Nanoscale Patchwork (Jigsaw): a new two-dimensional hybrid material

Angel Rubio
NanoBio Spectroscopy Group and ETSF Scientific Development Centre , Dpto. Física de Materiales, Universidad del País Vasco, CFM-CSIC-UPV/EHU and DIPC, 20018 San Sebastián. SPAIN and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Addressing a two-dimensional band-gap engineering by patching carbon and BN nanodomains opens a new avenue for optoelectronic devices.

Probably Carbon is the element that best represents the emergence of new phenomena and properties when dimensionality is reduced. From mechanical to electronic and thermal conductance, nanotubes [1], fullerenes[2], nanoribbons and graphene[3] just illustrate the carbon-only "lego" of nanoscience. Combining C with its neighbouring atoms in the periodic table (B and N) increases enormously the available lego component offering a host of different B-C-N configurations. Indeed, just after the discovery of nanotubes in the 90's [1] it was theoretically predicted that other inorganic B-C-N nanostructures could be formed [4]. These predictions were soon made a reality [5] fostering the emergence of the field of BCN-nanostructured based materials [6]. However, the phase diagram of B-C-N compounds is still rather unexplored and unfunded. From a general material science perspective, unveiling this rich phase diagram is one of the most challenging and exciting frontiers in materials science. On page ??? of this issue Liu et al [7] provide a novel systematic route to synthesize two-dimensional BCN hybrid structures consisting of a two-dimensional jigsaw "patchwork" of BN and C nanodomains. From a graphene perspective it provides a new opportunity to explore band gap engineering in 2D layered systems, rather than that given by dimensional confinement or doping alone.

Nanostructures of BCN form an exciting materials set with a rich variety of physical properties and numerous possible technological applications in the fields of nanoelectronics, optical and lasing devices, field emission, catalysis, and lubrication. They exhibit a large resistance to chemical degradation and oxidation whereas their mechanical and electronic properties could be tuned by changing the relative BCN composition. In spite of this exciting phenomenology of properties, the BCN systems are much less studied as they are much harder to synthesize than their carbon counterparts. The work of Ajayan's group [7] provides an elegant solution to this problem in two-dimensions using a thermal catalytic chemical vapour deposition method. The tendency of BN and C to segregate triggers the formation of randomly distributed hybrid domains, with variable composition from pure BN to pure graphene. The work in [7] constitutes only the first step showing that these structures can indeed be grown in only a few atomic layers like single and multilayer graphene. They used a copper substrate that is known to favour large area growth of graphene as well as hexagonal BN. Methane and ammonia borane were used as precursors. Interestingly the atomic ratio can be controlled by changing the experimental conditions of pressure, temperature and gas concentration, however in all cases B and N appear in a one-to-one ratio. The carbon content can be changed from as little as 10% to nearly full carbon content. High resolution transmission microscopy demonstrate that the samples consist of mainly two or three layers. To prove that the structure consist of C and BN nanodomains they perform detailed Raman, X-ray photoelectron and energy-loss spectroscopies. That data would be inconsistent with a h-BN/graphene stacked growth.

The new hybrid structures show electronic, optical and transport properties at variance with pure graphene and hexagonal BN. Electrical measurements on the samples shows that the conductivity increases with increasing carbon concentration (with a lowest nominal resistance of 10^{-3} Ω cm). Therefore the film electric properties can be moved from insulating to highly conducting. Moreover, the temperature dependent resistance shows an increase of ten times by reducing T clearly puts in evidence the semiconducting nature of the new BCN films. It is remarkable that the new BCN layers exhibit an ambipolar field effect transistor behaviour similar to that of graphene with an electron and hole mobility in the range between 5 to 20 $cm^2 V^{-1} s^{-1}$ that is much smaller than the one of graphane. This result supports the C-BN domain structure instead of a

stacked one, and it is consistent with first-principles studied performed by the authors of ref. [7] .

The realisation of hybrid layered structures opens the path towards having one-dimensional heterostructures with basically new properties dictated by their structure and composition. Moreover, looking at the BN domains as long-range scattering centres in an otherwise perfect graphene structure, many fundamental questions could be answered with the new synthesised layered materials, such as: i) study the transition from a weak to strong Anderson localization regime in 2D as a function of BN density ii) possible appearance of edge states localized at the BN-C interface that could be (or not) spin-polarised and lead to half-metallicity (as predicted for some graphene [8] and BCN ribbons [9]) iii) as pure BN is a very good light-emitter in the UV [10] it could address voltage-tuned optical and lasing devices (from UV to visible). The work of Ajayan's group will develop a whole new field that will be exciting for basic physics and electro-optic applications of low-dimensional B-C-N materials. By changing the processing conditions one should be able to find other stable or metastable phases with different relative compositions ($B_xC_yN_z$) and dimensionality (from clusters, to nanotubes to molecular solids and three-dimensional structures).

