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**ANALYSIS OF STRUCTURES OF SYMMETRICAL [001] TILT GRAIN BOUNDARIES IN SILICON AND GERMANIUM**

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Résumé - A partir de résultats expérimentaux obtenus par Microscopie Electronique Haute Résolution et relaxation numérique sur les joints  $\Sigma=5$ ,  $\Sigma=65$ ,  $\Sigma=13$ ,  $\Sigma=25$  et  $\Sigma=41$ , une analyse de la structure des joints de grains de flexion d'axe [001] dans le silicium et le germanium est réalisée. Le modèle habituel des unités structurales (Sutton) se révèle insuffisant pour expliquer tous les résultats expérimentaux obtenus dans ces matériaux. Toutefois le concept d'unité structurale-dislocation employé d'une façon plus générale permet de déterminer et d'analyser les nouveaux modèles expérimentalement observés.

Abstract - Using experimental results obtained by High Resolution Electron Microscopy (HREM) and numerical relaxation on  $\Sigma=5$ ,  $\Sigma=65$ ,  $\Sigma=13$ ,  $\Sigma=25$  and  $\Sigma=41$  grain boundaries in silicon and germanium, an analysis of the structures of the symmetrical [001] tilt grain boundaries is presented. The limitation of the usual structural unit model (SUM) when applied to this material is shown. However, the efficiency of the concept of structural unit-dislocation in determining and analysing new complex structures is demonstrated.

1 - INTRODUCTION

The first models of the symmetrical [001] tilt grain boundaries (GBs) were built by Hornstra using core dislocation notions /1/. But the most powerful formalism to construct and propose the most probable structures is the structural unit model (SUM) formalized by Sutton and Vitek in metallic GBs /2/ and applied in semiconductors by Kohyama /3/. Experience and energy calculations are the two tools to check the propositions of the SUM. The energies of several GBs have been calculated /3,4,5,6/. Until recently, few experimental results were obtained on <001> tilt GBs /7,8/. However, recently, the availability of new performant microscopes (JEOL 400KV) has permitted to determine the exact structure of several [001] tilt GBs /4,5,6/. New structures were observed, showing the limitations of the SUM. Two complications can limit the use of the SUM in real structures :

- i) some particular bordering conditions like external applied stresses or boundary faceting
- ii) the effect of temperature through the entropy terms.

In this paper, we summarize the recent experimental results /4,5,6/ and present a formalism that, using the notions of structural unit (SU) and dislocation, permits to construct and analyse all the observed structures. References to Sutton's concepts /2/ is often made.

2 - GEOMETRICAL DESCRIPTION OF SYMMETRICAL [001] TILT GRAIN BOUNDARY

As already done by Kohyama /3/ a symmetrical [001] tilt grain boundary can be represented by two integers  $k_1$  and  $k_2$ . Such a representation is very convenient because it sums up in a few formulas all the cases. In this paper we will adopt a slightly different notation that seems more adapted when referring to the diamond cell. We decide to represent by the couple  $(k_1, k_2)$  (where  $k_1$  and  $k_2$  are non zero integers with no common integer factor) the symmetrical

[001] tilt grain boundary having for boundary plane normal the vector :  $\vec{n}_1 = [k_1, k_2, 0]_1$

(coordinates written in the basis constructed on the diamond cell of the crystal 1). The theoretical periodicity of the interface in a direction perpendicular to the tilt axis is  $d_1 = \alpha[-k_2, k_1, 0]_1$ , where  $\alpha$  is equal to 1/2 if  $k_1$  and  $k_2$  are odd and equal to 1 if they have not the same parity. If  $(k'_1, k'_2)$  represents Kohyama's notations we have  $k'_1 = \alpha(k_1 + k_2)$ ,  $k'_2 = \alpha(k_2 - k_1)$ .

