4bn Hydrogen-Induced Crystallization of Diamond-Cubic Semiconducting Materials

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Thin films of semiconducting materials such as diamond and silicon have been researched for more than three decades for their wide range of electronic, photonic, and more recently, biological applications. Both these group IV materials are synthesized under similar conditions by CVD: the dissociation of a hydrocarbon gas (or SiH_4 in the case of silicon) heavily diluted in H_2 using plasma or hot-filament, creates reactive CH_x (or Si_xH in case of silicon) and H fragments, which react on a heated substrate to produce films that contain diamond (or silicon) crystals. Despite the tremendous research in the synthesis of thin films, the understanding of nucleation and growth is limited, which is necessary to gain control over crystallite fraction, defects and morphology in thin films for desired applications.

Recently, nucleation experiments were performed in a microwave plasma chemical vapor deposition (CVD) reactor that resulted in a large density of carbon nanocrystals, which were analyzed using electron nanodiffraction. These studies led to the discovery of two new crystalline phases of sp^3 carbon other than diamond: face-centered and body-centered cubic carbon. Nanodiffraction results revealed possible hydrogen substitution into diamond-cubic lattices, suggesting that these new phases perhaps act as intermediates in diamond nucleation. These results, further confirmed using simulations of electron diffraction, elucidate the role of hydrogen in the nucleation of diamond.

It is well-established that crystalline silicon films are obtained only when SiH_4 is highly diluted in H_2, or under conditions where SiH_4 is completely dissociated such that there is a high concentration of H in the gas phase. In fact, amorphous silicon films undergo disorder-to-order transition upon exposure to atomic hydrogen created by plasma or hot filament assisted dissociation of H_2. The mechanism of this disorder-to-order transition was uncovered recently; specifically, it was shown theoretically that hydrogen inserts into the strained bonds Si-Si bonds in amorphous silicon, and induces bond-breaking and bond re-forming reactions, which eventually lead to nucleation of crystalline silicon. This chemically-induced crystallization of silicon occurs in the 150-300 ^oC temperature range, where thermal effects are not expected.

Crystallization of silicon at room temperature was demonstrated for the first time as a result of hydrogen-induced crystallization. Nanocrystals of silicon were deposited at room temperature using an inductively coupled plasma source and SiH_4 highly diluted in H_2. *In situ* attenuated total internal reflection - Fourier transform infrared spectroscopy (ATR-FTIR) was used to monitor the surface and bulk silicon hydride species (SiH_x) and surface temperature. The film microstructure and thickness were monitored using in situ spectroscopic ellipsometry (SE). The deposited films were also characterized using *ex-situ* techniques such as Raman spectroscopy and transmission electron microscopy (TEM). Both *in situ* and *ex-situ* characterization techniques clearly indicated the presence of crystalline domains in the deposited films. *In situ* spectroscopic ellipsometry also revealed that the silicon nanocrystals nucleate in the bulk and grow beneath an amorphous silicon crust, which supports the theory of hydrogen-induced crystallization. Further improvement in crystalline fractions and morphology of thin films by controlling the ion and radical flux in the plasma would also be very desirable.

A similar strategy could also be applicable to obtain room temperature deposition of diamond (and possibly germanium) since amorphous carbon can undergo similar disorder-to-order transformation in the presence of hydrogen. Room temperature deposition of semiconducting materials is very attractive for flexible electronics, making them compatible for roll-to-roll manufacturing. Further more, thin films of diamond and silicon on flexible substrates will be attractive for a wide variety of electro-mechanical and biological wireless sensors that contour to a given surface.