Amorphous hydrogenated silicon films prepared from a glow-discharge

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Abstract. From a detailed study of electrical and optical properties of amorphous hydrogenated silicon prepared from a mixture of 10% silane and 90% hydrogen, it is shown that the properties of the films compare favourably with the best reported results on those prepared from 100% silane.

Keywords. Amorphous semiconductors ; solar cells.

1. Introduction

There has been a great deal of interest in recent years in the study of amorphous silicon films prepared by the glow-discharge decomposition of silane (SiH_4). It was first demonstrated by the Dundee group (Spear and Le Comber 1972, 1975; Madan *et al* 1976) that these materials contain very low density of states in the gap and can be doped *n* or *p* type by the addition of impurities. It is now established (Triska *et al* 1975) that these films contain significant amount of hydrogen which get attached to the dangling bonds thereby reducing the states in the gap. One of the interesting features of the so-called amorphous hydrogenated films (a-Si : H) is the fact that the optical band gap is between 1.6 to 1.8 eV and the absorption constant in the visible region of sunlight is much larger than that in crystalline silicon so that solar radiation can be absorbed in a film only 1 μm thick. This, coupled with the fact that this material has a reasonably large electron lifetime, makes it an attractive candidate for a solar cell material. In fact, a-Si : H solar cell has been fabricated with about 5.5% efficiency (Carlson and Wronski 1976) and a very intensive effort (Brodsky 1979) is going on to make viable solar cells using this material for large scale terrestrial applications. Simultaneously, there is a great deal of activities to understand the basic properties of the material (Brodsky 1969).

We have been working on the study of properties of a-Si : H films prepared by the glow-discharge technique. In this talk, I shall briefly describe some of the results that we have achieved.

2. Sample preparation

The glow-discharge technique involves the breaking of the molecular bonds of a suitable gas in a plasma. In the most commonly used method (Chittick *et al* 1969), a low pressure (0.1 to 1 torr) of pure silane is maintained in a glass chamber and the plasma is maintained inside the chamber by the application of a field. An r.f. field is very frequently used and the plasma can be maintained either by inductive or by capacitive coupling. It is also possible to decompose silane by d.c. capacitive discharge. It is now known that the reaction kinetics is quite complex and in the breaking up of silane, the plasma contains (Matsuda *et al* 1980) SiH , SiH_2 and SiH_3 and the property of the film depends critically on plasma conditions (Brodsky 1977) and the reaction of the plasma with the surface of the film being grown.

We have used d.c. capacitive discharge of a SiH_4 (10%)- H_2 (90%) mixture for depositing the films. The dilute mixture rather than 100% silane is used since it is inexpensive and less hazardous. The schematic experimental set-up is shown in figure 1. The substrate is placed on the cathode and the substrate temperature can be varied between 300 to 600 K. Typical parameters during deposition are as follows: pressure: 0.6 torr, substrate temperature: 600 K and flow rate: 1 cc/sec. The electrode separation is about 5 cm. A high temperature oven is kept between the reaction chamber and the rotary pump to crack up any unreacted silane. The reaction chamber is evacuated to 10^{-3} torr with a sorption pump and thoroughly baked before silane is introduced. Typical growth rates are about 1 Å per second.

3. Sample characterisation

Since the property of the film depends critically on plasma conditions, it is necessary to carry out a large number of measurements to characterise the film. The

Figure 1. Schematic diagram of experimental set-up for deposition of amorphous silicon.

activation energy and hence the position of the Fermi level can be determined by the measurement of conductivity as a function of temperature. Measurement of optical absorption near the fundamental absorption edge gives the optical band gap. In order to find out how much hydrogen has been incorporated in the film one can use a variety of techniques (Fang *et al* 1980). A very simple method is to use infra-red absorption (Brodsky *et al* 1977) since the stretching mode of silicon-hydrogen bond gives a peak at around 2000 cm^{-1} .

