Determination of Edge Purity in Bilayer Graphene Using μ-Raman Spectroscopy

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Polarization resolved μ-Raman spectroscopy was carried out at the edges of bilayer graphene. We find strong dependence of the intensity of the G band on the incident laser polarization, with its intensity dependence being 90° out of phase for the armchair and zigzag case, in accordance with theoretical predictions. For the case of mixed-state edges we demonstrate that the polarization contrast reflects the fractional composition of armchair and zigzag edges, providing a monitor of edge purity, which is an important parameter for the development of efficient nanoelectronic devices.

The recent discovery of graphene [1], a two-dimensional crystal comprised of a single layer of carbon atoms, triggered intensive research efforts in the physics and materials science communities. The high degree of crystallinity and outstanding electronic and thermal properties make graphene a promising candidate for nanoelectronic devices [2–4]. The addition of a second layer forms bilayer graphene with a largely changed electronic band structure resulting in field-tunable electronic band gaps [5] and strongly suppressed electronic noise [6]. Of particular importance for device applications are the underlying edge chiralities of bilayer graphene and graphene nanoribbons (GNRs), since the atomic edge composition influences the electronic structure and thus transport properties [7, 8] as well as chemical reactivity [9].

As a nondestructive technique, Raman spectroscopy has been widely utilized to determine the number of graphitic layers [10, 11]. Furthermore, since the chirality of graphitic edges and the orientation of the crystalline axis have a strong impact on phonon modes localized at the edges, Raman spectroscopy can also be utilized for edge state characterization [12–14]. Although previous experiments have addressed the issue of edge state identification by Raman spectroscopy using the D band around 1350 cm−1 [13], a detailed analysis and methodology to determine edge purity in the case of mixed edges has not yet been presented. Unlike the D band, the G band around 1580 cm−1 was recently predicted to show a strong polarization sensitivity with respect to armchair and zigzag edges, with Raman scattering amplitudes 90° degrees out of phase [12].

Here, we report on polarization-resolved μ-Raman experiments performed at the edges of bilayer graphene flakes. We find a strong dependence of the Raman intensity of the G-band on the polarization of incident laser light with respect to various edge orientations and we confirm that amplitudes of armchair and zigzag edges are 90° out of phase. Furthermore, we demonstrate that the varying polarization contrast of the G band is a useful monitor to characterize edges with mixed armchair/zigzag boundaries.

In these experiments, graphene flakes were mechanically exfoliated from a highly ordered pyrolyzed graphite (HOPG) block and deposited onto pre-patterned p+ silicon wafer with a thermally grown 300 nm silicon oxide. Room temperature μ–Raman spectra were obtained using a 2.33 eV laser diode with a spot size of about 2 µm. Half wave plates were used to rotate the plane of polarization with respect to the sample in the laser excitation path and to rotate the plane of polarization in the collection path back to its original configuration in order to eliminate any errors introduced by the dependence of the spectrometer’s grating and other optical components on the polarization of light.

The prominent spectral bands of graphene are shown in the Raman spectrum in Fig. 1b., whereas dashed horizontal lines show defect scattering; b) abridged Raman spectrum labeling the bands identified in a; c) G’ band Raman spectra obtained from several different flakes (offset for clarity) showing the dependence of the G’ band on the number of graphitic layers. The solid red line is the sum of the Lorentzian sub-components.
D’ band spectroscopy (see discussion below) and used as a
in Fig. 2a. Edge 6 was identified as being zigzag using D /
edges were selected from a single large area flake, as shown
flake obtained under the same polarization conditions. All
Figure 2b shows Raman spectra of different edges of a bilayer
D and D’ bands can be used for edge chirality determination.

The following investigation focuses on exfoliated flakes which have been identified
as bilayer graphene.

Figure 2: a) Scanning electron micrographs of different regions
of the graphene flake from which the spectra were obtained. b)
Raman spectra of the edges identified in ‘a,’ (offset for clarity).
The angle θ is measured between edge 6 and the edge from which
the spectra were obtained. The presence (absence) of the D and
D’ bands is indicative of armchair (zigzag) edge chiralities.

While the G’ band is useful in layer metrology analysis, the
D and D’ bands can be used for edge chirality determination. Figure 2b shows Raman spectra of different edges of a bilayer
flake obtained under the same polarization conditions. All
edges were selected from a single large area flake, as shown in Fig. 2a. Edge 6 was identified as being zigzag using D / D’ band spectroscopy (see discussion below) and used as a
reference for measuring all subsequent edge angles, identified as θ in Fig. 2. Interestingly, several of the edges possess pro-
nounced D (1350 cm⁻¹) and D’ (1620 cm⁻¹) bands, while others lack both bands. The D band originates from inter-
valley scattering that connects two adjacent K & K’ points at the Brillouin zone boundary via a second order process that
requires one iTO phonon and a symmetry break [16, 17]. The
D’ band is a weak intra-valley transition that
requires one iLO phonon and a symmetry breaking pertur-

b) 

![Diagram](image)

Figure 2b: Raman spectra of different edges of a bilayer graphene flake. The angle θ is measured between edge 6 and the edge from which the spectra were obtained. The presence (absence) of the D and D’ bands is indicative of armchair (zigzag) edge chiralities.

