Anti-Stokes Raman Spectroscopy for Probing Functional Groups in Amorphous Carbon Thin Films

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Amorphous carbon (a-C) is often utilized as a cost-effective barrier coating (10-100 nm thick) for silica optical fibers to protect them from harsh ambient. As a rule, these coatings consist of randomly oriented graphite-like crystals that make the structure of a-C film porous with a high concentration of defects. It is known edge defects of graphene fragments are chemically active and interact with water and its dissociation products in the ambient air. This leads to the enrichment of a-C films with hydrogen- and oxygen-containing functional groups [1], as a result, to a deterioration in the protective properties of carbon coatings.

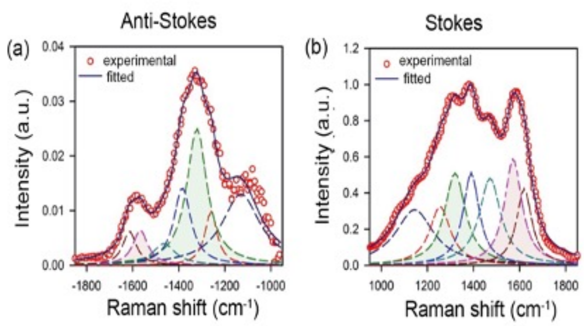

Figure 1: Anti-Stokes (a) and Stokes (b) Raman spectra of the a-C film (thickness 107 nm). Red circles show the measured spectra, dashed lines show the result of deconvolution, solid line is a sum of dashed lines

Raman spectroscopy is a powerful tool for diagnostic organic materials. This work is devoted to the development of a method for studying functional groups (hydroxyl, epoxy, carbonyl, and carboxyl) in a-C thin films. This method is based on anti-Stokes Raman scattering.

The objects under study were carbon-coated optical fibers. The fiber diameter was 125 microns, and the thickness of the carbon layer was 57 to 107 nanometers. To study the spectroscopic properties, red laser radiation with a wavelength of 632.8 nm was used. Figures 1(a) and (b) show the spectra of anti-Stokes and Stokes Raman scattering of a-C film with a thickness of 107 nm under laser irradiation with a power of 5 mW. As can be seen, the ratio of anti-Stokes and Stokes intensities does not predict Boltzmann's law. In particular, the IaS/IS value for the G band (1580 cm^{-1}) at room temperature was 1/10, which is 60 times higher than predicted by Boltzmann's law. We assumed that such behavior could be associated with resonant Raman scattering of light and photo-induced heating of a-C films upon excitation by CW laser radiation. To study the photo-heating of a-C under the action of continuous laser radiation, the dependence of the ratio IaS/IS on the laser power was measured. The resonant Raman scattering was estimated by introducing the resonance coefficient as the ratio of the anti-Stokes and Stokes scattering cross sections. We assumed that the observed resonant Raman scattering is related to the modification of the joint electron density of a-C states caused by water enrichment defects [2]. Thus, the resonance coefficient can be used to estimate the degree of enrichment/depletion of a-C films with hydrogen- and oxygen-containing groups. Understanding the physical mechanisms of anomalous anti-Stokes Raman scattering will improve Raman thermometry.

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References

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