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Hydrogen Radical-Annealing of CVD-Produced Amorphous-Silicon Film

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This paper shows that photo-generated hydrogen radical-annealing (HRA) is very effective for improving the film quality of CVD produced amorphous-silicon films. The relative change of photo-conductivity at AM1 100mW/cm^2 with respect to dark conductivity was improved from 100 of non-HRA sample to about 6×10^4 after HRA at 280°C. The TFT characteristics were improved also by the HRA. The best HRA conditions have been investigated.

1. Introduction

Amorphous-silicon thin-film transistors (a-Si TFTs) have been extensively studied for active elements in flat-panel displays[1]. The plasma enhanced chemical-vapor deposition (PCVD) method is widely used for depositing the active a-Si layers and gate insulators of the TFTs. There remain, however, serious problems; for example, degradation of a-Si quality by bombardment of high energy electrons and ions, generation of dense pin-holes due to many flakes caused by plasma-polymerization and low through-put because the substrates can not be stacked.

The thermal CVD method seems very attractive for a-Si TFTs since all problems mentioned above can be solved for the following reasons. Firstly, source molecules are thermally decomposed only near the surface of high temperature. There are no high energy particles and no plasma-polymerization problem. Secondly, high through-put can be expected since many substrates can be loaded in a stack-like manner into a chamber. The thermal CVD method, however, has been considered for a long time not applicable to the TFT process since it needs high temperature for decomposing the source materials. This technological barrier has been overcome by the recently developed higher silane gas such as disilane (Si_2H_6)[2] or trisilane(Si_3H_8)[3,4,5].

The thermal CVD method using higher silane gases has a potential to make a-Si film with quality better than PCVD since the partially cracked silane molecules can move for a long distance on the substrate surface to find a potential minimum point due to the higher substrate temperature in CVD than that in PCVD. Thus the tail state density will fall more rapidly with energy from the extended state edges to the midgap in CVD films than in PCVD films. This results in a improved field-effect mobility. However, the ESR spin density caused by the dangling bond near in the midgap is two orders in magnitude higher in CVD a-Si than that in PCVD a-Si due to a low hydrogen content. Thus, it is important to develop a new technique to hydrogenate the CVD films after

deposition. This should be done without a plasma[6], since plasma will cancel almost all advantages of CVD method mentioned above. This paper shows that the CVD a-Si devices have been drastically improved in their performance by photo-generated hydrogen radical annealing (HRA), for the first time.

2. Experimental Results

2.1 Apparatus

The HRA effects were studied using an apparatus whose reaction chamber was made of glass, as show in Fig. 1. There were two gas lines for introducing hydrogen into the chamber. The first was for introducing hydrogen with mercury and passed through a Hg reservoir kept at 85°C. The second was directly connected to the chamber for controlling H_2 and Hg partial pressures independently. The second was also used to introduce hydrogen for hydrogen annealing after HRA, which should be done for the purpose of reducing the Staebler-Wronski effect generated during HRA. The 253nm-long UV light was introduced through a 5mm thick quartz window located at the top of the chamber to excite hydrogen by the mercury sensitizing method. The substrate heater was located at 5mm below the quartz window. The standard annealing condition is listed in table I. The mercury partial pressure was 2.3 mTorr. In order to control the substrate temperature accurately, the sample was fixed on the substrate heater using an In-Ga alloy

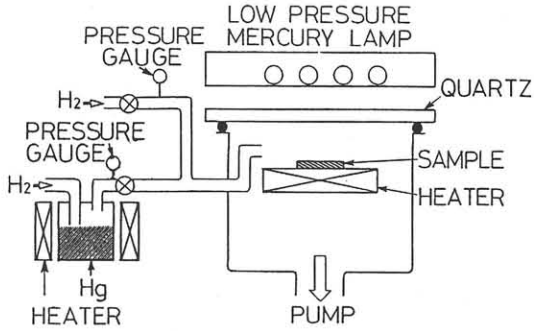

Fig. 1 Schematic view of annealing system.

Table I Standard HRA conditions and Post HRA conditions.

HRA	
H_2 flow rate(with Hg)	10 sccm
Total chamber pressure	5 Torr
Time	30 min
Sample temperature	225 °C
Hg reservoir	
Temperature	85 °C
Pressure	260 Torr
H_2 Annealing (Post HRA)	
H_2 flow rate	100 sccm
Chamber pressure	100 Torr
Time	30 min
Sample temperature	225 °C

which is liquid at room temperature and has a low vapor pressure. The planar type photo-cells with Al electrodes had a 80nm-thick CVD a-Si film deposited on glass substrate at 400°C by using trisilane-silane. The details of a-Si deposition conditions were reported elsewhere[5].

