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DEPOSITION TECHNIQUES FOR AMORPHOUS SILICON FILMS

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ABSTRACT

Chemical vapor deposition, sputtering, laser decomposition and glow discharge are some of the techniques utilized for the deposition of amorphous silicon. A broad outline of these deposition techniques will be given and the characteristics of the deposited material examined. Particular attention will be devoted to the glow discharge process which is the most widely utilized technique for the deposition of amorphous silicon utilized in the production of photovoltaic cells.

1. INTRODUCTION

Thin films of amorphous silicon, particularly those containing hydrogen in the solid network, (a-Si:H), posses considerable electronic properties for specific applications (solar cells, transitors for electronic devices, etc.). The processes by which one can deposit silicon films are numerous and very often confusing. One of the most recent comprehensive reviews covering many theoretical and practical aspects of thin film deposition is the book edited by J.L. Vossen and W. Kern /1/. Aim of this note is to provide a broad outline of some basic and practical methods for silicon film deposition, and to analyze some properties of the material produced.

The methods selected can be distinguished in: a) conventional processes (chemical vapor and sputter deposition) by which polycrystalline and amorphous films can be obtained - b) non conventional processes (Reactive sputter and laser deposition, plasma deposition) by which hydrogenated and doped films can be realized during the growing process.

2. CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is a method of film formation based on purely chemical processes in the vapor phase. It has been defined /1/ as material synthesis process in which the constituent of the gas or vapor phase reacts to form a solid film on a selected substrate.

The great variety of chemical reactions (pyrolysis, reduction, etc.) which can accour in CVD processes and the large number of simple or complex compounds which can be deposited have made this method one of the most important and versatile method of film deposition at relatively low temperature.

A reactor system for carryng out CVD processes must satisfy the following requirements: a) it must allow controlled transport of reactant and diluent gases in the reaction chamber; b) it must provide heat to the substrate to mantain a given temperature; c) it must remove safely the gas reaction products. The geometry and the material of the reactor are determined by the chemical and physical parameters of the process.

For silicon films deposition, reactors operating at low pressure in the range of 0.1 - 10 torr are commercially available. In fig. 1 a schematic drawing of a typical low pressure reactor is shown. A series of resistances provides the controlled heat to the reactor walls in the reaction zone; so that the same deposit as on the substrates is obtained on the reactor walls as a consequence of the thermal equilibrium. The density and the good adherence of the deposit to the wall, togheter with the vertical configuration of the substrate holder, reduce the possibility of film contamination.

Thin silicon films that can be prepared by CVD are generally the results of pyrolitic or thermal decomposition of silane at the hot susceptor surface or of reduction process of various chlorosilanes.

The reactants are injected in mixture with Hz , sometimes also with carrier gas He (generally 99% of carrier gas and 1% of reactant). The deposition temperature does not exceeds 600°C when silane is used, but can be up to 1200°C with chlorosilane.

The structure of the deposited films is directly related to deposition parameters (gas composition, pressure, substrate and its temperature etc.). Epitaxial or polycrystalline are the two most common structure which are obtained. Sometimes amorphous silicon is also obtained.

3. NON-REACTIVE SPUTTER DEPOSITION

Sputter deposition has become a generic name for a variety of processes. Fig. 2 shows a simplified cross section of a Diode Sputtering System, which uses a plate of material to be deposited as the cathod electrode of a glow discharge. The target is connected to a negative voltage supply and is faced to the substrate holder. The holder may be grounded, floating or biased. With this type of system, material can be transported from the target to the substrate and deposited as film. The sputtering gas is an inert gas, generally argon, which is introduced into the reactor chamber to provide the medium in which the glow discharge is initiated and maintained. Gas pressures from few millitorr to about 100 torr can be used. The surface of the deposited film is in constant contact with the plasma, so that the structure and the physical properties of the film will depend not only on the nucleation and growth mechanism, but also on the plasma species. When the glow discharge (which can be also radio frequency operated) is started, positive ions strike the target plate and remove mainly neutral atoms by momentum transfer. There is the formation of vapors of material target, which condense into thin film on the substrate.

For a given target material both rate and uniformity of deposition process are influenced by system geometry, target voltage, sputtering gas pressure and power input.

The main characteristic of the sputtering processes is the versatility, both in term of materials that can be deposited and process parameters that can be adjusted to tailor the properties of the films deposited.

In general the silicon films produced by sputtering contain a high overall level of gap states associated with dangling bonds in probably quite an extensive microvoid structure, with the consequence that the material presents low values of photoconductivity and is scarsely affected by doping. Some of these undesirable affects can be reduced if deposition is made by reactive sputtering.