The Coincident Site Lattice has a tetragonal centered cell having for generator vectors :

$$\begin{aligned} \vec{y}_1^c &= 1/2[k_1, k_2, 0] & \vec{y}_2^c &= 1/2[-k_2, k_1, 0] & \vec{y}_3^c &= [0, 0, 1] \quad \text{if } k_1 \text{ and } k_2 \text{ are odd } (\alpha=1/2) \\ \vec{y}_1^c &= 1/2[k_1+k_2, -k_1+k_2, 0] & \vec{y}_2^c &= 1/2[k_1-k_2, k_1+k_2, 0] & \vec{y}_3^c &= [0, 0, 1] \quad \text{otherwise } (\alpha=1) \end{aligned}$$

The theoretical rectangular cell of the boundary is then primitive when  $k_1$  and  $k_2$  are odd (interface on a face of the CSL cell) and centered otherwise (interface on a diagonal). The  $\Sigma$ -value is given by  $\Sigma = \alpha(k_1^2 + k_2^2)$ . The desorientation between the two crystals can be represented by a rotation  $\Omega_\theta$  having for axis the common direction [001] and for angle  $\theta$  :  $\cot(\theta/2) = k_1/k_2$ . The matrix of this rotation is :

$$\Omega_\theta = \frac{1}{k_1^2 + k_2^2} \begin{pmatrix} k_1^2 - k_2^2 & -2k_1k_2 & 0 \\ 2k_1k_2 & k_1^2 - k_2^2 & 0 \\ 0 & 0 & k_1^2 + k_2^2 \end{pmatrix} \quad \left( \begin{array}{l} \text{In that case the median plane of the} \\ \text{GB is (100), but other rotations may} \\ \text{be more judiciously chosen.} \end{array} \right)$$

An important vector for the boundary is the Burgers vector (BV)  $\vec{b}$  associated with the theoretical periodicity  $\vec{d}_1$  and the rotation  $\Omega_\theta$ . This Burgers vector can be determined graphically with Burgers circuits (FSRH in the reference lattice, the positive sense of the dislocation line being the [001] positive direction) or numerically using the equation /9/:

$\vec{b} = (\Omega_\theta^{-1} - I)\vec{d}_1 = \vec{d}_2 - \vec{d}_1$ .  $\vec{d}_2 = \Omega_\theta^{-1}\vec{d}_1$  represents the periodicity of the interface perpendicular to the tilt axis written in the coordinates of the crystal 2 topologically equivalent to the crystal 1. If we restrict to [001] rotations, the same interface has four different BVs (table I). The one to select, which we will call the Burgers vector of the interface (BVI), is the one leading to the minimum of energy.

In this paper we consider the dissociation of  $b$  into two types of structural unit-dislocation (SUD) having dislocation lines along [001] and BVs equal to  $1/2\langle 110 \rangle$ . When projected along the [001] axis, these units have a trigonal-pentagonal pattern (fig. 1). A-units represent the cores of edge dislocations, B units the cores of  $45^\circ$  dislocations. Depending on the chiralities and the orientations of these A and B units, 16 different SUDs can be determined (fig. 1). The  $B^{+0}$  unit has a BV equal to  $1/2[10\bar{1}]$ , the  $A^{+-}$  unit has a BV of  $1/2[1\bar{1}0]$  and a positive chirality, whereas the  $A^{--}$  has the same BV but a negative chirality. By decomposing the BVs  $\langle 100 \rangle$  and  $\langle 110 \rangle$  into two SUDs of A or B type and by applying an energetical  $b^2$  criterium we obtain the minimum energy rotation (table II) and thus the BVI (table I) (this is a "generalisation" of the results of /1/).

Due to the symmetry of the material, all kinds of symmetrical  $\langle 001 \rangle$  tilt GBs are described only once if we restrict  $k_1$  and  $k_2$  to the values :  $k_1, k_2 > 0$ . If we do so, we find a singular value at  $3k_2 = k_1$ , and two domains :  $k_1 \geq 3k_2$  and  $k_1 \leq 3k_2$ . Most of the experimental results have been obtained for the first domain.

