

CONTROL OF SILICON NETWORK STRUCTURE IN PLASMA DEPOSITION

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Controllability of the Si network structure ranging from amorphous to microcrystalline, polycrystalline, or epitaxial growth has been achieved in conventional glow discharge of silane by controlling the extent of hydrogen 'etching' during film growth. The concept of film formation as a balance between deposition and 'etching' of the growing surface is discussed. Since energetically unfavorable configurations are preferentially eliminated, 'etching' reduces the temperature required to remove weak or strained bonds and produces device quality a-Si:H. It is also responsible for achieving low temperature crystallinity.

1. INTRODUCTION

Plasma deposition is the most commonly used method for preparing device quality amorphous silicon (a-Si:H) films. Using non-conventional deposition methods of hydrogen radical enhanced chemical vapor deposition (HR-CVD), and spontaneous chemical deposition (SCD) where silane (SiH₄) is decomposed oxidatively by a gas phase reaction with F₂, Shimizu and co-workers showed recently that the propagation of Si network could be controlled to yield both amorphous and crystalline films by having SiH_nF_m precursors.^{1,2} We have found that such controllability of Si network structure can also be achieved in conventional plasma enhanced chemical vapor deposition (PECVD) of SiH₄ by H₂ dilution with SiH_n precursors. In fact structures ranging from amorphous to microcrystalline (μc), polycrystalline (poly), or epitaxial growth have been attained at low temperatures of 200-300°C. The key is to control the extent of 'etching' during film growth.

This paper discusses equilibrium and non-equilibrium film formation processes in the plasma deposition of Si and their effects on network propagation. The concept of film formation as a balance between deposition and hydrogen 'etching' of the growing surface is discussed, where 'etching' represents all reactions forming volatile species in the growth zone.

2. LOW TEMPERATURE CRYSTALLINITY

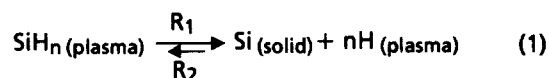
Adding large amounts of H₂ to SiH₄ in PECVD is known to produce μc-Si films.³⁻⁶ Previously, we

have studied the transition from amorphous to μc-Si, and reported the effect of hydrogen on the growth, structure, grain size, and properties of Si.^{7,8}

In addition to μc-Si, poly-Si^{7,8} and epitaxial films can also be obtained by H₂ dilution in PECVD, as shown in the cross-section TEM micrographs in Figs. 1 and 2, respectively. The dark field image in Fig. 1 shows columnar poly-Si grains of the order of ~1000 Å. The lattice images shown in Fig. 2 clearly demonstrate the epitaxial Si growth on Si (100) at a low temperature of 200°C. Thus, one can achieve a control of Si network structure in conventional PECVD having SiH_n precursors.

3. HYDROGEN 'ETCHING'

To understand such a controllability of network structure, film formation can be considered as a balance between deposition and hydrogen 'etching' of the growing surface.^{7,8} The net reaction can be expressed by the following:



where R₁ and R₂ correspond to the deposition and 'etching' rates, respectively. Similar concept was first proposed by Veprék and co-workers⁹ in explaining μc-Si film growth using chemical transport in a hydrogen plasma. Here we applied this idea to explain the controllability in the Si network propagation in PECVD with an emphasis on 'etching'.

The term hydrogen 'etching' here represents all reactions going in the reverse direction in Eq. 1 to

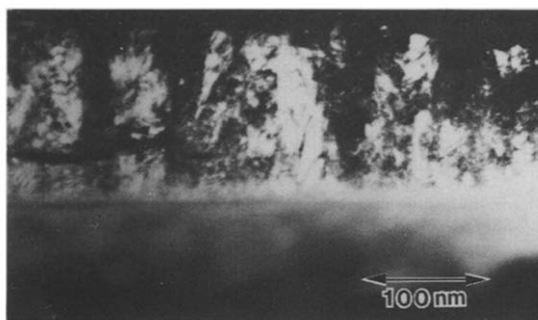
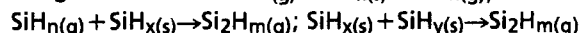


FIGURE 1

Dark-field cross-section TEM micrograph of polycrystalline Si films grown on Corning 7059 glass substrate at 200°C. (98% H₂, 10 W)

form volatile species. It takes place during film growth, and only occurs in the growth zone¹ consisted of Si segments with an abundance of H terminators. Thus it differs from the normal sense of etching that typically takes place after the film formation. Examples of such 'etching' reactions in the growth zone are: $H(g) + SiH_x(s) \rightarrow SiH_n(g)$;



Hydrogen dilution of SiH₄ pushes the reaction in the reverse direction, or increases R₂. This is evidenced by a strong reduction of the film growth rate with increasing H₂ dilution as shown in Fig. 3.

