Investigation of graphene using low energy positron annihilation induced Doppler broadening spectroscopy

V A Chirayath¹, M D Chrysler¹, A D McDonald¹, R W Gladen¹, A J Fairchild¹, A R Koymen¹ and A H Weiss¹

¹Department of Physics, University of Texas at Arlington, Arlington Texas 76019-0059, USA
Email: koymen@uta.edu

Abstract. We report the first measurements on 6-8 layers graphene using a low energy positron beam employing a high efficiency rare gas moderator. Doppler broadening of the annihilation gamma was measured from graphene over layers at positron kinetic energies as low as 2 eV. The efficient trapping of positrons on the surface state of graphene at these low energies has been utilised to get Doppler broadened gamma spectra predominantly from graphene over layer on Cu. The ratio of the annihilation gammas measured at low positron energies (a few eV) to that measured at 20 keV show features corresponding to carbon. W-parameter calculated from gamma spectra at different positron energies point towards trapping of positrons in defected graphene as well as at the interface of graphene over layer and Cu. This is the first ever measurements of graphene film of 2-3 nm thickness on a substrate with a depth resolved Doppler broadening spectroscopy at positron kinetic energies below 10 eV.

1. Introduction
The excellent ballistic conduction, mechanical strength, optical properties etc. of graphene is related to the linear band dispersion at the Fermi level and due to these favourable properties graphene is touted to be widely used in future electronic applications like flexible electronics, organic LED, high frequency transistors etc [1]. However, in real world scenario there can be modification to its properties at Fermi level due to the mismatch and subsequent strain at the interface or due to impurities at the interface of graphene with other materials. Thus it is important to investigate the defects or chemical impurities at the interface of the multilayer or single layer graphene with technologically important materials. Further research into deposited graphene layers has been motivated by the discovery that the choice of substrate on which graphene is deposited plays an important role in the electronic, magnetic and chemical properties of the film [2, 3]. Hence it is important to have a non-destructive probe which can investigate graphene over layers on various substrates without extensive sample preparation or probe modification of its chemical or physical properties. Variable energy positron beams have been used to non destructively investigate over layers on substrate by analyzing the Doppler broadening of the 511 keV annihilation gammas after implanting the positrons at various depths [4]. However all these studies have used positrons of kinetic energy greater than 100 eV which is good for over layers or thin films which are a few tens of nanometer thick. In order to investigate two dimensional materials like graphene it is important to trap the positrons predominantly in the surface state, so that the Doppler broadened annihilation gamma...
carry information from graphene or other two dimensional materials. If positrons are implanted at energies less than 10 eV then it is possible to get information from the top atomic layers of the sample as there is greater probability for trapping the positrons into the surface state as evidenced from positron annihilation induced Auger spectroscopy (PAES) [5].

We describe here first measurements of multilayer (6-8) graphene on polycrystalline Cu sample with an advanced positron beam attached with a high efficiency rare gas moderator. This positron beam system is under construction and when fully operational will allow for coincident PAES and coincidence Doppler broadening spectroscopy. The variable positron energy coincidence Doppler broadening system of the beam has been completed and was utilized for the present investigation. The spectra were taken with incident positron kinetic energies as low as 2 eV which allowed us to probe the surface state of graphene.

2. Experimental apparatus and sample

The advanced positron beam system consists of a high efficiency rare gas (neon) moderator system purchased from First Point Scientific Inc. and a positron transport system equipped with time of flight spectrometer. In the rare gas moderator system, crystalline neon is grown on a Cu cylinder kept at 6.8 K. The Cu cylinder also houses Na^{22}, the source of positrons that has an activity of 0.5 mCi. The Cu cylinder (moderator) is biased to a positive potential with respect to the ground. The slow positrons from the solid neon moderator are filtered from unmoderated fast positrons by bending the slow positrons through an aperture (offset from beam axis) on a tungsten barrier. The slow positrons are transported from the moderator to the sample using an axial magnetic field of ~60 Gauss. The positron beam system has a time of flight tube (~3 m) which will be utilized in the PAES experiments. This time of flight tube was utilized as a retarding field analyzer to find the kinetic energy of the positrons entering the sample chamber in this experiment. It was found that when the moderator is biased to 32 V, the kinetic energy of the positrons has a distribution which peaks at 33 eV and has an FWHM of ~2 eV [6]. The beam energy of the positron is defined as the peak value of the positron kinetic energy distribution i.e. in the case when moderator is biased to 32 V, the beam energy is defined as 33 eV. Lower energies are obtained by biasing the moderator to lower positive potentials with respect to the grounded sample. It was determined that both methods yield equal incident kinetic energies [6].

