ELEVENTH INTERNATIONAL CONFERENCE ON INTERGRANULAR AND INTERPHASE BOUNDARIES 2004

JOURNAL OF MATERIALS SCIENCE **40** (2005) 3163–3167

Relationship between structure, segregation and electrical activity in grain boundaries

A. LAMZATOUAR, O. PALAIS
Laboratoire TECSEN, UMR 6122 - CNRS, Faculté des Sciences et Techniques de St. Jérôme, F-13397 Marseille, Cedex 20, France

O. B. M. HARDOUIN DUPARC
LSI, UMR 7642 – CNRS – CEA, Ecole Polytechnique, 91128 Palaiseau Cedex, France
E-mail: olivier.hardouinduparc@polytechnique.fr

J. THIBAULT, A. CHARAÏ*
Laboratoire TECSEN, UMR 6122 - CNRS, Faculté des Sciences et Techniques de St. Jérôme, F-13397 Marseille, Cedex 20, France
E-mail: ahmed.charai@univ.u-3mrs.fr

Using the contactless microwave phase-shift technique (μW-PS) and High Resolution Transmission Electron Microscopy (HRTEM), we show that the twist and mixed parts of a $<110>\Sigma = 51(\theta = 16.10^{\circ})$ grain boundary in germanium (Ge) are electrically active. We also show that we can passivate the electrically active grain boundaries by sulfur segregation which has been studied by energy filtering HRTEM. Atomistic simulations show that the most favorable places for this segregation are the high energy sites of grain boundary.

1. Introduction

The presence of defects such as grain boundaries (GBs) can affect the electrical properties of polycrystalline semiconductors by introducing localized electronic states in the band gap. These states can act as centers of recombination for the charge carriers. The origin of these electronic states (band tails or deep levels) may be intrinsic (owing to large structural distortion and dangling bonds) or extrinsic (owing to segregated or precipitated impurities or dopants). The dangling bonds in GBs are the major contributor to the intrinsic electrical activity [1–3]. Atomic simulations have shown that the structural disorder in twist GBs in silicon is very likely to generate gap states [4].

This paper is a continuation of our early published work [5] on the theme of correlation between atomic structure, segregation and electrical activity in GBs. Here, we detail this study for a $<110>\Sigma = 51(\theta = 16.10^{\circ})$ GB in germanium which was grown by Chokralski method and which exhibits different structures. We use the contactless **M**icro-**W**ave **P**hase **S**hift technique [6] and we explain the origin of the observed electrical activity by analyzing the GB at the atomic scale by HRTEM. We also study the effect of sulfur segregation on the electrical activity and atomic structure of $\Sigma = 51$ GB in Ge.

2. Methods

The electrical characterization of germanium GBs is based on the measurement of minority carriers lifetime. Lifetime mappings obtained by the μW-PS technique enable observation of contrast between the homogeneous area of the bulk and the grain boundary area when the GB is electrically active. In this technique, carriers are generated by a laser diode which is modulated by a sine wave form function generator and the phase shift Φ between this optical excitation and the microwave power reflected by the sample is measured. Because the excitation is modulated by small amplitude sine waves, the technique is a quasi steady state one, and its main advantage is that it works at practically constant injection level. Trapping effects that can distort the lifetime measurement are thus strongly reduced.

It is possible to extract the bulk lifetime of minority carriers τ_b from the measured phase shift which is a function of the frequency of modulation f and of parameters of the sample under investigation. These parameters are the bulk lifetime of minority carriers τ_b, the front and the back surface recombination velocities S_f and S_b respectively, the diffusion coefficient D, the optical absorption coefficient α and the thickness of the sample t. One thus has for the phase shift Φ the following complex function (1) whose details can be found elsewhere [7]:

$$\Phi = F(\tau_b, S_f, S_b, D, \alpha, t, f) \quad (1)$$

Among the seven parameters, three are known α, t, f, and D can be easily evaluated. In general, to deduce the parameter of interest, τ_b, one needs to know the surface

*Author to whom all correspondence should be addressed.

