SURFACE REACTIONS IN SILANE DISCHARGES

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Discharges in silane are of considerable interest for the production of a-Si:H films for use in photovoltaics and as other photo receptors. The quality and characteristics of such films are known to be critically dependent upon the plasma parameters used in the film deposition. Thus, one would like to understand the sequence of gas and surface reactions responsible for the film production and the quality and morphology of the resulting films. I will describe here measurements made in my laboratory of the gas species present in these discharges by the use of mass spectrometry. While this might appear to be a study of gas processes, the results are in fact dominated by surface chemistry and surface reactions, because we find that in these low pressure discharges almost all of the chemistry occurs on the surfaces. I will first describe some of the measurements made during the discharges, in order to demonstrate how we determined this. I will then describe how we used surface sputtering as a diagnostic tool, in order to study the surface layers of the growing a-Si:H film.

Our overall model for the plasma chemistry and surface processes which take place in these discharges is shown in Fig. 1. Here, the

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Fig. 2. Ion and neutral molecules formed in the discharge are measured by mass spectroscopy. Off-axis neutral detection geometry is shown here.

The results obtained for all of the SiH\textsubscript{n} and Si\textsubscript{2}H\textsubscript{n} radicals are plotted in Fig. 3 for a discharge in silane and silane/argon mixed gases at approximately 0.1 Torr pressure and room temperature. In this diagram the radical densities are plotted as a fraction of the density of silane gas that has been depleted from the flow before leaving the discharge chamber, as this ratio tends to be nearly independent of discharge power. Note that the SiH\textsubscript{3} radical appears in an amount that is essentially independent of the mixture, and in data not shown we find that it is also independent of power and other parameters. Our explanation is that, as noted above, the decomposed SiH\textsubscript{4} produces almost exclusively SiH\textsubscript{3} from the initial silane decomposition and the ensuing radical and ion reactions. As can be seen, the other radicals are present in very small quantities in the pure SiH\textsubscript{4} discharge, but in very large quantities when doping small amounts of silane into argon. Our explanation is that almost all of these other radicals are actually produced by ion-bombardment.
Fig. 3. Density of radicals, relative to discharge-depleted silane density, for discharges in pure SiH₄, and in SiH₄/Ar mixtures.

Sputtering from the surfaces. In the argon mixture these argon-ion bombardments are much more frequent, relative to the gas source of SiH₄, hence these sputtered radicals appear in much larger quantities. Even in the pure silane discharge, some of the small quantities of other radicals can be attributed to surface reactions and residual ion sputtering. Thus, as these radicals drive the discharge chemistry, we are led to conclude that the sputtering of radicals from the surface is a major source of the discharge chemistry in the Ar/SiH₄ mixtures.

Another important observation is the fraction of Si₂H₆ relative to depleted silane. At low discharge powers 30-50% of the silicon atoms
depleted from the SiH₄ flow reappear as disilane (the remainder go into the film).² This fraction decreases as the surface temperature is increased, and in addition it is almost independent of the silane pressure. In particular, we even observe this fraction at silane pressures as low as 5 mTorr, such that almost all SiH₃ radicals produced in the gas arrive at walls before colliding with an SiH₄ molecule.² Thus, it is apparent that the Si₂H₆ must be made on surfaces, and furthermore, as SiH₃ is the dominant radical arriving at the surface it appears that two of these must react on the surface to form Si₂H₆. This is a sufficiently exothermic reaction to also yield Si₂H₄ and Si₂H₂ emission from the surface following the reaction of two SiH₃ radicals.

We have studied a number of the surface reaction energies and other steps in the surface reactions by the method of silane pyrolysis reactions with hot surfaces.³ Here we can trace the H₂-release, and silane-incorporation, and other film producing steps. The potential exists for future experiments of this type to delineate many of the important reaction steps with much higher precision than our current initial models can attain.

The next step in our diagnosis of these surface reactions has been to separate the deposition and sputtering. In this experiment, carried out by J. Doyle, C. H. Lin, and M. He, we first run a silane discharge to produce a film, then evacuate the silane and operate a pure argon discharge while detecting (with the mass spectrometer) the silane neutrals sputtered from the surface. As the sputtering continuously etches the surface we can thus detect the quantities of hydrogen-rich silicon molecules as a function of depth into the freshly deposited surface. The timing sequence and the types of signals observed are shown in the upper part of Fig. 4. The total quantity of H-rich species, sputtered in this
Fig. 4. Diagram of the post-deposition sputtering timing sequence, sample data, and total quantity of H-rich molecules, in units of surface layers, sputtered from a freshly deposited a-Si:H surface.

manner from the top layers of the film, is plotted at the bottom of Fig. 4, where we note that H is sputtered primarily as H₂ gas, the Si as primarily SiH₃, with a lesser amount of Si₂H₅. Note also, in the middle of the figure, that the Si₂H₅ is sputtered much more rapidly than SiH₃ from the top layers of the surface, implying a much weaker binding of the dangling disilane chains. H₂ is evolved even longer than SiH₃ due to the much larger surface coverage of H atoms, as well as diffusion from deeper layers to the surface when H atoms have been sputtered off the surface.
Fig. 6. Structured-surface diagram of converting a singly Si-Si bonded SiH₃, labeled S, into a doubly bonded SiH₂, labeled D.

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References