論文の内容の要旨

Thesis Summary

Developing Effective Code for Building CSL and Approximate CSL Interfaces of Any Two Lattices and Investigating the Phase Behavior in Interfaces of Diamond-structured Materials

（CSL および近似 CSL 粒界作成のための効率的コードの開発とダイヤモンド構造界面における相挙動の研究）

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Most materials with important applications in modern times exist as crystalline materials. It still seems to be a long way to eliminate all the barriers to ultimately understand the mechanism of all the crystalline materials' properties due to lacking in a full understand of the effects of crystalline interfaces, which often cause more extensive disparity in properties from the perfect crystal than other defects like point defects or dislocations. Atomic simulation is an effective way to investigate structure-property relationship of interfaces, which has provided important support in studies on both heterogeneous interfaces and GBs widely existing in many modern functional devices and engineering materials.

In chapter 2, I introduced a python code which is capable to eliminate two barriers existing in simulating interfaces. One is lacking in an effective and convenient package capable to build a CSL interface by only input crystallographic indices and cif files. Another is lacking in a package capable to compute the cell of non-identical displacement (CNID) of any CSL interface. The results in this chapter have shown that this package can be conveniently applied to generate both heterogeneous interfaces and grain boundaries of non-cubic lattice system; and the computed CNID can apparently lower the cost of some previous simulations on interfaces and GBs.

An interesting discovery of GB phases is that multiple GB phases can coexist in fcc metals[1]. One is capable to explore the fcc GB phases by varying the atomic density near the GB respect to the atomic number in a whole GB plane (GB energy – PAD relationship). The cusps in the GB energy – PAD figure correspond to GB phases which are capable to transform between each other. Similar studies were subsequently reported in bcc GBs as well[2]. Such a phenomenon was also verified by experimental observation in atomic-scale in an aluminium GB[3]. Despites the exciting achievements in fcc and bcc metals mainly with metallic bonds, it is of both scientific and practical importance to extend this research into other elemental materials. Diamond-structured materials are good candidates to do so.

In chapter 3, I applied two methods to explore the phases of a well-known symmetric tilt GB in carbon, silicon and germanium. One is the method frequently applied in optimizing fcc and bcc GBs without varying the atomic density respected to a whole GB plane (planal atomic density (PAD)). The other is that which has been applied to explore fcc GB phases with varying PAD. The former method resulted in an enormous number of GBs each with a well-defined unit structure showing that the carbon, silicon and germanium possess some common structures and properties. The latter method was similar with that applied in the previous studies on fcc and bcc GB phases which has explored several minimum cusps in the PAD – GB energy figure representing different GB phases with well-defined unit structures. However, the results by this method for the diamond-structured materials shown only one minimum cusp at the PAD = 0, which is identical to the most-stable GB structure explored by using the former method with all the GBs having PAD = 0. The much higher complexity of the ensemble of meta-stable GBs with well-defined unit structures in the diamond-structured materials than those in the fcc and bcc metals and the difference in the PAD – GB energy distribution in these two species of materials can be attributed to the disparate properties of their chemical bonds. The diamond-structured GBs can tolerant more point defects and they do not need phase transition to compensate these defects to make the system to be stabler.

In chapter 4, with first-principles simulation, I verified the reasonability of four selected GB phases explored in chapter 2 with well-defined structural units in carbon, silicon and germanium expect one in carbon without dangling bonds. This result makes this research to be reasonable to discuss these complex GB states or phases.

In chapter 5, through computing the GB free energy by quasi-harmonic-approximation and Frankel-Ladd-Path and by monitoring the GB structural similarity of the four selected GBs at elevated temperature, the disparate temperature-induced behaviours of the three meta-stable

GBs were illustrated. They performed different capabilities to transform to the Ground GB and different pre-melting preferences. The results not only presented a phase transition from the Meta-2 GB to the Ground GB, but also challenged the well accepted assumption in previous simulations of GBs that the meta-stable GBs should always be capable to transform to the most-stable GB so that those studies often ignored the explored meta-stable GBs and were often focused only on the explored GB with lowest GB energy. These disparate performances of different meta-stable GBs should be attribute to their different kinetic barriers of transition and of pre-melting and different entropy effects at elevated temperature. These results propose the significance to of kinetic barriers and entropy effects on the free energy in affecting the stability of different GB phases at non-0K environments especially when meta-stable GBs were generated and frozen occasionally from the synthesis process of the material.

In chapter 6, I confirmed that the Meta-2 GB did transform to the Ground GB at elevated temperature. This transition is by reconstruction of the unit structure. The reconstructed unit structure is identical to that of the Ground GB but it has two ‘orientations'. Such reconstruction mechanism enables us to use a division of the whole GB into a tessellation of transforming units to describe the transition mechanism of the whole GB. There exists an interaction between the adjacent units with effects on the reconstruction that the kinetic barrier of a reconstruction resulting in a transformed unit near a neighbor already transformed to the identical orientation (like growth) is lower than that resulting in an isolated transformed unit (like nucleation) or that resulting in a neighbor transformed to the opposite orientation (defined as mutation). This energy preference of the transition at different environments predicts an integral behavior of all the reconstruction unit to be a first-order like phase transition, which was subsequently verified by a dynamic simulation. The temperature-induced free energy variation of GBs distinct with orientation disorder shows that the orientation disorder significantly contributes to the entropy and free energy of the system, which predicts a second-order phase transition. An important insight from this result is that this research has found a structural transition of this well-known GB at elevated temperature which has not been reported before, and it suggests that such structural transition is also likely to be found in other covalent-bonded GBs with reconstruction units.

In chapter 7, I have shown that the appearance of meta-stable GBs can introduce quite different electronic properties with that computed only from the most-stable GB. The results show that the meta-stable GB is capable to make higher disparity in band structure from the perfect crystal than the most-stable GB to make a metallic-like property which can be contributed to the larger distortion of the atomic bonds. The results have shown the importance to discuss the meta-stable

GBs in order to fully understand the structure-property relationship of GBs in this material and propose possibility to manipulate the electronic properties by adjusting the composition of meta-stable GBs according to the annealing results from chapter 5. Combined with the suggestion in chapter 6, the reconstructing GBs provide possibility to make new functional devices.

This research is helpful for more effective interface simulation and has made new insights on understanding the effects of meta-stable GB phases on the properties of materials with covalent bonds

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