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Ding-Kun Peng, Chun-Lin Wang, Guang-Yao Meng. HIGH RATE DEPOSITION OF HYDROGENATED AMORPHOUS SILICON USING MICROWAVE PLASMA CHEMICAL VAPOR DEPOSITION PROCESS. *Journal de Physique Colloques*, 1989, 50 (C5), pp.C5-667-C5-672. 10.1051/jphyscol:1989578 . jpa-00229611

**HAL Id: jpa-00229611**

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Submitted on 4 Feb 2008

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## HIGH RATE DEPOSITION OF HYDROGENATED AMORPHOUS SILICON USING MICROWAVE PLASMA CHEMICAL VAPOR DEPOSITION PROCESS

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**Résumé** Des films de aSi-H ont été obtenus avec des vitesses de dépôt importantes (90 Å/sec) à partir de mélanges SiH<sub>4</sub>-H<sub>2</sub> dans un dispositif CVD à plasma micro-onde. L'influence des paramètres (puissance, pression, débit, polarisation, localisation) sur la vitesse de dépôt et les propriétés des couches a été examinée. Les films sont caractérisés par la conductivité et son énergie d'activation, le gap optique et l'absorption IR. Pour des dépôts obtenus à raison de 30 à 90 Å/sec, le signal de photoconductivité varie de 3.10<sup>0</sup> à 5.10<sup>5</sup>. Le rendement de dépôt par rapport au silane est voisin de 100%.

Abstract—Hydrogenated amorphous silicon(a-Si:H) films with high deposition rate up to 90Å/sec have been obtained by using microwave plasma chemical vapor deposition(CVD) from SiH<sub>4</sub>-H<sub>2</sub> mixtures. The effect of deposition parameters, such as, power, pressure, flow rate, bias and deposition site, on the deposition rate and film properties has been examined. Films were characterized by conductivity, dark conductivity activation energy, optical band gap, and Infrared absorption. In the deposition rate range of 30-90 Å/sec, the deposited films exhibited photoconductive gains between 3.0x10<sup>0</sup> to 5.0x10<sup>5</sup>. The deposition efficiency or silane use factor was found to be nearly 100%.

### 1-INTRODUCTION

Hydrogenated amorphous silicon(a-Si:H) has caught increasing attention since the work of W. E. Spear and P. G. LeComber/1/. However, the main obstacle to the application of a-Si:H, both technologically and economically to optoelectric devices, e.g., solar cells and photo receptors, is its low growth rate of about 1-5Å/sec and low deposition efficiency by conventional glow discharge processes. Therefore many researchers have been embarking on achieving high rate deposition of a-Si:H. It is believed that the production of the film growth precursors, SiH<sub>2</sub>(or/and SiH<sub>3</sub>), has direct influence on the deposition rate/2,3,4/.(However,S.Veprek has shown that the surface processes is the rate limiting step/5/.) Works have been carried on mainly in two ways, firstly, employing source reagents(Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>H<sub>8</sub>, etc)/2,3,4/ which are easier to be dissociated under the electron bombardment than SiH<sub>4</sub>, or reagents with longer radical lifetime(SiH<sub>2</sub>F<sub>2</sub>, SiF<sub>4</sub>+H<sub>2</sub>,etc)/6,7/ and high deposition rate up to 40Å/sec was achieved. The other way is, using deposition systems which can produce more energetic electrons to break down the chemical bonds of SiH<sub>4</sub> to yield more precursors, or perhaps plus more energetic bombardment on the growing surface. Many workers have focused on these methods/8,9/. Among them, microwave excited plasma CVD is a newly employed and emerged as an effective and encouraging method. This is because that, in microwave low temperature plasma, as both expected theoretically and proved experimentally, the rate of dissociation as well as ionization and ratio of electron temperature to gas temperature can be easily raised, and also microwave plasma can be sustained at higher total discharge pressure(yet low temp.), than ordinary GD. Following the work of S. R. Mejia et al/10/, a few experiments have been carried out with monosilane as the source reagent and deposition rate as high as 250Å/sec has been acquired by this method/11,12,13/. Also, the deposition efficiency has been markedly improved/12/. However, the deposition kinetics and mechanism as well as film properties still need further studies. This paper reports our results obtained in the deposition of a-Si:H films from SiH<sub>4</sub> and H<sub>2</sub> mixtures by Microwave Plasma Chemical Vapor Deposition method.