4. REACTIVE SPUTTERING

Reactive sputtering is a chemical sputtering which involves the raction of an excited neutral or ionized gas with a surface to form volatile compounds. This technique is mainly used for plasma etching of semiconductors material. The target is a nominally pure metal, alloy, or mixtures of species which can be transformed into compounds by sputtering in a pure reactive gas or an inert gas-reactive mixture. The reactive gas either is or contains the chemical species required to synthesize the desired compound.

W. Paul and his coworkers /2,3/ showed that, by adding hydrogen to the argon used in the sputtering process, a few atomic percent can be incorporated into the film. This has a marked effect on the electronic properties of the material in that the dangling bonds present in amorphous silicon are saturated by hydrogen atoms.

5. CHEMICAL TRANSPORT IN HYDROGEN PLASMAS

This system might be considered intermediate between chemical sputtering and CVD. It consists essentially in a hydrogen d.c. glow discharge, where in a zone (charge zone) of the positive column there are small pieces of crystalline silicon and in an another zone (deposition zone) there is the substrate on which the film is deposited. In the charge zone, volatile hydrides are formed, which then decompose on the hot substrate. The apparatus is shown in Fig. 3. With a similar system hydrogenated microcrystalline and amorphous silicon has been obtained by Veprek et al. /4,5/. They found that the deposition of hydrogenated silicon is the result of the following heterogeneous equilibrium: $Si(s) + x\,H \rightleftharpoons SiH_x(g)$, which is influenced by both the discharge current intensity and temperature gradient between the solid and gas phase. The forward reaction occours in the vicinity of solid silicon which is mantained at $\sim$ 10°C of temperature, while the reverse one, which is responsable of the film formation, take place in the deposition zone which is mantained at temperatures above 100°C. One has therefore a chemical transport of silicon from the charge to the deposition zone. The deposited silicon, which has been fully characterized, has been found to present electronic properties very similar to that deposited from SiH_4 glow discharge /6,7/.

6. DEPOSITION BY LASER PHOTODISSOCIATION

The use of laser source, in the infrared, visible and ultraviolet wavelength range, for deposition processes is becoming every day more promising.

One of the most recent use of this technique is the deposition of a-Si:H from SiH_4 by means of the resonant absorption of a CO laser radiation /8/. SiH_4 , in fact, presents a strong absorption, due to one of the fundamental modes (ν_4 bending at 913.3 cm^{-1}), for some high gain lines of the P branch emission of CO laser (λ = 10.59 m) and can be dissociated under appropriate operative conditions. The decomposition products of the photochemical process can lead to the growth of a-Si:H film. The hydrogen content within the film depends on the substrate temperature, which is generally kept below 400°C. This apparatus operates at SiH_4 partial pressure of few torr and total pressure above 10 torr, with total flow rate of about 5 sccm. The deposition rate of this system depends on laser intensity, SiH_4 pressure, substrate temperature and gas carrier (generally Ar or N_2).

7. PLASMA DEPOSITION

The technology of thin films produced by plasma deposition processes is fast outrunning the scientific understanding of their detailed properties. The physics of the deposition process, the chemical knowledge of the kinetics of formation, the nature of film microstructure are just some of the now emerging investigations on the subject.

Low pressure plasmas can contain electrons with energies between 1 and 10 eV and density of the order 10^{10} cm^{-3} . The electron temperature may be tens of thousands of degrees, while that of gas only few hundreds, so that the electrons posses sufficient energy to excite molecules, atoms, and break molecular bonds. One of the prime motivating factors in utilizing glow discharge plasma deposition is that the substrate can be kept at relatively low temperature. The films deposited by plasma reactions are generally amorphous or microcrystalline, with short-range structural ordering and contain variable amount of hydrogen incorporated. The reactor designs and the experimental conditions for thin film deposition are numerous. The basic components of a plasma system are: a) the reactor, generally a quartz or pyrex tube; b) the power source, generally radiofrequency; c) a matching network to transfer the power from the generator to the plasma gas; d) gas flow system, with regulators and controls; e) the pumping system with the pressure measurement instruments.

Most of the early work for producing silicon films have utilized rf electrodeless glow discharge, operated within a frequency range of 0.5-13.5 MHz, at power levels of some tens of watts, with SiH_4 flow rates of the order of few CM per minute (sccm), at pressure in the range 0.1-2 torr.

A better uniformity has been achieved with capacitive discharge systems, with parallel plate electrodes inside the discharge chamber. Deposition rates of several hundreds of Å min^{-1} can be obtained with both systems.

