Electronic Properties and Defects in Germanane

T.J. Asel[1], E. Yanchenko[1], S. Jiang[2], K. Krymowski[3], W. Windl[3] J. Goldberger[2], and L.J. Brillson[1,4]

[1] The Ohio State University, Department of Physics, 191 West Woodruff Ave., Columbus, OH 43210 USA

[2] The Ohio State University, Department of Chemistry, Newman and Wolfrom Lab,100 West 18th Ave., Columbus, OH 43210 USA

[3] The Ohio State University, Department of Materials Science and Engineering, 117 Watts Hall, 2041 N. College Rd., Columbus, OH, 43210

[4] The Ohio State University, Department of Electrical and Computer Engineering, 205 Dreese Lab, 2015 Neil Ave., Columbus, OH 43210 USA

We have used a combination of surface science techniques to study the electronic properties and defects in germanane, a chemically functionalized two dimensional (2D) material. With the advent of graphene there has been a focus on 2D materials due to their unique properties, and the ability to further manipulate them both chemically and mechanically. Similar to graphene and MoS_2, germanane is a 2D material with a direct band gap that can be manipulated by terminating with different ligands, making it an exciting candidate for optoelectronic applications. Germanane is synthesized by deintercalating $CaGe_2$ in an acid to result in a particular termination [1]. We applied depth-resolved cathodoluminescence spectroscopy (DRCLS)[2] to measure the electronic transitions including the band gap in hydrogen terminated germanane (GeH), methyl-terminated germanane ($GeCH_3$), dimethylether terminated germanane ($GeCH_2OCH_3$), and allyl-terminated germanane ($GeCH_2CH=CH_2$). Using surface photovoltage spectroscopy (SPS) and DRCLS we have directly observed defects in "bulk" germanane.

A key feature of germanane is that terminating the germanium lattice with different ligands can affect the size of the direct band gap. The combination of the effects due to ligand size and electronegativity. The electronegativity of the ligand is believed to determine the extent of electron density withdrawal from the germanium scaffold, which weakens Ge-Ge bonding and reduces the band gap. Large ligand size can introduce strain and as a result also reduce the band gap energy. We used DRCLS to examine this relationship. The electronegativity of each ligand decreases from $–CH_2OCH_3$ > -H > $-CH_3$ > $-CH_2CH=CH_2$. DRCLS finds the band gap energies increase from CH_2OCH_3 (1.47 eV) > $-CH_2CH=CH_2$ (1.50 eV) > -H (1.52 eV) > $-CH_3$ (1.62 eV). These values follow the trend in electronegativity with the exception of the allyl termination, which can be explained using strain as it is the largest ligand.

We used SPS and DRCLS to observe sub band gap optical states in $GeCH_3$. SPS shows E_C - 0.85 eV and E_V+1.05 eV. DRCLS shows complementary transtions due to gap states at 0.82, 0.96, 1.02, and 1.35 eV. Investigating $GeCH_3$ samples that have been deintercalated for one week and three weeks the 1.02 eV feature disappears in the sample that had been deintercalated for three weeks. This can be tentatively attributed to the removal of residual CaI_2 from interlayer spacing of the $GeCH_3$ layers. This demonstrates that defects can be identified and eliminated. through systematic chemical processing. This work supported by NSF MRSEC under award number DMR-1420451.

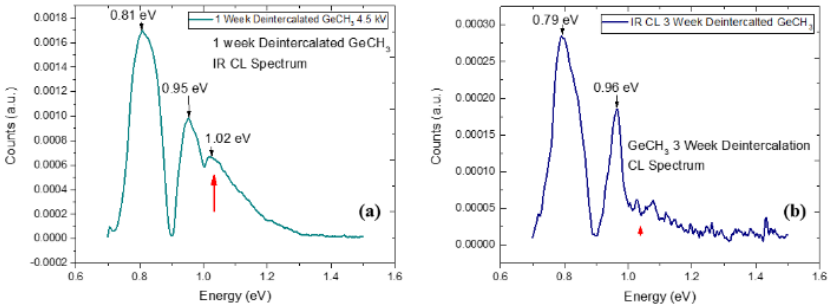

Figure 1: 1 Week deintercalated $GeCH_3$ (a) shows a prominent 1.02 eV peak. $GeCH_3$ that has been deintercalated for 3 weeks shows the absence of the 1.02 eV peak

[1] S. Jiang, S. Butler, E. Bianco, O.D. Restrepo, W. Windl, J. E. Goldberger, *Nat. Comm.* **5**, 3389 (2014).

[2] L. J. Brillson, *J. Phys. D: Appl. Phys.* **45**, 183001 (2012)