INTERFACIAL STRESS TRANSFER IN GRAPHENE-BASED NANOCOMPOSITES

R. J. Young[a*], L. Gong[a], I. A. Kinloch[a], K. S. Novoselov[b]

[a] *School of Materials, University of Manchester, Manchester, M13 9PL, UK*
[b] *School of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK*
**robert.young@manchester.ac.uk*

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Abstract

The deformation of nanocomposites containing graphene flakes with different numbers of layers has been investigated with the use of Raman spectroscopy. It has been found that there is a shift of the 2D band to lower wavenumber and that the rate of band shift per unit strain tends to decrease as the number of graphene layers increases. It has been demonstrated that band broadening takes place during tensile deformation for mono- and bi-layer graphene but that band narrowing occurs when the number of graphene layers is more than two. It is also found that the characteristic asymmetric shape of the 2D Raman band for the graphene with three or more layers changes to a symmetrical shape above about 0.4% strain and that it reverts to an asymmetric shape on unloading. This change in Raman band shape and width has been interpreted as being due to a reversible loss of Bernal stacking in the few-layer graphene during deformation.

1. Introduction

1.1. Graphene

Graphene is currently inspiring a whole range of research activities in a number scientific areas because of its interesting and unusual electronic and mechanical properties. Excitement was generated originally because monolayer graphene was the world’s first 2D atomic crystal and the thinnest material every produced. It was found to be extremely electrically conductive and to have unprecedented levels of stiffness and strength, consistent with theoretical predictions. Bilayer graphene, in which the two layers of carbon atoms are in so-called AB Bernal stacking has strikingly different electronic properties. Similar behaviour is found with ABA trilayer graphene making these multilayer Bernal-stacked graphene materials strong candidates for optoelectronic and nanoelectronic applications. The majority of the graphene prepared by mechanical exfoliation has a high proportion of few-layer Bernal-stacked material.

1.2 Raman spectroscopy

It is well established that Raman spectroscopy is one of the best methods of both characterizing graphene and following its deformation in nanocomposites. Strong, well-defined resonance Raman spectra are obtained even from single atomic graphene layers and the technique can be used relatively easily to differentiate between monolayer, bilayer, trilayer and few-layer material, from the shape and position of the 2D (or G') Raman band [2]. It is also found that the positions of the Raman bands in graphene shift with stress and that such stress-induced Raman band shifts can be used to determine the stress in the material and so determine its effective Young's modulus [1]. These stress-induced band shifts have been used to monitor the transfer of stress between a polymer matrix and the graphene reinforcement in model nanocomposites consisting of monolayer or few-layer graphene flakes sandwiched between thin polymer films.

The behavior of model monolayer nanocomposites has been shown to follow classical shear-lag behavior at low strains with evidence of failure of the graphene-polymer interface at higher strain levels [1]. In the case of model nano-composites reinforced with few-layer graphene the behavior has been found to be more complex with evidence of inferior levels of stress transfer even at low strains. This has been modeled in terms of poorer stress transfer between the inner graphene layers than between the polymer matrix and the outer graphene layers [2].

2. Results and Discussion

2.1. Monolayer graphene

In this present study we have followed the effect of deformation upon the 2D band in the Raman spectra of a number of model nanocomposites consisting of exfoliated monolayer, bilayer, trilayer and few-layer graphene flakes embedded in a polymer matrix on a poly(methyl methacrylate) (PMMA) beam [3]. We have monitored the changes with strain in position and FWHM (full width at half maximum height) of the bands fitted to a single peak. The behavior of the 2D band for monolayer graphene is shown in Figure 1. It can be seen that the band shifts to lower wavenumber and broadens as the tensile strain in increased, with some evidence of the band splitting at the higher strain levels [1].

2.2. Trilayer graphene

In contrast to the monolayer and bilayer materials the stress-induced band shift behavior of the trilayer graphene in the nanocomposite is quite different as can be seen from Figure 2. The band, which has been fitted arbitrarily to 6 peaks, shifts to lower wavenumber with tensile strain but narrows when fitted to a single peak (Figure 2(d)) indicating a loss of Bernal stacking in the trilayer material [3]. Moreover when the stress is removed the Raman band shifts back to lower wavenumber and the shape and width of the band reverts to that of the trilayer before deformation.

2.3. Deformation mechanisms

At this stage it is important to consider the process that must take place on the atomic level leading to the loss of Bernal stacking in the tri- and few-layer materials. The process is shown schematically in Figure 3 for a Bernal-stacked trilayer graphene nanocomposite. When the polymer matrix is deformed, stress is transferred by interfacial stress transfer to the two outer graphene layers (both will be A-type layers) as has been found before for monolayer and bilayer specimens. They will become elongated in the tensile direction and narrower in the transverse direction due to Poisson contraction.