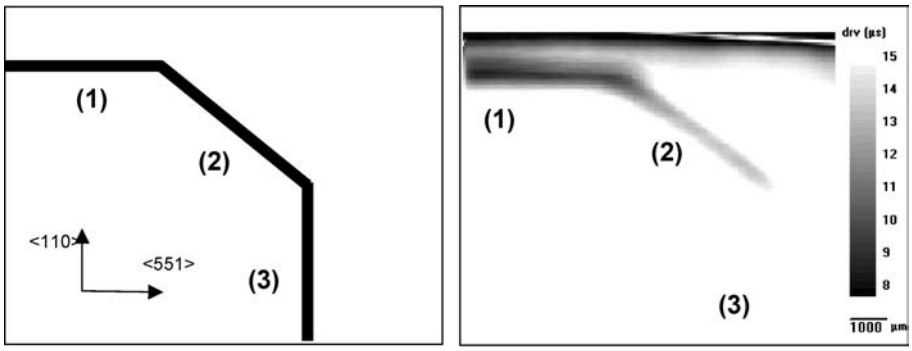

Figure 1 (a) Schematic shape of germanium bicrystal with three types of $\Sigma = 51$ GB: (1): Tilt GB; (2): Mixed GB; (3): Twist GB. (b) Lifetime scan map.

recombination velocity of the front and the bottom side, except if their influence can be strongly reduced. That is why during lifetime measurement, the electrical activity of surfaces is reduced by a solution of iodine. In this case τ_b is directly obtained by the relation (2) (see [7]):

$$\tau_b = \tan \Phi / 2\pi f \qquad (2)$$

However, if a quantitative determination of τ_b is not required, it is possible to obtain a relative variation i.e. an effective lifetime $\tau_{b,\text{eff}}$ without surface passivation. In this case, $\tau_{b,\text{eff}}$ is not the actual lifetime but allows relative comparison between the electrical activity of the bulk and the grain boundary, even if surface passivation is not achieved.

To obtain a lifetime scan map, the laser beam was focused on the front surface of the sample and the spot diameter was about 50 μm. The samples were mounted on an X-Y stage moved by step motors driven by a computer in order to map the sample.

After electrical measurement, the samples are studied at the atomic scale by HRTEM. Discs of about 3 mm in diameter were ultrasonically cut from the thin lamellas along the boundary and were then thinned further using standard mechanical grinding and ion milling procedures. HRTEM experiments were performed using a JEOL 4000EX electron microscope (CEA-Grenoble) operating at 400 kV. We also carried out chemical analyses using a JEOL 2010F, operating at 200 kV and equipped with a field emission source in order to take advantage of the small and intense analytical probe (∼0.5 nm). For chemical analyses, that JEOL 2010F is coupled to a Gatan Imaging Filter (GIF) to obtain Electron Energy Loss Spectra (EELS) and chemical images through energy filtering transmission electron microscopy (EFTEM). Energy filtered images were obtained by the three windows method (20 eV for each). The first window is centered on the L2,3 sulfur edge (corresponding to an energy loss of 165 eV) whereas the two others were positioned at two pre-edge positions to process the background subtraction.

3. Minority carrier lifetime measurements on different $\Sigma = 51$ GBs

We started our investigation on a bicrystal containing three types of $<110>\Sigma = 51(\theta = 16.10^\circ)$ GB, a pure tilt (GB (3) on Fig. 1a, a twist (GB (1) on Fig. 1a and a mixed (a mixture of tilt and twist GB) (GB (2) on Fig. 1a. The lifetime scan map shows no contrast between tilt GB and the bulk indicating that the pure tilt GB is not electrically active. However, the twist and the mixed GBs are recombinant since a lifetime contrast is clearly visible compared to the homogeneous grains (Fig. 1b). We note that the mixed $\Sigma = 51$ GB is less active compared to the twist GB; this can be explained by the fact that the tilt parts existing in mixed GB are inactive and only the twist parts are thereby responsible for the electrical activity of the $\Sigma = 51$ mixed GB. The observed electrical activity of $\Sigma = 51$ twist GB may be related to a great structural disorder, because chemical analysis (with a detection limit of 1%) using the JEOL 2010 F show neither impurities nor precipitates along to the grain boundary. According to atomistic calculations, twist GBs are characterized by strong structural disorder associated with excess energies considerably

