# Abnormal Linear Elasticity in Polycrystalline Phosphorene

Ning Liu, Ramana Pidaparti and Xianqiao Wang<sup>\*</sup> College of Engineering, University of Georgia, Athens, GA 30602 USA <sup>\*</sup>Corresponding author: <u>xqwang@uga.edu</u>

#### 1. Effect of grain number on mechanical performance

In the main text, the number of grains is fixed for polycrystalline phosphorene sheets with different grain sizes. However, the effect of grain number on mechanical performance is not discussed. Here we perform additional simulations to address this issue. As it is shown Figure S1(a), the number of grains varies from 8 to 16 while the grain size is fixed at 2nm. For each grain size, five samples with different grain orientation distribution are generated and annealed following the process described in details in the methodology section. Subsequently, all the samples are biaxially stretched to obtain corresponding mechanical properties. The detailed procedure is same as that in the main text, including the loading style and the strain rate. Figure S1(b) shows the mechanical properties of polycrystalline phosphorene sheets, which are normalized by that of samples with 8 grains. It can been seen that the stiffness fluctuates while both ultimate strength and fracture strain experiences minor decrease as the grain number increases. However, all of the variations are in the range of 10 percent. We should admit that the number of grains do affect the mechanical performance but the effect is marginal.

#### 2. Effect of annealing process on structural stability and mechanical performance

Our previous study has shown that the annealing process plays a vital role in the understanding of structural stability and mechanical properties of polycrystalline graphene.<sup>18</sup> It is desirable to investigate the efficiency of annealing process in polycrystalline phosphorene's structural stability and its corresponding effect on mechanical properties. Figure S2(a) shows the evolution of potential energy per area ( $\Delta \rho_E$ ) during the entire annealing process which can be divided into three stages. Note that the effect of time on the efficiency of the annealing process is briefly discussed in the supporting information. In the first stage,  $\Delta \rho_E$  increases as the temperature increases from 1 K to 800 K. Subsequently,  $\Delta \rho_E$  fluctuates and slowly decreases in the second stage when the temperature is controlled around 800K. Moreover, the decreasing trend becomes vague as the grain sizes increases. During this stage, breaking and forming of covalent bonds is prevalent on the grain boundaries. According to the Arrhenius equation, the reaction rate increases as the temperature increases. Physically speaking, with high translational energy at 800K, phosphorus atoms on the grain boundaries can easily overcome the activation energy and form new bonds, possibly leading to a more stable configuration than that of unannealed polycrystalline phosphorene sheet. Finally,  $\Delta \rho_E$  rapidly decays due to the decrease of temperature from 800 K to 1K in the last stage. To further evaluate the efficiency of the annealing process,  $\Delta \rho_E$  after annealing process is calculated and shown in Figure S2(b). It can be seen that as the grain size increases,  $\Delta \rho_E$  decreases. Moreover, the simulation results agree well with the fitting curve, indicating that  $\Delta \rho_E$  is proportional to the inverse of grain size. Geometrically, the percentage of atoms on the grain boundaries is also proportional to the inverse of grain size. The similarity of the varying trend of above two quantities versus grain size makes some sense. Compared with atoms inside grains, the

phosphorus atoms on the grain boundaries are loosely connected by covalent bonds, making them highly active in the high temperature range. Therefore, the breaking and forming of bonds between atoms on the grain boundaries is probably the cause of  $\Delta \rho_E$  after the annealing process. To validate our hypothesis, the snapshots of polycrystalline phosphorene sheets with grain size 6nm are taken before and after annealing process and shown in Figure S3. From comparison between Figure S3(a) and S3(b), it can be seen that the grain boundaries become harder to distinguish after the annealing process, indicating the obvious potential energy decrease. After observing the structure of grain boundaries in the zoomed-in snapshots (Figure S3(c) and S3(d)), one can see that the under-coordinated atoms form new bonds with adjacent atoms, strengthening the connections among grains and thus making the phosphorene sheets mechanically stronger.

