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# Grain Size Effect on Mechanical Properties of Polycrystalline Graphene

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**ABSTRACT:** Characteristics of nanocrystalline materials are known substantially dependent on the microstructure such as grain size, crystal orientation, and grain boundary. Thus it is desired to have systematic characterization methods on the various nanomaterials with complex geometries, especially in low dimensional nature. One of the interested nanomaterials would be a pure two-dimensional material, graphene, with superior mechanical, thermal, and electrical properties. In this study, mechanical properties of "polycrystalline" graphene were numerically investigated by molecular dynamics simulations. Subdomains with various sizes would be generated in the polycrystalline graphene during the fabrication such as chemical vapor deposition process. The atomic models of polycrystalline graphene were generated using Voronoi tessellation method. Stress strain curves for tensile deformation were obtained for various grain sizes (5~40 nm) and their mechanical properties were determined. It was found that, as the grain size increases, Young's modulus increases showing the reverse Hall-Petch effect. However, the fracture strain decreases in the same region, while the ultimate tensile strength (UTS) rather shows slight increasing behavior. We found that the polycrystalline graphene shows the reverse Hall-Petch effect over the simulated domain of grain size (< 40 nm).

**Key Words:** Polycrystalline graphene, Molecular dynamics, Mechanical properties, Fracture strain, Hall-Petch effect

## 1. INTRODUCTION

Carbon based materials such as fullerene, CNT and graphite are well known for their superior electrical, thermal and mechanical properties than many other materials [1]. Among these, graphene has been intensively investigated recently and utilized as a functional material because of its unique two-dimensional nature [2]. Since some fabrication method such as the chemical vapor deposition (CVD) unavoidably produces polycrystalline microstructure, many properties of the polycrystalline graphene are of great interest related with its grain size. And it is known various properties of composite materials are closely related to the microstructures, and they are interconnected via 'cross-property relation' [3].

Graphene has been known to possess the highest mechanical strength among the existing materials. However, due to its polycrystalline nature in realistic products, it has been highly required to predict the relation between the mechanical property and its microstructure such as grain size. Mechanical properties have been studied for single crystalline graphene via

experimental measurement [4] and computer simulations such as ab initio method [5] and molecular dynamics [6] as well. Here, while other quantities such as yield strain and tensile strength are rather dependent on the measurement method and the calculation conditions such as strain rate, the Young's modulus is nearly independent on such determination conditions. In most studies, Young's modulus turned out consistently to be ~1 TPa.

On the other hand, mechanical properties of "polycrystalline" graphene have been studied mainly using molecular dynamics calculation [7,8]. To treat computationally the polycrystalline models is still beyond the computational limit for the ab initio calculation. Grain size effects were addressed for the mechanical properties of Young's modulus, fracture strain and ultimate tensile strength (UTS). It was shown the Young's modulus and UTS increase and the fracture strain decreases as the grain size increases up to about 10 nm [9]. This behavior corresponds to reverse Hall-Petch effect observable in the small grain limit.

Toward the other limit of infinite grain size, which is single

crystal, it is interested to determine the mechanical properties. In many nanomaterials, it has been shown the Hall-Petch effect observable by decreasing some mechanical properties in this limit. For example, the Hall-Petch effect exists by showing certain crossover of grain size for optimal mechanical properties of polycrystalline copper [10]. However, some of previous studies on polycrystalline graphene did not sufficiently address it, thus we computationally determined in the large grain size limit.

In this study, we investigated mechanical properties for rather larger grain size for polycrystalline graphene. Molecular dynamics calculation was employed for the large polycrystalline models with large grain size. In this method, we obtained stress strain curves of the polycrystalline models under tensile deformation and calculated mechanical properties such as Young's modulus, fracture strain, and UTS.

## 2. SIMULATION MODELS AND METHOD

### 2.1 Modeling

For the atomic modeling of polycrystalline graphene, we used the Voronoi tessellation method. Each seed randomly generated in the two dimensional domain is regarded as the center of each grain, and then each grain has a shape of polygon. The shape of realistic grains created by CVD process may have curved grain boundaries, however, the straight grain boundaries in the simulation models would not give substantial effect on the mechanical properties of the polycrystalline models [7]. The size of the grains was determined by the diameter of an imaginary circle having same area with the corresponding polygon. Fig. 1 shows an atomic model of polycrystalline graphene. Note that each grain has different shape and crystal orientation.