Information regarding the states in the gap can be obtained from photoconductivity measurements (Anderson and Spear 1977). These experiments give us the $(\mu\tau)$ product where μ is the mobility and τ is the lifetime of the carriers and hence reflect the quality of the films. A more direct information regarding the states in the gap can be obtained from field effect measurements (Spear and Le Comber 1972; Madan *et al* 1976) where one applies a gate voltage perpendicular to the sample surface and the modulation in the conductivity can be related to the distribution of states in the gap. The other tests that can be used for checking the quality of the film are (i) the ideality factor of the conduction across the Schottky barriers (Deneuville and Brodsky 1979), (ii) the frequency dependence (Snell *et al* 1979) or the time dependence (Cohen *et al* 1980) of the capacitance of the Schottky barriers.

4. Experimental results

A typical plot of conductivity as a function of temperature is shown in figure 2. The plot is linear down to about 250 K indicating a low density of gap states. The

Figure 2. Plot of dark conductivity as a function of temperature.

activation energy is typically between 0.6 to 0.7 eV. Optical absorption (α) of the films has been measured and figure 3 shows the plot of $(\alpha h\nu)^{1/2}$ as a function of incident energy $h\nu$. Typical optical gaps are found to be between 1.8 to 1.9 eV. These results are in agreement with those reported for films prepared from 100% silane. In order to find out the hydrogen content in the film, we have measured the infra-red absorption spectra of films deposited on polished high resistivity silicon substrates. A typical spectrum is shown in figure 4. The stretching mode of singly bonded hydrogen at 2000 cm^{-1} is observed; the peak at around 630 cm^{-1} is due to the wagging mode. From the integrated absorption at 2000 cm^{-1} due to the singly-bonded hydrogen, we estimate the hydrogen content in the films to be around 30%.

We also note from the absorption spectrum that the peak at 2080 cm^{-1} which is associated with doubly bonded hydrogen (Brodsky *et al* 1977) is absent in our film. Since presence of doubly bonded hydrogen in glow-discharge films usually results in poor quality material, the observed absence is a desirable feature. We must add however that this interpretation is not unambiguous since in a-Si:H prepared from glow-discharge decomposition of silane-argon mixture, the presence

Figure 3. Plot of optical absorption as a function of incident energy.

Figure 4. Infrared absorption spectrum.

of doubly bonded hydrogen does not affect the quality of the film. A more direct test for the quality of our film is obtained from photoconductivity measurements. The room temperature photoconductivity for incident photon flux of $10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ from a He-Ne laser is 10^{-5} to $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. This compares favourably with the best results obtained from other laboratories. One should note that the magnitude of photoconductivity depends on the position of the dark Fermi level (Anderson and Spear 1977) and hence comparison has been made with material of similar activation energy. The intensity dependence of photoconductivity is shown in figure 5. One finds an intensity dependence of the form I^ν with ν close to 0.8 over the entire intensity range. This reflects a continuous exponential distribution of electron traps (Rose 1963) in the material and agrees with the results obtained by the RCA Group (Zanzucchi *et al* 1977) on d.c. discharge a-Si:H. We have also carried out field effect and photoluminescence measurements on our films. Field effect measurements show that the density of states at the Fermi level of our film is between $5 \cdot 10^{16}$ to $10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$. The photoluminescence intensity compares favourably with that obtained from a sample obtained from the Marburg Group of comparable thickness deposited by decomposition of 100% silane.

Table 1 summarises the properties of our films prepared from 10% SiH_4 -90% H_2 mixture; also shown are some of the best results reported for films prepared from 100% silane. We find that the results are comparable. This has interesting technological implications since the dilute mixture that we use is much cheaper and less hazardous than 100% silane. We have also established the device grade quality of our material by fabricating Pd-Schottky diodes (Pietruszko *et al* 1980) with barrier heights of 0.9 eV and ideality factor of 1.2.