Table I - Single periodicity  $\vec{d}_2$  in crystal 2 coordinates ( $\vec{d}_1 = \alpha[-k_2, k_1, 0]$ ) and BVs  $\vec{b}$  associated with  $\vec{d}_1$  and respectively with the four rotations of angles  $\theta'$  equal to  $\theta, \theta - \pi/2, \theta + \pi/2, \theta + \pi$ .

angle $\theta'$	$\theta$	$\theta - \pi/2$	$\theta + \pi/2$	$\theta + \pi$
$\cot \theta$	$k_1/k_2$	$(k_1+k_2)/(-k_1+k_2)$	$(k_1-k_2)/(k_1+k_2)$	$-k_2/k_1$
$\vec{d}_2$	$\alpha[k_2, k_1, 0]_2$	$\alpha[-k_1, k_2, 0]_2$	$\alpha[k_1, -k_2, 0]_2$	$\alpha[-k_2, -k_1, 0]_2$
$\vec{b} = \vec{d}_2 - \vec{d}_1$	$2\alpha k_2 [1, 0, 0]$	$\alpha(k_2 - k_1) [1, 1, 0]$	$\alpha(k_1 + k_2) [1, \bar{1}, 0]$	$-2\alpha k_1 [0, 1, 0]$

Table II - Minimum energy rotation associated with a " $(k_1, k_2)$  symmetrical (001) interface". The two last columns give the numbers of perfect units P and groups of A-A (or B-B) units in the simple models coming from the SUM. The BVI can be deduced from table I.

	rotation	P units	A-A units	
* $ k_1  \geq  k_2 $	if $ k_1  \geq 3 k_2 $ then $\theta' = \theta$	$2\alpha( k_1  - 3 k_2 )$	$12\alpha k_2$	
	if $ k_1  \leq 3 k_2 $ then	if $k_1 k_2 > 0$ $\theta' = \theta - \pi/2$	$2\alpha(3 k_2  -  k_1 )$	$\alpha( k_1  -  k_2 )$
		if $k_1 k_2 < 0$ $\theta' = \theta + \pi/2$	"	"
* $ k_1  \leq  k_2 $	if $3 k_1  \leq  k_2 $ then $\theta' = \theta + \pi$	$2\alpha( k_2  - 3 k_1 )$	$12\alpha k_1$	
	if $3 k_1  \geq  k_2 $ then	if $k_1 k_2 > 0$ $\theta' = \theta - \pi/2$	$2\alpha(3 k_1  -  k_2 )$	$\alpha( k_2  -  k_1 )$
		if $k_1 k_2 < 0$ $\theta' = \theta + \pi/2$	"	"

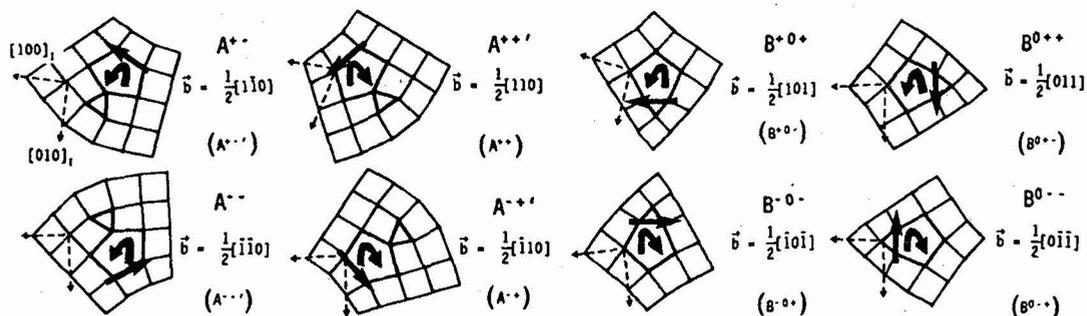


Fig. 1 - Schemes of the (001) projection of eight of the structural unit-dislocations of A and B type with their names (for instance  $A^{++}$ , see text for notation) and their BVs  $b$ . The lines represent bonds between atoms. Every atom is tetracoordinated. The notations in brackets design the units having similar projections but opposite chiralities.