### 2.2 Calculation Method

In this study on large atomic systems, we used a molecular dynamics simulator, which is large-scale atomic/molecular massively parallel simulator (LAMMPS) [11]. To examine the
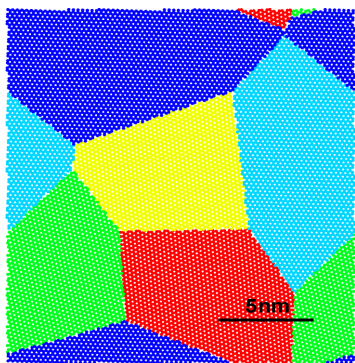
mechanical properties, we applied tensile deformations on the models subject to constant pressure (P = 0 Pa) and temperature (T = 300 K) ensemble (NPT). For the interatomic interaction, we used the AIREBO potential [12] known to describe carbon interactions more accurately than the Tersoff potential used in other previous studies. Grain size in the models was in the range of 5 to 40 nm. To achieve better statistics, we made five different configurations for each grain size and averaged the result.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Tensile Deformations

Fig. 2 shows the atomic models near the fracture or right after fracture under the tensile deformation of polycrystalline graphene with grain size 5 nm (a) and 20 nm (b) at the tensile strain of 0.08. It can be seen that the carbon atoms near the grain boundaries become unstable because of bond breaking and high energy is induced. As the Hall-Petch effect, it is seen that the crack propagation occurred in different sites depending on the grain size. For example, for the small grain size (a), cracks are generated usually at the grain boundaries. However, for larger grain size (b), the crack can be initiated inside the grains. That is, for small grain size, inter-granular failure is dominant but, for large grain size, intra-granular failure is
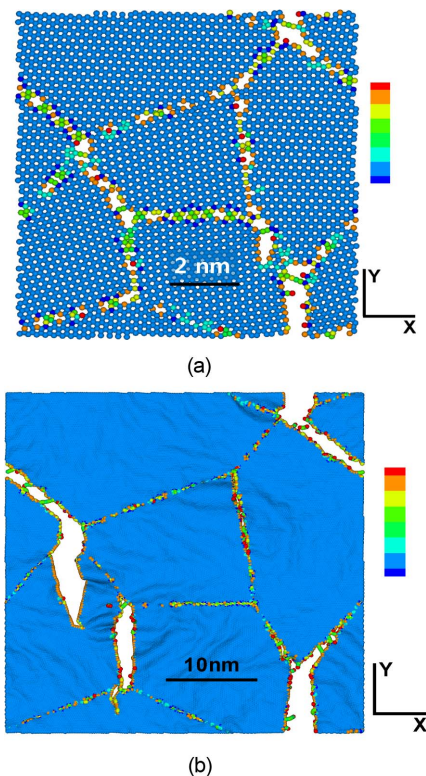


(a)



(b)

**Fig. 2.** Failure patterns under the tensile deformations of polycrystalline graphene tensile strain of 0.08 for the grain size of (a) 5 nm and (b) 20 nm. (color denotes energy of each atom: red for high energy and blue for low energy)
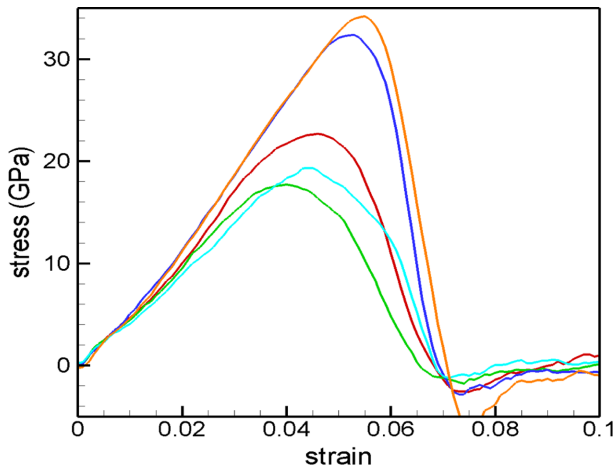


**Fig. 1.** An atomic model of polycrystalline graphene generated by Voronoi Tessellation

**Fig. 3.** Stress strain curves of polycrystalline graphene with grain size of 20 nm. Five different geometric configurations were determined in this plot



**Fig. 4.** Young's modulus vs grain size

more dominant just as in the case of polycrystalline copper [10].

Fig. 3 presents typical stress strain curves obtained for tensile deformations on the grain size of 20 nm. The initial slopes are nearly same for all five configurations and the slopes begin to slightly diverge as the strain increases. It is seen that the slope becomes stiffer after the strain of 0.02. The reason might be that the initial polycrystalline models have atomic rearrangements from sp2 to sp3 conversions caused by bond breaking at the grain boundaries. And the reconversion from sp3 to sp2 occurred under tensile deformation may show the initial small slope in the stress strain curves partially contributed by angular forces at the grain boundaries. It is also noted that the fracture strain and UTS vary with relatively large deviations, may be due to the deviation of geometric variations of the polycrystalline models.

### 3.2 Young's Modulus, Fracture Strain and UTS

Young's modulus is supposed to be approaching to that of single crystalline graphene as the grain size becomes large as. In Fig. 4, Young's modulus of the 5 nm grain model is about 200 GPa and increases to over 600 GPa for the grain size of 40 nm, which is somewhat lower than the value of single crystal (~ 1 TPa). This lower value may be due to the way of determination strain region for the modulus. As pointed out before, the polycrystalline model might have some sp3 carbons instead of sp2 carbons near the grain boundary, which later deformed only under angular force. Thus the modulus determined at the small strain region may be low estimated. Otherwise, the Young's modulus beyond the 40 nm grain size would approach to 1 TPa. The Young's modulus for the varying grain size monotonically increases and thus no apparent optimum grain size is observed.

