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Electronic properties of grain boundaries in semiconductors

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Résumé. — Le but de cette communication est la description des résultats principaux que nous avons obtenus ces dernières années sur les propriétés électroniques des joints de grain dans les semiconducteurs. L'étude, expérimentale et théorique, était centrée sur les principales caractéristiques électroniques, à savoir la densité d'états, les sections de capture optique, les sections de capture pour les porteurs (et la vitesse de recombinaison) à partir desquelles toutes les propriétés électroniques peuvent être déduites. Les résultats expérimentaux concernent principalement les bicristaux de Ge et Si bien que quelques expériences aient été faites sur du Si polycristallin. Comme les résultats obtenus sont en nombre important et détaillés dans des publications, on les discute ici brièvement en mettant l'accent sur l'idée directrice qui les sous-tend.

Abstract. — The aim of this communication is to describe the main results which we have obtained in the past years on the electronic properties of grain boundaries in semiconductors. The study, experimental as well as theoretical, has focused on the main electronic characteristics i.e. density of states, optical cross sections, carrier capture cross sections (and recombination velocity) from which all the other electronic properties can be derived. The experimental results concern mostly Ge and Si bicrystals although some experiments were performed in poly-Si. Since the results obtained are rather numerous and detailed in publications, here we discuss them briefly, focusing on the leading idea with connects them.

1. Introduction.

The potential applications of both single and polycrystals are governed by the electrical properties, for example the mobility and lifetime of the carriers, which are greatly influenced by the defects contained in the material. Hence the importance of the defect characterization (location of the energy level in the forbidden gap, capture cross section for majority and minority carriers). In polycrystalline materials, grain boundaries can play an important role, in addition to other defects which can also be encountered in single crystals such as point defects (impurities, complexes, intrinsic defects) and dislocations. In this paper, we report electronic characteristics of these boundaries, i.e. the density of states associated with a given type of grain boundary as well as the associated capture cross-sections (directly related to the recombination velocity).

The studies of the electrical and optical properties of polycrystalline semiconductors started in the Fifties, first on germanium, then on silicon and later on compounds [1, 2]. They showed the existence of

localized electronic levels at grain boundaries [3] which give rise to the formation of an internal potential barrier. Mostly based on the measurement of current-voltage characteristics on bicrystals, these studies were able to describe the mechanisms of electrical conduction through the boundary, to estimate the height of the associated potential barrier and to give qualitative informations on the density of states [4]. On an other hand, the recombination velocity S was deduced [5] from the collection of electron-hole pairs created by a localized excitation (photons or electrons) scanned in the vicinity of the grain boundary (the so called electron or light beam induced current technique), provided the diffusion length of the minority carriers in the grain is known. The value of S obtained by this technique, however, is only a rough estimate, because the variation of the induced current *versus* the distance from the boundary at which the excitation is performed is not very sensitive to the fitting parameter S .

Our contribution to the characterization of the electronic properties of grain boundaries consisted first to develop experimental techniques allowing to

get quantitative measurements of i) the density of states $n(E)$ of a given boundary ; ii) the associated capture cross section σ for majority carriers ; iii) the recombination velocity S . This was achieved for the first time by extending the so called Deep Level Transient Spectroscopy (DLTS) technique on a bicrystal [6] for $n(E)$ and σ and the light beam induced current (LBIC) technique [7] for S . These techniques were applied to several types of bicrystals [8, 9] or polycrystals [10,11]. Soon, it appeared that $n(E)$ is strongly dependent on the thermal treatment [12] and that, in addition to a broad distribution of states, it can also contain individual localized states whose characteristics are identical to those of point defects contained in the bulk material. This raised the question of the origin, intrinsic or extrinsic, of this density of states and therefore we developed a way to get the profile of the states in the vicinity of the boundary. Finally, a comparison of these results with theory was attempted. In a first step we calculated the properties (density of states, optical cross sections) of a broken bond, assumed to be the dominant intrinsic defect at an unreconstructed boundary, in order to look for eventual similarities with the experimental density [13, 14]. This comparison suggested, once again, that the origin of $n(E)$ was not intrinsic. A realistic calculation of the electronic structure of the incoherent $\Sigma = 3$ grain boundary in the frame work of a reconstructed model which reproduces the main features of the high resolution electron microscopy image it exhibits, showed [15] that such a boundary does not introduce states in the fundamental energy gap. These theoretical results, coupled with the experimental ones, thus clearly demonstrated that the electrical activity of a grain boundary should be attributed to impurity segregations and not to intrinsic structural effects.

