Structure of an incommensurate 90° Si grain boundary resolved with the help of a Cs-corrector for illumination

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Abstract. The atomic structure of an incommensurate (001)/(110) Si grain boundary (GB) or 90° Si GB has been studied by transmission electron microscopy (TEM) and refined by atomistic simulations (Stillinger-Weber potential). Samples were made by bonding one (001) Si wafer with one (110) Si wafer and carefully orienting the 2 wafers in order that they have a common [110] direction. In the interfacial direction perpendicular to [110], the [110]₁ direction of grain I is parallel to the [001]₂ direction of grain II and, as the ratio of this 2 vectors is √2, it is impossible to find 2 integers n and m such that n[110]₁=m[001]₂. The structure is incommensurate in this direction. Z-contrast images obtained in an FEI-Titan microscope equipped with a probe Cs-corrector easily resolve the Si dumb-bells in the two grains and allow us to determine the complex atomic structures of the interface. On the other hand, near on-axis high resolution TEM images obtained in a JEOL 4000EX microscope are very efficient to analyse the long range order of the interface.

1. Introduction
In many situations, energy is lowered by creating periodic structures. For instance, in Si polycrystalline materials, grains are generally not at all randomly distributed. Grain boundaries (GBs) with low energies tend to be created, and these low energy GBs correspond to particular orientations of the grains that produce periodic interfaces with short interfacial periods [1]. But what happen if the two crystals are bonded together in such an orientation that no periodic lattice is geometrically possible (what we call an incommensurate case)? Will the orientation of the grains be slightly changed in order to create a periodic lattice? Such a crystal has already been created in gold and its structure has been described as quasicrystalline [2]. In this work the fabrication, characterization and simulation of an incommensurate grain boundary in Si is reported.

2. Experimental details
The incommensurate grain boundary in silicon was made by bonding together one (001) 4” Si wafer, with one (110) 4” Si wafer. The two mirror-like wafers were first cleaned to remove any organic contamination or particles. Secondly, both surfaces were hydrophilic recovered by a native oxide with rms roughness of ~1.5nm. Thirdly, the surfaces were passivated by hydrogen using HF vapour. Then the two wafers were placed face to face and carefully oriented in such a way that they had a common

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direction. The bonding was initiated by pressing gently one edge of the wafer. From the pressed point, a wave front propagated and started to bond the two wafers together [3]. The bonding was then fixed by annealing at high temperature (about 1000°C).

[110] cross-sections were then classically realized by mechanical thinning and ion milling. Samples were observed either with a JEOL 4000EX microscope equipped with a LaB$_6$ filament or with a FEI-TITAN microscope fitted with a CEOS probe Cs-corrector.

Atomic models of specific configurations were manually built starting from models determined from experimental images by using the V_Sim software [4]. The energy of these configurations was finally minimized by using a Stillinger-Weber potential and by periodising the structure [5-6].

3. Experimental results

3.1. HRTEM images

Figure 1 is a high resolution transmission electron microscopy (HR-TEM) image of the grain boundary (GB) obtained with the JEOL 4000EX. The GB is observed along the common [110] direction. Perpendicular to [110], the [110] direction of the first grain ([110]$_1$) is parallel to the [001] direction of the second grain ([001]$_2$) (fig. 1). As the ratio of the norms of these two vectors is equal to $\sqrt{2}$, it is mathematically impossible to have a common period along these directions and the GB is said to be incommensurate along that direction. Grain 2 can be deduced from grain 1 by a rotation of 90° around the common [110] axis. From images such as fig. 1, it is very difficult to solve the atomic structure of the interface because, due to the limited resolution of the microscope (0.17 nm at Scherzer defocus), not all the atomic columns are resolved and because the structure is not really periodic although some features are repeated. Indeed it is rather difficult to determine what is repeated and what is not. These periodicities are best seen by slightly disorienting (2 or 3°) the sample away from the [110] common direction. The contrasts in the two grains are then slightly different and the two grains are easily distinguished (fig. 2). Long range order is then analyzed more easily.