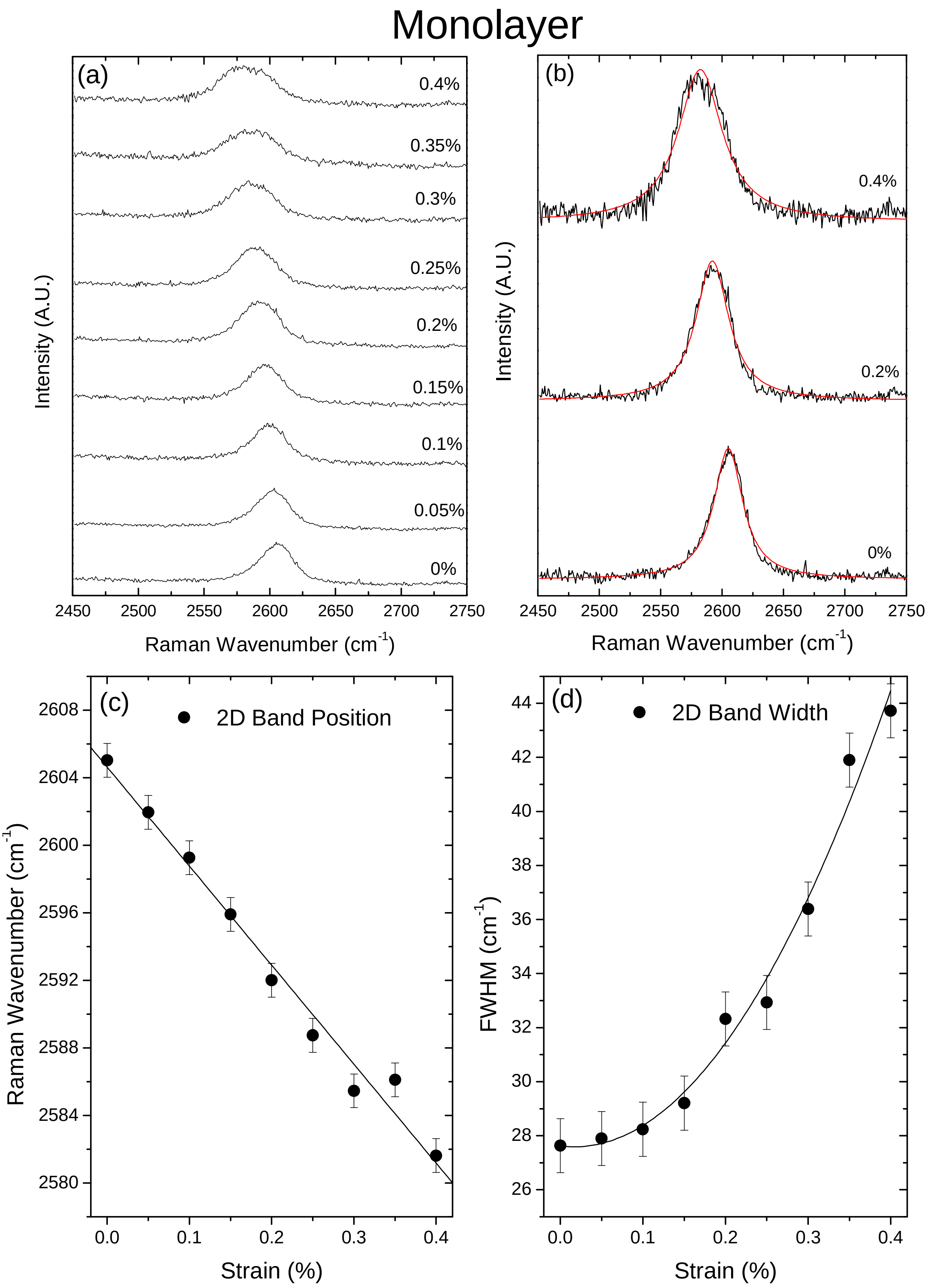

Figure 1. Shift of the 2D Raman band with strain for a graphene monolayer flake in a model nano-composite. (a) Overall band shift for the monolayer, (b) Details of the band for the monolayer, (c) Shift with strain of the bands fitted to a single peak, (d) The variation with strain of the FWHM (full width at half maximum height) of the bands.

