

Structural band-gap tuning in g-C₃N₄

— Supplementary Materials —

Sebastian Zuluaga,¹ Li-Hong Liu,² Natis Shafiq,² Sara Rupich,²
Jean-François Veyan,² Yves J. Chabal,² and Timo Thonhauser¹

¹*Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA*

²*Department of Materials Science and Engineering, University of Texas at Dallas, Dallas, Texas 75080, USA*

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I. ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

Ultraviolet photoelectron spectroscopies (UPS) were obtained on a PHI Versa Probe II scanning XPS microprobe, Physical Electronics, equipped with a Prevac UV source (UV40A). The UPS radiation is generated by a He-gas discharge lamp (He I = 21.22 eV; UV source settings: $I_{\text{emis}} = 100$ mA, $U_{\text{source}} = 0.52$ kV, $P_{\text{He}} = 9.6 \times 10^{-2}$ mbar), and measurements were made using the He I excitation (21.2 eV) and recorded with a constant pass energy of 1.75 eV in the ultrahigh vacuum chamber of the XPS instrument. Samples were placed at normal incidence to the analyzer. The source to analyzer angle was set to 45°. During the measurement, both e-gun and Ar gun were turned on for neutralization. The pressure in the main chamber was 2.6×10^{-7} Pa. Samples were loaded in the UHV chamber overnight to allow sample degassing and to let the UHV pressure drop below 1×10^{-6} Pa.

Figure S4 shows a series of UPS spectra for the four g-C₃N₄ samples prepared at 500, 550, 600, and 650 °C in the valence band region. In particular, the E_{VB} positions, based on linear extrapolation, are shown and numerical values are collected in Table S1. Because the samples are insulators at room temperature, their work function cannot be measured by standard bias techniques using UPS.

TABLE S1. Band gap, E_g , and the positions of the valence and conduction bands, E_{VB} and E_{CB} , in eV with respect to the Fermi level for the four g-C₃N₄ samples prepared at different temperatures.

Temperature	E_g	E_{VB}	E_{CB}
500 °C	2.75	-0.90	1.85
550 °C	2.69	-0.90	1.79
600 °C	2.68	-0.90	1.78
650 °C	2.62	-1.13	1.49

II. FIGURES

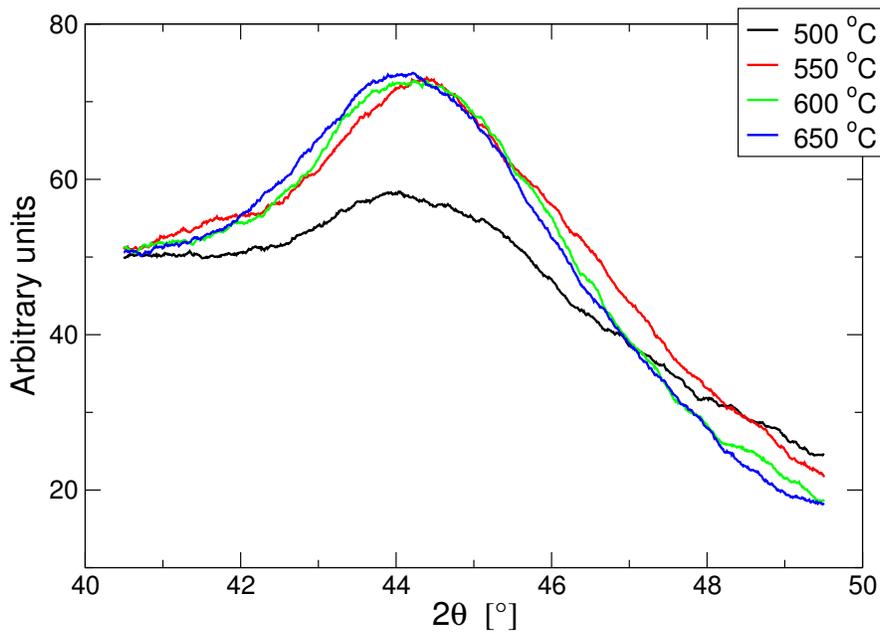


FIG. S1. Enlarged experimental XRD spectra around the peak at $\sim 45^\circ$ for the $g\text{-C}_3\text{N}_4$ samples prepared at 500, 550, 600, and 650 °C.