3 - SUMMARY AND COMMENTS OF EXPERIMENTAL RESULTS

3.1 - The singular value  $(k_1, k_2) = (3, 1) : \Sigma = 5(310)$ , a favoured boundary

Two minimum energy rotations can be associated to this interface (table II). The rotation with angle  $\theta' = \theta = 36.37^\circ$  gives a BVI  $b = [100]$  that can be decomposed into two A units ( $A^{++}$  and  $A^{--}$ ) or two B units ( $B^{+0+}$  and  $B^{-0-}$ ). These two decompositions lead to the respective models Z and S (fig. 2b). The second rotation  $\theta' = \theta - \pi/2 = -53.63^\circ$  gives a Burger vector  $[1\bar{1}0]$  that can only be decomposed into two  $A^{--}$  units. Depending on how these two units are arranged (linearly or in a zigzag manner) we obtain the two previous models S and Z (fig. 2b). So the two different rotations lead to the same structures.

Experimentally, only the Z structure has been observed /4,7/ (fig 2a). Statics energy calculations /3,4/ also show that this model has an energy lower than the S model (fig. 3c). So at first only this Z model will have to be considered in the SUM.

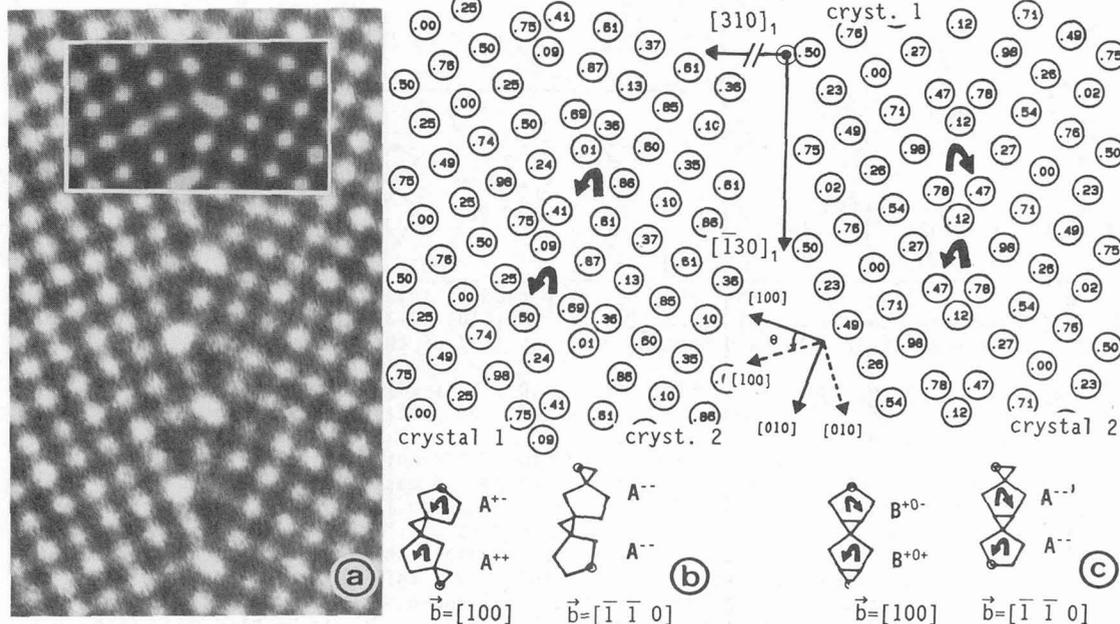


Fig. 2 a) Simulation of the  $\Sigma = 5(310)$  GB superposed on the experimental image (defocus -42nm, thickness 7nm). Each spot represents a tunnel, the big ones are the pentagonal tunnels of the Z model. b) (001) projection of the Z model analysed in term of  $A^{++}$ - $A^{--}$  units in the bottom left scheme (rotation  $\theta$ ) and in term of  $A^{--}$ - $A^{--}$  units in the bottom right one (rotation  $\theta - \pi/2$ ). c) (001) projection of the S model analysed in term of  $B^{+0+}$ - $B^{+0+}$  units in the bottom left scheme (rotation  $\theta$ ) and in term of  $A^{--}$ - $A^{--}$  units in the bottom right one (rotation  $\theta - \pi/2$ ). The figures in the circles gives the heights of the atomic sites in units of  $a[001]$ .

