Thermo-optic coefficient of chemical vapor deposited graphene multilayers

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Date Received: 11-01-2022 Date Accepted: 04-05-2023

Abstract

Observation of strong inelastic light-matter interaction and large thermal conductivity of novel two-dimensional graphene has invigorated the present research. Herein, the thermo-optic coefficient of graphene multilayers is obtained from their nonlinear refraction coefficients calculated from Z-scan experiment in closed aperture geometry. The refractive optical nonlinearity was obtained employing a continuous wave He-Ne laser and occurs due to thermal lensing effect. The graphene multilayers behave as the diverging (concave) lens giving rise to self-defocusing effect leading to negative sign of refractive nonlinearity. Accordingly, a large negative thermo-optic coefficient (-2.43×10^{-3} K^{-1}) inferred for the graphene multilayers suggests its utility for thermo-optic device applications.

Keywords: *Graphene, Optical Nonlinearity, Thermal lens, Self-defocusing, Thermo-optic coefficients*

1. Introduction

The successful manufacturing of optical limiting and optical switching devices necessitates an understanding of nonlinear absorption coefficients and nonlinear refractive indices. The optical materials' refractive index is not a constant parameter. Various optical materials show electro-/acousto-/thermo-optic phenomenon, and optical nonlinearity effects, where the variation in refractive index is generated by interaction of electric/acoustic fields with the optical waves within the crystal, or temperature. Among them, the thermo-optic effect is extremely important in fabricating various thermo-optic switches/modulators, and temperature sensors (Agrawal et al., 2016). Low-cost temperature sensors can be created using suitable optical materials with high thermo-optic coefficients. To achieve switching functionality, thermo-optic switching makes use of the temperature dependence of the refractive index. Small thermally induced changes in the refractive index can have a large impact on the light-intensity distribution. Depending on the material quality, positive or negative thermo-optic coefficients can be obtained. Materials with negative thermo-optic coefficients are suitable candidate materials for athermalization, which is required to compensate for thermal expansion.

For such thermo-optical applications, graphene has established itself as a potential candidate material because of its high heat conductivity and strong light-matter interactions [Kim et al., (2013); Li et al., (2020); Gan et al., (2015)]. It is worth mentioning here that when a strong laser light is incident on the sample, a percentage of this intense light is absorbed by the sample, resulting in a temperature gradient within the illumination section, which may give birth to convection current. The dissipation of this heat from the sample causes the creation of a sample lens, implying a redistribution of density within the material. On the basis of material's nature, heat can escape from the centre of the lens or from the periphery, resulting in convex or concave lens development, which can be investigated by determining the nonlinear refractive index obtained using effective far-field closed aperture z-scan experiment. The emergence of a peak-valley (valley-peak) configuration is a symptom of self-defocusing (self-focusing) action and hence diverging (converging) lens behavior, which leads to negative (positive) optical nonlinearity [Sheik-Bahae et al., (1989)]. In a previous work, we demonstrated negative refractive optical nonlinearity for chemical vapor produced graphene multilayers using the same z-scan approach performed under closed aperture geometry with He-Ne laser source operating in continuous wave (CW) mode [Agrawal et al., (2020a); Agrawal and Yi., (2020b)].

Various researchers have theoretically and practically determined thermo-optic coefficients for various two-dimensional (2D) materials (graphene or MoS_2, for example) utilizing techniques such as temperature dependent Raman spectroscopy, photothermal detection techniques, and so on [Wu et al, (2018); Yang et al., (2019)]. However, manipulating the flow light in graphene-based 2D materials in the visible spectrum regions, where most of the fascinating optoelectronic and thermo-optic features have been demonstrated, remains a significant challenge. In light of this, and using our previous findings, an attempt has been made to calculate the thermo-optic coefficient of graphene multilayers.

2. Materials and methods

For the current study, graphene multilayers were formed on copper foil utilizing ultra pure methane (CH_4) gas and hydrogen (H_2) gas serving as carbon precursor and ambient gas, respectively. For graphene growth, a four-stage growth model was used, with stage I involving ramping of the furnace temperature to a constant high temperature of 980^{o}C. During this stage, 10 sccm H_2 gas was flown at a constant rate within the furnace; stage II is the annealing stage, where the temperature of the furnace is kept constant

(980°C) for a certain time period under the same gas flow; and the III stage corresponds to graphene development, in which CH_4 gas with an flow rate of 10 sccm was added into the furnace, however there is an increase in the flow rate of H_2 gas to 100 sccm; finally, IV stage is natural cooling stage. Following stage IV, the graphene layers generated on copper foil were removed from the furnace and placed onto quartz substrate using wet-transfer method. More information about the growth can be found elsewhere [Agrawal et al., (2020a)]. Figure 1 depicts all four stages, as well as their temperature-time profiles.

