Probing the strain in epitaxial graphene grown by different methods with Raman spectroscopy

K.Grodecki [1,2], W.Strupinski[1], A.Wysmołek[2], R.Stępniewski[2], and J.M.Baranowski [1,2]

[1]Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland

[2]Faculty of Physics, University of Warsaw, Hoza 69, 00-681 Warsaw, Poland

<kacper.grodecki@fuw.edu.pl>

The difference between epitaxial graphene layers on 4H-SiC(0001) obtained by two different growing techniques have been investigated with micro Raman spectroscopy. The first one, commonly used is based on sublimation of Si from SiC(0001) surface at high temperature (S-EG). The second method has been developed by chemical vapor deposition technique (CVD-EG). This new technique involves controlling the dynamic flow of argon in the reactor, which stops Si sublimation and uses propane gas as the carbon precursor.

The micro Raman maps have been created with 3μm light spot using 530 points measured on 2,3 x 2,3 mm area in the center of the sample. The wavelength of the light used was 532nm. Micro Raman maps allowed to make histograms, on which number of points with the same 2D line frequency v+/- 1cm^{-1} were plotted against frequency v. It was found that there are two main differences between maps obtained on the S-EG and CVD-EG layers. The histogram for typical S-EG sample has shown that the mean position of the 2D line is located at frequency 2743cm^{-1}(Fig 1). Such a shift of the 2D line (blue shift up to 63cm^{-1}) in comparison to free unstrained graphene, in which the 2D line is at frequency 2680cm^{-1}, indicates that the S-EG layer is under strong compressive strain. On the other hand, histograms for the CVD-EG have shown that mean position of the 2D line is at frequency 2708cm^{-1} (Fig 1). This reveals that CVD growth of graphene produces much less strained layers (blue shift up to 28cm^{-1}). The effect is dramatic – the compressive strain in the CVD-EG is two times smaller than in the S-EG. Similar effect observed for the position of the G line confirmed the results for 2D line. Another important difference between Raman spectra of samples produced by this two growth modes is that the layers grown by CVD are much more uniform in comparison to the S-EG ones. This is noticeable from the half-width of histograms shown in Fig.1: the one for CVD-EG is much more narrow than the one for the S-EG. This proves that the quality of graphene layers grown by CVD-EG technique is significantly higher.

Discussion on the unexpected different compressive strain obtained for the S-EG and CVD-EG layers has also been presented. It has often been argued, that the origin of compressive strain in S-EG comes from the different thermal expansion coefficients for graphene and SiC. In the case of S-EG growth, the origin of Si sublimation from SiC surface is probably connected with atomic steps and also with all kind of defects present on the SiC surface, in particular with dislocations. Thus, the graphene layer can be pinned to the SiC surface at many randomly distributed points. This will inevitably lead to much larger strain in the S-EG layers and eventually to their poorer quality. In the case of CVD-EG the nucleation sites of graphene layer are probably connected only with atomic steps of SiC surface and will be much less sensitive to surface defects. Subsequently grown layers will weakly interact with the ones already grown, and may more easily relax the strain. It may explains superior quality of the CVD-EG layers.

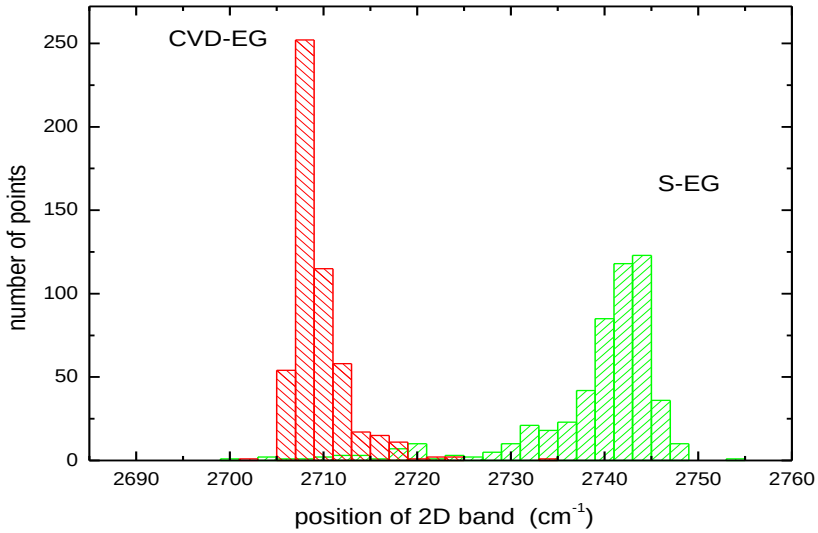

Fig1. Typical histograms obtained from micro Raman maps for epitaxial graphene layers grown on 4H-on axis SiC(0001) by chemical vapor deposition (CVD-EG) – red area, and by conventional Si sublimation (S-EG) – green one.