### 2-EXPERIMENTAL

The microwave plasma CVD method used is illustrated in Fig.1. The distributions of electron energy and ion density as well as gas temperature in discharge zone for various often-used discharge gases has been carefully examined. Microwave was conducted to discharge chamber in TE<sub>10</sub> mode. The quartz tube has an internal diameter of 35mm. Hot-wall heating around the tube can heat the whole discharge zone up to 400°C. The substrates were: polished c-Si wafers for IR measurements; quartz and Corning 7059 glass for conductivity and optical band gap(E<sub>opt</sub>) measurements; stainless steel sheets for substrate bias effect studies. Before each run, the chamber was pumped and baked, refilled with purified H<sub>2</sub>(99.9999%), then pumped and refilled

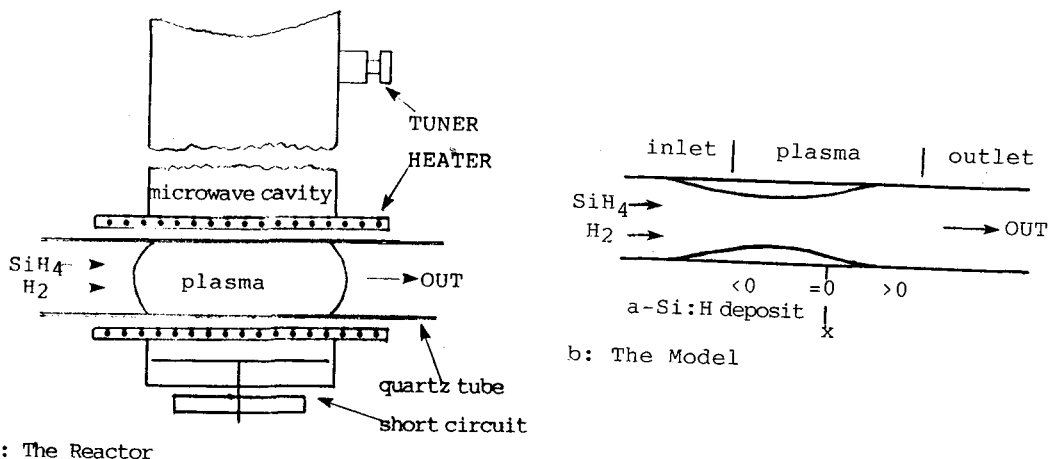


Fig.1. A schematic view of the deposition system (a), and of the resulting deposition profile (b).

three times to minimize the effect of the background gases. Prior to the inlet of  $\text{SiH}_4$ , discharges were ignited using  $\text{H}_2$  under the same conditions except  $\text{H}_2$  instead of  $\text{SiH}_4\text{-H}_2$  as the later depositions to further clean the deposition zone by plasma bombardment and heat up the substrates to the deposition temperature. Stable and homogenous plasmas were obtained by adjusting three tuners and short circuit terminal on the waveguide. After 5-10 minutes bombardment heating,  $\text{SiH}_4\text{-H}_2$  mixtures were introduced into the chamber. Each run was lasted for 30 to 60 minutes. After each depositions, deposited films were cooled down to room temperature in situ under  $\text{H}_2$  atmosphere.

Typical deposition parameters were:  $\text{SiH}_4$  flow rate 3-30 SCCM;  $\text{H}_2$  10-30 SCCM; discharge concentration of silane 5-20%; power dissipated 50-150 w; total pressure 1.0-10Torr; deposition temperature 100-400°C without intentional substrate heating, i.e., by plasma bombardment, and was estimated by a thermometer and from former measurements.

