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Correlation between electrical activity and various structures of Ge grain boundaries

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Abstract

The links between the electrical activity and the atomic structure of various Ge grain boundaries (GBs) are investigated. The atomic structure is studied using high resolution electron microscopy, while the electrical activity is evaluated thanks to the measurement of minority carrier lifetime by means of the contactless microwave phase shift technique. Results show that in the $\Sigma = 51$ GB the electrical activity depends on the atomic structure connected to the configuration of the grain boundary, i.e. tilt, twist or mixed. Lower energy structures such as $\Sigma = 3$ and 9 GBs appear not to be recombinant.

1. Introduction

Electrical properties, atomic structure and chemical composition are key parameters in the semiconductor engineering field. Usually, these parameters are investigated independently from each other, although they are strongly interdependent. Indeed, often the electrical properties of a semiconductor depend directly on structural defects and impurities. Many studies have been performed to correlate electrical properties with impurities, but few to correlate electrical properties with structural defects. The purpose of this work is to couple means of investigation allowing direct correlation between the electrical activity of an extended defect and its own atomic structure. We have chosen germanium bicrystals for this study because Ge ingots are very pure, free of contaminant which could distort the electrical charaterizations. The investigations were carried out on the $\Sigma = 51$, 3 and 9 Ge GBs, which are GBs with clearly defined atomic structures. Moreover the atomic structures of these GBs are totally reconstructed with non-recombinant centres for minority carriers like dangling

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bonds. However, if additional extended defects such as steps are present, such structures can become distorted and their energy increases. In the present paper, we will correlate electrical activity of various GBs to their atomic structures and show that it is possible to detect structural defects by means of electrical contactless measurements.

2. Experimental details

2.1. High resolution electron microscopy.

To study the GBs on an atomic scale high resolution electron microscopy (HREM) has been performed, using a JEOL 4000EX electron microscope operating at 400 kV. Ge thin foils, few nanometres thick, were prepared by means of a mechanical thinning followed by an ion thinning.

2.2. Contactless measurement of the electrical activity

Electrical properties of GBs were locally measured by means of the microwave phase-shift technique (μW-PS) that gives both the bulk lifetime (τ_b) and surface recombination velocity (S) of minority carriers. The μW-PS is a non-destructive contactless technique that does not require any sample preparation thanks to the use of microwaves as a probe. This makes it possible to directly measure minority carrier bulk lifetime on as-grown samples. For measurement, minority carriers are generated by means of an optical excitation, sine modulated, at one fixed wavelength. The sinusoidal variation of the carrier density induces a sinusoidal variation of the reflectivity coefficient of the microwaves and thus the phase shift (Φ) between the modulated exciting light and the reflected power of microwaves is measured. From the measurement of Φ, τ_b and S are deduced [1]. This technique is able to map τ_b and S with a lateral resolution up to 20 μm. In the present work we focus on the bulk properties of various GBs, then in order to minimize the effects of surfaces on the bulk lifetime measurements, a 1550 nm laser diode has been used for carrier excitation (at this wavelength the optical absorption coefficient is only about 3×10^2 cm^{-1} in germanium [2]).

Notice that μW-PS is sensitive to the electrical activity of a defect, that is why extended defects, even thinner than the spatial resolution, such as GBs, are clearly visible with the lifetime scan maps if they are electrically active.

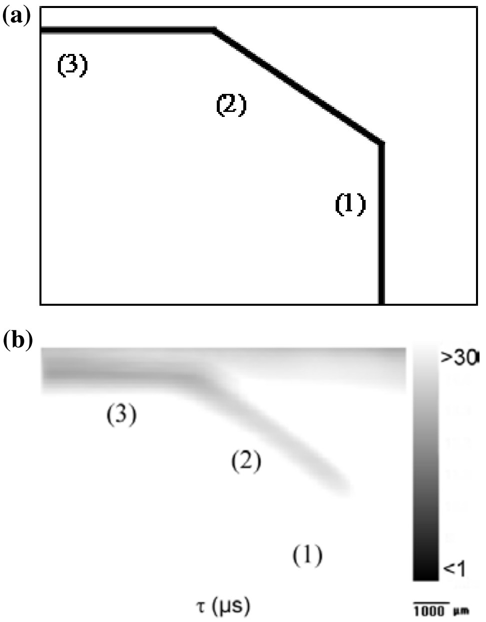
2.3. Ge samples investigated

The samples investigated in this work are intrinsic Czochralski grown germanium bicrystals and tricrystals, coming from ingots about 2.5 cm in diameter.

We took advantage of the accidental structure modification which occurred during the growth of the ingot $\Sigma = 51\{551\}\langle 110\rangle(\theta = 16.10°)$ pure tilt GB containing, for study a $\Sigma = 51$ GB in three atomic configurations: tilt GB, twist GB and mixed GB, as illustrated by figure 1(a). A triple junction of one $\Sigma = 9\{221\}$ GB and two $\Sigma = 3\{111\}$ GBs as shown by figure 4(a) was also investigated.

3. Results and discussions

For each GB configuration we performed an electrical analysis by means of measurement of minority carrier lifetime τ_b. Among the samples investigated the one described by figure 1(a) is very useful for this work due to its variety of $\Sigma = 51$ GB configurations. The minority carrier



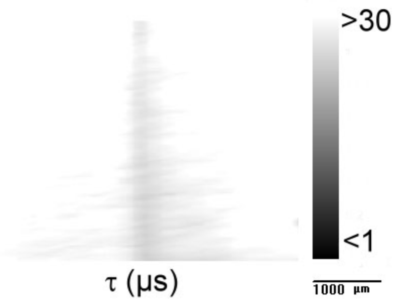


Figure 1. (a) Schematic shape of germanium bicrystal with three types of $\Sigma = 51$ GB: (1) tilt GB; (2) mixed GB; (3) twist GB. (b) Lifetime scan map.

