MASS SPECTROMETRY OF GLOW DISCHARGES IN ATMOSPHERES CONTAINING SILANE, PHOSPHINE OR DIBORANE

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ABSTRACT

The dependence of the amounts of di- and trisilanes existing in a monosilane plasma on the r.f. power and on the silane flow was investigated. Deposited doping atoms are partly released in a plasma containing H₂ and form a doping profile in the growing a-Si:H layer. After the reactor has been cleaned in a CF₄/O₂ plasma etching process, F atoms are left on the walls and react with SiH₄, influencing the properties of subsequently manufactured solar cells.

1. INTRODUCTION

Thin films of hydrogen containing amorphous Silicon (a-Si:H) formed by a low pressure glow discharge are a fundamental material for solar cells. The properties of the deposited doped and undoped a-Si:H layers depend on the composition of the plasma. We have therefore investigated neutral and ionic particles in SiH₄, PH₃ and B₂H₆ r.f. glow discharges by mass spectrometry.

2. EXPERIMENTAL

The investigations were carried out in a stainless steel reactor. A differentially pumped quadrupole mass spectrometer (MS) was mounted at the side similar to the system in /1/. The r.f. power (13.5 MHz) was capacitively coupled to the plasma. The electrodes could be heated (250°C), their diameter was 13 cm, their distance 4 cm. The gases used were pure SiH₄ as well as mixtures of 10 % PH₃ in H₂ and of 10 % B₂H₆ in H₂, and the etching gas CF₄/O₂. The typical pressure was 0.2 mbar.

3. RESULTS

3.1 SILANE

Silane is dissociated completely in the ionization chamber of the MS at ionization voltages = 30V. Only the particles SiHₓ (x = 0 - 3) are detectable. While a glow discharge is burning the relative portions of SiHₓ depend only on the ionization voltage of the MS and not on the r.f. power.
in the plasma (≤20 W) in analogy with Turban's findings /2/.

In addition di- and trisilanes Si_2H_x (x = 0 - 6) and Si_3H_x (x = 0 - 8) appear in the plasma. If the reactor is filled with SiH_4 up to a pressure of 0.2 mbar and if after closing all valves a glow discharge is started, then time dependent concentrations of the gaseous species appear as is shown in Fig.1. The concentration of disilanes increases quickly during the first three minutes and then the ratio of the intensities of di- and monosilanes remains nearly constant. This ratio decreases slightly after about 12 minutes. The reason for this may be the increasing hydrogen pressure.

When the glow discharge is interrupted, the intensities of all neutral particles SiH_x, Si_2H_x and Si_3H_x do not change, and remain constant for at least one hour. Therefore it can be assumed that during the discharge only the stable neutrals SiH_x, Si_2H_x, and Si_3H_x reach the quadrupole, whereas neutral radicals cannot be detected.

In steady state operation concentrations of polysilanes are formed, which result from the generation rate depending on the used r.f. power, and from the removal, which depends on the gas flow (Fig.2). The time in which the steady state condition is reached depends on the silane flow and on the volume of the reactor. It amounts to about one minute in our experiments (flow = 20 sccm, volume = 20 l), in accordance with investigations by means of optical emission spectroscopy /3/. This relatively long time produces variable properties of the a-Si:H in the first sheets of the layer, as they are known from the dependence of the electrical properties on the layer thickness /4/.

It is known /5/ that a-Si:H film deposition rates compared to SiH_4 are about 20 times greater for Si_2H_6 and Si_3H_6. As the concentrations of the polysilanes depend on gas flow, r.f. power, and reactor volume, the deposition kinetics are remarkably influenced by these parameters.

3.2 DOPING GASES

PH_3 is partly dissociated in the ionization chamber of the MS. The relative portions of the neutral particles PH_x (x = 0 - 3) in a phosphine plasma (10 % PH_3 in H_2) do not depend on the r.f. power in the plasma (≤20 W), whereas the relative portions of neutral diphosphines P_2H_x (x = 0 - 4) formed in the plasma depend slightly on the power. For an r.f. power ≤15 W the neutrals PH_3 and P_2H_x appear additionally (Fig.3). Thus, in contrast to the silane plasma, neutral radicals can be detected in this case. The triphosphines P_3H_x (x = 0 - 6) were observed in ionized form only.

The ion mass spectrum of a silane-phosphine plasma is a superposition of the spectra of the single gases. However, the ion mass intensities with the mass numbers 65 and 95
are clearly stronger. These additional ions can be defined as \( \text{SiPH}_6^+ \) and \( \text{SiP}_2\text{H}_5^+ \) (or \( \text{Si}_2\text{PH}_8^+ \)), respectively.

In a diborane plasma (10\% \( \text{B}_2\text{H}_6^+ \) in \( \text{H}_2 \)) polyborane ions can be found in the shape of \( \text{B}_x\text{H}_y^+ \) (\( x \geq 1 - 6 \)). These polyboranes can be deposited as high polymers on walls causing the known disadvantageous delayed Boron escape leading to uncontrolled incorporation in the a-Si:H layers. In the ion mass spectrum of a silane-diborane plasma the \( \text{SiBH}_4^+ \) ion is present additionally.

If a \( \text{H}_2 \) plasma is started after the deposition of a pure P or B layer and after the reaction gas has been pumped down, phosphines or diboranes respectively reappear in the neutral mass spectrum (Fig. 5). We can conclude from this result that, after a deposition of doped a-Si:H during the deposition of pure a-Si:H, doping atoms from the walls are released. These atoms are then incorporated in the intrinsic a-Si:H layer and thus form a doping profile.

If a multichamber system is used, this effect can be reduced but not eliminated completely. For it is true that in this case doping atoms no longer stay on the walls, but exist nevertheless on the substrates. This effect has to be taken into account if a well-defined B profile is to be adjusted in the 1-layer for optimized efficient and stable cells /6/. As undoped a-Si:H typically shows a slight n-type conductivity, it is desired to carry off B atoms, but not P atoms. This carrying off is the reason that pin solar cells usually have better electrical properties than nip cells.

3.3 CF\(_4\)/O\(_2\) ETCHING GAS

While it is possible to clean the inner parts of experimental reactors, after they have been demounted, by a wet chemical etching process, it is easier to clean an in-line system in a plasma etching process by means of an etching gas containing fluorine. After such an etching process in a CF\(_4\)/O\(_2\) plasma, fluorine atoms are left on the reactor walls and can not even be removed by an \( \text{Ar} / \text{H}_2 \) glow discharge lasting one hour. If an a-Si:H deposition is carried out after the etching process, the silane reacts with the fluorine atoms while it is flowing in. In the mass spectrum appear Si-F-H compounds (Fig. 5). The concentrations of these compounds decrease during one hour of a-Si:H deposition, but they do not disappear completely. The supposition that fluorine atoms are incorporated in the a-Si:H layer could be confirmed by SIMS analysis /7/. These fluorine atoms can influence the electrical properties of the layers. This result was used to find conditions for the manufacturing of solar cells, so that their performance is uneffected after the plasma etching process in a multichamber plant /7/.
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REFERENCES


Fig. 1: Time dependence of the concentrations of mono- and disilanes after starting a silane glow discharge
Fig. 2: Disilane portions in silane glow discharges

Fig. 3: Mass spectral intensities of neutral particles
Fig. 4: Concentrations of neutral $P_xH_y$ and $B_xH_y$ particles

Fig. 5: Concentrations of F containing particles during a-Si:H deposition after a plasma etching process with $CF_4/O_2$