Second harmonic generation from graphene and graphitic films

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Optical second harmonic generation (SHG) of 800 nm, 150 fs fundamental pulses is observed from exfoliated graphene and multilayer graphitic films mounted on an oxidized silicon (001) substrate. The SHG anisotropy is observed as a sample is rotated about the surface normal. For p-polarized fundamental and SHG light, the isotropic SHG from a graphene layer only slightly interferes with the fourfold symmetric response of the underlying substrate, while other samples show a threefold symmetry characteristic of significant SHG in the multilayer graphitic films. The dominance of the threefold anisotropy is maintained from bilayer graphene to bulk graphite. © *2009 American Institute of Physics*. [doi:10.1063/1.3275740]

In recent years there has been intense interest in the quantum and transport properties of graphene,[1,2] bilayer graphene, and few-layer graphite for reasons related to fundamental physics and the possible development of nanoelectronic devices.[3,4] The family of thin films with different number of layers (hereafter referred to as C-films) can be produced using micromechanical exfoliation of bulk graphite (e.g., with tape) and typically attached to a substrate. It has been found theoretically that the properties of graphene evolve to those of bulk graphite in less than ten layers.[5] Natural graphite consists of graphene layers stacked in a hexagonal Bernal, or (AB) arrangement. Another common method of producing graphene, epitaxial growth, involves the vacuum graphitization of SiC at high temperatures.[6,7] This technique generally produces 5–40 layers of graphene with a non-Bernal stacking arrangement, albeit with a larger defect density.[7]

Optical techniques have played a major role in diagnosing the quality and properties of C-films. For example, although a single graphene layer only absorbs approximately 2% of visible/infared light, when C-films are placed on a layered substrate such as SiO_2/Si, optical interference effects in reflection permit the determination of the exact number of layers for sufficiently thin samples.[8,9] Raman spectroscopy has also been used to distinguish between one, two, and three layer materials, as well as detecting defects.[10,11] Pump-probe spectroscopy has been used to determine the carrier dynamics of epitaxial graphene and the family of C-films.[12–14] In this letter, we present results from studies of SHG from C-films mounted on an oxidized Si(001) substrate with the aim of determining how the SHG response and its rotational anisotropy vary with the number of layers.

Nonlinear optical techniques are well-known to provide insight into the properties of surfaces or interfaces,[15–20] particularly between centrosymmetric media where bulk dipole sources of SHG are symmetry forbidden. The observation of SHG provides another tool for C-film research with possible applications to studies of structure, doping, charge transfer, adsorbate effects, etc.

The surface of (AA) stacked graphite (not naturally occurring) has C_{6v} symmetry (sixfold rotational symmetry with no inversion symmetry). Similarly, graphene on a substrate has C_{6v} symmetry, and dipolar interface SHG is, in principle, permitted. Nonetheless, only an isotropic response is allowed from mounted graphene as the sample is rotated about the surface normal since dipolar SHG is governed by a third rank susceptibility tensor ($\chi^{(2)}$) and is not sensitive to the presence of a C_n rotation symmetry operation with $n>3$. The surface of multilayer C-films has C_{3v} symmetry ($n=3$), and so dipolar interface SHG is permitted, and may be anisotropic. Such SHG may occur at both of the C-film interfaces. For sufficiently thick samples, there may be a bulk contribution to the SHG, attributed in first order to electric quadrupole/magnetic dipole sources governed by a fourth rank tensor. Such bulk sources are capable of showing rotational anisotropy behavior associated with a threefold rotation symmetry axis. For all C-films mounted on $SiO_2/(001)Si$ substrates, isotropic SHG might arise from the SiO_2/Si interface and bulk Si, while fourfold symmetric contributions can arise only from bulk Si electric quadrupole/magnetic dipole sources.[17]

When all sources of SHG are taken into account, the total p-polarized SHG field, $E_{2\omega}$, generated from a fundamental p-polarized field E_ω is of the form[17]

$$\frac{E_{2\omega}(\phi)}{E_\omega^2} = a_0 + a_3\cos[3(\phi+\phi_0)] + a_4\cos(4\phi), \qquad (1)$$

where ϕ is the azimuthal angle of rotation about the normal relative to the Si (100) axis, ϕ_0 represents the orientation of the graphene relative to the silicon lattice, and a_n are complex coefficients which depend on various susceptibility tensor elements and linear optical properties of the thin-film system. The SHG intensity is then found from $I_{2\omega}/I_\omega^2 \propto |E_{2\omega}/E_\omega^2|^2$. For reasons mentioned above, for both the bare substrate and graphene on the substrate, $a_3=0$, while for sufficiently thick graphite, where the silicon is effectively optically shielded, $a_4=0$.

