Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information of

Rapid Thermal Thinning of Black Phosphorus

Shangqing Fan, Haicheng Hei, Chunhua An, Wei Pang, Daihua Zhang, Xiaodong Hu, Sen Wu and Jing Liu**

Dr. S. Fan, H. Hei, C. An, Prof. W. Pang, D. Zhang, X. Hu, S. Wu, J. Liu

State Key Laboratory of Precision Measurement Technology and Instruments, School of Precision Instruments and Opto-electronics Engineering

Tianjin University, No. 92 Weijin Road, Tianjin, 300072, China

E-mails: senwu@tju.edu.cn; jingliu_1112@tju.edu.cn;

1. Direct sublimation of black phosphorus (BP) in N_2/H_2 mixture flow

We exfoliated a few-layer BP flake from bulk crystal and transferred it onto Si/SiO_2 substrate. The optical image of the freshly exfoliated BP flake is shown in Fig. S1a. The sample was then directly annealed in N_2/H_2 mixture flow at 360 ^oC for 2 min. The optical image of the sample after annealing is presented in Fig. S1b. No obvious thinning effect can be observed by comparing Fig. S1a and b.

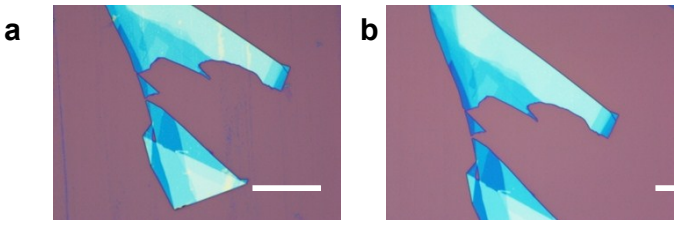

Figure S1. Optical images of mechanically exfoliated BP flakes before (a) and after (b) rapid annealing in N_2/H_2 mixture (V:V, 98:2) at 360 ^oC for 2 min.

2. Selectivity of the thermal thinning method

We prepared few-layer MoS_2, ReS_2, $MoSe_2$, WSe_2, $MoTe_2$, WS_2 samples on Si/SiO_2 substrate (the freshly exfoliated sample are shown in Fig. S2 A-F), respectively, and treated them by the two-step thermal annealing method. The detailed thermal annealing recipe was: 2 min air annealing followed by 0.5 min N_2/H_2 mixture annealing at 390^oC. After thermal annealing, as shown in Fig. S2a-f, none of samples show obvious thinning effect, demonstrating the great selectivity of this two-step method for BP thinning.

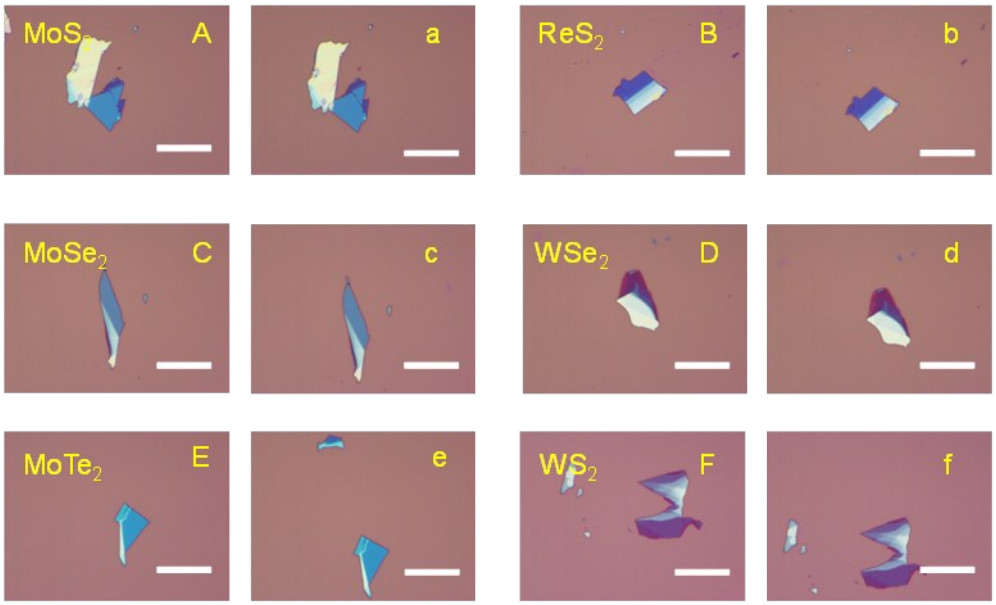

Figure S2. Optical images of MoS_2, ReS_2, $MoSe_2$, WTe_2, $MoTe_2$, WS_2 flakes before (A)-(F) and after (a)–(f) annealing, respectively.