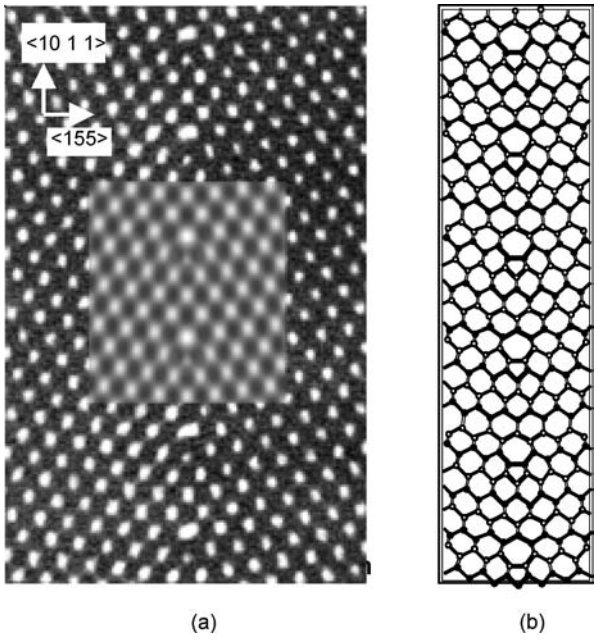

Figure 2 (a) HRTEM image of perfect $\{551\}\Sigma = 51$ tilt GB observed along the [011] common axis in Ge. The inset in (a) shows a simulated HRTEM image of the model shown in (b) (conditions of simulation: focus: −52 nm, defocus spread: 10 nm, semi-divergence angle: 0.9 mrad, and thickness: ∼2.5 nm). The atomic columns appear as dark spots. (b) Atomic model of $\{551\}\Sigma = 51$ tilt GB.

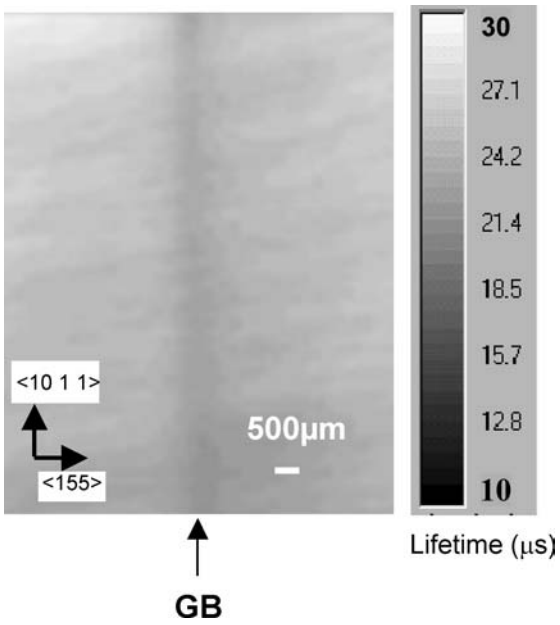

Figure 3 Lifetime scan map of $\Sigma = 51$ tilt GB in Ge before sulfur segregation. Note the contrast between the homogeneous area of the bulk and the grain boundary.

larger than those of the tilt GBs [4], which may explain the reason why twist GBs are seldom found in polycrystalline semiconductors.

The number of recombining centers (due to the structural disorder) in twist GBs is also likely to be larger than the corresponding amounts in mixed GBs and this can explain the difference in the lifetime scan map between mixed and twist $\Sigma = 51$ GB.

4. HREM imaging and atomistic simulations of the pure tilt symmetrical GB

We have studied the pure symmetrical tilt part of the $<110>\{551\}\Sigma = 51$ GB by HRTEM, it shows no steps nor any defects. This is consistent with the inactivity of this part of $\Sigma = 51$ GB. It has already been shown in several studies [3, 8, 9] that the perfect atomic structure of $\Sigma = 51$ pure tilt GB does not contain strongly distorted bonds or dangling bonds. Our numerical calculations actually show that the maximum bond length distortion is only 3% compared to the ideal bond. In Fig. 2a, a HRTEM image of a $\Sigma = 51\{551\}$ pure tilt GB is shown in such conditions where the atomic columns appear as dark spots. The atomic structure which can be deduced from this image is identical to the one already proposed [3, 8, 9]. It is made of only two well defined structural units labeled C (two six-atom rings) and L (five-seven-atom rings). One period can be represented by {CCCL.CCCL} (Fig. 2b). The L-unit can be described as a Lomer-dislocation core. Once numerically optimized as indicated in [8] using the Ding-Andersen potential [10], the atomic positions can be treated with the EMS code (Electron Microscopy Simulation) [11] to simulate their corresponding HRTEM images. The comparison between simulated and experimental HRTEM images shows a perfect match and confirms the fact that all the atoms are tetracoordinated (see inset in Fig. 2a).

