Hydrogen induced microstructural variation in diamond and diamond like carbon thin films

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Abstract. Hydrogen plays a crucial role in the growth of micro-crystalline diamond (MCD) and diamond like carbon (DLC) thin films grown by plasma assisted chemical vapour deposition (PACVD) processes. It selectively etches graphite phase and helps in stabilizing the diamond phase. The presence of various hydrocarbon species in the plasma and their reaction with atomic, excited or molecular hydrogen on the substrate surface decide the mechanism of diamond nucleation and growth. Several mechanisms have been proposed but the process is still not well understood.

Control of hydrogen and other deposition parameters in the PACVD process leads to deposition of yet another class of materials called diamond like carbon. By varying the concentration of hydrogen it is possible to produce purely amorphous carbon films on the one hand and amorphous hydrogenated carbon films (with as high as 60% hydrogen) on the other. Very hard, optically transparent and electrically insulating films characterize the diamond like behaviour. The proportion of hydrogen and its bonding with carbon or hydrogen in the film can be varied to obtain very hard to very soft films which could be optically transparent or opaque. The microstructure of these films have been investigated by a large number of techniques. The results show interesting situations.

This paper reviews the work on the role of hydrogen on the growth, structure and properties of MCD and DLC thin films.

Keywords. Diamond; hydrogen; microstructural variation; graphite; plasma assisted chemical vapour deposition; amorphous; microcrystalline; epitaxy; insulator; optical properties; supersaturation; nucleation and growth.

1. MCD thin films

Extensive research is being carried out, all over the world, on the growth of diamond and diamond like carbon thin films using PACVD techniques employing various hydrocarbon sources. Major breakthroughs in low-pressure diamond deposition technology have been possible mainly due to the addition of hydrogen in the reactive gas mixtures. The best quality microcrystalline diamond (MCD) thin films have been obtained in hydrogen atmosphere containing only small amount (e.g. 1% or less, of methane) of hydrocarbon in the reaction mixture.

A variety of processes have been used for MCD thin films deposition. These include microwave/rf/dc plasma CVD processes employing methane, acetylene, butane, benzene, acetone, methyl alcohol etc. as the source of carbon. All these hydrocarbon sources contain plenty of hydrogen and it is released during the plasma decomposition process. A large number of radicals and ions are produced in the plasma as a result of reaction between the hydrogen and the dissociation products of the hydrocarbon (Frenklach 1989). Thus, in the CH₄–H₂ plasma the chemical species produced are CH₄⁺, CH₃⁺, CH₂⁺, CH⁺, C⁺, H₂⁺, CH₂⁻ and H₃⁻ as well as neutrals CH₃, CH₂, CH, C, H and the excited species. These active species can react on the substrate surface and lead to nucleation and growth of the diamond microcrystals. At low pressures (atmosphere or below) diamond is metastable, the stable phase being the graphite.
The free energy difference between the graphite and the diamond is only 0.02 eV/atom (500 cal/mole). As a result in a growth process, diamond phase is formed in a continuous competition with the thermodynamically favoured graphite phase. The probability of nucleation and growth of diamond is negligibly small as compared to that of graphite.

In a typical PACVD process of diamond growth several overlapping elementary processes work together. These may be classified in three groups — (1) dissociation of the hydrocarbon source and the formation of the necessary intermediate species, (2) transport of the reactive species to the substrate surface and the occurrence of the nucleation process and (3) stabilization of the diamond phase on the surface of the growing film. Knowledge of the reaction pathways and the ability to control the rate determining step are crucial for consistent and reproducible film characteristics (Inspector et al. 1989).

In addition to the above factors, hydrogen plays a very important role in diamond synthesis and this is due to the preferential etching of graphite in contrast to diamond in hydrogen plasma environment. The relative gasification rates of diamond and graphite are known to be different by orders of magnitude (Setaka 1989). As a result the nucleation and growth of graphite is inhibited due to the presence of atomic hydrogen in the plasma environment. There are numerous variations on this theme. Calculations show that at least some of the experimental data can be rationalized if one assumes that in the presence of atomic hydrogen diamond is kinetically stable relative to graphite (Sommet et al. 1989). The second important effect of hydrogen is to satisfy dangling bonds of surface carbon atoms keeping them in the $sp^3$ configuration and thus preventing the diamond surface from reconstruction into graphitic $sp^2$ or carbynic $sp^1$ structures. Thus, for example, Yang et al. (1993) have shown formation of monohydride surface structure with one hydrogen atom per surface carbon atom on diamond (100).

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**Figure 1.** Free energy difference and activation barrier for graphite and diamond phases.