The two collinear 511 keV annihilation gammas are detected by a NaI (Tl) detector and a high purity germanium (HPGe) detector kept at diametrically opposite positions with respect to the sample. The HPGe detector has a resolution of 0.98 keV for the 356 keV line of Ba^{133}. The HPGe detector is gated with the output from NaI(Tl) detector for coincidence measurements. The measurements were carried out from positron kinetic energies of 2 eV to 20 keV in both coincidence and non coincidence mode. In coincidence mode, the lowest count rate obtained was ~ 8 cps under the 511 keV peak as detected by the HPGe detector. The annihilation gamma line shape was parameterized using the W parameter [7] which is defined as the ratio of counts in the wing region of 511 keV gamma peak to the total counts under the peak (defined within ±10 keV of 511 keV). The wing region in these experiments has been defined at two regions. The first wing region, corresponding to the W1 parameter was defined from 512.5 keV to 513.5 keV on the high energy side of the 511 keV peak and from 508.5 keV to 509.5 keV on the low energy side of the 511 keV peak. The second wing region, corresponding to the W2 parameter was defined from 513.5 keV to 518.5 keV on the high energy side of the 511 keV peak and from 503.5 keV to 508.5 keV on the low energy side of the 511 keV peak.

2.1. Sample

The 6-8 layers graphene sample, purchased from ACS materials, was grown using the CVD technique on polycrystalline Cu. The sample was characterized by Raman spectroscopy using 532 nm laser light. The resulting Raman spectrum is shown in Figure 1. The presence of multilayer graphene was confirmed from the shape of the 2D band at ~ 2700 cm^{-1} in comparison to that obtained from highly oriented pyrolytic graphite [8]. The Raman spectrum also shows the presence of defect peak at ~1320
cm$^{-1}$ and the graphitic peak at ~1580 cm$^{-1}$. AFM images of the sample shows that it was covered uniformly with flakes of multilayer graphene (Figure 2). The polycrystalline Cu substrate was heated to 1100 K before graphene growth and hence no interfacial contamination is expected. PAES experiments conducted independently also gave evidence of no significant interfacial contamination. The analysis chamber was kept at a vacuum of 6.7×10$^{-8}$ Pa during measurements.

![Figure 1. Raman spectra collected from multilayer graphene and highly oriented pyrolytic graphite using a 532 nm laser. A graphitic peak corresponding to sp$^2$ hybridisation is seen in both samples at ~1582 cm$^{-1}$. The 2D band of graphite (~2700 cm$^{-1}$) consists of two peaks which is absent in graphene and is an indication of the presence of graphene layers. Graphene also has a defect peak (~1320 cm$^{-1}$) which shows the presence of defects in the multilayer graphene sample.](image)

![Figure 2. AFM image of multilayer graphene sample taken in contact mode. The scan was repeated in different areas of the sample which shows that flakes of graphene multilayer cover the sample almost uniformly.](image)

3. Results
The gamma spectra collected in coincidence mode at positron kinetic energies of 5 eV and 20 keV is shown in Figure 3. The background has been subtracted from the data using the algorithm suggested by Mogensen et al. [9]. The ability of variable energy positron beam based Doppler broadening spectroscopy to distinguish between bulk (20 keV) and surface states (5 eV) is brought out from the difference in the peak and the wing regions of the annihilation gamma at two different positron energies. It shows that at the surface, positron has a greater probability to annihilate with the low momentum valence electron resulting in a sharper 511 keV annihilation gamma peak in comparison to the broader annihilation gamma peak from the bulk. The large changes observed in the Doppler broadening suggest that the spectra can be utilized in obtaining chemical information from the surface.

The chemical information in the gamma line shape is brought out by the ratio of the annihilation gamma line measured at various energies to that taken at 20 keV (Figure 4). The 511 keV gamma spectrum at an incident positron energy of 20 keV is approximated to be coming entirely from positron annihilation in the bulk of the Cu substrate. The x-axis of the plot is expressed in $p_L$ representing the longitudinal component of the momentum of the annihilating electron positron pair [10]. A straight line at a ratio equal to one would represent bulk Cu. It can be seen that the gamma spectra at lower positron kinetic energies (energies are given in legends) have higher intensity at low momentum and a large dip at around ~15 × 10$^{-3}$ m$_0$c. Analyzing the ratio curves given by Brusa et al for bulk carbon and bulk Cu [11], it can be seen that the dip at 15 × 10$^{-3}$ m$_0$c corresponds to a highly reduced probability of positron annihilation with 3d electrons in Cu. As the positron kinetic energy is increased, the depth of
the feature at $15 \times 10^{-3}$ $m_0c$ reduces and by 15 keV, the ratio curve corresponds to annihilations from bulk Cu. PAES spectra collected from the same sample using positrons of low kinetic energy (less than 10 eV) with the time of flight PAES spectrometer connected to a second positron beam system at University of Texas at Arlington [12] show an Auger electron peak from the KVV transition in carbon at 263 eV and no signature of the Cu Auger peak at 60eV due to the M2,3VV transition. Hence, the dip at $15 \times 10^{-3}$ $m_0c$ is due to enhanced annihilation of positrons with electrons of carbon atoms and reduced annihilation with 3d electrons of Cu atoms.

