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COMPARISON OF AMORPHOUS SILICON (a-Si:H) PREPARED IN RADIO AND MICROWAVE FREQUENCY GLOW DISCHARGES

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ABSTRACT

Amorphous silicon has been prepared in electroded and electrodeless glow discharges at several frequencies. The sample materials have been characterized using a variety of physico-chemical techniques, which clearly show that some properties are substantially less structure-sensitive than others. Samples made by electrodeless discharges tend to be quite rich in C and O contaminants; it is felt that these are introduced after deposition, and that they correlate with columnar morphology. The lesser incidence of these defects in samples from electroded discharges is felt to be related to ion bombardment annealing of the sample during growth.

1. INTRODUCTION

Over the past ten years, research on amorphous hydrogenated silicon (a-Si:H) has increased dramatically, since this material has proven to be very attractive for use in photosensitive devices, particularly low-cost solar cells (1). Many workers have prepared a-Si:H from silane (SiH_4) using d.c., audio- or radio-frequency (r.f.) plasmas. This laboratory is among the few to also use microwave discharges(2).

In plasma deposition processes, a sizeable number of fabrication variables must be controlled; this is particularly critical in the preparation of a-Si:H having photoconductive properties. The primary purpose of the work reported here was to examine the effects of frequency and coupling of the applied exciting field on the production of photoconductive material. Several deposition systems have been used: A capacitively coupled (electroded) radiofrequency (r.f.) reactor operating at f_1 = 450 kHz; an electrodeless reactor system in which an inductively coupled r.f. plasma (f_2 = 13.56 MHz) or a microwave (m.w.) plasma (f_3 = 2.45 GHz) could be generated. The electron-neutral collision frequency, ν, being about 100 MHz in Ar at 200 mTorr(3), f_1 and $f_2 < \nu$, and $f_3 > \nu$. On this basis one might expect fundamental plasma-physical and -chemical processes to differ in the two cases. Furthermore, as f_2 and f_3 are ISM frequencies, they are of particular interest for potential commercial production of a-Si:H.

2. EXPERIMENTAL

The electroded and electrodeless systems have been described in detail(4). The only difference is that, in this work, the microwave applicator was

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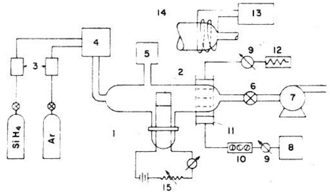

Fig. 1: Schematic diagram of electrodeless deposition system. 1, Reactor vessel; 2, heated sample holder; 3, electronic flowmeter/controllers; 4, mixing manifold; 5, capacitive manometer; 6, automatic throtting valve; 7, turbo-molecular pump; 8, 2.45 GHz power supply; 9, power monitors; 10, triple stub tuner; 11, slow wave microwave applicator; 12, dummy load; 13, 13.56 MHz power supply; 14, inductance; 15, substrate heater supply.

placed transverse to the reactor axis, permitting us to confine the plasma to a narrow region downstream from the sample holder (Fig. 1); the same is true for the inductor.

As in earlier work, Ar-SiH$_4$ mixtures were used as feed gas; in the present case, however, the mixture was richer in Argon:

$$1.5 < X_g < 9; \quad X_g \equiv \frac{F[SiH_4] \times 100\%}{F[SiH_4] + F[Ar]} \qquad (1)$$

where F designates flow rate in sccm.

The temperature in all cases was kept at 300°C, with plasma deposition in the electroded system carried out at a pressure of 360 mTorr and an applied power of 2W. In the electrodeless system, the pressure was maintained at 180 mTorr, with the applied power depending on the frequency: for f_2 = 13.56 MHz, the applied power was kept at 60W while, for f_3 = 2.45 GHz, the applied power had to be raised with increasing X_g, from 70 to 200W, in order to maintain a stable plasma.

In what follows, we shall describe results obtained using quadrupole mass spectroscopy and emission spectroscopy as plasma diagnostics. Concentration profiles of light elements (H, C, O) in the a-Si:H films have been obtained with nuclear elastic recoil detection (2,5) and scanning electron microscopy (SEM) was employed to examine their morphologies. We will discuss measurements of the optical absorption coefficient, α, as a function of the photon energy, of the d.c. dark conductivity as a function of temperature, and of photoconductivity.

3. RESULTS AND DISCUSSION

3.1 Structural Characteristics

In the case of the electrodeless system, substantial differences between the r.f. and the m.w. procedures soon become evident from the appearance and behaviour of the plasma. M.w. plasmas tend to be harsh, and can readily give rise to powder formation unless special care is taken. We have therefore adopted the following geometry (see also figure 1): the sample holder instead of being immersed in the plasma, is just upstream from the glow region, and the film is formed by active species which diffuse to or are formed at the sample surface. The relative abundance of these species (as measured by the film deposition rate) is a sensitive function of distance between the sample holder and the glow region. It can range from a few tens of Å min^{-1} for a distance of about 5 cm, to several hundred Å min^{-1} when the sample just contacts the glow zone. In the case of r.f., however, deposition rate varies much more slowly with distance from the excitation source: for 140W of applied r.f. power the glow fills the entire reactor, but is seen to have little effect on the corresponding deposition rate (Table I).

