SUPPLEMENTARY INFORMATION: DETECTION OF DEFECT POPULATIONS IN SUPERHARD SEMICONDUCTOR BORON SUBPHOSPHIDE $B_{12}P_2$ THROUGH X-RAY ABSORPTION SPECTROSCOPY

This document contains supporting informating for the publication entitled "Detection of defect populations in superhard semiconductor boron subphosphide $B_{12}P_2$ through x-ray absorption spectroscopy" by S.P.Huber *et al.* with DOI: 10.xxx/xxx

A. X-ray Diffraction

The crystalline nature of samples L1-L5 has been assessed by x-ray diffraction (XRD), using a Panalytical Empyrean diffractometer with Cu-Kα_1 radiation (λ = 1.5406 Å). To assess crystal structure and orientation of the samples, diffraction spectra were recorded in thin film geometry, i.e. 2θ scans at various fixed incident angles. Before each scan, other geometric parameters were optimized iteratively, such that the intensity recorded at a diffraction angle $2\theta = 22.5°$, which corresponds to the (0003) orientation of the $B_{12}P_2$ crystal structure, was at a maximum. The optimized geometric parameters included the incident beam angle ω, the angle of the sample surface with respect to the diffraction plane ϕ, the sample surface height z and the angle χ, denoting the rotation of the sample surface around the axis intersecting the diffraction plane and sample surface. The optimization process revealed that the samples are strongly textured, since only within a very narrow range of values would significant intensity be detected at the expected (0003) orientation.

After optimizing the geometric parameters, they are fixed during the $\theta - 2\theta$ scans, which are shown in Fig. S1 for samples L1-L3. For sample L1 a diffraction peak is found at 22.5° which corresponds to the (0003) orientation. The peaks for L2 and L3 have a significantly lower intensity indicating that they have an inferior long range order compared to sample L1. The position of the peak for L2, and to a lesser extent for L3, appears to be shifted slightly. This can potentially be due to built up stress in the grown films. The $B_{12}P_2$ crystal lattice has about a 2.5 % lattice mismatch with the 4H-SiC substrate, and given the hardness of the $B_{12}P_2$ crystal structure, large strains can be built up within the film, even to the point where it has been found to be able to introduce cracks into the SiC substrates[S1].

The intensities of L2 and L3 are comparable with that of L3 being slightly larger, despite it being deposited at a lower temperature and our presupposition would have expected the reverse. However, the difference is rather small and more detailed work on the effect of deposition temperature and the resulting crystallinity, has shown that the relationship is not necessarily linear[S1]. It should also be noted that the deposition conditions used in this work are now known to not be optimal for perfect crystal growth. This also explains why the XRD scans do not resemble what would be expected for crystals of high quality and we can conclude that the $B_{12}P_2$ films described in this work do not posses a long range order. This applies especially to the samples deposited at the lowest temperature, L4 and L5, in whose x-ray diffraction scans the (0003) peak was almost indiscernible from the background signal.

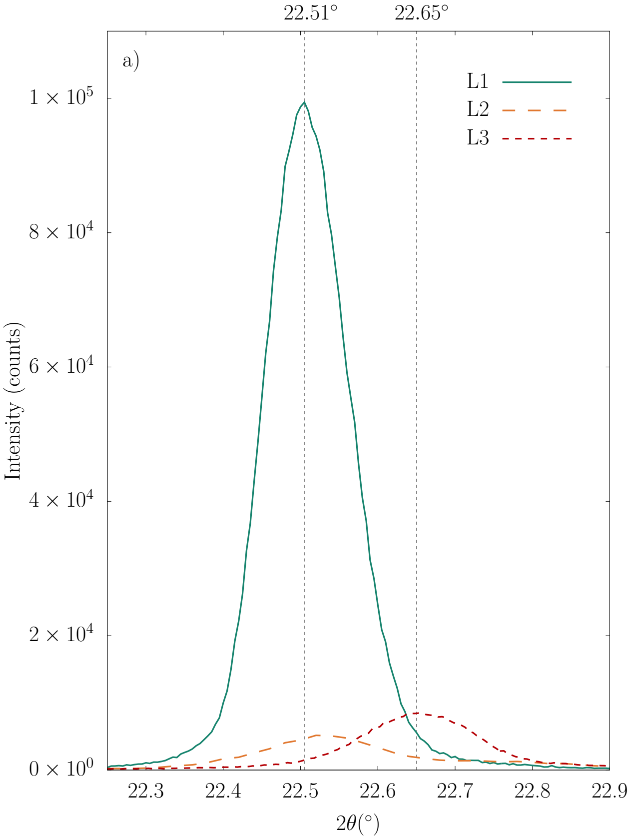

FIG. S1. (a) X-ray diffraction spectra in thin film geometry for samples L1, L2 and L3 at optimized values of ϕ, χ, 2θ and z.

In conclusion, due to the strong texturing in all samples and their thin film nature, it is impossible to quantitatively assess their absolute or even relative crystallinity from this data with certainty. However, the fixed $\theta - 2\theta$ scans do show that the intensity of the (0003) peak decreases significantly as the deposition temperature of the film decreases, which indicates that the long range crystalline order decreases for lower deposition temperatures. Even to the point where the film may not even have a polycrystalline structure any longer, as would indeed seem to be the case for samples L4 and L5. XRD is a diffractive technique and is therefore sensitive exclusively to long range order, whereas XANES contrastingly only probes short range order, which explains how the differences in the x-ray absorption spectra of the samples can be relatively small, while simultaneously having very distinct diffraction spectra. A thin film without any appreciable long range order may still possess crystalline structure on small length scales. These findings do support the statements about the relative differences in crystallinity of the grown films, made based on their x-ray absorption spectra, as posited in the main text of the manuscript.

[S1] C. Frye, C. Saw, B. Padavala, R. Nikolić, and J. Edgar, Journal of Crystal Growth **459**, 112 (2017).