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Effect of doping on the growth and electronic properties of graphene-carbon nanotube hybrid

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Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], there has been great excitement among material scientists and engineers due to its unique structure and properties. In particular, field emission (FE) from CNTs is one of the most promising properties as far as its practical application is concerned. Although number of studies explored CNTs as the promising candidate for FE devices, the FE is believed to predominantly occur from the tips rather than the side walls. A report by Konishi *et al.*[2] suggests that the intensity of electric field concentrated on the tip of CNT is 2.8 times higher than the side walls. The FE of CNTs is also problematic because they burn out during emission, ceasing the emission completely, i.e., they have less FE stability. In order to achieve the FE enhancement, CNT-graphene hybrid (g-CNTh) with graphene layers protruding from the CNT have been synthesized by many researchers with a vision to create more emission sites and exceptional FE performance than individual CNT [3-5]. This composite made of CNT and graphene is a three-dimensional conductive carbon network which offers the advantage of high surface area frame work of CNT coupled with the high edge density of the graphene sheets.

In order to enhance or control the electron emission characteristics of g-CNTh, doping is considered as one of the most feasible technique. Amongst various potential dopants, nitrogen is the most popular dopant of the carbon nanomaterials as it has similar atomic radii as that of carbon. Plasma enhanced chemical vapor deposition (PECVD) is considered as the most viable technique for the synthesis of nitrogen doped g-CNTh as it exhibits better control over the g-CNTh structure at relatively low temperatures and also offers the advantage of g-CNTh structure modification by nitrogen plasma treatment. In the present work, a theoretical model is developed to describe the growth of CNT and thereafter nucleation and growth of graphene sheets on CNT in the presence of $CH_4/H_2/N_2$ plasma. The defects generated on the CNT surface during its growth are considered as the nucleation sites for the growth of graphene sheet on CNT surface. The model incorporates the charging rate of the g-CNTh, kinetics and energy balance of all plasma species i.e., electrons, positively charged ions and neutral atoms along with the nitrogen doping species, and growth rate of the g-CNTh. Numerical calculations on the effect of nitrogen doping on the growth of g-CNTh have been carried out for typical glow discharge plasma parameters. It is found that the graphene sheet nucleation density, i.e., defects density on CNT surface increases via nitrogen doping and moreover, the dimensions of graphene sheets, i.e., height and thickness decreases upon nitrogen doping. We have also estimated the FE characteristics of the nitrogen doped and pristine g-CNTh and found that the FE of g-CNTh gets enhanced upon nitrogen doping due to increase in emission sites and high field enhancement factor of the protruded graphene sheets on the CNT surface. Some of the results of the present investigation are in accordance with the existing experimental observations [5,6].

References

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