Our experiments were performed with a Ti:sapphire oscillator, providing 1.0 nJ, 150 fs pump pulses at 800 nm. The incident pulse energy was attenuated to ~0.06 nJ (well below the damage threshold), and monitored with a calibrated photodiode. The fundamental beam was focused at an angle of incidence of 60° onto the samples using a 0.12 numerical aperture microscope objective, generating a spot-size of approximately 7 μm × 10 μm. The 400 nm SHG light was collected, optically filtered, and detected using a cooled pho-

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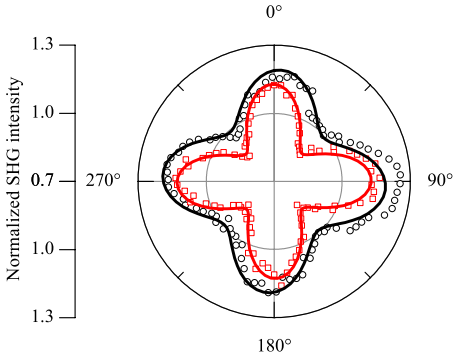

FIG. 1. (Color online) Normalized SHG signal from $SiO_2/(001)Si$ (red squares) and graphene on $SiO_2/(001)Si$ (black circles) as a function of azimuthal angle ϕ. Both data sets are fit to Eq. (2) (solid curves) and have the same normalization. The absolute angle is arbitrary, but corresponds to the same physical orientation for both samples.

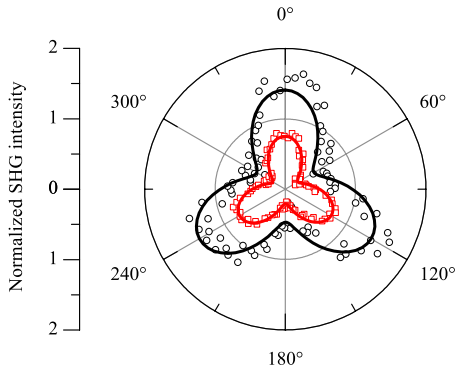

FIG. 2. (Color online) SHG signal from bilayer graphene (black circles) on $SiO_2/(001)Si$ and from bulk graphite (red squares) as a function of azimuthal angle ϕ. Both data sets are fit to Eq. (3) (solid curves) and are normalized such that the isotropic component of the SHG signal from silicon would be unity. The absolute angle is arbitrary for both curves.

tomultiplying tube and photon-counting electronics. The polarization states of the fundamental and SHG beams were controlled using high quality polarization optics. While s- and p-polarized SHG was observed from all samples for s- and p-polarized fundamental beams, the highest intensity signals were observed for p-polarized fundamental and SHG beams, and we focus on these results here.

C-films of at least 20 μm diameter were mounted on a 300 nm film of SiO_2 on a (001)Si substrate to make the samples visible as described above. The samples were mounted on high precision translation and rotation stages such that they could be rotated about the normal axis while keeping the beam focus within a particular sample. The SHG intensity was measured as a function of ϕ. Samples were imaged in a confocal arrangement with a charge coupled device camera to ensure that the focal spot coincided with the axis of rotation of the sample—although due to mechanical limitations the exact center of the axis of rotation could vary by several microns relative to the sample. For each sample, the SHG signal was normalized to the isotropic component of the SHG signal obtained from the adjacent bare SiO_2/Si substrate. SHG signals were observed from various samples, from single layer (graphene) samples to bulk graphite, but here we focus on samples with 0 (bare), 1, and 2 layers on the SiO_2/Si substrate, and bulk graphite (>100 layers). For all samples, the SHG intensity was observed to vary with the intensity of the fundamental beam as $I_{2\omega} \propto I_{\omega}^{n}$ with $n=2.0\pm0.3$ for incident pulse energies up to those used.

