135b Analysis of Chemical Reactions between Radical Growth Precursors Adsorbed on Plasma-Deposited Silicon Thin-Film Surfaces

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Hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon thin films grown by plasma-assisted deposition from silane-containing discharges are used widely in technological applications, including the fabrication of solar cells and flat panel displays. Device-quality a-Si:H films are typically deposited under conditions where the SiH_3 radical is the dominant deposition precursor. Upon impingement on the a-Si:H film surface, SiH_3 radicals may either react chemically with the surface at the point of first contact or diffuse on the surface prior to reaction with surface Si atoms or other surface hydrides. Development of systematic strategies for depositing silicon thin films with desirable properties requires a fundamental understanding of the interactions between reactive radicals originating in the plasma and the growth surface, as well as between the adsorbed radicals themselves.

In this presentation, we use first-principles density functional theory (DFT) calculations on the crystalline Si(100)-(2x1):H surface in conjunction with molecular-dynamics (MD) simulations on a-Si:H surfaces to investigate the interactions between SiH_3 radicals adsorbed on Si thin film surfaces. Both calculation methods reveal the existence of two reaction channels: two SiH_3 radicals may either form disilane (Si_2H_6) that desorbs from the surface or disproportionate resulting in formation of an SiH_2 radical that is incorporated in the film (surface dihydride), and a silane (SiH_4) molecule that is released in the gas phase.

The DFT calculations show that Si_2H_6 formation from reaction between two adsorbed SiH_3 radicals is virtually barrierless if both radicals are in a “diffusive state”, i.e., if they are attached to overcoordinated surface Si atoms. On the other hand, disilane formation exhibits a moderate (0.46 eV) activation energy barrier if one of the two SiH_3 radicals is attached to an overcoordinated surface Si atom, while the other one is chemisorbed on the surface (i.e., it is bonded to a four-fold coordinated surface Si atom). Finally, activation energy barriers in excess of 1 eV are obtained for two chemisorbed SiH_3 radicals. We find that disproportionation displays a similar tendency associated, however, with reaction barriers in excess of 0.4 eV for all possible configurations of the reactants. MD simulations confirm that disilane formation and disproportionation reactions also occur on a-Si:H growth surfaces, preferentially in configurations when at least one of the SiH_3 radicals is in a “diffusive state”. Our results are in agreement with experimental observations and plasma process simulators showing that the primary source for disilane in low power plasmas may be the substrate surface. Moreover, the results are used to discuss reactions of disilane molecules with hot a-Si:H surfaces.