Fig. 5 shows fracture strains vs the grain size of polycrystalline graphene. Initially, the fracture strain is obtained about
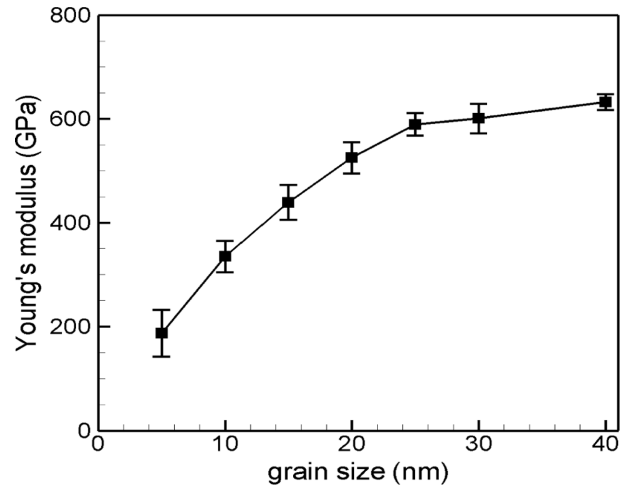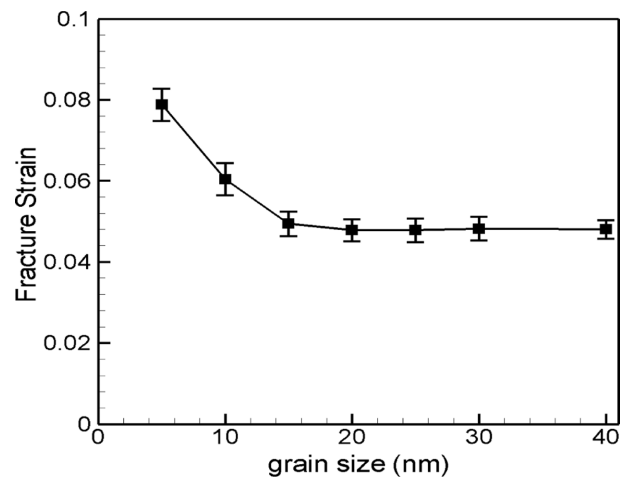


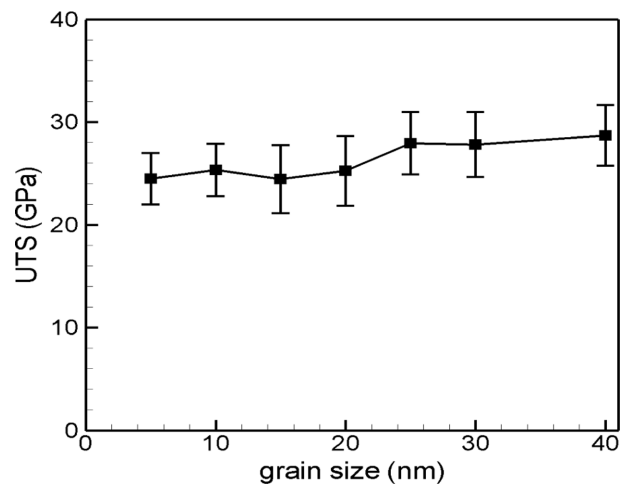**Fig. 5.** Fracture strain vs grain size



**Fig. 6.** UTS vs grain size

0.08 and decreases as the grain size increases. After the grain size is about 15 nm, the fracture strains are saturated around 0.05. The ultimate tensile strength (UTS) shown in Fig. 6 slowly increases as the grain size increases. It is obtained between 20~30 GPa and the deviation is shown rather large. This large deviation is suspected to come from geometric variations of the randomly generated models. That is, for each grain size of a given model is not well uniform but have mixed grain sizes and even smaller grains can exist for certain configurations. For example, some configuration including smaller grains than the averaged grain size may increase the fracture strain as shown in the figure.

## 4. CONCLUSIONS

In this study, we have investigated mechanical properties of polycrystalline graphene under tensile deformations. As the grain size of the atomic models increases, it is shown that Young's modulus and UTS increase monotonically and on the other hand fracture strain decreases. This grain size effect (reverse H-P effect) observed in previous studies (< 10 nm) remains the same up to the larger grain size of 40 nm. We conjecture that this result may hold up to the limit of infinite grain size corresponding to the single crystalline graphene. Similarly, the other limit of small grain size corresponding to the amorphous materials [13,14] can be addressed as well. Some other mechanical properties such as fracture energy and the interfacial characteristics between the grains will be investigated for deeper understanding of fracture mechanism and optimal design of polycrystalline graphene.

## ACKNOWLEDGEMENT

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