5. Electrically active defects along the tilt parts of $\Sigma = 51$ GB

Another sample of the same ingot containing only a $\Sigma = 51$ tilt GB parallel to {551} plane, has been investigated and we measured the minority carriers lifetime. Surprisingly, the lifetime scan map shows a difference of contrast between the GB and the bulk (Fig. 3); we note a shorter minority carrier lifetime in the GB compared to the bulk. This result shows clearly that this GB contains recombining centers, and as a consequence it is electrically active. It is very likely that the GB contains active defects or precipitates. The contactless microwave phase shift technique not being able to determine the origin of the electrical activity of $\Sigma = 51\{551\}$ tilt GB, we studied the GB at the atomic scale using the HRTEM coupled to chemical analysis. This latter does not reveal any precipitates, but our HRTEM observations show the existence of defects along the $\Sigma = 51\{551\}$ tilt GB, these defects are steps perpendicular to the $<110>$ tilt axis which lead to twisted portions along the tilt $\Sigma = 51\{551\}$ GB (Fig. 4). These twisted parts are revealed by the presence of Moiré patterns corresponding to the superimposition of two crystals twisted by 16.10° around the $<110>$ common

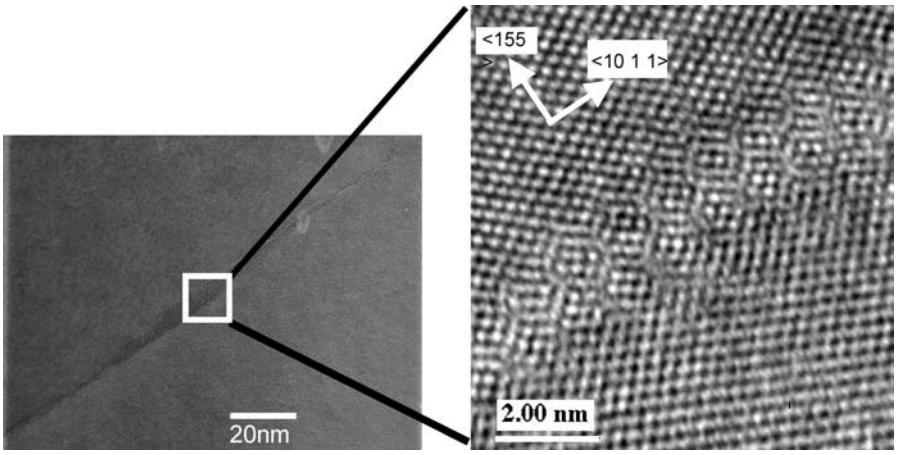

Figure 4 HRTEM images showing parts of $\Sigma = 51$ twist GB in $\Sigma = 51$ tilt GB in Ge. The tilt GB has steps perpendicular to the tilt axis which are revealed by the moiré pattern corresponding to the superimposition of two crystals rotated by 16.10°.

axis. These twisted parts are thereby responsible for the electrical activity of this "tilt" $\Sigma = 51$ GB.

