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► To cite this version:

A. Goltzené. Electron paramagnetic resonance of plastically deformed semiconductors : a short review. *Revue de Physique Appliquée*, 1987, 22 (6), pp.469-471. 10.1051/rphysap:01987002206046900 . jpa-00245562

HAL Id: jpa-00245562

<https://hal.science/jpa-00245562>

Submitted on 1 Jan 1987

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Classification
 Physics Abstracts
 76.30M — 81.40L

Electron paramagnetic resonance of plastically deformed semiconductors : a short review

A. Goltzené

Laboratoire de Spectroscopie et d'Optique du Corps Solide, Université Louis-Pasteur,
 5, rue de l'Université, 67084 Strasbourg Cedex, France

(Reçu le 17 novembre 1986, accepté le 13 février 1987)

Résumé. — Des spectres de résonance paramagnétique électronique, corrélés avec une déformation plastique, ont été mis en évidence dans Si, Ge et GaAs. Au moins pour Si et GaAs, le comportement de ces signaux, attribués à des défauts localisés, soit dans le cœur de la dislocation, soit proche de celui-ci, est très semblable ; une différence entre élément et composé devrait cependant se manifester, plus de phases pouvant apparaître lorsque le réseau du composé se réarrange.

Abstract. — Electron paramagnetic resonance spectra correlated to plastic deformation have been evidenced in Si, Ge and GaAs. At least for Si and GaAs, a similar behaviour is observed for these signals, ascribed to defects localized on, or near, the dislocation core ; however, we stress that the difference between the element and binary compound should also yield a difference while the lattice is reordering, as more than one phase can appear in a compound.

1. Introduction.

Electron paramagnetic resonance (EPR), and the derivated coupled magnetic resonance methods, have been useful in the determination of the electronic and nuclear structure of the defects in semiconductors. Most of the results are devoted to intrinsic or extrinsic point defects. Only few trials have been done in the case of extended defects, for instance microprecipitates or dislocations.

The main reason is certainly due to the low intensity of the signals which could be correlated to dislocations, and therefore most perfect crystals are required : we will therefore only be able to give a short review of the data obtained on Si, Ge and GaAs, and of course a provisional one, especially for the latter.

A further difficulty is related to the precise location of the paramagnetic defects, on the dislocation core or away from it : the EPR signal is integrated over the whole sample, a major drawback there.

For a dislocation, the core should correspond either to dangling bonds or to rebound ones. In the latter case only some localized, uncompensated,

dangling bonds should be observed near defects, for instance jogs ; in the former one, one should have a one-dimensional metal [1]. At this point one may however point out that for more covalent matrices, there is a strong tendency toward rebonding, even forming wrong bonds as shown by the stability of the antistructure defects, i.e. ions on wrong lattice sites as for instance GaAs, and the amorphous phases ; the limit for the latter has been given as a function of the ionicity and anion over cation radius ratio by Phillips [2]. The same should hold for the anti-sites [3].

2. The data.

Si : The main features are known now. The first EPR signal was obtained in 1965 [4]. The spectrum consists in two sets of lines, labeled Si-K1 and Si-K2 [5-8]. They correspond to the spectrum labelled D by the Russian group [9, 10]. The concentration corresponds only to a small fraction of the expected dangling bond concentration along an undistorted dislocation core, in the 1 % range.

K1 and K2 show an opposite behaviour under light excitation [6], the former being the main signal

in the dark. At low temperature (15 K), the effect persists for hours after switching off the light, and fast recovery occurs only at $T > 140$ K. The spectral dependence itself shows a strong increase of K2 for $0.56 \text{ eV} < h\nu < 0.66 \text{ eV}$. This led to the attribution of both set of lines to two ionization states, and therefore spin states, of one defect located on the dislocation ; 0.56 eV corresponds then to the transfer of one electron from the valence band to the K1/K2 level, and 0.66 eV to the transfer of one electron from the dislocation state to the conduction band. Similar experiments on doped Si confirmed the presence of these nearly midgap levels [6].

Thermal anneals at $T > 650^\circ\text{C}$ are necessary to decrease the intensity of K1 and K2 : the corresponding defect is therefore more stable than the irradiation induced vacancy complexes [8, 11].