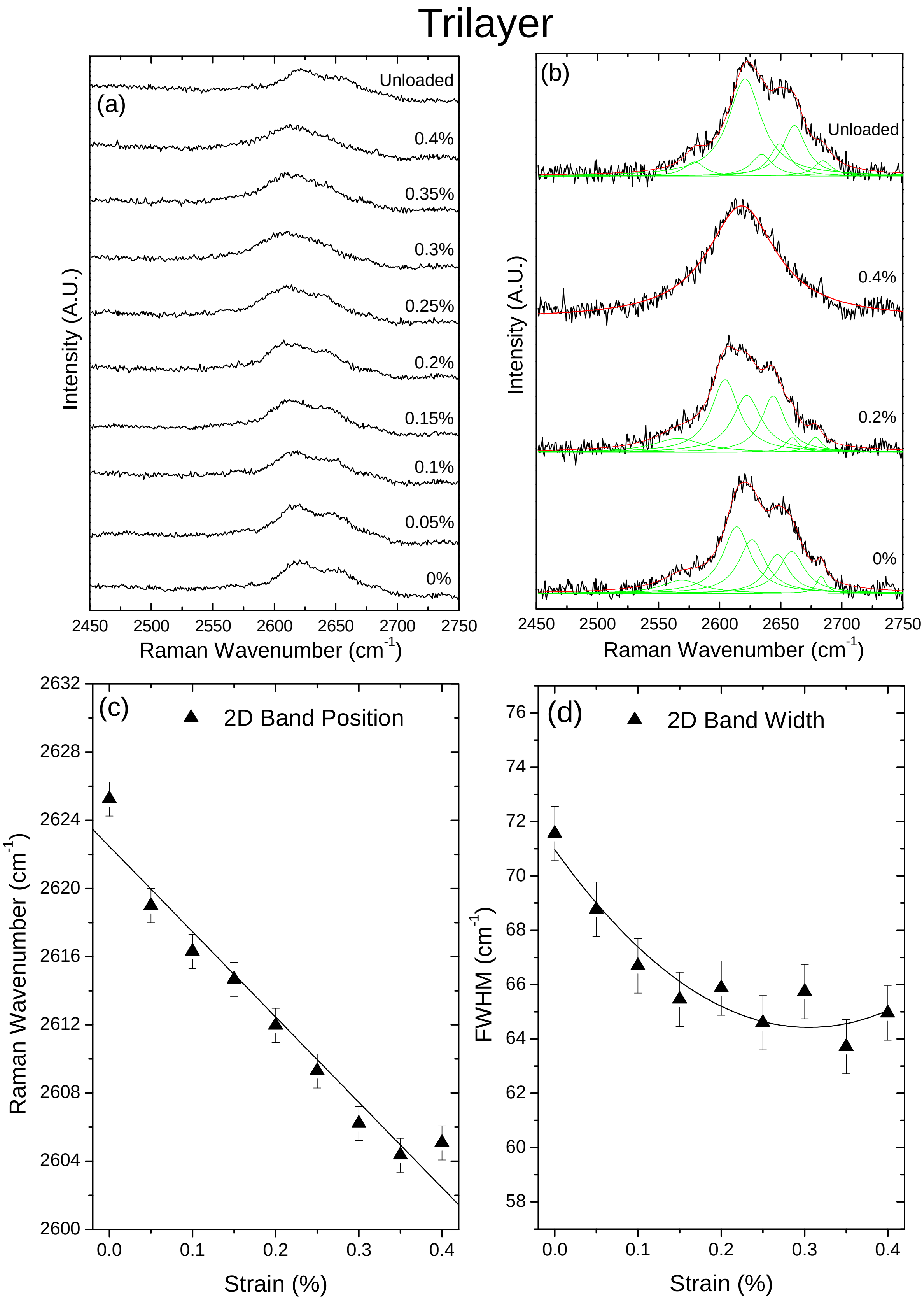

Figure 2. Shift of the 2D Raman band with strain for a graphene trilayer flake in a model nanocomposite.

Stress transfer to the inner B-type layer can only take place by shear from the two outer A-type layers. If this does not take place efficiently then the two A-type outer layers will become deformed and the inner layer will remain relatively undeformed, as shown in Figure 3(b). The consequence of this is that the Bernal stacking will be lost. On unloading the outer layers will revert to their original form and Bernal stacking will be regained. It is envisaged that a similar process will also occur for few-layer material investigated in this study. It should be noted that the Bernal stacking is not lost in the case of bilayer specimens as both graphene layers have interfaces with the polymer matrix that remain intact up to 0.4% strain [3].

