An Optical Excitation Study of Pure and Ru-doped Bi$_{12}$SiO$_{20}$ Crystals with Graphene Coating

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Abstract. CVD-grown graphene was transferred onto polished crystal plates of pristine and Ru-doped bismuth silicate (Bi$_{12}$SiO$_{20}$:Ru), which are well known inorganic materials possessing very high carrier mobility and photo conductivity. The heterostructures obtained were investigated by optical absorption and Raman spectroscopy. We examine the influence of photoinduced phenomena in the crystal substrate on the graphene layer with possible implications for optical doping of graphene through photo-induced space-charge field.

1. Introduction

Sillenite Bi$_{12}$SiO$_{20}$ (BSO) single crystals are of special interest due to their photochromic and photorefractive properties enabling applications as reversible recording media for holography and image processing.

Bismuth silicate and bismuth titanate (BTO) crystals (Bi$_{12}$SiO$_{20}$, Bi$_{12}$TiO$_{20}$) are well-known as perfect photoconductors for spatial light modulator (SLM) devices due to their excellent photoconductivity and high dark resistivity [1,2]. Doping with transition metal elements (Ru, Rh, etc.) significantly improves the response time yielding fast photoconductive materials in the near infrared spectral range [3–5]. So far, despite sensitivity improvement, only a limited number of near infrared operating SLM have been demonstrated based on Rh-doped BTO [6] or some semiconductors [7,8], all of them operating with ITO electrodes. However, as it is well known, ITO has limited and variable transparency throughout the near infrared spectral range [9], which is of particular importance for the development of near infrared operating devices.

Recently, graphene has emerged as a next generation material for photonics and optoelectronic applications due to its excellent conductivity, low sheet resistance and very high transparency in a broad spectral range. Beyond its role as a photoactive layer in solar cells, in organic light emitting diodes and field-effect transistors, graphene has been considered as a promising candidate to replace expensive and requiring complicated processing ITO contacts [10]. Moreover, as compared to ITO, graphene can provide higher mechanical and chemical stability and flexibility [11]. Based on the above exceptional properties, graphene becomes an attractive transparent conductive electrode in liquid crystals devices.

Recently, a highly photosensitive, near infrared operating SLM device using graphene-based electrodes was demonstrated [12]. Its high performance was attributed to a reversible space-charge generation and surface charge distribution under non-uniform light illumination leading to slight
electrostatic doping of the graphene layer. To further examine the underlying mechanism of these phenomena we performed optical and Raman studies on graphene-coated BSO crystal plates. BSO crystals of various forms and sizes as well as a polished plate representative for the substrates used in the present study are shown in figure 1.

![Figure 1. BSO ingots and crystal plates of various size.](image)

2. Experimental

The graphene was grown on a Cu foil using a low-pressure chemical vapor deposition (LPCVD) method. LPCVD is widely used approach to grow high quality graphene, over a large area and with a controlled thickness. The growth process was performed in a quartz tube using 50 sccm high purity hydrogen and 20 sccm methane flow at a temperature of about 1000°C. After completing the growth process, the graphene was transferred on the target substrates by means of poly(methyl-methacrylate) PMMA (4% in anisole) as a supporting layer. The Cu foil was etched out in an iron trichloride solution, the resultant film of PMMA and graphene was transferred on polished Czochralski-grown pure BSO and BSO:Ru crystal plates, followed by removal of the PMMA using acetone at 60°C.

The presence of graphene on both crystal plates was verified by Raman spectroscopy as shown in figure 2. The Raman spectra were measured in backscattering geometry using HORIBA Jobin Yvon Labram HR visible spectrometer equipped with a Peltier-cooled charge-coupled device (CCD) detector. The 633-nm line of a He-Ne-laser was used for excitation. The laser beam was focused on spots of different size using microscope optics.

The samples thus obtained were examined with optical absorption and Raman measurements in pristine state and after being irradiated for 15 min. with an UV lamp in order to excite the photochromic effect in the BSO crystal substrates. The setup for UV irradiation is shown in figure 3. In order to drive the substrates to their pristine state after irradiation the samples were annealed for 1 hour at 100°C.
Figure 2. Raman spectra of the structures pure BSO/graphene (black trace) and BSO:Ru/graphene (red trace). The spectra are vertically offset for clarity.

Spatially resolved Raman measurements were performed on both samples in the pristine state of the substrates and after UV irradiation and the positions of the main graphene peaks were determined.

Figure 3. A schema of the UV irradiation setup.

3. Results and discussion
A similar study on graphene-coated samples of lithium niobate [13] revealed that an optical gating of graphene through non-uniform irradiation of such samples can indeed be achieved. In our case the effect of non-uniform irradiation was sought by using non-continuous graphene layers consisting of grains that are only partially connected to each other. The presence of such layers was verified with electrical measurements yielding sheet resistances of the order of 100 kOhm. Furthermore, the Raman spectra taken from different points exhibited variable intensity of the graphene peaks and there were also points with a very faint to missing graphene signal.
The results of the optical absorption measurements in the form of transmission spectra are depicted in Figure 4. Reference spectra of the substrates from spots without graphene coating are also shown. It is seen that UV irradiation increases the absorption of the graphene layer by about 50% on pure BSO and several times on BSO:Ru. On the other hand, Ru doping is known to enhance the photochromic and the photorefractive effect in BSO [5,14] and to form levels connected to charge transfer [15].

Figure 5. Graphene G-peak positions as determined from spatially resolved Raman spectra.

We further show results for the graphene G-peak frequency determination (figure 5) from spatially resolved Raman measurements on the BSO:Ru/graphene sample. For this sample, the G-peak frequency tends to slightly increase upon UV radiation. Under the same conditions, the BSO/graphene sample does not exhibit any net irradiation-related shift in G-peak position (not shown). It can thus be assumed that the G-peak position shift for graphene on BSO:Ru is related to the more strongly pronounced enhancement of the photochromic effect in the doped BSO substrate. On the other hand, it is logical to assume that both photochromic and photorefractive effects are excited together by the UV radiation. These two effects have vastly different relaxation times but their subtle interplay could create transient space-charge fields capable of electrostatically doping the graphene layer on the surface.
4. Conclusion
CVD-grown graphene was transferred onto polished crystal plates of pristine and Ru-doped bismuth silicate with subsequent characterization of the samples by optical absorption and Raman spectroscopy. The influence of photoinduced phenomena in the crystal substrate on the graphene layer manifested by increased graphene absorption and G-peak position shift is tentatively explained with optical doping of graphene by possible transient photo-induced space-charge fields.

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