A dc discharge in SiH_4 has also been used to deposit a-Si:H film.

The electronic properties of the deposited films are critically dependent on a great number of variables such as the substrate temperature, gas flow rate, pressure, power input, feed composition /9/.

With this film deposition technique, doping from the gas phase can easely be achieved by adding to silane small, but accurately measured amounts of V or III group hydrides (such as PH_3 or B_2H_6).

The introduction of halogen atoms into hydrogenated silicon films has been found to give a better thermal and electrical stability to the deposited material /10/.

Hydrogenated silicon films with chlorine atoms incorporated have been prepared in our laboratories by feeding the glow discharge with mixtures of $SiCl_4$ and H_2 /11/.

A schematic drawing of the apparatus used is shown in Fig. 4. The reactor is capacitively coupled to the radiofrequency generator (35 MHz) by means of two external annular electrodes and the substrate (sapphire, alumina, tantalum, corning glass, crystalline silicon, fused quartz and stainless steel) are placed on a holder which is temperature controlled. A system of laser interferometry allows the determination "in situ" of the film thikness and deposition rate during the growing process. The main deposition parameters with the relative ranges investigated, are: Total Flow Rate, Φ_T (sccm) 30-120; Feeding Ratio, R_{SiCl_4} 0.03-0.15; Power, W(watt) 15-200; Pressure, P(torr) 0.5-4.5; Deposition Temperature, T (°C) 175-430.

A wide characterization of the material obtained has been carried out /12-14/. The structural analysis, /13/ has shown a material of microcrystalline nature with grain size ranging between 40-200 Å, with hydrogen contents ranging between 1 and 4 at.% and chlorine ranging between 1 and 3 at.%. Visible absorption spectra have been used to derive absorption coefficient, refraction index and optical gap, the values of which have been found to be very close to those obtained on silicon films deposited from silane /15/.

The dependence of the deposition rate on the discharge parameters (pressure P, $SiCl_4/H_2$ ratio R_{SiCl_4}, and substrate temperature T_D) have indicated that although the crystallite sizes of the deposited films depend in a complex way on all discharge parameters, at the end they are strictly related to the deposition rate. These results have been interpreted on the basis of a simplified reaction scheme, which involves an equilibrium between deposition and etching processes /16/.

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CAPTIONS TO THE FIGURES

Fig. 1 - Schematic diagram of a low pressure CVD reactor. (After ref. 1).

Fig. 2 - Schematic diagram of simple diode sputtering system.

Fig. 3 - Simplified diagram of chemical transport reactor.

Fig. 4 - Apparatus for plasma deposition of a-Si:H,Cl from $SiCl_4/H_2$ gas mixtures.

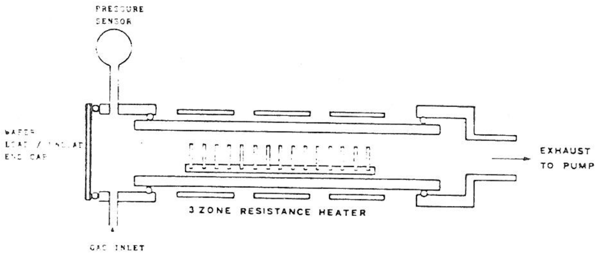

Fig. 1.

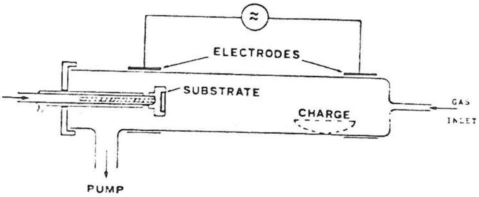

Fig. 2.

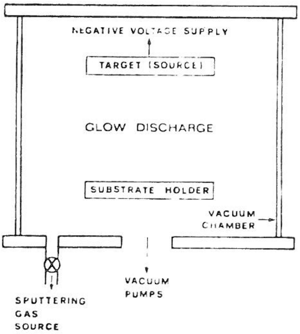

Fig. 3.

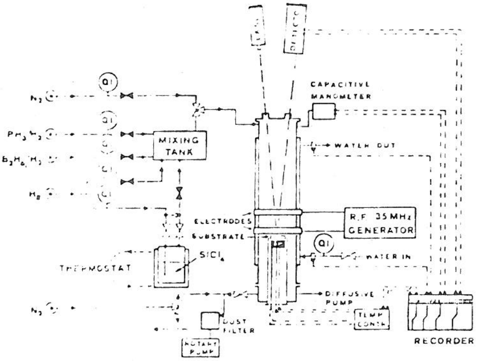

Fig. 4.