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ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES

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Résumé.- Les joints de grains des isolants, des semiconducteurs et des métaux présentent des propriétés électriques très différentes que nous exposons de manière succincte dans le cas des isolants et des semiconducteurs et de manière plus détaillée dans celui des métaux.

Abstract.- The electrical properties of grain boundaries are very different in insulators, semiconductors and metals. We present them briefly in the case of insulators and semiconductors and with more details in the case of metals.

INTRODUCTION

The properties of a polycrystalline material are different from those of a monocrystalline one. These property variations are generally attributed to the grain boundaries, i.e. to the localized defects which separate the grains of different orientations, rather than to the differences of orientation themselves. To explain the electrical properties both these hypothesis must be retained. The first, due to the local atomic disorder and to segregation, is a short range effect. The second, due to the orientation change, is a long range effect.

For an infinite monocrystal the elementary electronic theory gives us the very useful band concept to explain the electrical behaviour difference between insulators, semiconductors and metals. Based on the translation invariances of the infinite crystal, this theory fails for finite real crystals or polycrystals, however its principal result, the band concept, is a physical reality which is not essentially modified. The most important alteration induced by grain boundaries is the presence of localized states or narrow bands in the previously forbidden band. In insulator and semiconductors these localized states potentially increase the conductivity; in metals it can often be neglected. When an electric field is applied the distribution of the electronic states near the FERMI level changes. This variation contributes to the conductivity, its value is controled by the density of these states and their scattering. These scatterings arise from the atomic disorder of the grain boundaries (short range effect), the change of periodicity between grains (long range effect) and other defects. Using the real monocrystal as a reference a conductivity increase can be expected if the increase of the state density near the FERMI level is large (insulators and semiconductors), or conductivity decrease if the grain boundaries increase predominantly the electronic diffusion (semiconductors and metals).

A grain boundary is also a region of low ionic density and in its vicinity a redistribution of the charge carriers occurs reducing the electrostatic energy. The higher the charge carrier density is, the more the screening is efficient (1). Thus in metals, the ionic and electronic width are nearly the same, but in semiconductors and particularly in insulators the electronic width is higher than the ionic one. In these last materials the grain boundary is a region of electric field heterogeneity which can exert a repulsion on the charge carriers. This effect explains the decrease of the conductivity and the capacitive behaviour of the grain boundary.

In insulators and specially at high temperature an ionic grain boundary conductivity can occur and frequently it is the most important part of the total conductivity. The electronic properties of the grain boundaries are thus determined by the intergranular diffusion.

Generally grain boundaries damage the electrical properties of materials. Polycrystalline metals are less conductive and polycrystalline insulators more conduc-
tive than monocrystalline ones. Semiconductors grain boundaries can be a region of high or low resistivity and in these two situations they decrease the electrical properties.

ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES IN INSULATORS

Insulators with very high electrical properties (conductivity, electrical breakdown...) are glass or liquids, that is to say materials without grain boundary (2). In technical crystalline insulators the notion of grain boundary is often confused with the notion of a binding phase provided by impure composites or requiments of the elaboration processes. Only a few recent papers are mentioned to illustrate the more important properties of insulator grain boundaries.

HOU et al (3) measure the total conductivity (ionic + electronic) of pure aluminia by conventional d.c. techniques and the ionic conductivity by the electrochemical method. The ionic conductivity does not vary with the grain size. The electronic conduction is, in fact, a hole conduction due to a localized state at 1.85 eV above the top of the valence band. This part of the conductivity decreases with the grain size until 10 μm and remains constant for the higher sizes. The grain boundaries increase the hole conductivity and the change of behaviour above 10 μm is attributed by the authors to the disappearance of the higher energy grain boundaries during the recrystallization.

In ceria where the electronic conductibility is negligible WANG and NOWICKS (4) investigate the electrostatic properties of grain boundaries. They measure the impedance from d.c. to 13 MHz. The shape of the complex impedance plot suggests an equivalent schema where the effects of electrodes, grain boundaries and bulk can be separated and each effect described by a resistance and a capacity. From the ratio of the grain boundary capacity to the bulk one they estimate the electrical width of the grain boundaries to be close to 10 nm. The physical meaning of this width is not clear because the authors use the same dielectric constant for all the material disregarding its electrostatic heterogeneity. In ceria grain boundaries decrease the conductivity of the sample. The authors notice an increase of the grain boundaries effect associated to an increase of the sintering time, but they do not give information about the changes of the grain size and of the grain boundary nature.