Photoconductivities were measured by coplanar electrode method under the illumination of  $10^5$  Lux with a water filter to eliminate heat effect. Dark conductivity activation energies were obtained by measuring its dark conductivities (in pure  $\text{N}_2$  ambient) vs temperatures. Band gaps were obtained with Shimatz Company UV-240. Infrared absorptions were conducted with NICOLET 170-SX. X-ray identifications were done with D/Max-1A (Nippon RIKA) and also SEM and Refractive Index measurements were used for the structure and morphology examinations. Finally, film thicknesses were determined by micrography, both interfering and transversal to ensure the accuracy (within  $\pm 3\%$ ).

### 3-RESULT AND DISCUSSION

#### 3.1 Influence of deposition parameters

It was found that the deposition rate and film properties depended greatly on the deposition site in the deposition chamber. However, the highest deposition rate did not occur at the center of the discharge zone where both electron energy ( $T_e$ ) and ion density (Ni) are the highest. This might be due to the consumption of the source materials (i.e.,  $\text{SiH}_4$ ) along its propagation or flow direction. This was supported by the fact that the highest rate positions were pushed ahead with the increasing silane flow rate (Fig.2). It also showed that the discharge pressure had its influence on the rate distribution. The lower the pressure, the smoother the distribution curve. These were all in the same trend with  $T_e$ , Ni as we found in plasma diagnostics/14/. The discharge power, on the other hand, showed no pronounced effect on the deposition rate. (However, it did have great influence on properties by the virtue of deposition temperature, see later). This is probably due to the fact that in microwave plasma, electrons, both their density and energy were high enough to dissociate or/and ionize all the source molecules entered the discharge zone. This argument was supported by the results we got in plasma diagnostics which showed that under the deposition pressure, both  $T_e$  and Ni didn't change significantly with the discharge power varied from 100w to 600w/14/. And the nearly unity deposition efficiency regardless of power (see later) was apparently in agreement with this phenomenon. This may suggest that the power needed was only asked by Paschen's law. As mentioned above, the silane flow rate (or total flow rate times silane percentage) had a direct control over the deposition rate, both its spatial distribution and value. The higher silane flow rate was obviously responsible for the higher deposition rate (Fig.3).

#### 3.2-Substrate Bias

Substrate bias exhibited its influence to some extent on deposition and rate. The gas phase

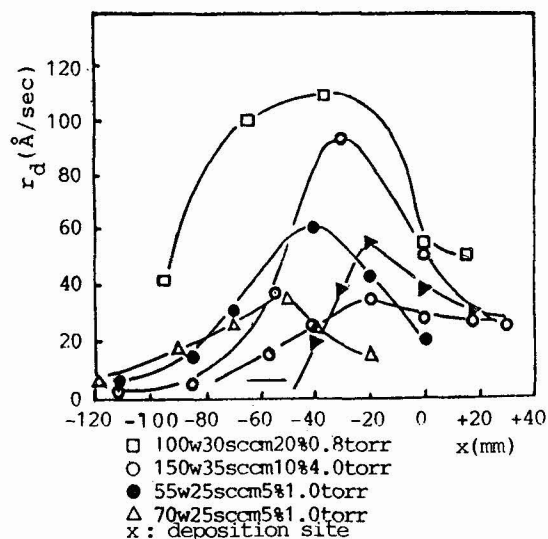


Fig.2-The relationship between deposition rates and Substrate position under various conditions

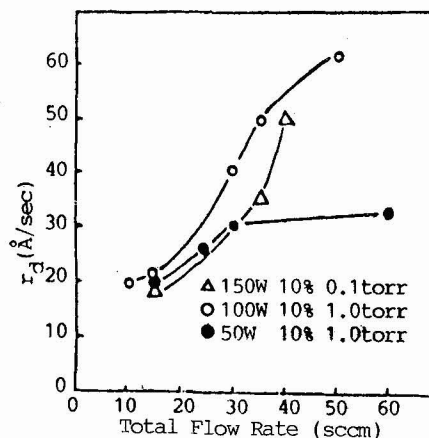
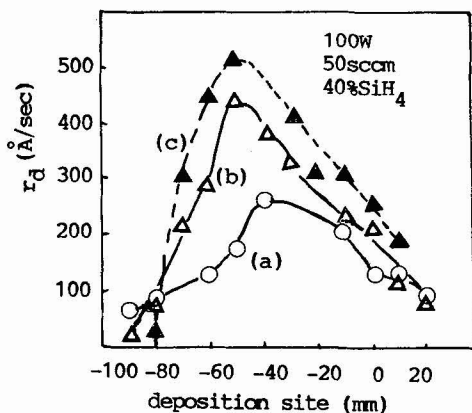