3.2 - The range  $k_1 \geq 3k_2 > 0$  :  $0 \leq \theta' = \theta \leq 36.87^\circ$

These interfaces having a desorientation between  $\Sigma=5$  (310) and the perfect crystal  $\Sigma=1$  composed of square shape P units, the models constructed with the SUM will have  $A^{+}$ ,  $A^{+}$  and P units /2/. The decomposition of BVI indicates that at least  $2\alpha k_2$  groups of  $A^{+}$  -  $A^{+}$  units are necessary per period  $\vec{d}_1$  (table II). In order to keep the interface as planar as possible it is necessary to arrange the A units in a zigzag manner like in the Z model. As a zigzag  $A^{+}$  -  $A^{+}$  grouping covers a distance equal to  $1/2[130]$  and that a P unit "measures"  $1/2 [010]$ ,  $2\alpha(k_1 - 3k_2)$  P units (table II) are necessary for covering the whole distance  $\vec{d}_1$ . Several models can be built with these units. The SUM tries to predict the lowest energy structure with the principle of continuity (PC) /2/. This PC comes down to alternating more often and more regularly the SUs. In our case the facts that  $A^{+}$  and  $A^{+}$  are not strictly equivalent and that  $A^{+}$  -  $A^{+}$  groupings may be favoured complicate the PC.

3.2.1 A non-favoured GB nearly in agreement with the principle of continuity :  $\Sigma=65$  (11 3 0) This interface is characterised by  $k_1=11$  and  $k_2=3$  ( $\alpha=1/2$ ). The minimum energy rotation ( $\theta'=\theta=30.57^\circ$ ) defines a BVI  $\vec{b}=3[100]$ . A single periodicity of the GB contains 3 groups of  $A^{+}$  -  $A^{+}$  units and two P units (table II). The PC favors the  $Z_{3,3}$  model, whereas a mixture of PC and pair association would prefer the  $Z_{4,2}$  model (fig. 3). In fact, some periods of the two last models have been experimentally observed. It is interesting to note that the energies of these two models are very similar and lower than any other ones. There is a competition between a pure PC and an adapted PC taking into account the  $A^{+}$  -  $A^{+}$  groupings.