2. The density of states.

2.1 EXPERIMENTAL STUDIES. — In the past, most informations on the density of states of a grain boundary were obtained through the study of current-voltage characteristics [16] as a function of temperature and doping. Such an electrical technique gives directly the height of the potential barrier associated to the grain boundary but not the detailed energy dependence of the concentrations of localized states. A first improvement in the determination of $n(E)$ was reached by the introduction of spectroscopic techniques. With photoinduced capacitance changes [17] $n(E)$ is obtained by differentiating the electrical charge with respect to the photon energy. Using the so called admittance spectroscopy [18] i.e. the frequency dependence of the admittance, $n(E)$ is extracted through the use of an equivalent circuit. The main drawback of this last

technique is that the resulting $n(E)$ depends on the analysis i.e. on the equivalent circuit chosen and on the assumed potential fluctuations (i.e. on the spatial distribution of the localized traps at the grain boundary).

Because of the existence of a space charge region in the vicinity of the boundary, which can be modified by the application of an electric field as in the case of a Schottky barrier (a charged grain boundary is equivalent to two Schottky barriers in series and of opposite polarity), it is possible to fill on empty localized traps located on the grain boundary or in the vicinity of it, by the application of voltage steps. From the study of the emptying process, i.e. the emission of localized carriers into a band, which can be monitored through changes of the capacitance of the boundary space charge region, it is easy to obtain $n(E)$ through the analysis of the kinetics of the emission, performed at various temperatures [6, 10]. This analysis is made using the so called Deep Level Transient Spectroscopy (DLTS). Although equivalent in principle to the admittance spectroscopy technique, the DLTS procedure provides $n(E)$ without the introduction of an equivalent circuit, and it has been shown in the case of Si-SiO₂ interfaces that it has a larger energy range accessible, a higher energy resolution and a better sensitivity [19]. In addition, by a proper choice of the applied voltage and of voltage pulses, the DLTS technique allows one to study separately the traps on each side of the boundary, to perform profiling measurements and to differentiate between localized states at the grain boundary and in its vicinity [20]. However, the DLTS technique should be applied with caution and the apparent results must often be corrected for spurious effects [21, 22].

The results obtained on Ge bicrystals can be found in [6] and [8] ; those on Si bicrystals are described in detail in this volume. Here, we only wish to stress some general features.

i) Capacitance-voltage characteristics are often asymmetric, i.e. the capacitance values measured for two equal voltages of opposite polarity are not identical. This observation implies that the charged traps are not all located on the boundary itself but that there are also localized states in the vicinity of the boundary which are not equally distributed on both sides of this boundary.

ii) $n(E)$ is not a broad distribution of states located near the middle of the forbidden gap, as we should expect (see Sect. 2.2) in case it originates from dangling bonds or from strongly distorted bonds ; it is rather constituted by a sum of isolated localized states.

iii) In case of Si bicrystals, $n(E)$ is very sensitive to thermal treatments and to the nature of the atmosphere in which this treatment is performed.

iv) Some of the localized states which constitute

$n(E)$ are clearly located outside of the plane of the boundary. In case of a Ge bicrystal one of these states is related to a trap which has been identified by an independent study as being a defect containing oxygen.

2.2 THEORETICAL STUDIES. — All these observations strongly suggest that the localized states which compose $n(E)$ are not of intrinsic origin but are rather associated with isolated impurities or impurity segregation, as suggested by transmission electron microscopy observations. Obviously, one of these impurities is oxygen but one should expect carbon to be also involved since infrared spectroscopy studies have shown that carbon is a dominant impurity in the Si bicrystals we studied. However, these experimental results alone cannot demonstrate that $n(E)$ is of purely extrinsic origin since it can be the result of the interaction between intrinsic defects and impurities. For this reason we were led to perform calculations of the density of states one should expect in the case it is of intrinsic origin.

In a first step, we looked for the electronic properties associated with a dangling bond in Si. It is easy to understand in a simple tight binding approximation [23] that a « pure » dangling bond will lead to a localized state in the middle of the forbidden gap. Thus, dangling bonds surrounded by a more or less perturbed environment should give rise to a broad distribution of states centred approximatively in the middle of the gap. A realistic calculation [13] has been made as follows: we used a tight binding approximation limited to second neighbour interactions. The tight binding parameters are adjusted in order to reproduce the band structure. A perturbation is introduced, which cuts the bonds between an atom and its neighbours. The Green's function method is used to calculate the resulting localized states and we obtain the wellknown A1 and T2 levels of the vacancy. The energy difference between these two levels being due to the interactions between the four dangling bonds characteristic of the vacancy, we then applied a new perturbation which amounts to suppress these interactions. Then, the electronic states of the isolated dangling bond are derived through the use of Dyson's equation.

We thus obtained the local density of states of the isolated dangling bond which has the following characteristics: it can exist in three charge states, positive (D^+), neutral (D^0) and negative (D^-); the corresponding energy levels, in the absence of any relaxation are $\varepsilon(0/+)$ = 0.05 eV and $\varepsilon(-/0)$ = 0.7 eV with conventional notations; 60% of the electron density is localized on the trivalent atom and this for the three charge states.