Figure 1 shows the SHG signal from the bare substrate as well as from the substrate with a graphene layer on it. In both cases a fourfold symmetry pattern with a strong underlying isotropic response is observed. The anisotropic contribution is significantly weaker than the isotropic contribution and so $|a_0| \gg |a_4|$ in Eq. (1). Thus, for the bare substrate and graphene/SiO_2/Si system, the SHG intensity azimuthal dependence may be approximated as

$$\frac{I_{2\omega}(\phi)}{I_{\omega}^{2}} \approx A_0 + A_4 \cos(4\phi), \tag{2}$$

where A_n are phenomenological constants corresponding to the nth elements of a Fourier decomposition of the azimuthal pattern, and where, of course their value is sample dependent. Equation (2) has been used to fit both data sets.

For the bare substrate the anisotropy parameter $A_4/A_0 = 0.13 \pm 0.03$ whereas for the graphene/SiO_2/Si, $A_4/A_0 = 0.08 \pm 0.03$. As Fig. 1 also indicates, the normalized SHG intensity from the graphene system is slightly higher than that of the bare substrate. These differences are related to differences in the linear optical properties of both systems or a possible contribution of the graphene layer to isotropic SHG. However, if the isotropic contribution to the SHG were negligible, linear optical properties alone would not lead to a reduced anisotropy for the graphene sample since linear properties would affect isotropic and anisotropic contributions of the SHG in the same way. Hence there is evidence for a (weak) isotropic contribution to the SHG from the graphene layer. It is nonetheless not possible from the present data alone to clearly determine the relative influence of differences in the linear optical properties at the fundamental and SHG frequencies for the two systems versus the additional isotropic contribution from the graphene layer.

The SHG signal from a bilayer graphene sample on the substrate shows a qualitatively different azimuthal pattern than that from graphene on $SiO_2/(001)Si$; Indeed the pattern is now dominated by a threefold symmetry as shown in Fig. 2. For multilayer C-films, one could expect that the anisotropic contribution from the C-films dominates that from the substrate, $|a_3| \gg |a_4|$ in Eq. (1). This obviously would occur for sufficiently thick samples where little light reaches the substrate, but Fig. 2 suggests that this is also true for bilayer graphene. If $|a_3| \gg |a_4|$ and $|a_0| \gg |a_3|$ then one would expect the SHG intensity to be of the form

$$\frac{I_{2\omega}(\phi)}{I_{\omega}^{2}} \approx A_0 + A_3 \cos[3(\phi + \phi_0)] \tag{3}$$

where A_0 and A_3 are layer-dependent coefficients. The SHG signal from bilayer graphene is shown to fit well with Eq. (3) as the figure indicates. This shows that the degree of anisotropy from the bilayer graphene dominates that from the substrate with anisotropy parameter $A_3/A_0 = 0.6 \pm 0.1$. Also shown is the SHG response from bulk graphite. Not unexpectedly the threefold symmetry dominates but now with $A_3/A_0 = 0.5 \pm 0.1$

Although not shown, preliminary observations of several other samples of different numbers of layers show a dominant threefold symmetry, since they all have C_{3v} symmetry, although the magnitude of the isotropic and threefold com-

ponents vary with the number of layers, partly due to the linear optical properties and interference effects.

Note that the offset angle ϕ_0 can easily be determined (not shown here) by comparing the SHG anisotropy pattern from the C-films with that from the $SiO_2/(001)Si$ substrate. In Fig. 2 the offset angle is chosen arbitrarily to produce a maximum at $\phi=0$.

The magnitude of Fourier components in $I_{2\omega}(\phi)/I_{\omega}^2$ other than the zeroth and third [suggested by Eq. (3)] were found to be comparable to the noise, and are not analyzed here. In all cases part of the signal variation is likely due to imperfections in the samples, and is generally greater in samples with visible defects, and samples which are small enough that the focal spot clips the edge of the sample while it is being rotated.

In summary, we have observed SHG signals from graphene and multilayer graphite films mounted on a SiO_2/Si substrate. Samples with >1 layer show the threefold symmetry inherent to the AB stacking arrangement, while single-layer samples do not. This is understood in terms of rank-3 (surface dipole) and rank-4 (bulk quadrupole) tensor properties. Thus, SHG may be used as a diagnostic for the layering structure of graphene and few-layer graphite. This technique may yield qualitatively different results for expitaxial graphene (non-AB stacking) and may also be used to study charge transfer effects, induced dc field effects, the influence of adsorbates, and other external influences.

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