To further validate the efficiency of the annealing process, biaxial tensile tests are performed on phosphorene sheets with grain size 7 nm before and after the annealing process. The results are shown in Figure S4. From Figure S4(a), one can tell that the annealing process barely has no effect on the stiffness. However, the fracture strength becomes bigger after the annealing process. To strength the above conclusion, we have conducted biaxial stretching on five independent samples with different grain orientation distributions before and after the annealing process. The results are normalized with the average stiffness/strength of annealed samples and shown in Figure S4(b). It can be observed that the differences between stiffnesses before and after annealing process are neglible:  $68.9 \pm 0.9$  GPa and  $69.4 \pm 1.3$  GPa, respectively. However, the ultimate strength of the annealed samples ( $4.52 \pm 0.26$  GPa) are bigger than that of the unannealed samples  $(3.87 \pm 0.33 \text{ GPa})$ . As we have mentioned before, the breaking and forming of the covalent bonds during the annealing process heal the defects and reconstruct the grain boundaries, making the polycrystalline phosphorene sheet mechanically stronger. With less dangling bonds and undercoordinated atoms on the grain boundaries, the annealed samples can sustain more loads than the unannealed ones. In summary, we have demonstrated the efficiency of the annealing process on stabilizing the phosphorene sheets and enhancing the mechanical properties, providing a good foundation for investigating the effect of grain size on mechanical properties of phosphorene sheets.

### 3. Effect of grain orientation on biaxial tensile stiffness

To verify our statement that the biaxial stiffness  $S_g$  of a crystalline phosphorene grain is independent on grain orientation  $\theta$ , biaxial tensile simulations are performed on single crystalline phosphorene sheet sized 15×15nm with different orientations ranging from 15 to 75 degree as shown in Figure S5(a). The grain orientation is defined as the angle between armchair direction and x axis as it is shown in Figure 5(a). The strain rate is the same as that used in the main context which is mentioned in the "Methods" section. The obtained stiffness is shown in Figure 5(b) from which we can tell that the differences among stiffnesses of

different grain orientations are marginal. However, it is noted that the stiffness  $S_g$  is around 100 GPa, which is still much higher than the value estimated in Figure 4(a), 73.3GPa. The above mismatch may come from the irregular shape of grains in the polycrystalline phosphorene sheets. The single crystalline phosphorene studied here are squares while the grains in the polycrystalline sheets are polygons. One can expect that the upper limit of stiffness *S* of polycrystalline phosphorene with square-shaped grains should be almost identical to that of biaxial stiffness  $S_g$  of single crystalline phosphorene.

## Figures



**Figure S1** (a) Top view of the polycrystalline phosphorene sheets with different grain numbers (All the sheets have the same average grain size 2nm) (b) Comparison among mechanical properties of polycrystalline phosphorene sheets with different number of grains.



**Figure S2.** (a) Potential energy density evolution during the annealing process of polycrystalline phosphorene; (b) Potential energy density differences after the annealing process versus grain size (Note that the blue line represent the fitting result while the solid circles with error bars represent results from simulations)



**Figure S3.** Potential energy profile of the polycrystalline phosphorene sheet with grain size d=6nm (a) before the annealing process; (b) after the annealing process; Zoomed-in snapshot of an area highlighted by a red dash square in subfigure (a): (c) before the annealing process; (d) after the annealing process.



**Figure S4.** (a) Average biaxial stress-strain responses for annealed and unannealed polycrystalline phosphorene sheets with grain size d=7nm. (b) Relevant normalized mechanical properties of the polycrystalline sheets derived from the stress-strain curves in (a). (Note that the normalized mechanical properties are obtained through dividing the physical values of mechanical properties by the corresponding values from the annealed samples.)



**Figure S5.** (a) Schematic view of the simulation set-up of biaxial tensile tests for single crystalline phosphorene (b) Stiffness of single crystalline phosphorene versus grain orientation  $\theta$ .