Odd multiples corresponding to edges with opposite chirality [13], we identify edge 5, being 120°degrees with
respect to edge 6 (a zigzag edge) as zigzag, while edge 1, which is 90° with respect to edge 6 as an armchair edge.

However, the D band does not provide unambiguous in-
formation about edge purity. For example, a lower purity is
expected for the case of edge 2 and 3 with 72° and 78° respec-
tively as is evident from the schematic in Fig. 3 c, but the D
band does not change its oscillator strength accordingly and
was found not to exhibit strong polarization dependence.

Following the initial identification of the edge chiralities in
our sample, we now focus on the G band around 1580 cm⁻¹.

The G band arises from a doubly degenerate intra-valley pro-
cess that originates from scattering of an iTO phonon or an
iLO phonon at the center (Γ-point) of the Brillouin zone
[10]. For pure zigzag edges, the intensity of the G band
is expected to be maximum for an excitation beam polar-
ization that is perpendicular to the edge. Conversely, for
armchair edges its intensity maximizes for the incident exci-
tation beam polarization that is parallel to the edge. This
phenomenon is still present for mixed edges, however, the
degree of the polarization contrast is diminished and is pro-
portional to the amount of mixing of zigzag and armchair
boundaries. Purely random edges, i.e. edges comprised of
equal amounts of zigzag and armchair boundaries, are not
expected to exhibit any polarization dependence [17].

The polarization dependence of the G band obtained from
edges 1 (armchair) and 6 (zigzag) is shown in Fig. 3a. We
find that the intensity of the G band of the armchair and
zigzag edges has a strong polarization dependence, that is
90°out of phase with respect to each other. The intensity
dependence of the armchair edge varies according to
I_G ∝ sin^2 ϕ (solid red line in Fig. 3a), while for the zigzag
edge it varies according to I_G ∝ cos^2 ϕ (solid blue line in
Fig 3a), where ϕ is the angle between the edge of the flake
and the polarization axis of the excitation beam [13]. Note
that the data in Fig. 3a have been corrected for a nonva-
nishing background of about 2800 counts to emphasize the
polarization contrast, while Fig. 3b shows raw data without
any background substraction.

Furthermore, the G band shows no polarization depend-
ence far from the edges (≥ 3µm), as shown by the black
circles, obtained at the center of the flake. Similar non-
polarized data were obtained at numerous different points
away from the edges and across the entire flake. Earlier
experiments on the G band found a variation in ampli-
tude when scanning across a flake at various interior points
[12, 21], which is related to Kohn anomalies and an underly-
ing non-uniform strain or deformation potential [22]. Conse-
sequently, the lack of polarization dependence at interior points
(in basal plane of graphene) is indicative that the observed
phenomenon in our experiments arises from the different al-
lowed and forbidden phonon modes at the edges of the flakes
and not from strain-related effects.
The presence (absence) of the D band is strongly correlated to 30° multiplicity of the edges as shown above. This effect originates from the fact that only the longitudinal (transverse) optical phonon mode is a Raman active mode near the armchair (zigzag) edge. Since the physical mechanism that gives rise to the G band originates from scattering of a doubly degenerate ITO and an LO phonon at the Brillouin zone boundary, the G band should be better suited for the determination at that edge; c) schematic representation of the edges.

In contrast, the intensity of D band showed little sensitivity on the incident photon polarization (data not shown). More precisely, edge 1, which is 90° to the dominant zigzag edge has the highest (50%) polarization contrast and the closest odd multiplicity ($\frac{2\pi}{30}$ = 3) while edges 2 and 3 have 26% and 10% polarization contrasts with multiplicities of $\frac{2\pi}{90}$ = 2.6 and $\frac{2\pi}{72}$ = 2.4 respectively. It should be noted that, in all cases, the polarization dependence of the G-band tends to a minimum value, but never vanishes, suggesting that although the edge is comprised of mostly armchair constituents, it is not atomically clean within the detection area (2 µm spot size). This verifies prior experimental results [13], which show that atomically smooth edges are very rarely obtained using micromechanical exfoliation.

In summary, we found that the Raman G band in bilayer graphene is particularly sensitive to the laser polarization with its intensity dependence being out of phase by 90° in the armchair and zigzag case. In addition, for mixed-state edges we observe that the G band polarization contrast reflects the fractional composition of armchair and zigzag edges and provides thus information about the purity of the edge. This knowledge is crucial for the development of graphene-based electronic devices and could serve as a convenient process monitor to characterize the degree of edge state purity in GNRs created with various fabrication techniques such as exfoliation, electron beam lithography, or local anodic oxidation.

During the review process of this manuscript we became aware of a recent work by Cong et al. [23], showing a similar polarization dependence of the G-band using monolayer graphene. The combined knowledge of our work and the work by Cong et al. suggest that the polarization dependence in mono- and bilayer graphene is of the same origin. In addition, our work considers the case of mixed edges which are most relevant for technological applications.

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Figure 3: a) Polarization dependence of the edges E1 (armchair, blue triangles) and E6 (zigzag, red squares). The black circles correspond to the data obtained at the center of the flake, which shows no polarization contrast. b) polarization contrast of 3 armchair edges (E1, E2, & E3) showing variable polarization contrast $C^2_\theta$ which is correlated to the expected amount of zigzag contamination at that edge; c) schematic representation of the edges.
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