The Raman spectroscopic characterization result [Figure 2 of ref. (Agrawal et al., (2020a)] confirms the creation of graphene multilayers as well as the presence of sp^2 hybridized carbon and sp^3 hybridized carbon atoms, with sp^3 indicating the presence of defect and/or disorderness in the generated graphene multilayers [Agrawal et al., (2020a)].

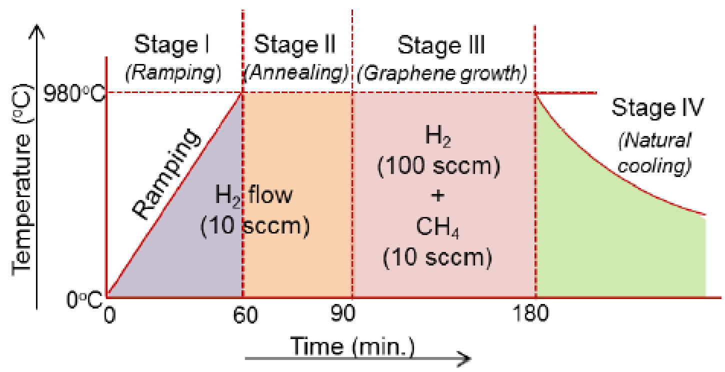

Figure 1: Temperature-time profile for the four-stage growth of graphene multilayers; Stage I: Ramping; Stage II: Annealing; Stage III: Graphene growth; and Stage IV: Natural Cooling. Modified from [Agrawal et al., (2020a)].

Furthermore, the thermo-optic coefficient of graphene multilayers was obtained from the knowledge of its nonlinear refractive index coefficients which can be extracted by performing closed aperture Z-scan experiment. In this technique, the sample is mounted on a translation stage which is placed in the z-direction of an intense laser light source and a tight focusing lens is placed in front of the sample. The sample is then translated in the positive and negative direction with respect to the focal length of the tight focusing lens and this creates an intensity variation in the z-direction. Also, for measuring the transmitted light in closed aperture geometry, an aperture is placed in front of the detector which allows only the on-axis transmitted light to be detected. In present situation, the far field closed aperture z-scan experimental result was obtained by utilizing a He-Ne laser (operating wavelength = 633 nm; beam waist = 26.77 µm; and Rayleigh range = 3.55 mm) and the tight focusing lens has a focal length of 12 cm. to detect the transmitted light, Thorlab PM 100 detector having an accuracy of 1% has been employed. Figure 2 shows the actual Z-scan experimental setup to determine the nonlinear refractive index coefficients and hence the thermo-optic coefficients.

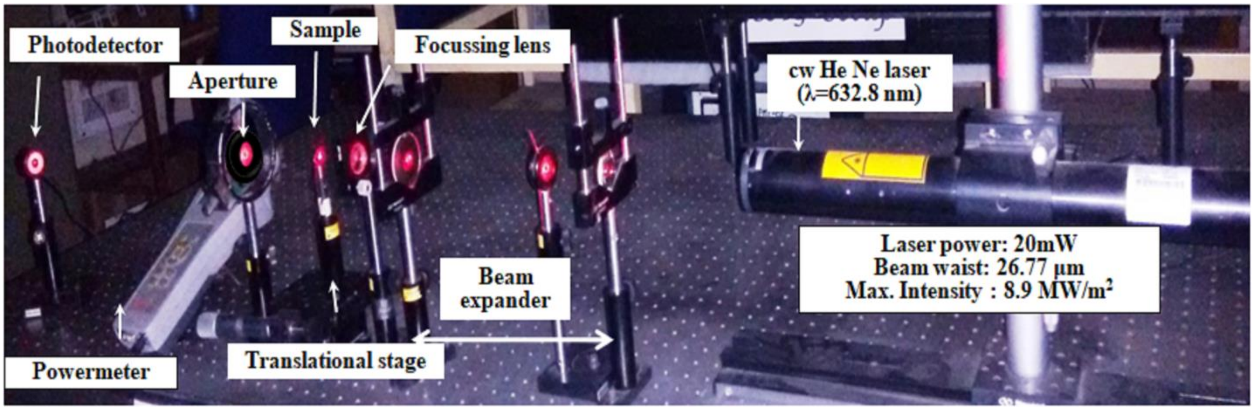

Figure 2: Photograph of the actual Z-scan experimental setup to determine the nonlinear refractive index coefficients and hence the thermo-optic coefficients.