Another interesting property of the film that we make is the absence of significant light-induced change in dark conductivity. It has been observed by several

Figure 5. Plot of photoconductivity as a function of light intensity.

Table 1. Comparison of properties of a-Si films prepared from 100% silane and 10% silane-90% hydrogen mixture.

	Pure silane	Silane-hydrogen mixture
High temperature activation energy	0.6 to 0.8 eV	0.6 to 0.7 eV
Room temperature dark conductivity	10^{-9} to 10^{-7} ohm $^{-1}$ cm $^{-1}$	10^{-9} to 10^{-8} ohm $^{-1}$ cm $^{-1}$
Room temperature photoconductivity at intensity 10^{15} cm $^{-2}$ sec $^{-1}$	10^{-5} ohm $^{-1}$ cm $^{-1}$	10^{-5} to 10^{-4} ohm $^{-1}$ cm $^{-1}$
Optical gap	1.6 to 1.8 eV	1.8 eV
Absorption constant at		
(1) 2000 cm $^{-1}$	$5 \cdot 10^2$ to 10^4 cm $^{-1}$	1 to 2 10^3 cm $^{-1}$
(2) 2080 cm $^{-1}$	Nil	Nil
Photoluminescence intensity (arbitrary units)	1	1
Density of states at Fermi level from field effect	$5 \cdot 10^{16}$ to 10^{17} cm $^{-3}$ eV $^{-1}$	$5 \cdot 10^{16}$ cm $^{-3}$ eV $^{-1}$

groups (Staebler and Wronski 1977; Fuhs *et al* 1978; Tanielian *et al* 1978) that films prepared by r.f. or d.c. discharge of silane or silane-argon mixture show a drastic change in dark conductivity on exposure to AMI sunlight for some time. As for example it has been shown by the RCA group (Staebler and Wronski 1977) that an exposure to AMI light for 4 hr decreases the dark conductivity by as much as four orders of magnitude. The original conductivity can be restored by annealing at 150° C for a few hours.

We have carried out experiments to study the effect of light exposure on our samples. The samples are heat dried at 150° C before exposure and the experiments are carried out when the samples are in vacuum. We find that exposures of AMI light for 2 hr reduces the dark conductivity typically by a factor of five (figure 6). This is much smaller than the reported results on 100% silane deposited films. The original conductivity can be restored by annealing at 150° C.

Various mechanisms have been put forward to explain this effect which is not very desirable from the device point of view. These are (i) existence of band bending at the film substrate interface (Solomon *et al* 1978), (ii) existence of band bending at the film-vacuum (air) interface (Goodman *et al* 1980) and (iii) creation of traps in the bulk of the material due to photo-structural changes (Staebler and Wronski 1977). In the first two cases, it is assumed that positive charges at the surface or interface give rise to accumulation layers of higher conductivity which dominate the conduction in the film. The electrons generated on exposure to light neutralise these charges thus removing the band bending; the conductivity in this case is the true bulk conductivity. While it is true that presence of accumulation layers at the top or bottom of the film can give rise to light effects, there is evidence from measurements on Schottky barrier diodes (Jousse *et al* 1980) that light degradation may come from bulk effects. The absence of light-induced effects in our film indicates that none of the three mechanisms that can contribute to this effect is important. From field effect experiments, we have observed that

Figure 6. Conductivity of the sample before, during and after exposure to light.

there is no significant band bending at the film-substrate interface; in a properly heat dried sample, the band bending at the top is also absent (Guha *et al* 1980). The absence of significant light degradation effect also shows that photostructural changes are not very important in our films.

5. Conclusions

We have been able to prepare high quality amorphous hydrogenated films by glow-discharge decomposition of a SiH_4 (10%)- H_2 (90%) mixture. Since a dilute mixture rather than 100% silane is used, the method is more inexpensive and less hazardous. The films are found to be more stable against prolonged light exposure.

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