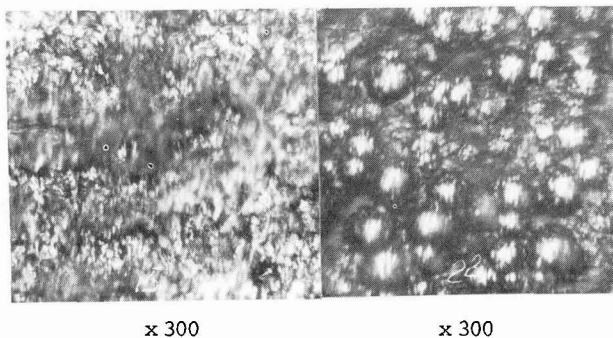
Fig.3-Effect of flow rate on the deposition rate

polymerization is a well-known phenomenon in GD deposition of a-Si:H. In microwave plasma deposition with two competitive factors, i.e., higher  $T_e, N_e$  to break down  $(SiH_2)_n$  groups and higher  $SiH_2$  and/or  $SiH_3$ ,  $SiH$  radical densities more feasible to form  $(SiH_2)_n$  groups, this polymerization also haunts. In present work, we found that under high silane flow rate, yellowish powders were deposited. However, by exerting substrate bias up to  $-300V$ , we successfully depressed the polymerization (Fig.4).



- (a)  $V_{bias} = -300V, 0.8Torr$   
 (b)  $V_{bias} = -300V, 1.5Torr$   
 (c)  $V_{bias} = 0V, 1.5Torr$  (powder)

Substrate: Stainless steel



- (a)  $V_{bias} = 0V, x = -25mm$  (b)  $V_{bias} = -300V, x = -25$

Fig.4-Effect of substrate bias on deposition Fig.5-The influence of bias on the deposited films

Under negative bias, positive ions were accelerated by the electric field across the sheath and obtaining an extra kinetic energy of about  $60eV$  according to M. Konum et al ( $E = 0.2 - 0.3 \times V_{bias} (eV) / 15$ ). Ions with such energy would therefore decompose the polymerized groups within the sheath adjoining the growing surface, on the other hand, they transferred their kinetic energy to the growing network enabling it to rearrange its structure to denser ones. Moreover, ions also would sputtered away those loosely combined or simply attached parts, left behind a rough surface dotted with hillocks (dense area) (Fig.5). Nevertheless, substrate bias played little role in promoting the deposition rate. It was estimated, from both the ion current density towards the growing surface and the rate difference between with and without bias, that ions ( $SiH_2^+$  or/and  $SiH_3^+$ , etc) contributed less than 20% to the deposition rate. So we conclude that the deposition mechanism may be generally the same as that of GD case, i.e., the film

growth precursors were mainly neutral radicals.

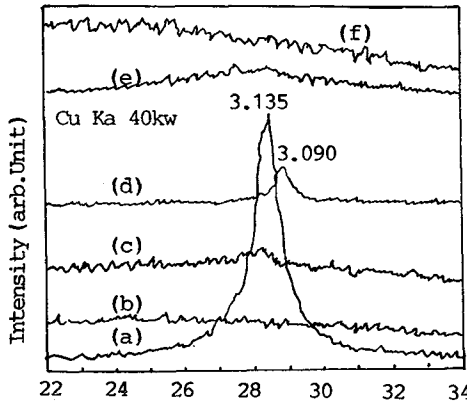
3.3-Deposition Efficiency

By integrating the deposition rate spatial distribution curves through the whole deposition zone and with a reasonable assumption that the deposition was axial symmetric, we found that the deposition efficiency or silane use factor was almost unity regardless of silane percentage. Consequently, there was no detectable silicates in the collection vessel put at the end of the exhaust pipe after many runs. Therefore, this method is also a safe process even using pure silane as the discharge gas and need not to dilute the exhaust gas with inert gases.