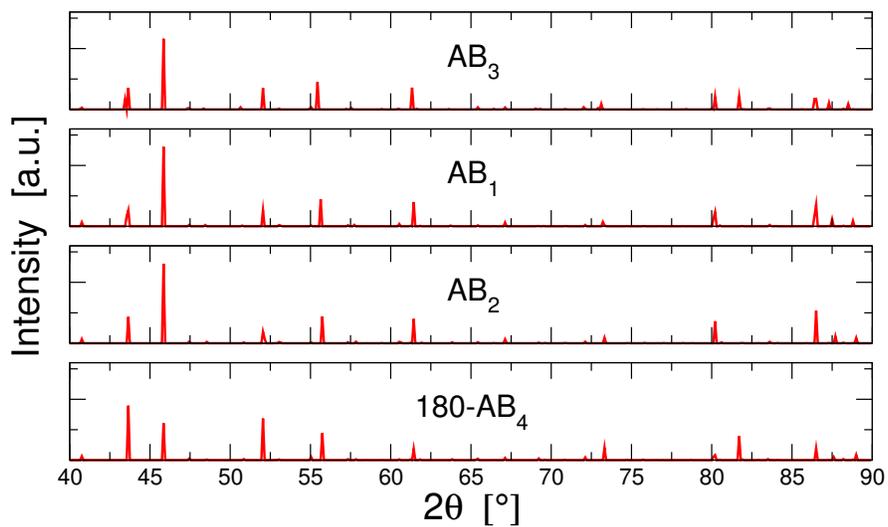


FIG. S2. Calculated XRD spectra at higher angles for the four $g\text{-C}_3\text{N}_4$ stacking configurations.

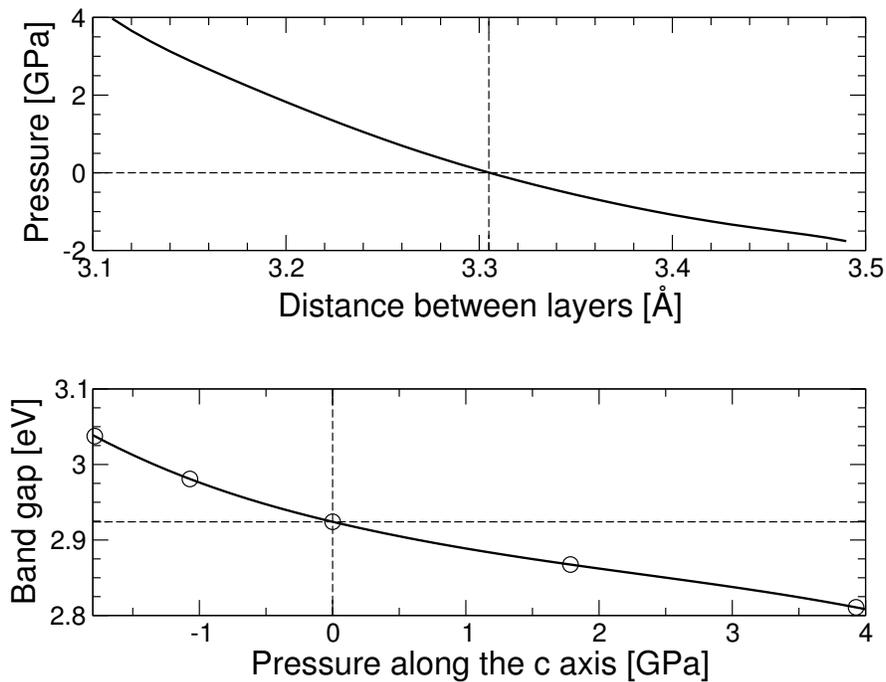


FIG. S3. (top) Pressure vs. layer separation d in the AB_1 stacking of $g\text{-C}_3\text{N}_4$. (bottom) Band gap of AB_1 as a function of the applied pressure along the c axis.

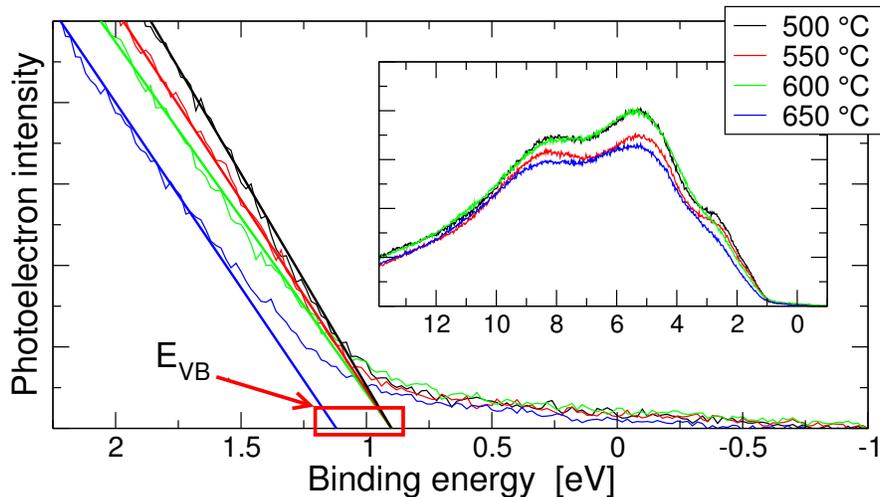


FIG. S4. UPS spectra in the valence band region of the four $g\text{-C}_3\text{N}_4$ samples prepared at 500, 550, 600, and 650 $^{\circ}\text{C}$. The inset shows the full spectra between -1 and 13 eV.