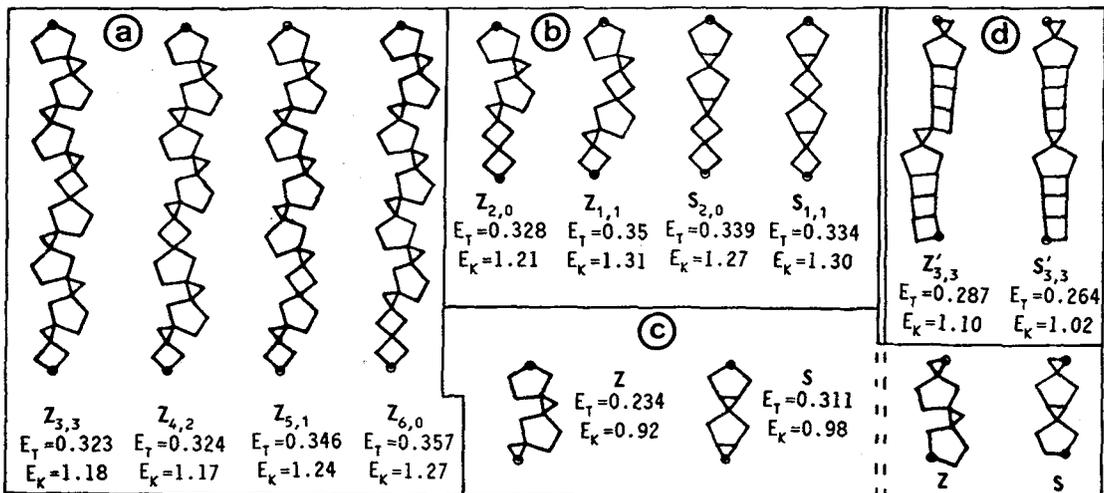


Fig. 3 - Schemes representing the SUDs of one period of several [001] GBs models : a)  $\Sigma=65$  (11 3 0)  $\theta'=30.57^\circ$ , b)  $\Sigma=13(510)$   $\theta'=22.62^\circ$ , c)  $\Sigma=5(310)$   $\theta'=36.87^\circ$ , d)  $\Sigma=13(320)$   $\theta'=-22.62^\circ$   $E_T$  and  $E_K$  are the Tersoff /10/ and Keating energies /11/ of the GBs in  $J/m^2$  /4,5,6/.

3.2.2 Breakdowns in the SUM :  $\Sigma=13$  (510),  $\Sigma=25$  (710),  $\Sigma=41$  (910)

The simple models (fig. 3b) coming from the SUM and containing a minimum of two SUs per period have not been observed.

For the  $\Sigma=13$  (510) interface, we mainly found two different structures /4,5,6/. The first one (fig. 4) contains six SUDs per period and was only observed over short distances and associated with an asymmetrical interface /4/. The use of SUDs eases the construction and the analysis of such more "complex" models i.e. models with more SUDs than the necessary minimum number. For instance, the figure 5b shows the  $IH^*$  model with three SUDs. A few periods of this structure were observed in a very thin region of the sample. On the other hand, the  $I_1$  model of fig. 5d has a BVI [101] whose screw component is incompatible with table I, and it must be rejected. Models with 4, 5 ... SUDs can be also made (fig. 5c). The second (510) interface is more complicate (fig. 5a). The variability of the contrast of the HREM images of this interface observed in two perpendicular directions /5/ reveals that this interface is not strictly periodic. It is composed of a stable part periodically repeated and of a variable core where some atoms can have several stable positions. It is worth noting that this new kind of interface can be analysed as a mixture of periods of periodic models which can be determined using SUDs. The main models involved in this entirely tetra-coordinated mixed model are the  $IH^*$  and  $IH^*$  models /5/ (fig. 5c).

The  $\Sigma=25$  (710)  $\theta'=16.26^\circ$  and  $\Sigma=41$  (910)  $\theta'=12.68^\circ$  GBs were observed to have the same structure as the particular and new mixed model /4/. Instead of being uniformly distributed among the other SUDs., the P units gather themselves resulting in a localisation of all the distortions in a variable core region.

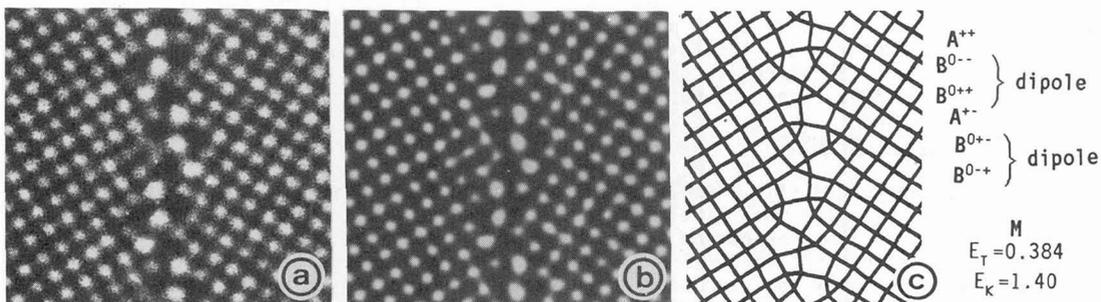


Fig. 4 - Experimental (a) and simulated (b) images of a  $\Sigma=13(510)$  GB (defocus -42nm, thickness : 7nm, the tunnels are white, Ge). c) Scheme of 2 periods of the M model corresponding to the a) and b) images. Bonds between atoms are drawn. A possible decomposition of a period in term of SUDs is indicated.  $E_T$  and  $E_K$  are the Tersoff and Keating energies in  $J/m^2$ .