De JONGHE (5) investigates the grain boundary properties in sodium 6 alumina from both the electrical and the structural point of view. This material is a good ionic conductor where conduction occurs only in a set of crystallographic planes. If the grain boundary allows the continuity of these planes (symmetrical tilt grain boundary with a suitable tilt axis) its electrical effect is low, but on the contrary its influence can be very high. Before annealing in polycrystals 90% of the resistivity is due to grain boundaries. But when, by annealing, the grain size is increased by a factor of 100 the resistivity only decreases by a factor of 10. To understand this result it is necessary to take into account an increase in the proportion of grain boundaries which block the current, this increase is observed by TEM. In this material the great variety of electrical properties of grain boundaries explains the relative failure of methods based on equivalent schemas which in fact expect all the grain boundaries to be identical. To overcome this difficulty and to enable more reliable studies to carried out De JONGHE (5) proposed experiments on well characterized bicrystalline samples.

ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES IN SEMICONDUCTORS

In semiconductors the localized states due to dangling bonds, which exist in reticular defects and specially in grain boundaries, are perturbing states. Their effects are minimized by the use of good quality, but expensive, monocrystals. Economical reasons incite the use of polycrystalline semiconductors and it is very important to understand the electrical grain boundary behaviour in order that it does not have a harmful effect on the properties. In a review AMELINCKS and DEKEYSER (6) describe the electrical properties of grain boundaries in semiconductors. In n-type materials, the grain boundary exhibits, perpendicularly to the grain boundary plane, an increase in resistivity which is thermally activated. After a conversion to p-type this effect disappears. In a parallel direction to the grain boundaries the resistivity is lower than in the bulk; this resistivity is not thermally activated and it is controlled by the charge carrier diffusion caused by the defects near the grain boundaries.
From a theoretical point of view a grain boundary induces a localized state near the middle of the forbidden band. For p-type semiconductors the FERMI level is below the localized state which is empty and inoperative. For n-type semiconductors the FERMI level is above the localized state which is filled. The grain boundary is then an acceptor region and for adjacent grains an electron depletion occurs; eventually a p-type slice can appear at the grain boundary. This charge carrier redistribution induces an electrostatic energy which is responsible for a bending of the bands near the grain boundary and, as in insulators, for a capacitive behaviour. PIKE and SEAGER (7) give a way to determine this band bending and find a relation between the shape of the current-voltage characteristic and the shape of the state density. The strong non-linear tendency of the characteristics (varistor-like behaviour) is explained as a consequence of a very localized state in the gap. In silicon ORR (8) gives an experimental verification of the PIKE and SEAGER's band schema by measuring with a photo-voltage method the local grain boundary resistivity; he observes a decrease of this resistivity by p-dopage. The assisted voltage asymmetry of the electric field near the grain boundary is used by REDFIELD (9) to visualize the electrical active grain boundary at a sample surface previously covered by a liquid crystal. BRONIATOWSKI (10) performs a detailed study of the electrical charge of grain boundary in germanium and claims that the electrostatic energy and the charge carriers entropy are dominant factors in determining the filling of the grain boundary states. Using DLTS (deep level transient spectroscopy) BRONIATOWSKI and BOURGOIN (11) obtain the position and the filling of the localized states in a germanium tilt grain boundary previously studied by TEM. A connexion between the chemical and the electrical properties of silicon grain boundaries is proved by KAMMERSKI (12). After fracture of a grain boundary under ultra high vacuum the maps of the potential surface and of the segregation repartition determined by AES and SMIS are compared. The increase of the electrical activity of silicon grain boundaries after annealing is attributed to oxygen segregation. In silicon MAURICE and LAVAL (13) carry out a similar study where the samples are not broken but thinned in order to observe grain boundaries by STEM and perform their chemical analysis by EDS and EELS. The electrical behaviour is depending of the grain boundary nature. Coherent twin boundaries have no effect, sub-grain boundaries tend to annihilate the photocurrent and incoherent grain boundaries decrease the photocurrent and increase the resistivity.

ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES IN METALS

1- Experimental studies. The increase of resistivity induced by grain boundaries can be measured by two methods. The first one is reserved for bulk samples. The resistivity of several samples with various grain boundary areas per unit volume are measured. Resistivity plotted against area per unit volume is generally a straight line; its slope defines the specific grain boundary resistivity \( \rho_g \) which is measured in \( \Omega \cdot m^2 \). The typical value for normal and noble metals is about \( 10^{-14} \Omega \cdot m^2 \). The second method is well adapted to polycrystalline thin films. In monocrystalline thin films the influence of external surface is well described by FUCH's theory (14). In polycrystalline thin films this theory fails, but MAYADA and SCHATZKES (15) derived an adaptation of this theory by describing the electron grain boundary diffusion with a mean reflexion coefficient which is closely related to the specific resistivity. In these two methods the result is a mean result over all the grain boundaries in the sample disregarding of their individual orientation with respect to the electric field and of the structure of the grain boundaries.

The experimental values measured in these ways are shown in table I. A great dispersion is immediately noticed from 0.15 to 230 \( 10^{-16} \Omega \cdot m^2 \). for the various metals. This dispersion is reduced if, as proposed by BROWN (16), we use the adimensional specific resistivity \( g \) defined by:

\[
\rho_g = g \cdot \frac{\hbar \cdot k_F}{2 \cdot n \cdot e}
\]

with \( k_F = (3 \pi^2 n)^{1/3} \), \( \hbar \) the reduced PLANCK constant, \( n \) the electronic concentration and \( e \) the proton charge. The values of \( g \) are not very different from its mean value 0.75 which can be used to obtain an estimation of grain boundary resistivity for metals where no experimental data is available. For the same metal the results are
often quite different. In the case of aluminium KASEN (25) shows there are no differences between his results and those of ANDREWS et al (18) if the same formula to obtain the volumic surface of grain boundary from the grain size measurements is used and if the purity difference is taken into account.

<table>
<thead>
<tr>
<th>Group</th>
<th>Metal</th>
<th>$\rho_s$ $\times 10^{-16}$ cm$^2$</th>
<th>$\varrho$ without dimension</th>
<th>samples type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B. bulk</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T.F. thin films</td>
<td></td>
</tr>
<tr>
<td>IB</td>
<td>Cu</td>
<td>4,8</td>
<td>0,73</td>
<td>B.</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,12</td>
<td>0,47</td>
<td>B.</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,58</td>
<td>0,54</td>
<td>T.F.</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>3,5</td>
<td>0,42</td>
<td>T.F.</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4,4</td>
<td>0,52</td>
<td>T.F.</td>
<td>21</td>
</tr>
<tr>
<td>II B</td>
<td>Zn</td>
<td>50</td>
<td>1,29</td>
<td>B.</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>0,10</td>
<td>T.F.</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6,5</td>
<td>0,17</td>
<td>T.F.</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>17</td>
<td>0,36</td>
<td>B.</td>
<td>22</td>
</tr>
<tr>
<td>III B</td>
<td>Al</td>
<td>2,45</td>
<td>0,30</td>
<td>B.</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,35</td>
<td>0,16</td>
<td>B.</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,1</td>
<td>0,13</td>
<td>T.F.</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3</td>
<td>0,28</td>
<td>T.F.</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,6</td>
<td>0,44</td>
<td>T.F.</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>23</td>
<td>2,07</td>
<td>B.</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,5</td>
<td>0,22</td>
<td>T.F.</td>
<td>28</td>
</tr>
<tr>
<td>IV B</td>
<td>Sn</td>
<td>7,6</td>
<td>0,38</td>
<td>B.</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0,15</td>
<td>0,01</td>
<td>T.F.</td>
<td>29</td>
</tr>
<tr>
<td>V B</td>
<td>Bi</td>
<td>87500</td>
<td>5,33</td>
<td>B.</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11500</td>
<td>0,70</td>
<td>T.F.</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Yb</td>
<td>60</td>
<td>0,38</td>
<td>T.F.</td>
<td>32</td>
</tr>
<tr>
<td>VI B</td>
<td>W</td>
<td>20</td>
<td>0,97</td>
<td>T.F.</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>0,97</td>
<td>T.F.</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>140 à 230</td>
<td>16,9 à 27,7</td>
<td>B.</td>
<td>35</td>
</tr>
<tr>
<td>VII B</td>
<td>Co</td>
<td>4,6</td>
<td>0,63</td>
<td>T.F.</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>1,36</td>
<td>T.F.</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>28</td>
<td>4,66</td>
<td>T.F.</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Permalloy</td>
<td>12</td>
<td></td>
<td>T.F.</td>
<td>39</td>
</tr>
</tbody>
</table>

Tableau I - Experimental values of the specific grain boundary resistivity for 14 metals and an alloy.