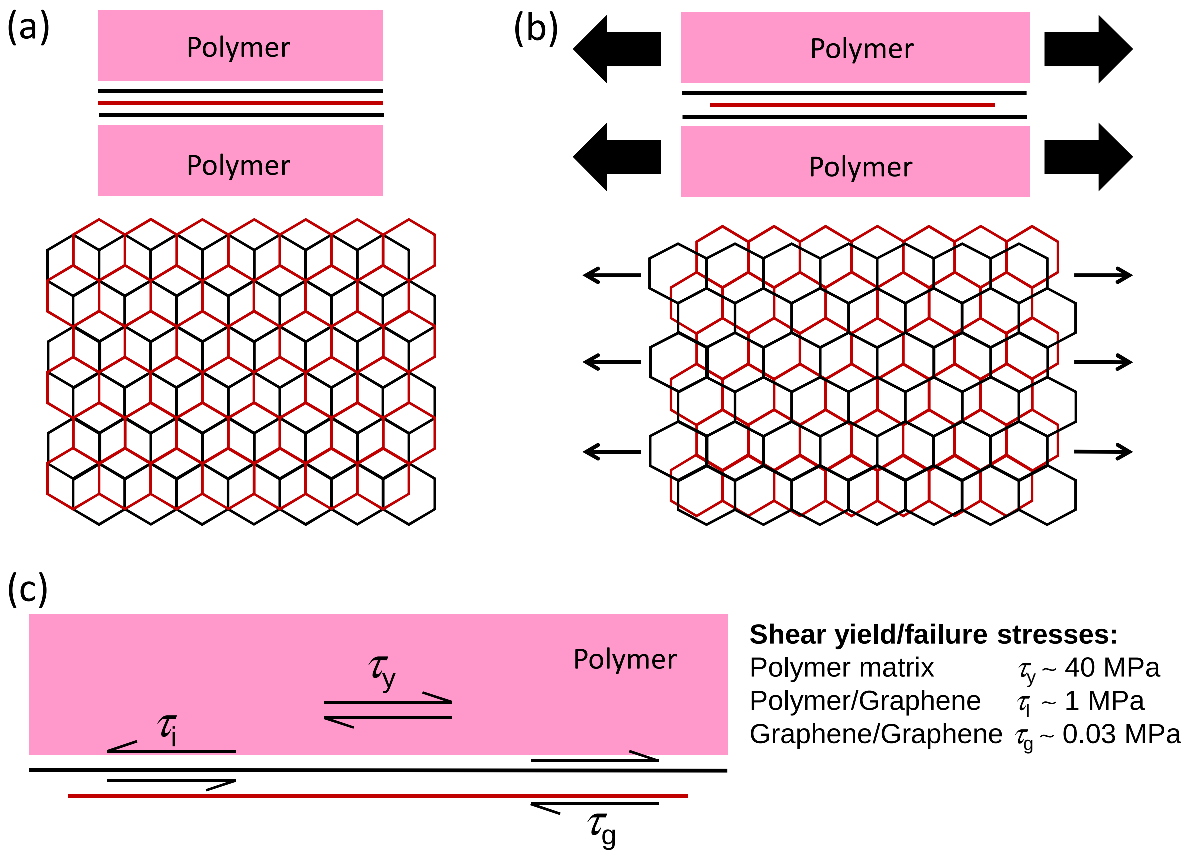

Figure 3. Schematic illustration of the loss of Bernal stacking during the deformation of trilayer graphene in a nanocomposite. (a) Undeformed structure. (b) Deformed structure showing the loss of Bernal stacking through affine deformation. (c) The shear process that take place at the different interfaces along with their values at yield or failure. (The A layers are colored black and the B layer is colored red).

This stress transfer in composites takes place through shear at the interfaces between the different components as shown schematically for the nanocomposite in Figure 3(c). Stress transfer will take place from the polymer matrix to the outer graphene layer and this is then transferred to the inner layers by shear between the outer graphene layer and the next layer as indicated. It has been found in a previous study that transfer between the inner graphene layers is no more than 70% efficient, leading to a reduction in effective Young’s modulus as the number of graphene layers is increased above two.

3. Conclusions

It has been demonstrated that few-layer graphene undergoes a reversible loss of Bernal stacking upon shear deformation in nanocomposites. This behavior leads to a reduction in the effective Young's modulus of the graphene that has been observed as the number of layers increases. It has been shown that the process can take place through the formation of arrays of partial dislocation and stacking faults between the graphene layers [3]. As well as having major consequences for the mechanical properties of graphene nanocomposites, it is also likely that the phenomenon may lead to a method of reversibly modifying the electronic structure of few-layer graphene.

References

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