Carbonization mechanism of PMDA-ODA-type polyimide

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PMDA-ODA-type polyimide has been utilized as a precursor of synthetic graphite. Carbonization process of PMDA-ODA-type polyimide synthesized from pyromellitic anhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA) has been studied for decades, but various reaction mechanisms have been reported and it is still unclear. It is essential to understand the carbonized structure of PMDA-ODA-type polyimide to estimate the defect structure of graphite. In this work, the carbonization mechanism of polyimide film heated at 1273 K or lower was analyzed by X-ray photoelectron spectroscopy (XPS), infrared (IR) and Raman spectroscopy, elemental analysis, calculation of spectra, and molecular dynamic simulation (ReaxFF). At 813 K, nitrile formed as observed by IR and N1s XPS. Between 813-873 K, oxygen content decreased from 13 to 9 at.% as results of elemental analysis. In addition, the percentage of C=O decreased and C-O-C formed as results of IR and XPS. The formation of nitrile originates from the scission of C-N bonding in PDMA and the formation of ether originates from the crosslinking between molecules by C=O as estimated by ReaxFF. Between 873 and 1073 K, the nitrogen content decreased from 19 to 14 at.% as results of elemental analysis. This decrement of nitrogen is caused by the formation of nitrogen-containing gas via the formation of isoimide as estimated by ReaxFF.