The gamma-ray spectra collected at different positron energies were parameterized by the W (wing)-parameter [7]. The parameter is reflective of the fraction of positrons annihilating with high momentum electrons. A decrease in the W-parameter is indicative of the presence of defects or surfaces in the material as the density of higher momentum electrons attached to the nuclear core are reduced in these regions. The variation in the W-parameter can also be due to changes in the chemical environment at the site of positron annihilation. The variation of the W-parameter calculated from gamma-ray spectra collected at various positron energies (2 eV-20 keV) for multilayer graphene is shown in Figure 5. Two different W parameters (W1 and W2) were defined. The parameter W1 was defined as the ratio of the integrated counts in the regions 1.5 keV to 2.5 keV above and below the central peak at 511 keV to the total peak count and is reflective of annihilation with outer most 2p electrons in C. Whereas W2 was defined as the ratio of the intensity in the region 2.5 keV to 7.5 keV from the central 511 peak. This region is reflective of annihilation with 3d electrons in Cu [11]. The calculated W-parameters (W1 and W2) have been normalized to their respective values at 20 keV representing bulk Cu. It can be seen that both W-parameters increase from a low value at the surface to a higher value in the bulk as the annihilation probability increases with higher momentum electrons in the bulk Cu. However, the W1 and W2 parameters show a difference in their variation with beam energy. The steady increase of W2 with beam energy is consistent with the variation seen in the ratio curve and is reflective of the increase in the fraction of positron annihilation with the Cu 3d electrons as the positrons are implanted more deeply and fewer of them return to C/Cu interface. On the other hand, W1 rises sharply and then levels off beyond 7.5 keV pointing to the fact that W1 is more
reflective of annihilation with the C 2p electrons. This can explain why the major change in this parameter takes place over the incident positron energy range in which the fraction of positrons trapping in the C over layer is changing. The sharp dip in W1 at ~5 eV as seen in Figure 6 is proposed to be due to positrons annihilating in 6-8 layers graphene. We hypothesize that the fact that W1 has a lower value for incident positron energy of 5 eV than for 2 eV is due to the differences in the gamma-ray spectra caused by the trapping of positrons in defects within 6-8 layers of graphene. As the positron energy is increased more positrons are implanted near the graphene-Cu interface resulting in the increase of W1. It can be seen that the W1 values from 15 eV to 25 eV are equal within the experimental error pointing to annihilation of positrons at the same site which in this case can be graphene-Cu interface. This hypothesis is being currently tested by comparing the results to that obtained from measurements in polycrystalline Cu substrate after sputter cleaning the multilayer graphene. The influence of positronium formation on the surface of 6-8 layers graphene as a function of incident positron energy also needs to be investigated to further clarify on the trapping of positrons in graphene defects.

Figure 5. Variation of W-parameters W1 and W2 (defined in the text) as a function of incident positron kinetic energy which is varied from 2 eV to 20 keV. It can be seen that the variation of W2-parameter follows the typical trend for metals and reflects the increasing annihilation probability of positrons with 3d electrons. The variation of W1 is reflective of changes in the annihilation probability with 2p electrons of C. (color online)

Figure 6. Variation of W1-parameter (defined in text) as a function of incident positron kinetic energy shown here from 2 eV to 100 eV. It is posited that the sharp dip in W1 at 5 eV is due to positrons annihilating in the 6-8 layers graphene over layer film on Cu.
4. Conclusion
Doppler broadening of the annihilation gamma-rays produced after implanting positrons at different energies (from 2 eV to 20 keV) in a multilayer graphene film on Cu substrate has been measured using an advanced positron beam system equipped with a high efficiency rare gas moderator. The measurements at low positron energies show the chemical sensitivity of the technique to a 2-3 nm thick graphene over layer on Cu substrate. The results also show the capability of the technique to deduce depth resolved information about positron trapping centres in graphene and at the interface of graphene and Cu substrate. These results suggest that it should be possible to utilize positron beam spectroscopy to characterize defects and chemical structure in nanometer thick 2D materials.

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