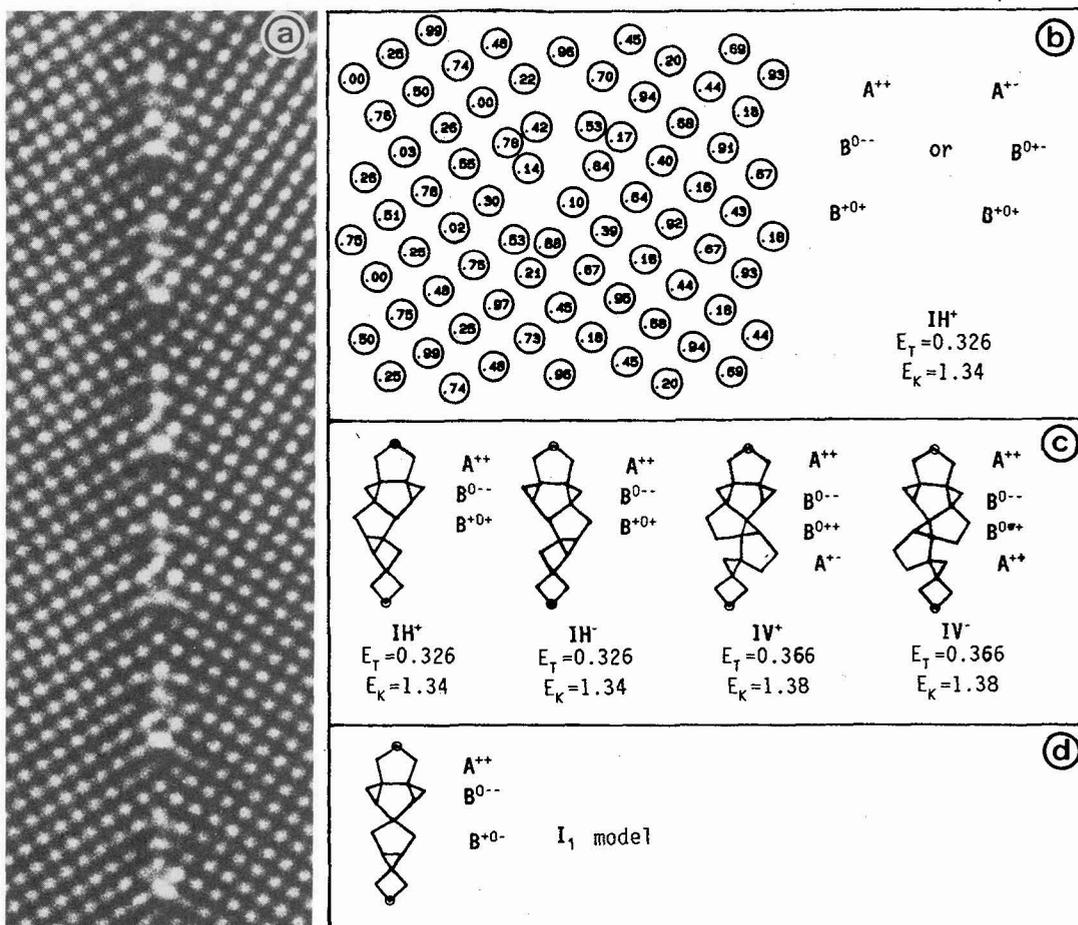


Fig. 5 - a) Experimental image (defocus -42nm, thickness about 8nm, germanium) of the second type of (510) interface. b) (001) projection of the  $IH^+$  model. The two possible decompositions of a period of the structure in term of SUDs are given. c) Scheme of four models of the (510) GB with 3 and 4 SUDs per period. d) Incorrect model with a  $[101]$  BVI having a strong screw component.  $E_T$  and  $E_K$  are the Tersoff /10/ and Keating energy /11/ in  $J/m^2$ .