3. Fabrication of single BP flake with different thicknesses

We transferred a few-layer BP flake on Si/SiO_2 substrate, as shown in Fig. S3a. The sample was then partially covered by a hexagonal boron nitride (h-BN) flake on top and underwent 2 min air annealing and 0.5 min N_2/H_2 mixture annealing at 340 ℃. The optical image of the sample after thermal annealing is presented in Fig. S3b. In this image, the area of the BP flake covered by h-BN remains the same bluish color as before annealing (because the thickness of this area may not change), while the area of the BP flake without h-BN coverage turns into purple color (because this area becomes thinner). After removing the covered h-BN flake, the color distribution of the BP flake presented in Fig. S3c keeps the same as in Fig. S3b. This indicates that the area of the BP flake covered by h-BN is not thinned after thermal annealing.

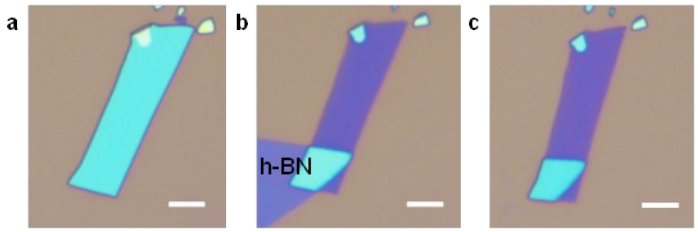

Figure S3. Optical images of (a) as-exfoliated BP flake, (b) the same BP flake partially covered by a flake of h-BN after thermal annealing, (c) the same BP flake after removing the h-BN on top.

4. Calibration of thinning rates

We prepared 15 BP flakes exfoliated from BP bulk crystal with thicknesses ranging from 10 nm to 20 nm. Each of these samples was partially covered by a flake of hexagonal boron nitride (hBN). Then, these samples were divided into 3 groups (5 samples in each group), which were thinned at 300 ^oC, 330 ^oC and 360 ^oC, respectively. The 5 samples in each group were sequentially annealed in air for time durations of 0.5 min, 1 min, 1.5 min, 2 min, 2.5 min, respectively, and in N_2/H_2 for 0.5 min. During annealing, the covered part was not thinned due to the protection of hBN, while the non-covered part was thinned down (which is demonstrated in Fig. S3). After annealing, the hBN flakes were removed. By comparing the thickness differences between the covered and non-covered part, we calculate the thickness that is thinned under different temperatures with various time durations. The AFM images of the 15 BP samples after annealing are presented in Fig. S4.

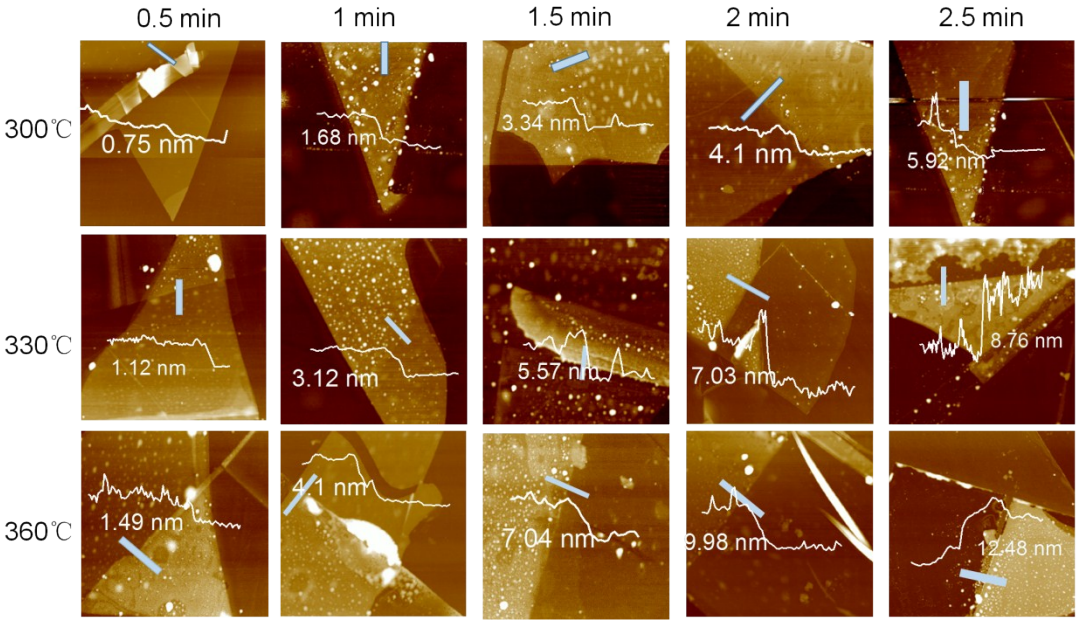

Figure S4. AFM images of 15 BP samples after annealing and removal of partially covered hBN. The samples presented in the same line were annealed under the same temperature marked on the left, while the samples in the same column were annealed in air for the same time duration marked on the top.