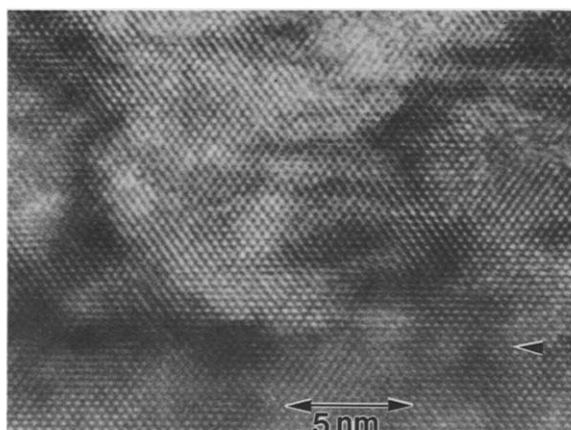


FIGURE 2

High resolution TEM micrograph of epitaxial Si films grown on Si (100) substrate at 200°C obtained by employing the lattice imaging techniques. The location of the film-substrate interface is indicated by the arrow. (98% H₂, 10 W)

The crystalline phase corresponds to the shaded region with strong H₂ dilution. Such a reduction is not due to the depletion of SiH₄, since a relatively high flow rate (~400 sccm total) is used in a small reactor with ~10 cm electrodes operated at a low rf power of 10W. The fact that comparable dilutions by inert gases such as He (Fig. 3), or Ar⁷ did not reduce the growth rate is also consistent with this explanation. Recently, van Oort found that H₂ plasma etched a-Si:H ~ 5-10 times faster than μc-Si.¹⁰

An advantage of 'etching' is the selectivity of stable configurations by preferential elimination of energetically unfavorable configurations. This explains the observed low temperature crystallinity.

'Etching' is also responsible for forming device quality a-Si:H by reducing the temperature required to remove weak or strained bonds.⁸ This is similar to the concept of 'chemical annealing' discussed by Shimizu in this volume.¹¹

Presumably F has a similar effect in controlling the network propagation as in HR-CVD and SCD.^{1,2}

4. EQUILIBRIUM & NON-EQUILIBRIUM PROCESSES

Under normal deposition conditions for a-Si:H, Eq. 1 is far from chemical equilibrium. Previous work showed that film formation processes in PECVD of a-Si:H have PVD and CVD-like regimes.¹² The main difference between the two is the larger R₁ in the former, partly due to the large sticking

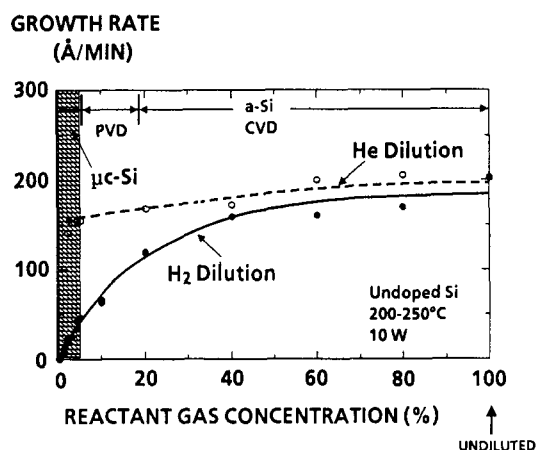


FIGURE 3

Film growth rate as a function of the reactant gas (SiH₄) concentration for hydrogen dilution (lower curve) and helium dilution (upper curve).

coefficient species involved. In both cases R_2 is too small to cause the nucleation and grain growth of the crystalline phase. Nevertheless, 'etching' is present even in the non-equilibrium processes. The finite R_2 eliminates weak or strained bonds, which is responsible for producing device quality a-Si:H at low temperature. However, such a small R_2 is insufficient to reduce most defects as R_1 becomes large in the PVD-like process.

Under the condition of large hydrogen concentration in the plasma, the reaction approaches a dynamic equilibrium,⁹ resulting in low temperature crystallinity. Since μ c-Si is often associated with slow growth^{6,8} one asks if crystallinity requires slow growth or certain levels of 'etching'. The correlation of the conductivity (σ) and growth rate is shown in Fig. 4, where σ was used as an indication of the crystallinity since the corresponding amorphous films are $\sim 10^3$ times less conductive. The result indicates that the crystalline structure was maintained although the growth rate was increased by ~ 5 times. Thus we believe that having certain minimum levels of 'etching' is more important for low temperature crystallinity than slow growth alone. If R_2 is increased by efficient generation of the etching species, one can obtain fast growth of the crystalline phase. In fact this is

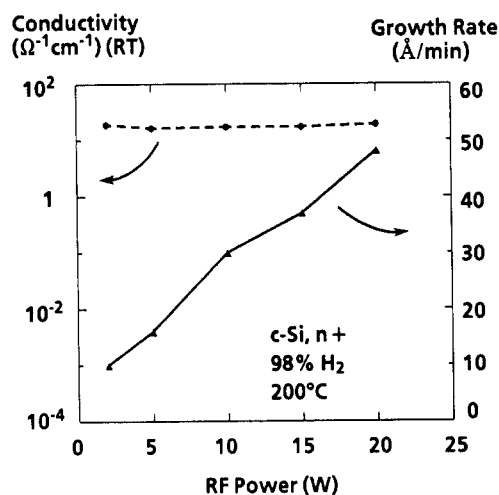


FIGURE 4

Room temperature conductivity and growth rate of n+ PECVD Si films vs. the rf power. Corresponding a-Si:H films have $\sigma \sim 10^{-2} \Omega^{-1} \text{cm}^{-1}$.

believed to be the case in HR-CVD or SCD.^{1,2}

5. CONCLUSIONS

The controllability of Si network structure ranging from amorphous to microcrystalline, polycrystalline, or epitaxial growth has been achieved in conventional PECVD at a low temperature of 200-300°C. And the key is to control the extent of hydrogen 'etching' during film growth. The concept of film formation as a balance between deposition and 'etching' of the growing surface has been discussed. The preferential elimination of energetically unfavorable configurations by 'etching' is believed to be responsible for achieving low temperature crystallinity, and producing device quality a-Si:H.

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