3. Results and Discussion

It is worth mentioning here that graphene exhibits overwhelming linear and nonlinear optical properties owing to- (i) unique electronic band structure, and (ii) linear energy dispersion in the vicinity of the K point. In our earlier report, far-field closed aperture result for as-grown graphene multilayer shows the existence of peak and valley at pre-focal and post-focal positions (Agrawal et al., (2020a)), respectively. Accordingly, self-defocusing behavior and hence the negative refractive nonlinearity has been observed in the grown graphene multilayers with a nonlinear refractive index coefficient (n_2) -14.5×10^{-9} m^2/W (Agrawal et al., (2020a)). It should be noted here that when the optical nonlinearity is examined via a laser source operating in CW mode then there is an involvement of thermal phenomena in optical nonlinearities. Herein, when CW laser radiation was incident on graphene multilayer sample, a part of this radiation gets absorbed leading to the production of sufficient amount of heat within the local area of the sample, giving rise to convection current and asymmetrical temperature gradient. Depending upon the nature/internal behavior of the graphene multilayer, this generated heat will escape from the peripheral part of the sample, indicating a redistribution of local density within the sample. Consequently, this creation of refractive index gradient with respect to temperature is known as thermo-optic coefficient, designated as *dn/dt*. The sign of the thermo-optic coefficient is another indication for the converging or diverging lens behavior of the material. Hence, the evolution of the thermal lens effect is also a medium characteristic. The thermally induced refractive index can be expressed in the form [Boyd (2003); Agrawal et al., (2015)];

$$n = n_o + \frac{dn}{dt}\Delta\theta;\ \frac{dn}{dt} \neq 0 \tag{1}$$

where n_o being the refractive index in linear regime, $\Delta\theta = (\theta - \theta_o)$ denotes the enhancement in local temperature of the illuminated portion within the sample, θ_o being the room temperature (300 K) and θ is the total local temperature.

Under steady state approximation, the maximum temperature difference achieved by a laser beam of beam waist radius R will be given by;

$$\Delta\theta_{max} = \frac{\alpha_o R^2 I_o}{\kappa} \tag{2}$$

Here, α_o is the linear absorption coefficient, R (= 26.77 μm) is the laser beam waist at the focal plane, I_o is the maximum laser intensity and κ represents graphene's thermal conductivity [5300 W/mK, Balandin et al., (2008); Pop et al., (2012)].

Knowing all the parameters of equation (2), one can determine the local temperature of the illuminated portion within the sample which when plotted as a function of transverse distance can facilitates in determining the behavior of the temperature variation of the sample upon approaching the focal plane of the tight focusing lens. Accordingly, the dependence of the total temperature within the illuminated region on the traversed distance of the graphene sample has been depicted in figure 3. This figure clearly indicates an increase in the local temperature of the sample as it approaches towards the focal plane of the tight focusing lens which is an indication of self-defocusing behavior. The maximum increase in the local temperature ($\Delta\theta_{max}$) that was created within the illuminated region was found to be 37.24 K.

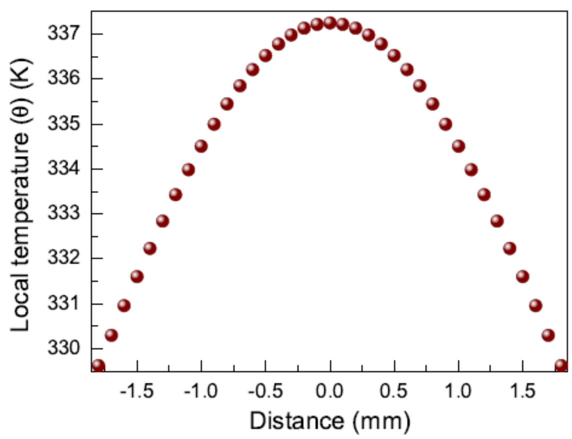

Figure 3: Temperature-transverse distance profile for graphene multilayer, showing the rise in local temperature upon approaching the focal plane.

The thermo-optic coefficient of a material depends on the nonlinear refractive index coefficient, maximum laser intensity and the local temperature and can be obtained using the equation [Boyd (2003)];

$$\frac{dn}{dt} = \frac{n_2 I_o}{\Delta\theta} \tag{3}$$

Using the above equation, the thermo-optic coefficient for graphene multilayers was found to be -2.43×10^{-3} K^{-1}. This value is even larger than that of various semiconductor oxides including ZnO [Agrawal et al., (2016); Agrawal et al. (2017)], MgZnO [Agrawal et al., (2016)], NiZnO [Dar et al., (2016)], etc. Such a large thermo-optic coefficient of graphene multilayers suggests that it could be used in thermo-optic switching or thermo-optic modulator device applications [Chen et al., (2020); Sun et al., (2016); Yang et al., (2022)]. The obtained large thermo-optic coefficient of CVD grown graphene multilayers was attributed to the larger coefficient of nonlinear refraction which is highly temperature dependent, high heat conductivity and strong light-matter interactions in graphene based two-dimensional materials.

4. Conclusion

In conclusion, the thermo-optic coefficient of chemical vapor deposited graphene multilayers has been determined from the knowledge of maximum rise in the local temperature within the illuminated region of graphene multilayers. Towing to the large thermo-optic coefficients, the grown graphene multilayers can be useful for fabricating thermo-optic switching or thermo-optic modulators etc. Furthermore, the thermo-optic coefficient's negative sign indicates that they are widely used to lessen the effect of thermal expansion.

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