6. Electrical passivation by sulfur segregation

Is it possible to passivate an electrically active GB? This is another principal objective of this work. For that, we performed a sulfur treatment on a sample containing the electrically active $\Sigma = 51$ "tilt" GB. The sulfur introduction was carried out through annealing of the sample at 540°C for 9 days under a H_2/H_2S gas mixture following a controlled protocol previously set up [12, 13]. The minority carriers lifetime scan maps measured after sulfur segregation show that the contrast between the homogeneous area of the bulk and the $\Sigma = 51$ GB has disappeared. The GB became electrically inactive after sulfur segregation. This shows that the sulfur has passivated the recombining centers of the twist parts observed in $\Sigma = 51$ tilt GB. Thus sulfur segregation seems to be very efficient in reducing carrier trapping in GBs. One can assume that the passivation of the electrically active GB is due to the saturation of strongly distorted or dangling bonds by the segregated atoms of the sulfur. It is of course difficult to prove experimentally this assumption because it is very difficult to determine exactly the atomic structure of twist GBs either before or after sulfur segregation. Instead, we investigated the perfect tilt parts (electrically inactive), before and after sulfur segregation. Before sulfur segregation, we obtained HRTEM images of $\Sigma = 51\{551\}$ pure tilt GB, it is like the one presented in Fig. 2a which shows a perfect atomic structure. After sulfur segregation, we note that the contrast changes in the HRTEM image of $\Sigma = 51\{551\}$ pure tilt GB. This change is located on the L-unit (Lomer dislocation core) (Fig. 5). Using the image filtering method, chemical imaging indicates clearly the presence of sulfur enrichment along the GB (Fig. 6). This result strongly sustains that a structural change is owed to sulfur segregation into the $\Sigma = 51$ tilt GB. Accordingly, the L-unit (dislocation core) can be considered as a favorable place for sulfur segregation due to

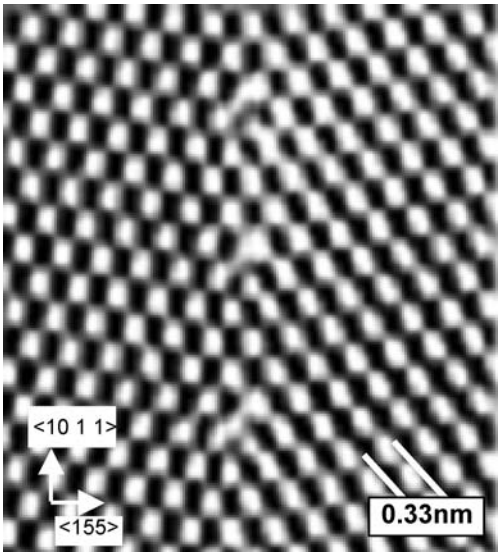

Figure 5 HRTEM imaging on sulfured $\Sigma = 51\{551\}$ pure GB in Ge showing a structural atomic change at the L unit level.

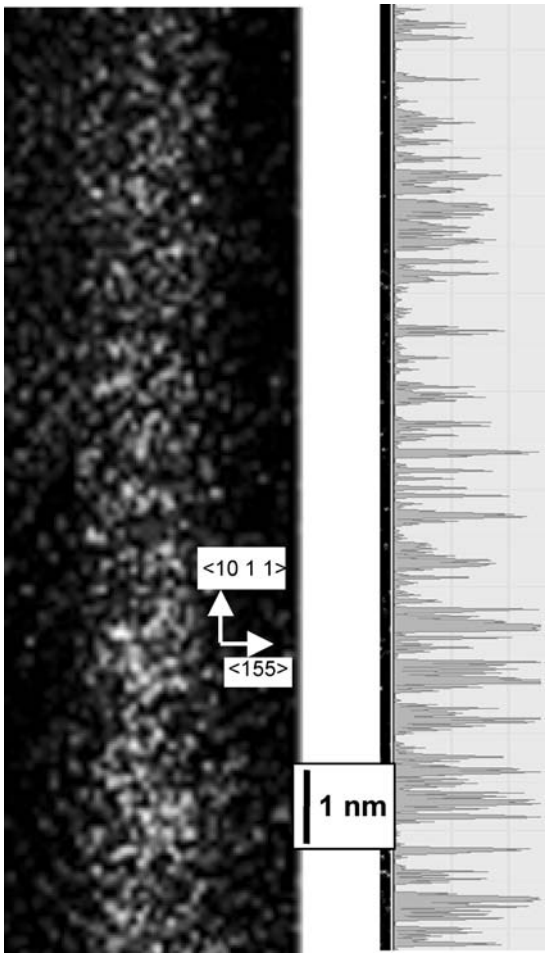

Figure 6 EFTEM image that indicates sulfur segregation in $\Sigma = 51$ GB in Ge.