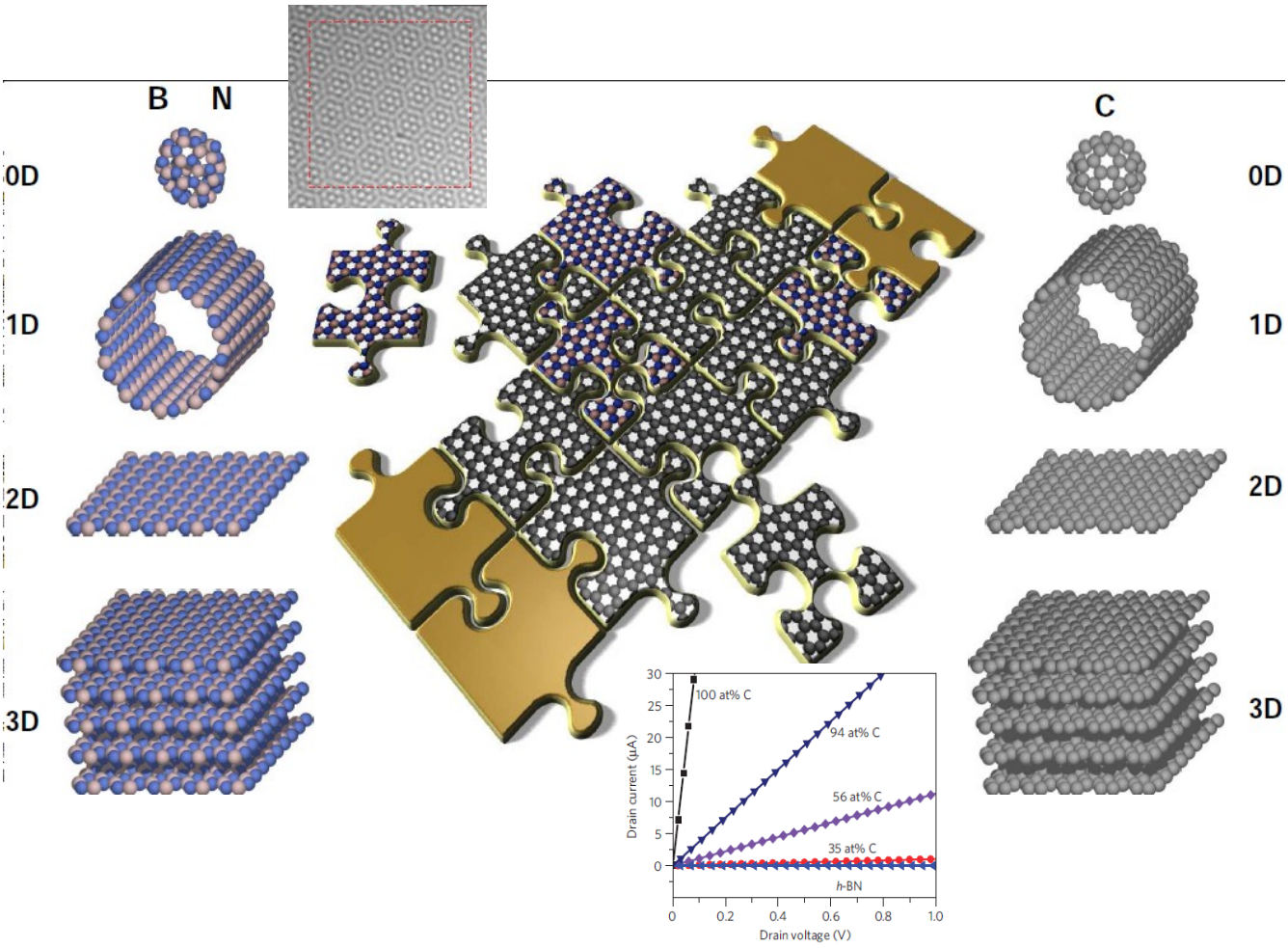

Figure: Schematic of the BN-C phase diagram illustrating the contribution of the work in [7] from the 2D case, many more new structures with unexpected properties could be formed by combining the different compositions, dimensionality and structures. Ref. [7] provides a chemical route to patched BN and C nanodomanis (filling a 2D jigsaw). The measured transport curves put in evidence the more resistive response when increasing the amount of BN domains. Blue, grey and light violet balls on the puzzle pieces denote N, C and B atoms respectively, whereas in yellow we represent the gold leads. (Courtesy of Dr. Duncan Mowbray).

References

[1] Iijima, S. Nature (London) **354**, 56 (1991)
[2] Kroto, H.W. et al Nature 318, 162 (1985).
[3] Geim, A.K. Science **323**, 1530 (2009)
[4] Rubio, et al, Phys.Rev. B**49**, R5081 (1994); Y. Miyamoto et al, Phys.Rev.B**50**, 4976 (1994)
[5] Z.W. Sieh et al Phys. Rev. B**51**, 11229 (1995);
[6] B-C-N Nanotubes and related nanostructures, Ed. Y.K. Yap, Lecture notes in Nanoscale science and technology, Springer (2009)
[7] Ci, L. et al, Nat. Mat. (2010)
[8] Son, Y.W, et al Nature **444**, 347 (2006)
[9] Kan, E.J et al J. Chem. Phys **129**, 084712 (2008)
[10] Watanabe, K. et al, Nat. Mat. **3**, 404 (2004); Attacalite, C et al Phys. Stat. Solidi **244**, 4288 (2007)