3.4-Characteristics of Films

a. X-ray diffraction

Films were generally X-ray amorphous, however, when substrate temperature was higher than 350°C, microcrystalline emerged(Fig.6).



- (a) Ts-450°C;50w;10%;+10mm
- (b) Ts-200°C;100w;5%;-2.5
- (c) Ts-350°C;200w;10%;+20
- (d) Ts-650°C;300w;70%;-10
- (e) Ts-150°C;300w;70%;-90
- (f) Ts-50°C ;50w ;10%;-50

Fig.6-X-ray diffraction patterns of films deposited under different conditions

The grain sizes were estimated by Scherrer formula to be: (a):100Å;and (d):200Å. It is interesting and may be of great importance to note that in Fig.6(d) the deposition rate of this structure was 70Å/sec. This may suggest that microwave plasma might be also a useful tool to deposit uc-Si at high rate.

b. Conductivity

Film photoconductivities( $\sigma_{ph}$ ) and dark conductivities( $\sigma_d$ ) are plotted against the deposition site and rate(Fig.7).

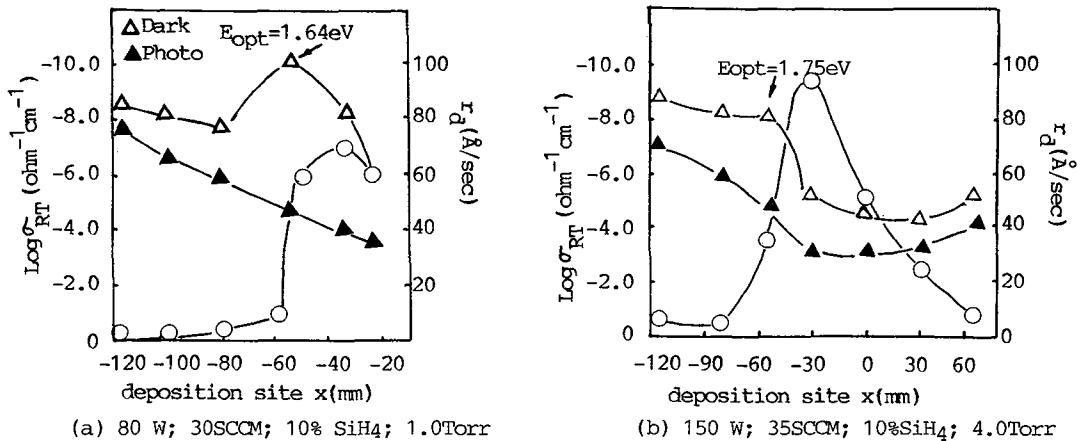


Fig.7-Influence of deposition parameters on film photoelectronic property

Generally, in the deposition rate range  $R_d=10-40\text{\AA}/\text{sec}$ ,  $ph/d$  had a gain of  $10^3-10^5$ . The highest photoconductive gain of  $5.0 \times 10^5$  was obtained on the sample prepared on glass substrate held at 100°C and its deposition rate, optical gap were 45Å/sec and 1.64eV respectively. Both conductivities varied with the change of deposition site. Near the discharge center the conductivities were relatively high and with the increase of distance from the center conductivities went down. This trend is mainly due to the change of their optical band gap  $E_{opt}$ (Fig.8). Narrower band gap therefore resulted in higher conductivities. Besides, this also lay with the variation of electron mobility. Nearer the discharge center the substrate temperature was

