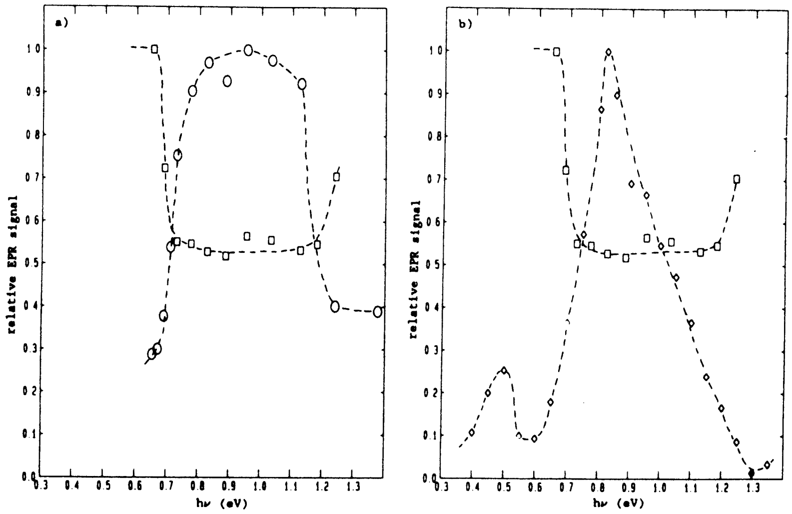

Figure 1. Photo-EPR spectra of **a)**: ZnCu (□) and Si-NL39 (○) and **b)**: ZnCu (□) and Si-NL34 (◇).

could be quenched with the same characteristic energy of ~ 0.67 eV. The intensity of the EPR signal could be lowered to about half of its initial value with the actual quenching ratio being, to a limited extent, sample dependent. The illumination of the sample with the band gap light restored the EPR signal to its original (non-illuminated) intensity. The onset energy value for the quenching of the NL34 signal is very similar to the -/-- electrical level of zinc as determined by DLTS measurements. Although such correlation could be coincidental, it is also possible that it indicates the situation in which the presence of a nearby copper atom has only limited influence on the properties of the zinc atom leading to small modifications of its energy levels. The quenching of the NL34 EPR spectrum was found to be in each case correlated to the generation of other zinc-related centres. These were further studied in more detail. In case of the measurements presented in Fig. 1a quenching of the NL34 resulted in simultaneous generation of a previously unknown spectrum, labeled here Si-NL39.

The Si-NL39 signal could be observed exclusively under the illumination. The angular dependence of the new spectrum is presented in Fig.2a. As can be seen the spectrum is composed of many lines and its full analysis is at this moment still not possible. Nevertheless its similarity to the quenched NL34 spectrum, as depicted in Fig.2b for easy comparison, is apparent with the anisotropy being slightly bigger. Therefore we tentatively identify the Si-NL39 centre as a zinc-copper complex of monoclinic symmetry. The work currently in pro-

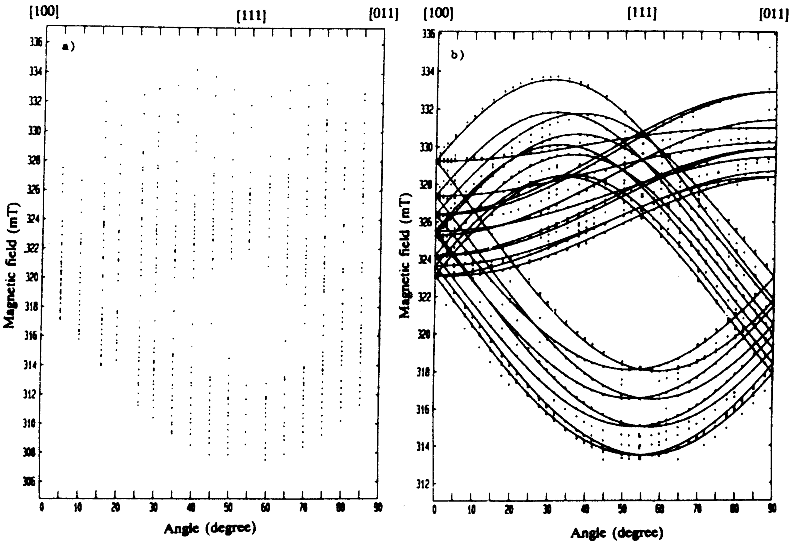

Figure 2. Angular dependence of **a)**: Si-NL39 and **b)**: Si:ZnCu (Si-NL34).

gress will aim at substantiating this identification.

It is tempting to explain the observed photo-EPR data as light-induced transition between two charge states of the same ZnCu complex. Such interpretation appears however to be greatly oversimplified in view of the (most probably) identical S=1/2 spin value for both centres and also an obviously large variety of zinc-related complexes. This is further evidenced by the results of the photo-EPR experiment for different material, as depicted in Fig.1b. As can be seen the quenching of the NL34 signal is in this case accompanied by the simultaneous generation of a different Zn-related EPR spectrum, namely Si-NL36 [7]. The angular dependence of the NL36 spectrum has been studied and is presented in Fig.3. It reveals orthorhombic symmetry of the centre; additionally, a small misorientation of the sample may be seen. The microscopic identification of the centre is not yet available but there is substantial evidence of the involvement of zinc and chromium atoms.

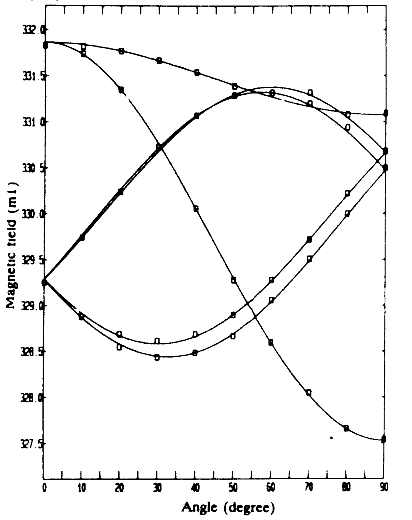

Figure 3. Angular dependence of Si-NL36 EPR spectrum.

Combined, the photo-EPR data for both materials are most readily explained if the quenching of the NL34 signal and the generation of the other NL36 and NL39 spectra are related to different processes i.e. one to the capture and the other one to the emission of an electron. The quenching of the NL34, which is a dominating mechanism most probably due to the general abundance of this centre, could then be, for example, accomplished by a hole capture process while simultaneously generated electrons would be captured by the electron traps available in the given sample - ZnCu or ZnCr complexes as depicted in Figs.1a and 1b, respectively.

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