512c Hydrogen-Induced Crystallization of Silicon at Room Temperature

Radhika C. Mani and Eray S. Aydil

Nanocrystalline silicon (nc-Si) films are alternative to amorphous silicon in solar cells and thin film transistors for flat panel displays. In addition, nc-Si films may have novel applications in Si-based light emitting diodes and in single electron memory devices. The dissociation of SiH_4 and H_2 gases using plasma or heated filament, creates reactive SiH_x and H fragments, which react on a heated substrate to produce films that contain silicon nanocrystals. Depending on the deposition conditions, the nc-Si films contain either nanocrystals that are abutted against each other, or sparse nanocrystals embedded in an amorphous matrix. While nc-Si films have been deposited at or above 200 ^{o}C for at least three decades, whether such films can be obtained at room temperature has remained an open question. The ability to deposit crystalline silicon at room temperature would be very attractive for electronics on flexible (plastic) substrates.

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 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 dissociation of H_2. The mechanism of this disorder-to-order transition was uncovered recently; specifically, it was shown 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 temperature 150-300 ^{o}C range. However, despite extensive experimental studies, unambiguous room temperature nucleation and growth of nc-Si has not been demonstrated.

We demonstrate the deposition of thin films containing nanocrystals of silicon using an inductively coupled plasma source and SiH_4 diluted in H_2 at room temperature on silicon and GaAs substrates. *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 revealed that the silicon nanocrystals nucleate in the bulk and grow beneath an amorphous silicon crust, which validates the theory of hydrogen-induced crystallization. Crystal size distribution obtained through high-resolution TEM show a broad distribution that depends on the growth duration rather than the substrate temperature. Crystals as large as 100-150 nm were observed at room temperature at the end of one hour deposition. Thus, silicon nanocrystals not only nucleate but also grow substantially in the bulk at room temperature.