KASEN (25) also proves that impurities increase the specific grain boundary resistivity by approximately $0.35 \times 10^{-16}$ cm$^2$ per p.p.m. For the three other experimental works on aluminium, the same method is used but the thin film substrates are different (silica (15), glass (26), calcite (27)) and consequently the texture and therefore the proportion of different type of boundaries are different. These differences
are sometimes brought to our attention but not always examined in detail.

2- Theoretical studies. For SEEGER and SCHOTTKY (40) the grain boundary is a region of low ionic density associated to a rectangular potential barrier which repulses the electrons to assure the electrical neutrality. This barrier scatters the conduction electrons and so increases the resistivity. These authors do not consider all the lattice effects and use the free electron theory to calculate a grain boundary resistivity. Their result is about a twentieth of the experimental data. VAN DER WOORT and GUYOT (41) use the same theoretical base but they describe the grain boundary as a wall of regularly spaced cylindrical voids. They also assume that the individual contributions are independent and they compute the grain boundary resistivity by the phase shift method. This method requires six phase shifts to converge and gives approximately the same results as the precedent. The failure of these two attempts show that the low ionic density of the grain boundaries (short range effect) is not the most important factor. ZIMAN (42) suggests taking into account the most important characteristic of a grain boundary: the difference in orientation of the two adjacent crystals (long range effect). In this spirit GUYOT (43) carries out a semiquantitative balance of the electronic reflexions caused by the anisotropy of the FERMI surface and its two different orientations in the two adjacent grains. For copper he obtains a specific grain boundary resistivity about five times higher than in his other work and thus gives a proof of the prevalence of the long range effect. BROWN (16,44) performs a resistivity estimation of the grain boundary based on its description by a network of dislocation. This study presents some similarities with that of VAN DER WOORT and GUYOT (40) but symmetry arguments allow the author to use only one phase shift. In these conditions the concordance with the experimental data is very satisfying for several metals. Nevertheless BROWN takes into account the structure of the grain boundary only by a symmetry argument and he assumes the electron diffusion by the grain boundary dislocations identical to those of the dislocations in the bulk.

Our recent studies (45-47) make use, as do those of MARTIN and ZIMAN (48) for aluminium dislocation and FREEMAN (49) for zinc stacking fault, of the theoric of pseudopotentials and that of first order perturbations. In this framework (50) the computation of the excess of resistivity, due to the defects contained in a volume V, is equivalent to the computation of the structure factor of atoms contained in the volume V. Thus the knowledge of all the atomic positions in the volume V enables the computation of the resistivity of this group of atoms in the usual approximations of the MATTHIESSEN rule. The only requirement for V is to respect cyclic boundary conditions. A volume V can be built for grain boundaries by considering only biperiodical grain boundaries and associating them in pairs of parallel grain boundaries symmetrical to each other. If the boundaries are parallel to one face of V the description is simplified.

With this method we have first (45) checked that a hypothetical grain boundary with no desorientation but just a compactity defect gives a resistivity of the same order of magnitude as SEEGER and SCHOTTKY (40) and that a coincidence tilt boundary (with a low Σ to minimize the role of atomic relaxations) exhibits a resistivity close to the experimental one. The influence of the distance between the two boundaries of the volume V is very important when the distance is small. When this distance increases (above 20 nm) the resistivity reaches an asymptotic value (46) which is independent to the size of the adjacent grains. For non relaxed tilt grain boundaries, the computed resistivity does not tend to zero when the desorientation angle tends to zero (46). The absence of relaxation introduces important and artificial defects in the grain boundary and it is their resistivities which are computed. Thus it is very necessary to have an accurate knowledge of the atomic positions near the grain boundaries to obtain a reliable computed grain boundary resistivity. For the (112) twin boundary of b.c.c. lithium, BEAUCHAMP (51) has computed two stable structures. For these two boundaries the computed grain boundary resistivities are nearly the same and reasonably in agreement with the one available experimental data (52). But for these two boundaries the distribution of transitions at the FERMI surface is very different (46). From the result of HASSON (53) about the structure of aluminium grain boundaries, it is possible to compute the grain boundary resistivity for 27 symmetrical tilt grain boundaries (fig. 1).
Figure 1. Computed specific resistivity of symmetrical tilt boundaries around <110>, <111> and <100> in aluminium as a function of the tilt angle. Only dots are computed.

