Anomalous anti-Stokes Scattering in Amorphous Carbon Thin Films

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Abstract. This work is devoted to a study of temperature-dependent Raman scattering of amorphous carbon (a-C) thin films. An anomalous rise of the anti-Stokes intensity in respect to the Stokes intensity was observed. This result comes from the resonant enhancement of anti-Stokes scattering of defects of graphite-like crystals. The observed discrepancy is quantified through a coefficient, $a$, defined as a ratio of the anti-Stokes and Stokes scattering cross sections. Understanding the mechanism for anomalous enhancement of anti-Stokes scattering provides a way for correct probing the temperature of the a-C thin films exposed to cw laser illumination.

1. Introduction

Due to the flexible rearrangement of physical and chemical properties depending on the ratio of diamond and graphite-like phases, amorphous carbon thin films demonstrate the versatility in large area of applications: from protective coatings in highly sensitive fiber-optic sensors to functional elements in modern nanoelectronic devices [1]. However, an important problem limiting their widespread use is the chemical heterogeneity and structural instability [2] of the material under high temperatures and pressures. In particular, under such conditions the hermetic properties of carbon films degraded that leads to the inefficient operation of an electronic device. Therefore, it becomes an important task to control the evolution of the structural and morphological properties of a carbon film with temperature.

Raman thermometry demonstrates very unique advantages in thermal measurement than traditional methods, especially for measurements at the nanoscale. However, Raman-based temperature probing is material-specific. In this work, we consider the critical factors and define the coefficients for determination the temperature of an amorphous carbon film of via Raman spectroscopy measurement.

2. Experimental part

As the studied samples, we used curved glass substrates – in the form of cylinders with a diameter of 125 μm, covered with a carbon layer of various thicknesses – from 3 to 107 nm. The carbon coating was applied by chemical vapor deposition method with the same precursor-gas – propylene. The Raman spectrum was recorded using linearly polarized light with a wavelength of 632.8 nm. To prevent photothermal heating of the samples of interest, the incident laser radiation power of 5.6 mW was set. A Raman
spectrum was registered in the spectral range of 150–2000 cm$^{-1}$. The exposure time was 20 seconds. In this work was utilized an experimental setup that was realizing a reflection-based feedback mechanism. This mechanism allows one to reliably exclude side-effects due to thermal expansion and the inertia of surrounding constituents while doing the Raman measurement. The focus was set onto a specimen under study in an optimal way and measures the maximal response from a photomultiplier. Then, based on the feedback mechanism, a z-correction was made with a xyz piezoscanner in such a way that the focus size would not exceed that defined by the setpoint. To reduce its offset range of piezoscanner due to heating of the surroundings, the hot plate was covered with a thermal shield.

3. Results and discussion

Figure 1 shows a Raman spectrum of the 107 nm a-C coating at room temperature and decomposition into seven elementary peaks assigned to different species of graphite-like and disordered phases. Stokes and anti-Stokes component of Raman spectra were normalized to the intensity of the Stokes line. A blue solid curve is a sum of all peaks. It fits the experimental data of anti-Stokes and Stokes Raman spectra with a correlation coefficient of 0.996 and 0.998, respectively.

It is known that the temperature of a carbon sample can be spectroscopic determined from the shift of G-mode, the linewidth broadening, the changes of the intensities of the anti-Stokes and Stokes components of the Raman spectrum. Due to the complex structure of Raman spectrum of amorphous carbon the intensity of lines is the most sensitive temperature indicator. Using the Boltzmann distribution for the mean number of phonons with energy $\hbar\Omega$ he temperature of sample can be determined using the following relationship [3]:

$$T = \frac{\hbar c\Omega}{k_B \ln \left[ \frac{I_S}{I_{AS}} \left( \frac{\omega_0}{\Omega} \right)^{a} \right]},$$