![Figure 1](image-url)

**Figure 1.** [110] HRTEM image of the (001)/(110) incommensurate Si GB. Defocus is about 50 nm, and atoms are black. The Si dumb-bells separated by 0.135 nm are not resolved.
Figure 2. Slightly off-axis HRTEM image of the (001)/(110) incommensurate Si GB (defocus is about 50 nm, atoms are black).

The interface is not flat but has a zigzag shape. The interface is not periodic, but composed of a limited number of segments distributed at first glance with no apparent order. These segments are characterised by their respectively vectors $p_1 = k_1/2[110]$ and $p_2 = k_2[001]$ in the lower and upper crystals (convention of figure 2). Figure 2 shows the more frequent $(k_1, k_2)$-segments: (7,5), (10,7), (13,9) and (3,2). It can be checked that the $k_1/k_2$ ratios are good approximants to $\sqrt{2}$ although they do not all belong to the diophantian series [2]: (1,1), (3,2), (7,5), (17,12). However, it was impossible to solve the atomic structure of these segments by analysing HR-TEM images because the structures are too complex. In Figures 1 and 2, atoms are black. The Si dumb-bells separated by 0.135 nm are not resolved. Tunnels are white and it is impossible to really separate where the hexagonal, pentagonal and heptagonal tunnels are. We had to use Z-contrast images to do it.

3.2. STEM images

Figure 3 is a high resolution scanning TEM (HR-STEM) image of the GB. This image was acquired on the TITAN microscope (300 kV) with a Fishione HAADF detector by using a spot size of 6, a gun lens of 6, an extraction voltage of 4300 V, a convergence angle of 20 mrad, a collection angle of 40 mrad, and a scanning time of 20 s. To enhance the contrast the image was filtered using a 7x7 pixels mask with weights of 32, 4, 2 and 1 for the central, first, second and third adjacent pixels, respectively. The atomic structure can be directly deduced from figure 3: each white spot corresponds to an atomic column and Si dumb-bells, composed of two columns separated by 0.135 nm, are mostly resolved.

Figure 3. High resolution STEM image showing several periods of the (7,5) segment. The common [110] direction of the two grains is the direction of observation. Arrows points towards atomic columns that have special reconstructions (no dumb-bell) doubling the period along [110]. The white squares outline specific tunnels composed of rings of 7 atoms (heptagonal tunnels).
Figure 3 contains several consecutive (7,5) segments. Several isolated columns can be seen and correspond to a special reconstruction doubling the period along [110]. The atomic structure of others segments have been solved but are not reported here.

3.3. Atomistic simulations
The atomic structure of a (7,5) segment is shown in figure 4. All the Si atoms have 4 neighbours. Some columns (pointed by arrows in fig. 4) have special reconstructions (no dumb-bell) along [110]. On these special columns, one bond is parallel to [110] and the 3 others are nearly in the (110) plane. These special reconstructions lead to a doubling of the period along the [110] direction: the period is 110 instead of ½[110] (fig. 4b).

Figure 4. (a) Atomic model of the (7,5) segment projected on to the (110) plane showing atoms and bonds between neighbours. Vertical white line determine the size of the periodic box used for simulations, of size 7/2[110] in the lower grain 1 and 5[001] in the upper grain 2) The white square outlines the heptagonal tunnels of Fig. 3. Arrows points towards atomic columns that have special reconstructions along [110]. (b) Section of the GB view along the directions [001] // [110] and taken near the atomic column corresponding to the arrow situated at the bottom left of fig. 4a. The periodicity in grains 1 and 2 is outlined by the two small ½[110] vectors. The [110] period of the interface is outlined by a vertical vector.

4. Conclusion
Thanks to the combination of electron microscopy techniques and atomistic simulation, the atomic structure of a complex non-periodic grain boundary has been resolved. The Si tetracoordination (4 neighbours) is kept at the interface. The interface is formed of quasi-period (k1,k2) segments.

Cs-corrected STEM was an efficient technique to solve the atomic projected structure of these segments. However, it is easier to determine the long range (k1,k2) segment ordering in slightly off-axis HR-TEM image because the two grains have slightly different contrast and because larger fields of view are more easily obtained.

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