These results are consistent with the electron paramagnetic resonance observation of the dangling bond at the Si-SiO₂ interface. The difference in the

localization of the wave function (80% instead of 60%) and in the value of the energy levels (experimentally $\varepsilon(0/+)$ = 0.3 eV and $\varepsilon(-/0)$ = 0.9 eV) can be accounted for by the atomic relaxation. But, the predicted correlation energy, as measured by the Coulomb term $U = \varepsilon(-/0) - \varepsilon(0/+)$, is practically equal to the experimental one. Moreover, the theory predicts [14] an optical ionization cross-section for the transition between the $\varepsilon(0/+)$ level and the valence band which has the correct order of magnitude. Its shape is accurately described by including the broadening due to the electron-lattice interaction using a Franck-Condon shift of 0.3 eV.

In a second step, we calculated the electronic structure of the incoherent (211) $\Sigma = 3$ grain boundary in Ge, for which the analysis of high resolution electron microscopy experiments has made possible a good determination of the atomic positions [24]. Among those grain boundaries for which the position of the atoms can be determined from available experimental data, the (211) $\Sigma = 3$ grain boundary is the one to which are associated the largest atomic perturbations, i.e. deviations of the atomic positions with respect to the perfect lattice arrangement.

First, the atomic structure has been determined by energy minimization in the Keating model. These calculations provided a reconstructed structure which reproduces the main features of the high resolution electron microscopy it exhibits; in particular it accounts exactly for the existence and position of the observed six fold rings of atoms. Then, for this optimized geometry, the electronic structure has been computed using the recursion method.

The result is clear: there are no localized states introduced in the fundamental gap. The main perturbation induced by the distortions of the bonds is a ~ 1 eV shift of the maximum of the density of the p states pointing in the direction in which the translation symmetry is broken, too small to push these states in the gap. This is in agreement with another direct calculation on distorted bonds [25].

Thus the electrical activity i.e. the presence of localized states at this grain boundary cannot be attributed to intrinsic structural defects. Since there are no broken bonds the density of states cannot be attributed to complexes involving intrinsic defects and impurities: it can only result from impurity segregation, i.e. impurity trapping in the strain field caused by perturbed atomic sites.

3. Capture cross sections and recombination velocity.

One of the main effect of a grain boundary is related to its ability to attract minority carriers and to induce their recombination with majority carriers. This occurs through the associated localized traps and is characterized by a so called recombination velocity

S , directly related to the capture cross sections for electron and holes.

Using the DLTS technique, briefly recalled in section 2.1, it is possible to measure the quantity n of the traps, which are filled when a voltage pulse of a given duration t_p is applied, and to select the region in which the traps are filled, by a proper choice of the applied voltage and of the pulse amplitude. Then, the majority carrier cross-section σ_M can be extracted [6] from the filling kinetics $n(t_p)$. The minority carrier cross section σ_m cannot be obtained in a similar fashion, mostly because it is not easy to measure accurately a concentration of injected minority carriers. However, σ_m can in principle be obtained indirectly, once σ_M has been measured, through a deconvolution of S (i.e. taking into account the fact that, since there is a distribution of traps, S corresponds to a series of parallel recombination processes).

We therefore developed a technique which, contrary to LBIC, allows a quantitative determination of S , L , and the diffusion length independently [7] (in conventional techniques, these quantities are obtained through a fitting procedure). The technique is based on the measurement of the abrupt change of the light induced current collected in a junction when the excitation beam is scanned through the grain boundary. Then S is given by

$$S = 2 \frac{I_2 D}{I_1 L}$$

where I_1 and I_2 are the currents collected on both sides of the boundary. The diffusion length L is obtained in a conventional way (from the slope of

the logarithm of the collected current *versus* the distance from the grain boundary) and the diffusion velocity D is calculated from the Einstein relation. From this technique S is measured with a 10 % accuracy.

No systematic studies of σ_M and S were performed when it was made clear that the states involved in the recombination were not related to dangling bonds.

4. Conclusion.

Thus the development of new techniques to determine quantitatively the electronic properties of a grain boundary, their application to well defined cases (bicrystals), coupled with a theoretical determination of the density of states, allowed us to deduce that, at least for the cases investigated, the localized states located at a grain boundary are extrinsic in nature, i.e. related to the presence of impurities. This result is fundamentally important and is related to the efficiency of the reconstructions which leads to the absence of broken bonds in the plane of a boundary (of course this result might not be true at the intersection between two boundaries of different orientations or in real grain boundaries where secondary dislocations might play an important role). It is also important on an applied point of view since this result implies that an electrically inactive grain boundary will only be obtained with a « pure » material i.e. a material which does not contain the impurities which have the ability to get trapped on a boundary or in its vicinity. Moreover we cannot expect a passivation process to be very simple, such as in the case of the H passivation of a dangling bond.

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