Dominant Reaction Channels and the Mechanism of Silane Decomposition in a H₂–Si(s)–SiH₄ Glow Discharge

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Chemical relaxation mass spectrometry has been used to study the kinetics and mechanism in the silane–hydrogen–solid silicon system under conditions of glow discharge. The emphasis was on the main processes related to the deposition of amorphous and nanocrystalline silicon thin films. It is shown that under conditions of the deposition of a-Si and nc-Si the dominant reaction channel is the electron impact induced fragmentation of silane into molecular hydrogen and SiH₂ radical. The role of other processes, such as hydrogen abstraction, is discussed.

KEY WORDS: Silane/silicon/hydrogen glow discharge; kinetics and mechanism; a-Si and nc-Si deposition; silicon etching.

1. INTRODUCTION

Amorphous (a-Si) and nanocrystalline silicon (nc-Si; also sometimes called “microcrystalline,” μ-c-Si) became important materials for a wide variety of devices as well as for fundamental solid state studies.¹ In order to achieve a better control of the properties of the deposited films, much work has been devoted to studies of the kinetics and mechanism of silane discharges (see, e.g., Refs 2 and 3 for a review). Worth mentioning in particular is the work of Turban et al.⁴,⁵ and the recent paper by Bruno et al.⁶a and by Robertson and Gallagher.⁶b The difficult problem associated with kinetic and mechanistic studies of this kind is the high complexity of the processes taking place under conditions of glow discharge. Thus, even an extensive experimental study using the conventional technique of plug flow⁶c or a closed system⁶d leaves a critical researcher with many open

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questions since, as a rule, the experimental kinetic data can be fitted by more than one theoretical model. These problems are mainly due to the fact that the time-dependent changes of the concentrations of the reactants and product species are followed on the macroscopic scale, i.e., one observes only the integral effects of many complicated microscopic processes.

A significant improvement has been achieved by using the chemical relaxation technique\(^{(9-11)}\) which has been recently adapted to mass spectrometric studies under glow discharge plasma conditions far away from thermodynamic equilibrium.\(^{(12,13)}\) This technique allows one to follow, on the microscopic time scale, the response of the concentration of various species (neutral and charged) present in the reactive plasma to a sudden, small change of the steady state of the complex system. In such a way, most of the problems associated with the above-mentioned experimental approaches are avoided and, in many instances, unambiguous results can be obtained.

In this paper we shall first summarize some previous data in an updated, more quantitative way and, afterwards, present new results of our kinetic and mechanistic studies. These will show clearly that in a weak discharge, which is typically used for the deposition of a-Si, the electron impact fragmentation of silane into \(\text{H}_2\) and \(\text{SiH}_2\) radical is the dominant reaction channel of silane decomposition. The conditions under which hydrogen abstraction may be important will be discussed on the basis of the experimental data.

The experimental results will be complemented by calculations of the rates of several subsequent steps in the complex reaction system. Their comparison allows us to propose the dominant mechanism of silicon deposition as a function of the reactor geometry and silane concentration.

Our primary goal is to find conditions under which polymerization in the gas phase is suppressed and only SiH\(_x\) monomers reach the surface of the substrate. It is well known that the homogeneous nucleation in the gas phase has to be avoided if good quality films are to be deposited.

2. EXPERIMENTAL

The experimental apparatus used in the present studies was described in our previous paper.\(^{(12)}\) For the present work the following improvements have been made:

1. The signal processing has been performed with the help of a personal computer (Apple II E) connected directly to the Datalab model 4000B signal averager. Typically several ten thousand scans were sampled and averaged in the Datalab signal averager, and the resultant signal with a sufficient signal-to-noise ratio has been used for the evaluation of the kinetic