Nanoscale physics

Raman and EPR spectroscopic studies of chromium-doped diamond-like carbon films

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The diamond-like carbon (DLC) and chromium-doped DLC (Cr-DLC) films were studied using Raman and electron paramagnetic resonance (EPR) spectroscopic methods. The films (~ 100 nm thickness) were prepared by a hybrid technology using a combination of pulsed laser deposition and magnetron sputtering using graphite target and formed on SiO_2 substrates. The Cr content varied from 1 at. % to 12 at. % (measured by WDS). From Raman study it was found that with the increase of Cr content the D-G band shifts to lower frequency, broadens and decreases in intensity. The Raman results agree with the XPS results showing that carbon sp^2/sp^3 ratio increased with the Cr concentration. Incorporation of Cr atoms results in the formation of some chromium carbides. In DLC films the EPR signal from the conduction electrons hopping between neighboring carbon dangling bonds was observed. We have established that there is a coupling between conduction electron spins and localized spins in DLC films. The *g*-value found for localized spins corresponds to the non-bonding π-electrons localized at the marginal regions of a nanographite sheet having a zigzag shape. In Cr-DLC films two EPR signals were observed: a narrow one from the carbon related defect (CRD) in the sp^3 hybridization state and the broad signal attributed to the P_{b0} center, which appears due to the presence of the oxygen and formation of the oxidized Si on the interface between the Cr-DLC film and SiO_2 substrate. A superhyperfine coupling between CRD and surrounding Cr nuclei in Cr-DLC films was suggested. The sp^3 coordinated CRD EPR signal intensity dramatically decreases with the increase of Cr content that is consistent with Raman and XPS data. The work supported by MEYS SAFMAT LM2015088 and LO1409 projects.