Models of the defects were inferred first from the symmetry of the EPR spectra. The centre responsible for K1 is symmetrical to the two (111) planes whose line of intersection gives the Burgers vector of the dislocation, in that case 30° partials. The distortion with respect to simplest crystal axis for a dangling bond ([111] in tetrahedral structures) is a hint of the presence of an associated point defect, for instance a vacancy. However at this point, we may notice that the g tensor of both K1 and K2 fall into the range corresponding to point defects with one or two parallel broken bonds, not tetrahedrally coordinated bonds, in the charts given for Si [12] ; this too fits with spins localized on a dislocation core. The thermal stability should, on the other hand, correspond to that of the associated point defect, and not that of the dislocation, which explains that for $T > 750^\circ\text{C}$ no paramagnetic defects are created after a deformation [7, 11].

Finally, whether limited segments of coupled unpaired electrons exist is not clear at present. One may note that some of the persistent spin-dependent recombination processes [13, 14] may require a high local spin concentration. Hints are given by the fact that the ESR intensity does not follow a Curie-law but shows an anomaly near 50 K, ascribed to a transition toward a Mott-Hubbard insulator with a very narrow band [15, 16]. Combined resonance [17] experiments are certainly important in this respect, and one may suggest a correlative monitoring of both carrier types by means of cyclotron resonance [18].

Ge : Surprisingly, as indeed for point defects, much less has been done in Ge, though excellent crystalline material is available ; moreover, the g values of the different defects are « spread out », in contrast with Si, for which Landé factors are nearly equal to the free electron value g_e .

The [111] axis of the spectrum which has been obtained corresponds to one dangling bond, and the dislocation line, perpendicular to [111], corresponds

to a 60° dislocation of the shuffle set [19]. As for Si-K1, a slight (1.2°) tilt has been ascribed to a local distortion. The signal is detected through the spin-dependent photoconductivity effect on the resonant cavity response, through the interaction between the dangling bonds of the dislocation core and the photocarriers trapped along the dislocation. As for similar experiments in Si, these signals correspond to a very low concentration of defects. The large $g_{\parallel}$ and $g_{\perp}$ shifts, with respect to g_e , are of the same sign and order of magnitude as for donors in Ge [20, 21], unlike the Si case.

GaAs : The first results have been obtained in 1980 [22, 23] : three lines labelled D_1 , D_2 and D_3 were correlated to the strain. These D lines proved to be [24] three out of the four lines identified later as the AsGa antisite signature in asgrown [25] or irradiated material [26, 27]. However EPR parameters and saturation behaviour show definite differences between these antisite spectra [28-30]. This recalls the Si case, where K1 and K2 are specific to the stressed samples. This is however a tough task to evidence in GaAs, as the lines are very broad. It has been suggested that these defects are not on the dislocation cores but are formed by gliding dislocations [31-33]. Photo EPR experiments [24] show two photoexcitation thresholds which led to a double donor model, eventually related to the main midgap donor EL2, a point which remains still controversial. The same persistent effects are observed as for Si and even a similar temperature threshold of some 110-140 K [34].

Such a parallel behaviour is surprising as there is a major difference between Si and GaAs : the latter is a compound and the former an element. This should have some consequences : on one hand, two types of ions may form the dislocation core, and on the other, separate phases may segregate, for instance As or Ga. Finally, the resistivity of disordered, i.e. amorphous, Si remains high, which is the case of neither GaAs [35], nor any As or Ga phase. This latter point should be evidenced for instance in the spin-dependent recombination effects which may yield fruitful data in stressed GaAs, but introduce another difficulty when trying to evidence any metallic-like behaviour of dislocation cores.

3. Conclusion.

For Si, Ge and GaAs, EPR spectra could be unambiguously related to deformation effects, therefore to defects induced by dislocations. Whether these paramagnetic states are located on the dislocation core or not remains an open question at least for GaAs, for which deformations at temperature lower than 400°C , or higher than 600°C , would certainly help, as the range $400^\circ\text{C} < T < 600^\circ\text{C}$ corresponds to the decrease of the antisite concentration in the

stressed [34] and irradiated [36] material. However the main problem remains the eventual occurrence of ordered parallel spins along limited segments and of high conductivity phases during the thermally

induced reconstruction. At least for GaAs, both may be highly detrimental to the electronic properties in the device applications.

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