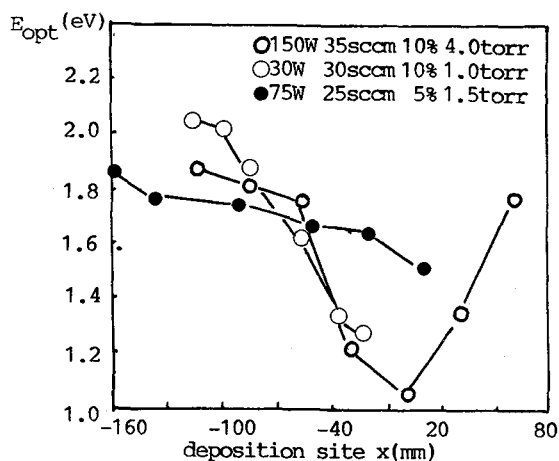


Fig. 8-Optical band gaps of the films corresponding to those in Fig. 7

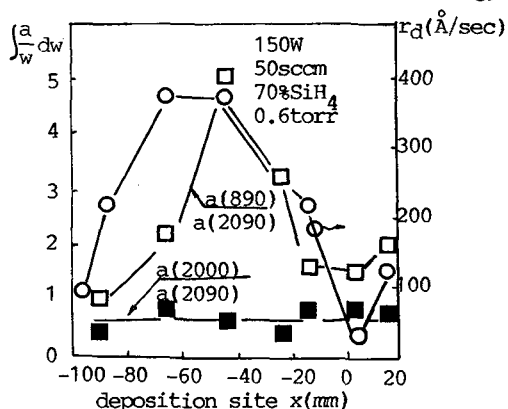


Fig. 9-Normalized IR absorption intensity of typical deposited a-Si:H film

higher, therefore the precursors had higher surface migration energy to find themselves better sites and make better crosslinkage. This was true as discovered by SEM. Electrons in this region would find themselves in a circumstance with smaller potential fluctuations and lower trap density, so they would exhibit higher mobility. Dark conductivity activation energy was found to be 0.23-0.88eV in the temperature range 10-200°C. This are typical values of a-Si:H corresponding to expanded states conductivities where electrons get enough energy jumping from  $E_f$  to  $E_c$  and above  $E_c$ , according to Chittick et al/16/ and LeComber et al/17/. However, under higher deposition rate (say, higher than 100Å/sec), samples showed poor or even no photoconductive gains and exhibited coarse columnar SEM structures. This might be due to the imperfect or had crosslinkage of film precursors under higher deposition rate. This resulted in higher defect density and consequently poor gains. Ogawa et al and Matsuda et al have also revealed in RF discharge that the photoelectric properties of deposited films were getting poorer with the rising discharge power and deposition rate/3,4/. In microwave discharge, Kitagawa et al. had found a deposition rate of 6Å/sec,  $\sigma_{ph}/\sigma_d$  of  $10^2/18$ . Nevertheless, the effect of deposition conditions and deposition rate on the photoelectric properties of the deposit still needs much works.

### c. IR Absorption

Fig. 9 shows a typical IR integrated peak intensities with respect to deposition sites and rates. It had been shown by M. Hirose that  $(SiH_2)_n$  bending vibration mode at  $890cm^{-1}$  could be correlated with the film density. The lower density gets stronger  $890cm^{-1}$  peak/19/. Fig. 9 shows clearly that with the increased deposition rate the density of deposited films decreased. This was also confirmed by SEM and refractive index measurements. It also reveals that the amount of  $(SiH_2)_n$  groups seems to change almost likewise as Si-H regardless of position and rate. This may serve as an approval to calculate the total hydrogen content just by integrating IR  $630cm^{-1}$  peak intensity which is the wagging vibration mode of Si-H bond. The hydrogen contents were calculated and estimated to be 2-30at% and had a drop in the discharge central region where the temperature were higher.

### 4-CONCLUSION

High rate deposition of a-Si:H from  $SiH_4+H_2$  mixtures was achieved by using microwave plasma chemical vapor deposition. The deposition rates were one to two orders of magnitude higher than those of RF case under comparable conditions. The deposition efficiency was almost 100%. Samples exhibited fairly good photoelectric and mechanical properties even at the rate as high as 90Å/sec. The discharge conditions affected the deposition different in some ways with RF case, but the deposition mechanism was thought to be similar. Further optimization of deposition conditions would make it possible to fabricate a-Si:H at high rate and yet better properties.

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