Studies of pure and doped tetrahedral amorphous carbon films deposited by a novel filtered cathodic vacuum arc technique

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The amorphous carbon (a-C) films have a mixture of sp^3, sp^2 and sp^1 bonded carbon where sp^3 content decides about the mechanical properties and sp^2 content decides about the optical and electronic properties. The properties of such films depend very strongly on the ratio of sp^3/ sp^2. The well known hydrogenated amorphous silicon (a-Si: H) and a-Si have only sp^3(tetragonal) bonding. The high sp^3 bonded carbon content present in a-C films may be up to 85 % and these films are then termed as tetrahedral amorphous carbon (ta-C) films.

Among the techniques used for the deposition of a-C films, cathodic arc evaporation of graphite has been reported to be a suitable process. The cathodic vacuum arc evaporation of a pure carbon source has the advantage that variables such as evaporation rate, substrate temperature and substrate bias can be independently managed. The key issues with the cathodic arc are the production of macro particles, which must be filtered out to produce defect free coatings and control of the arc location to acceptable areas. Magnetic filter is the widely used technique in which a magnetic filed is used to deflect and / or confine the plasma beam while the macro particle flux remains unaffected. Toroidal filter is the most widely studied filter which has 90^o (L) bend. For further enhancing the efficiency of filtering, one can also use the S bend filter which can be made by joining together two 90^o (L) bend filter. The combined use of cathodic vacuum plasma arc and a magnetic filter for the removal of macro particles is known as filtered cathodic vacuum arc (FCVA) technique. The cathodic arc offers the unique opportunity of growing various form of carbon ranging from highly diamond-like to graphitic-like and various intermediate materials like ta-C: H, ta-C: N, nano clustered, nanocomposite and nanotubes etc.

The aim of this thesis has been to study the pure and doped tetrahedral amorphous carbon (ta-C) films deposited by a novel filtered cathodic vacuum arc (FCVA) process. The S bend FCVA process used for the deposition of such films has been custom designed and indigenously made in the laboratory as well as in the country for the first time.

The work done in this thesis has been summarized in the following.

Chapter 1 gives a comprehensive review on the existing knowledge relating to growth, characterization and material aspects (like structural and other properties) of the carbon allotropes and carbon based structures like DLC, ta-C, carbon nanotubes and their deposition techniques and applications. Chapter 2 gives the existing models and theory of vacuum arc concerning the cathodic spot followed by the details of the S Bend FCVA process used in the deposition of undoped and doped ta-C films together with other experimental techniques used in their characterization. Langmuir diagnostic probe has been used to evaluate the plasma parameters of the vacuum arc.

Chapter 3 deals with the effect of substrate bias on the properties of as grown ta-C films. The electrical conductivity, activation energy, optical band gap, stress, sp^3content, density of states, field-emission threshold, emission current density etc are found to depend on the substrate bias applied during the growth of ta-C films which peak at 200 V substrate bias. Ion energy or the substrate bias is thus found to be a single important parameter, which controls the properties of ta-C films.

Chapter 4 investigates the effect of hydrogen (H) incorporation on the properties of as grown ta-C films deposited using an S bend FCVA process at a high substrates bias of 300 V for the first time. H incorporation reduces the electrical conductivity, density of states and field-emission threshold and increases the activation energy and optical band gap. Hydrogen enters in the tetrahedral structure in the network and increases the sp^3 content. The effect of hydrogen on ta-C is, therefore, to give a modest gain in semi conducting properties by passivating some of the defects.

Chapter 5 describes the effect of nitrogen (N) incorporation on the properties of as grown ta-C films deposited using an S bend FCVA process at a high substrate bias of 300 V for the first time. No compensating effect has been observed in controlling the electrical conductivity and activation energy in our study. N appears to enter the tetrahedral network in the present study in the range of the N content studied and it increases the sp^3 content and the electrical conductivity which is accompanied by the decrease in activation energy without changing the band gap of as grown ta-C films. It reduces the field-emission threshold and the residual stress and also increases the emission-current density. Small amount of N incorporation compensates the p-type nature of as grown ta-C films which reduces the density of states but at larger amount of N incorporation it acts like n-type dopant giving rise to the increased values of density of states .

Chapter 6 describes the effect of boron (B) doping on the properties of as grown ta-C films deposited using an S bend FCVA process at a high substrate bias of 300 V for the first time. B doping up to 2.0 at % decreases the activation energy continuously whereas the electrical conductivity is increased only by one order. The band gap of the material is not affected due to the addition of B and it remains the same as that of undoped ta-C films. B doping increases the $E_{turn-ON}$ and decreases the values of emission current density. The tetrahedral nature of the carbon network is not destabilized up to 2.0 at.% B.

Chapter 7 describes the effect of phosphorous (P) doping on the properties of as grown ta-C films deposited using an S bend FCVA process at a high substrate bias of 300 V for the first time. Incorporation of P in ta-C films decreases the activation energy and increases the electrical conductivity by one order only without affecting the optical band gap. P doping increases the $E_{turn-ON}$ and decreases the emission current density. It acts as n-type dopant. At low levels of P incorporation (up to 1.0 at % or less), the network is essentially tetrahedral in nature but at high level of P beyond 1.0 at % the tetrahedral nature is diminished drastically and it destabilizes the network.

Chapter 8 describes the effect of substrate bias on the properties of as grown ta-C films and the effect of N content on the properties of ta-C: N films deposited using a pulsed unfiltered cathodic vacuum arc process. The properties of as grown ta-C films are found to depend on substrate bias and N content in ta-C: N films. Pulsed arc process offers the advantage of depositing ta-C films with higher controllable and repeatable deposition rates and lower macro particles. Unfiltered pulsed arc also leads to lower macro particles than a continuous arc and also the higher deposition rate and ion throughputs. Finally, chapter 9 compares the properties of ta-C films (a new semiconductor) deposited using an S bend FCVA process (in the present thesis) to the properties of ta-C films deposited by L bend FCVA process and widely studied a-Si:H material in literature. In the end, scope of future work is also given.