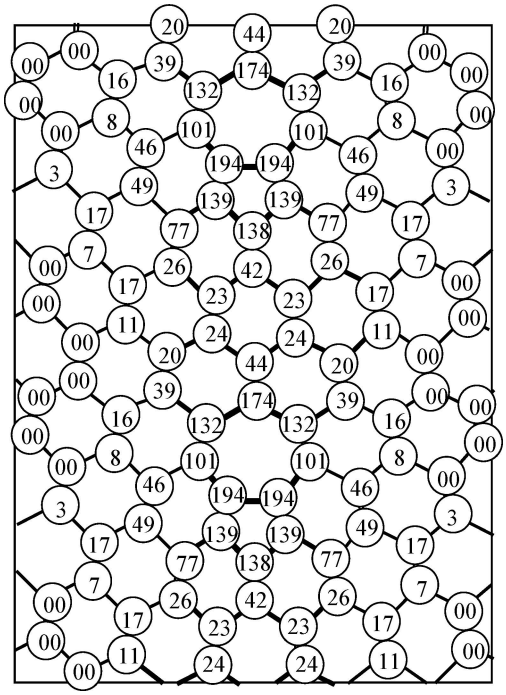

Figure 7 Energies of atomic sites of $\Sigma = 51$ GB in Ge. Note the high energy values in the two common atomic sites between seven and five-fold rings, (the energy values are calculated using the Ding-Andersen potential).

the existence in it of high energy sites (Fig. 7). This shows that, even if $\Sigma = 51\{551\}$ tilt GB contains neither great structural disorder nor dangling bonds, sulfur acts on the atomic structure particularly in the high energy sites. We suggest the same thing for the GBs with much distorted bonds such as $\Sigma = 51\{110\}$ twist GB.

7. Conclusion

To conclude, this work demonstrated that the μW-PS technique is an efficient mean for detecting the electrically active defects such as GBs and checking if a normally low atomic structure energy GB contains accidental structural defects. Using this technique, we showed that the $\Sigma = 51$ mixed and twist GB in Ge are electrically active. Complementing μW-PS with HRTEM and EELS observations and analyses allowed us to additionally locate the origin of this electrical activity. We also evidenced the distribution of sulfur segregation along the GB and showed its ability to passivate an electrically active GB.

Acknowledgements

The authors would like to thank W. SAIKALY (CP2M, Marseille) for helpful discussions.

References

1. T. PAXTON and A. P. SUTTON, *Acta Metall.* **37** (1989) 1693.
2. P. SUTTON and R. W. BALLUFI, in "Interfaces in Crystalline Materials" (Oxford Science publication, Oxford, 1995).
3. J. THIBAULT, J. L. ROUVIÈRE and A. BOURRET, "Grain boundaries in Semiconductors," in Handbook of Semiconductor Technology, edited by K. A. Jackson and W. Schröter (2000), Vol. 1, p. 375.
4. M. KOHYAMA and R. YAMAMOTO, *Solid State Phenomena* **37** (1994) 55.
5. O. PALAIS, A. LAMZATOUAR, O. B. M HARDOUIN DUPARC, J. THIBAULT and A. CHARAÏ, *J. Phys. Condens. Matter* **16** (2004) 207.
6. O. PALAIS, J. GERVAIS, E. YAKIMOV and S. MARTINUZZI, *Eur. Phys. J. AP.* **10** (2000) 157.
7. M. ORGERET and J. BOUCHER, *Rev. Phys. Appl.* **13** (1978) 29.
8. A. CHARAÏ, M. BENAISSA, C. ALFONSO, L. FARES, O. B. M. HARDOUIN DUPARC, J. L. ROUVIÈRE and J. THIBAULT, *Phil Mag.* **81** (2001) 1821.
9. H. M. MICHAUD, X. BAILLIN, J. PÈLISSIER, J. L. PUTAUX and J. THIBAULT, *Microsc. Microanal. Microstr.* **4** (1993) 221.
10. P. STADELMANN, *Ultramicroscopy.* **21** (1987) 131.
11. A. CHARAÏ, L. FARES, C. ALFONSO, L. ROUSSEL and J.-L. ROUVIÈRE, *Surf. Rev. Lett.* **5** (1998) 43.
12. J. CABANÈ and F. CABANÈ, in "Interface Segregation and Related Processes in Materials," edited by J. Novotny (Trans Tech. Publisher, 1991) p. 1.
13. K. DING and H. C. ANDERSEN, *Phys. Rev. B.* **34** (1986) 6987.

Received 29 July 2004
and accepted 31 January 2005