The variations of the resistivity with the desorientation are nearly the same as the energy variation. If we except the special case of the (111) twin boundary, the specific grain boundary resistivity varies between 0.3 and 3.7 $10^{-16}\,\Omega\,m^2$ and the average of the computed values is very close to the average of the experimental data. By handling the structure factor it is also possible to make the notion of effective structure factor of just one grain boundary appear and thus to compute the excess resistivity tensor of a grain boundary. For aluminium tilt grain boundaries this excess resistivity tensor is given on figure 2 with both the corresponding bicrystal and the reference frame. Also indicated on this figure are the eigen elements of the tensor.

Figure 2. Representation of the excess resistivity tensor for a tilt grain boundary.
The most important term is $\alpha$, or $\lambda$, it is the usual grain boundary resistivity. The two other eigenvalues have opposite signs, this feature denotes a selective scattering of the electrons in the grain boundary plane. Before leaving this subject it is important to indicate that this description allows us to distinguish between two types of electronic transitions. The first one is that of specular transitions; the momentum transfer between electrons and grain boundary occurs always normally to the grain boundary plane. The second is that of the diffuse scatterings where the momentum is not normal to the grain boundary plane. Only these last transitions can explain the intergranular electromigration.

3- Other properties. A more fundamental study has been carried out by Goncalves da Silva (54) who computes the electronic structure of two different (130) symmetrical tilt grain boundaries in aluminium with a tight-binding s-like Hamiltonian. He obtains a localized state just above the top of the conduction band and so quite far from the Fermi level. In iron Hashimoto, Ishida, Yamamoto, Doyama and Fuwara (55) compute the local density of states of d electrons by the recursion method for a (130) tilt grain boundary. They show that the local density of states near the center of the band increase while the peaks on either side of the bulk band shift inwards. This particular behavior disappears in the bulk metal one or two atomic layers away from the boundary.

When a direct occurs is applied to a metal an oriented grain boundary migration can occur generally towards the cathode. This phenomena is observed in several metals (Ag, Co, Cu, Au, Ni, Pd, Pt) (56) in the vicinity of the melting point and in aluminum (57) and gold (58) at lower temperature. This migration is a consequence of the exchange of momentum between electrons and grain boundary atoms. For these atoms the jump frequency is increased towards the anode and consequently the grain boundary moves towards the cathode.

The momentum transfer between electrons and grain boundary atoms is also the cause of the intergranular electromigration. The technological consequences of this phenomena are very important. In effect metallic thin films used in integrated circuits to connect together the active components, are traversed by relatively high current density. The resultant electromigration induces the failure of the circuit and decreases its reliability.

CONCLUSION

The most common electrical properties of grain boundaries have been extensively studied and the principal features are on the whole well understood. Nevertheless there are few studies where experimental and theoretical investigations are carried out on well characterized grain boundaries. However such studies are increasing (5, 11-13). Only the compilation and the comparison of such studies can give the necessary information in order to understand the grain boundary electrical behaviour and to predict it in new situations created by technological needs.
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DISCUSSION

C.L. BAUER: Measurements of resistivity of polycrystalline specimens are not particularly satisfying because only an average grain boundary resistivity is reported, while it is suspected that resistance of individual grain boundaries can vary by large amounts. I would like to ask:

(1) Over what range is it expected that grain boundary resistivity can vary?
(2) Is it possible to compute (estimate) grain boundary resistivity of a specific structure from a knowledge of the position of atoms in the vicinity of the boundary?

G. LORMAND: The results of our actual computations give a partial answer to the first part of the question. The computed specific resistivity of symmetrical tilt grain boundaries of aluminium varies from 0.3 to $3.7 \times 10^{-16} \text{ cm}^2$ if we do not retain the particular case of the (111) twin boundary. For asymmetrical grain boundaries no result is available but the change of periodicity along the grain boundary normal lets to expect a higher grain boundary resistivity.

For the second point I have surely not sufficiently specified that I take into account all the atomic positions far and near the boundary. The knowledge of the atomic positions near the grain boundary is important. It avoids to introduce some artificial defects in the grain boundary and to add their resistivity to the grain boundary one.