Table I - Sample Characteristics

f(Hz)	P(W)	X_g	Thickness (Å)	Deposition Rate (Å/min)	Sample Composition (Atomic%)		
					$[H]^a$	$[C]^{a,c}$	$[O]^{b,c}$
13.56 MHz	50	1.6	8200	170	6.4	3.8	5.7
"	60	3.0	6400	230	6.5	2.2	2.7
"	60	3.6	8300	270	8.5	3.0	1.9
"	60	7.5	12800	430	---	---	---
"	140	7.5	8000	400	---	---	---
2.45 GHz	70	1.5	3800	60	9.0	1.2	3.1
"	100	3.8	7800	130	8.8	3.4	4.5
"	200	8.8	8000	160	9.9	12	13

a. concentration ± 10%
b. concentration ± 20%
c. average values for first 200 Å

Table I shows various sample characteristics, for samples covering the range of X_g studied, in particular, the average concentrations of H, C and O, determined by ERD(2). H is the most important among these constituents as it plays an important role in the semiconducting properties of a-Si:H(1). M.w. samples are slightly richer in H than their r.f. counterparts; H concentration profiles through the sample thickness, indistinguishable between the two sample types, resemble those already published(2).

The relatively high C and O concentrations are surprising at first glance: the deposition system was scrupulously cleaned and free of possible organic contaminants; mass- and emission spectroscopy showed only traces of OH (presumably from adsorbed humidity), but no carbon. From this we would conclude that these elements were incorporated when the freshly prepared films were first exposed to atmosphere. It is well known that residual free radicals in plasma polymer films readily react with atmospheric constituents(6). The observed tendency for m.w. samples to be richer in C and O than r.f. samples is probably related to the fact that they have a greater propensity for forming columnar growth structures, which are also known to have higher concentrations of free radicals(7).

By comparison, the electroded system gives significantly lower levels of C and O: < 0.5%. The corresponding material is free of columnar structure, in contrast to material deposited in the electrodeless system (particularly m.w. samples) supporting the relation between the existence of columns and contaminants suggested in the previous paragraph. This, in turn, may be related to ion bombardment which is more pronounced in the electroded system (due to high sheath potentials) than in the electrodeless system. Ion bombardment has been shown(8,9) to eliminate rough surface morphology and structurally unstable growth which gives rise to columnar structure, presumably through the mobilization and rearrangement of reactive species on the surface during film growth.

3.2 Electro-optical properties

On the basis of a pseudo-crystalline model with a parabolic density of gap states(10), the optical absorption coefficient, α, is related to the optical gap, E_g, by

$$\alpha h\nu = C(h\nu - E_g)^2 \qquad (2)$$

where C is a constant.

Figure 2 shows a plot of $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) for r.f. and m.w. samples made in the electrodeless system; they have almost identical behaviour. Deviations from linearity between 1.7 and 1.9 eV are due to interference effects associated with these thin samples. Discounting these, E_g found by graphical extrapolation is close to 1.7 eV, in agreement with values in the literature for a-Si:H$^{(5)}$. Thus, E_g is clearly not a structure sensitive parameter and cannot be used to evaluate the functionality of a-Si:H.

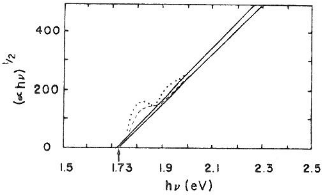

Fig. 2: The determination of the optical gap E_g for r.f. (.) and m.w.-(-) samples having the same X_g of ~ 3.5.

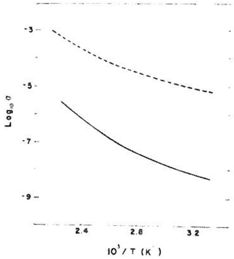

Fig. 3: Arrhenius plots of conductivity for r.f. (--) and m.w. (—) samples having the same X_g of ~ 3.5.

Figure 3 shows a plot of log σ versus 1/T, where σ is the dark conductivity and T the temperature, for the same $X_g \simeq 3.5$ r.f. and m.w. materials. The two curves are typical for other r.f. amd m.w. samples listed in Table I. Dark conductivity is seen to be considerably more structure-sensitive than optical gap. Of the samples listed in Table 1, the m.w. samples are somewhat more conductive and show a lower activation energy than capacitively coupled r.f. samples, and some m.w. samples reported earlier$^{(4)}$. The inductively coupled r.f. samples are even more highly conductive. This may be related to the high growth rate, and the resulting columnar structure and contamination.

Photoconductivity is even more structure sensitive. All samples of Table 1 show less than an order of magnitude conductivity increase in 0.3 AM2, whereas our capacitive r.f. samples show an increase of 10^3. Preliminary results indicate that at least 10^2 can be obtained with m.w. samples even further upstream from the applicator (and consequently grown far more slowly) than the samples described here. Schottky diodes made with these materials have efficiencies near 3% and 1%, respectively.

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