Figure 2. Lifetime scan map of $\Sigma = 51$ pure tilt GB, before sulfur segregation.

lifetime scan map shows that the pure tilt GB (GB (1) in figure 1(b)) is invisible, pointing out no recombinant activity. This is in agreement with our calculations using the Keating potential [3] showing that the maximal variation of bond length is 2.25%; this indicates the absence of dangling bonds. However, figure 1(b) shows lower lifetime around the twist and mixed GBs, indicating that they are electrically active. This activity may be related to the presence of dangling bonds in the twist GB [4]. The number of dangling bonds may increase going from the pure tilt GB to the twist GB via the mixed one. We can observe indeed that the mixed GB is less recombinant that the twist one, because it contains parts of pure tilt $\Sigma = 51$ that are electrically inactive. Nevertheless, the pure tilt $\Sigma = 51$ GB (figure 2) coming from another part of the same ingot should also be electrically inactive, but the electrical characterization shows a weak contrast around the GB, pointing out a recombinant activity. This result is apparently in contradiction with the first observations of the previous pure tilt $\Sigma = 51$ GB. However, the electrical activity measured around this GB is not surprising in view of the HREM observations that show the existence of steps (figure 3). Indeed, these steps could be described as segments of $\Sigma = 51\{110\}$ twist GB and may be the origin of the recombinant centres [4]. Consequently, the knowledge of the misorientation angle and the coincidence parameter Σ is not sufficient to predict the electrical activity of the corresponding GB. The presence of extra defects or possibly change of GB planes must be taken into account. Nevertheless, the electrical characterization by means of the μW-PS technique allows easy and quick determination of the specificity of an as-grown GB and a check of whether a normally low atomic structure energy GB contains accidental structural defects.

In order to passivate recombinant centres of the electrically active step containing $\Sigma = 51$ GB (of figure 2), a sulfur segregation was carried out, by annealing at 540 °C for 9 days under H_2/H_2S gas mixture. More details of sulfur segregation can be found elsewhere in [5, 6]. After this treatment the lifetime contrast around the GB has disappeared, indicating

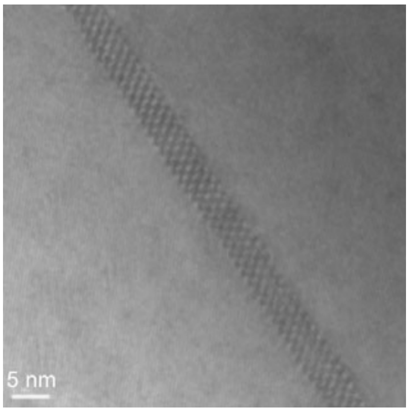


Figure 3. HREM image showing a step observed in a $\Sigma = 51$ tilt GB viewed along the [011] common axis in Ge.

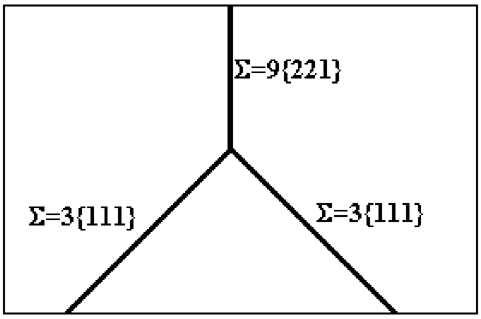


Figure 4. Schematic shape of the sample with a triple junction of one $\Sigma = 9$ and two $\Sigma = 3$ tilt GBs, viewed along the [011] common axis in Ge.

the saturation of the dangling bonds. Work is underway using HREM and electron energy loss spectroscopy (EELS) to confirm this interpretation.

Electrical features of lower energy GB structures were also investigated by studying a triple junction of one $\Sigma = 9\{221\}\langle 011\rangle$ ($\theta = 38.94°$) tilt GB and two $\Sigma = 3\{111\}\langle 011\rangle$ ($\theta = 70.53°$) tilt GBs (figure 4). The measurement of the lifetime of minority carriers, showing that this sample is electrically inactive, is in agreement with our predictions, because $\Sigma = 9\{221\}$ and $\Sigma = 3\{111\}$ have atomic structures that are totally reconstructed and among the less distorted. This result confirms that a lifetime contrast is only visible if a GB is electrically active. This result shows clearly that the dissociation of $\Sigma = 9$ into two $\Sigma = 3$ occurs without any creation of electrically active defects.

These observations show a correlation between the electrical properties and the atomic structure configuration. The scale analysis is a pertinent parameter to know what kind of defect (distortion, dangling bonds, steps...) introduces recombinant centres for minority carriers.

4. Conclusions

We have shown in this paper that the coupling HREM technique and minority carrier lifetime engineering enable us to correlate the electrical activity to the atomic structure of Ge GBs. In the case of the electrically active pure tilt $\Sigma = 51$ GB, this activity depends mainly on the existence of extra defects such as steps. We observed that sulfur segregation suppresses the recombinant centres of minority carriers. The most important finding consists in demonstrating that μW-PS is able to evaluate the recombination rate of a grain boundary and establish whether it is a low energy or a distorted atomic structure, possibly containing extra defects.

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