### 3.3 - The range $0 < k_1 \leq 3k_2$ : $-53.13^\circ \leq \theta' = \theta - \pi/2 \leq 0^\circ$

We illustrate this domain with the  $\langle 320 \rangle$  interface which is the only GB of this domain we have experimentally observed. Starting from the Z model which in this range must be decomposed into two A<sup>-</sup> units arranged in a zigzag manner, we obtain from the SUM the model  $Z'_{3,3}$  of figure 3d. On the contrary if the S model is considered we form the  $S'_{3,3}$  model. Geometrically this last structure has the advantages of being more planar and of having the real periodicity of the CSL which is centered. Experimentally it is this structure that we have observed on small  $\langle 320 \rangle$  facets of our (510) bicrystal. Its energy is also lower (fig. 3d).

## 4 - DISCUSSION AND CONCLUSION

The SUM is a powerful and simple tool that permits to construct some tetracoordinated models of any  $\langle 001 \rangle$  tilt GBs. The most likely structures could belong to these models, because they contain a minimum of SUDs per period and are then likely to have the lowest energy.

Effectively for some GBs ( $\Sigma=65(11\ 3\ 0)$  and  $\Sigma=13(320)$ ) the structures predicted by the SUM have been experimentally observed and do have the lowest energy. The favoured  $\Sigma=5$  GB is a singular value delimiting two different domains. For  $k_1 < 3k_2$ , the models would be deduced from the non-observed S model. For  $k_1 \geq 3k_2$ , they would prefer to come from the Z model. However, in that last domain, the principle of continuity could not be strictly used because the two A units of the Z model are not strictly the same.

But the major point is that in the range  $k_1 \geq 3k_2$  there is a domain where the SUM is not applicable. If the samples are pure enough to neglect the segregation of impurities at the GBs, two points limit the application of the SUM in the case of real structures. Firstly, particular bordering conditions could favoured more complex (i.e. with more SUDs than the minimum number) periodic structures. For instance the large scale boundary faceting certainly stabilizes the M structure of figure 4 /6,8/. In the case of  $\langle 011 \rangle$  GBs, two structures of the  $\Sigma=11(233)$  GB have been observed /12/. One of them which was observed in a deformed bicrystal is favoured by external applied stresses. Secondly, entropy terms could stabilize new structures. This is the case for the mixed models. The fact that one of the delimiting boundaries is the perfect crystal is likely to be important in these new kinds of interface. The perfect P units prefer to gather themselves periodically in order to form "vast" nearly undeformed stable zones and to localise all the distortions in a variable core region.

Even when the SUM does not work, a method using the concept of SUD can be applied to build the observed structures. It consists in associating to every basic SU a Burgers vector of the perfect crystal and forming what we call a structural unit -dislocation (SUD). Two main steps are then needed to make a model. Firstly, the Burgers vector of the interface (BVI) must be decomposed into SUDs. Secondly, for a given decomposition the different SUDs are arranged and the model is completed with perfect P units. As the BVI decomposition and the SUD arrangements are not unique, numerous entirely tetracoordinated models can be built. This method is not predictive. Its aim is to build all the possible models among which the experimental structures will be found. The most likely models are the ones proposed by the SUM because they have a minimum of SUDs and follow the PC. The same formalism can be used to construct and analyse the asymmetrical [001] GBs. It could be adapted to others GBs. In the case of the  $\langle 011 \rangle$  tilt GBs, as a BV of the perfect crystal cannot be assigned to every SU (for instance the boat shape 6 atoms rings do not define dislocation cores of the perfect crystal) the formalism should be generalized introducing partial or "pseudo" dislocations.

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