

Growth and Characterization of Hydrogenated Amorphous Silicon Thin Films

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Crystalline silicon (c-Si) is a well known semiconductor material used in numerous device applications. While c-Si is exceptionally useful in solid state electronics, it cannot be efficiently and cheaply deposited over large areas. Thus, c-Si is unsuitable for the production of devices requiring large area semiconductor film deposition, such as the photovoltaic cells used in solar panels and the thin film transistors used in flat panel liquid crystal displays.¹

In 1969, Chittick discovered that amorphous silicon thin films produced via the decomposition of silane (SiH_4) gas had superior electronic properties to films produced by evaporation.² Despite this progress, the properties of amorphous silicon (a-Si) remained substantially worse than c-Si. The primary impediment to device quality electronic performance was the existence of large numbers of dangling bonds within the a-Si film bulk. Dangling bonds arise from structural defects present in the film, giving rise to undesirable localized energy levels in the middle of the band gap. Subsequent research by Lewis suggested that hydrogen acts to terminate many of the dangling bonds, and thus reduces the number of defect states, yielding a higher quality hydrogenated a-Si (a-Si:H) film.³ In 1975, Spear and LeComber successfully doped a-Si:H with boron, a p-type dopant, and with phosphorous, an n-type dopant, making a-Si:H a viable material for semiconductor device applications.⁴

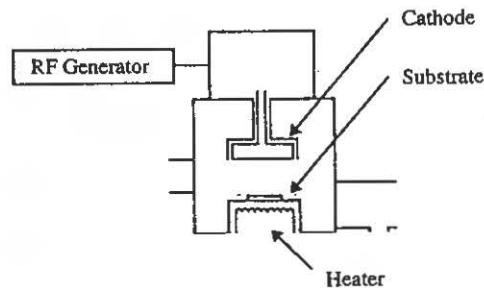


Figure 1
PACVD Apparatus

Since then, a-Si:H thin films have become important components in the photovoltaic cells used in solar panels, and in thin film transistors, which are used for switching operations in flat panel liquid crystal displays. Today, industrially produced a-Si:H thin films are grown exclusively by plasma assisted chemical vapor deposition (PACVD), in which an argon plasma is used to dissociate silane gas into reactive species that form a thin film when they impinge on the substrate (Figure 1).⁵ PACVD is used industrially rather than conventional (thermal) CVD because of the significantly lower temperatures to which the substrate can be subjected for successful film deposition. In fact, film deposition by PACVD even occurs at room temperature, though optimal film properties generally require a substrate temperature of 220 - 300 °C.

Numerous reactive species have been detected by a variety of characterization methods in plasmas containing silane and hydrogen gases.^{5,6} Most of these species, however, are short-lived or exist at low concentration. Mass spectral data reveals that an SiH_3 species is the silane

fragment present in the greatest abundance.⁷ While the fragmentation pattern of silane dissociation by electron impact has not been observed directly, calculations based on kinetic models of reaction and diffusion rates have suggested that SiH_3 is a product of secondary silane dissociation reactions, rather than being a primary dissociation product.⁸

Lin et al. have shown that a-Si:H film surfaces are rich in hydrogen.⁹ This suggests that SiH_3 species impinging on the film surface may react either by attaching to a dangling surface bond to become part of the film, or by abstracting a hydrogen atom from the surface, leaving a dangling surface bond and desorbing as silane.¹⁰ During film growth, hydrogen is incorporated into the amorphous film bulk, causing Si-H bonds in a-Si:H films to exist in a wide variety of environments. This diversity is evident when comparing the width of the infrared bands due to Si-H stretching modes to the sharp Si-H stretch peak produced by the ideally hydrogen terminated c-Si(111) surface.¹¹

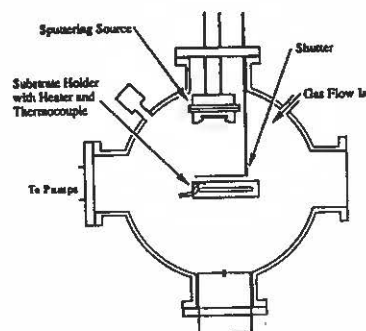


Figure 2
RMS Apparatus

The biggest disadvantage of PACVD is the need for the silane source gas, which, being toxic and flammable, poses a variety of safety hazards. As a result, alternatives to silane-based deposition techniques have been studied for some time. Only recently, however, have any of these techniques proved to be capable of depositing device quality a-Si:H films. In 1986, Rubel reported the silane-free growth of device quality films by the sputtering of a silicon target in the presence of hydrogen gas and a magnetically confined argon plasma.¹² This technique, known as reactive magnetron sputtering (RMS), has not yet been used in industrial production, but seems to be an attractive alternative to current PACVD deposition techniques (Figure 2).¹³ The utility of RMS deposition for low temperature device fabrication was recently demonstrated by McCormick and co-workers.¹⁴

Mass spectral data indicates that RMS deposition is dominated by energetic Si and SiH species being sputtered from the film.¹³ These species have multiple dangling bonds, and therefore have a high probability of reacting and being incorporated into the film immediately upon reaching the film surface.¹⁵ Infrared spectroscopy reveals that, as in PACVD grown films, Si-H bonds in RMS grown a-Si:H films exist in diverse environments.¹⁶

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