where $I_S$ and $I_{AS}$ are Stokes and anti-Stokes intensities; $\omega_0$ is the excitation frequency; $\Omega$ is a phonon frequency; $\hbar$ is the Planck constant; $c$ is the speed of light; $k_B$ is the Boltzmann constant; $a$ is coefficient that is specific to material. In general case, the coefficient $a$ in equation (1) contains the anti-Stokes to Stokes scattering cross sections ratio. In spontaneous Raman scattering of light these cross sections are equal to each other. However, under resonance conditions, the system can have different scattering cross sections for the ground and the excited vibration state that leads to an anomalous relationship between the Stokes and the anti-Stokes intensities.
Figure 2 (a) shows both the anti-Stokes and the Stokes Raman spectra of 31 nm thick film recorded at different temperatures. It can be seen that the Stokes part changes uniformly with temperature, while the anti-Stokes part grows anomalously in comparison with the predictions of Boltzmann's law. Two-dimensional (2D) temperature map calculated using the equation (1) shows the anti-Stokes to Stokes intensities ratio versus phonon mode frequency of carbon materials excited by the laser with a wavelength of 632.8 nm (figure 2 (b)). It can be seen that the maximum of the anti-Stokes to Stokes intensities ratio is achieved at low values of the vibration frequency and at elevated temperature. At room temperature the anti-Stokes to Stokes intensity ratio at characteristic vibrations frequencies of carbon materials should be only 1/600.

Figure 2. a) Temperature-dependent anti-Stokes and Stokes Raman spectra captured for a carbon film; b) 2-D temperature map of carbon materials.

In a number of articles, such anomalous behaviour is discussed within the framework of the vibration pumping [4], the correlated Stokes-anti-Stokes photon pair generation [5], and the charge transfer [6]. Usually, the contributions of the vibration pumping are reflected in the linear dependence of the anti-Stokes to Stokes intensities ratio on laser power. However, based on results of our spectroscopic investigations for the samples, the dependence was clearly approximated by an exponential function; therefore, the contributions of the vibration pumping are small. For the realization of the effect of correlated Stokes-anti-Stokes pairs the highly-oriented structures are necessary, such as highly crystalline graphite or nanodiamonds. However, the investigated carbon surface comprises crystalline and amorphous domains in concordance with results of atomic-force microscopy. Therefore, a phonon that generates photon pair quickly decay inhibiting the Stokes-anti-Stokes correlation. Also to estimate the contribution of heating under laser illumination of the carbon film to total temperature of the sample we investigated the dependence of \( \ln(I_{\text{as}}/I_{\text{s}}) \) on the incident laser power by using laser with wavelength of 632.8 nm. It was found that a significant photoinduced heating occurs in the carbon film at an illumination power of more than 6.0 mW. Samples of interest were exposed to a laser light with the wavelength of 632.8 nm and the power of 5.6 mW. So, contribution of the photoheating is negligible small. Therefore, we believe that anomalous behavior of anti-Stokes to Stokes intensity ratio caused by resonance anti-Stokes Raman scattering in disordered carbon film. Moreover, the resonance is the sensitive to the phonon mode (figure 3(a))
Figure 3. a) Dependence of the coefficient $a$ on temperature for a 12 nm thick carbon film; b) Dependence of the coefficient $a$ on thickness of carbon film.

The strength of this effect depends on the carbon film thickness. Figure 3 (b) shows a mean value of a coefficient $a$ in formula (1) calculated for a graphite vibration mode. The accurate estimation of crystallinity degree in the highly disordered carbonaceous material containing a huge amount of structural defects and dopants consisted of the different phases by means of Raman spectroscopy is challenging [7]. Since it was shown in our previous study the smaller thickness results in larger concentration of the defects that related to the chemical inclusions, such epoxide, carbonyl, carboxyl functional groups [8]. That leads to the modification of potential surface of vibrations [9]. So, the possibility of the involvement of an electronic transition resonance in the anti-Stokes spectral domain increases. Tending toward thicker films (on the order of microns), this effect is waning and the temperature of the film will exactly correspond to the Boltzmann distribution with the coefficient $a$ which has a value of unit.

Thus, in this work, we estimated the critical factors that contribute to the total temperature of the sample probed by means of Raman spectroscopy.

4. Conclusion
In this work, the temperature of the amorphous carbon films was probed by Raman spectroscopy. We found that the anomalous enhancement of the anti-Stokes Raman scattering of the a-C thin film. This effect is related to the resonant enhancement of the anti-Stokes scattering. This result opens a unique possibility for probing the temperature of a-C thin films exposed to cw laser illumination.

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