The TFT used in this experiment was fabricated on a highly doped single crystal silicon with 130 nm thick thermally grown SiO_2 layer as the gate insulator. The active layer was about 80nm thick CVD a-Si. Al source and drain electrodes were formed directly on the active a-Si layer in order to operate the device in ambipolar mode. Channel length and width were 200μm and 2mm, respectively.

2.2 Optimization of HRA Temperature

The photo-conductivity σ_p was evaluated by applying 10V between the electrodes under AM1 100mW/cm^2 irradiation conditions. The conductivity change γ was defined as the ratio of photo-conductivity and dark-conductivity. Figure 2 shows γ as a function of the HRA temperature T_a. The reason why we have plotted γ and not the real σ_p value is that the effect of band-bending, which will play a very important role in thin-film characteristics, should be cancelled. The γ value of the as-deposited

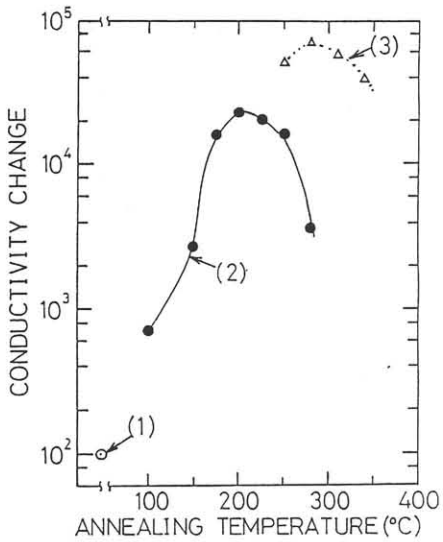

Fig. 2 Photo-conductivity normalized by the dark-conductivity as a function of HRA temperature.

cell was about 100. However, after HRA, the γ value was increased up to about 2×10^4 at T_a=200∿225°C as shown by curve(2) in Fig.2. For T_a more than 250°C, the γ value decreased again due to alloying of a-Si with the Al electrodes. In order to overcome this alloying limitation, we have added high T_a HRA before depositing the Al electrodes. The dotted curve(3) represents the results as a function of HRA temperature T_a before Al evaporation. In this case the γ value continued to increase with T_a and took a maximum value of about 6×10^4 at 280°C.

2.3 Optimization of the Hg Partial Pressure

Figure 3 shows the γ value as a function of Hg partial pressure. The γ value was normalized by its peak value. In the high pressure region, the UV light was absorbed very near the quartz window. Thus, radicals are formed far from the substrates and the number of them finally reaching the substrate is low due to collisions. Thus the γ value decreased with increasing pressure. In the low pressure region, UV light was not absorbed and sufficient number of radicals could not be generated. The γ value took the maximum at about 1/5 of standard Hg

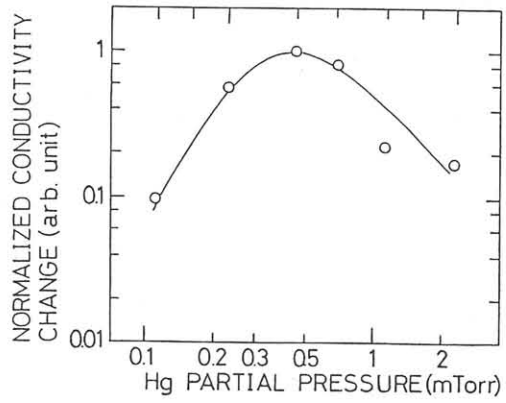

Fig. 3 Conductivity change γ as a function of Hg partial pressure. The Hg partial pressure under standard annealing conditions is 2.3mTorr. The γ value was normalized to its maximum value.

partial pressure and the γ value was about 6 times higher than that in standard HRA conditions.

2.4 Optimization of H_2 Pressure

Figure 4 shows the γ value as a function of the total H_2 pressure. The γ value was also normalized by its peak value. The Hg vapor pressure was kept at the standard value. In the high pressure region i.e. more than 20 Torr, the γ value decreased rapidly. This is because generated hydrogen radicals collide with neutral hydrogen molecules many times and then can not reach the sample surface. On the other hand, in the low pressure region below 20 Torr, Hg radicals

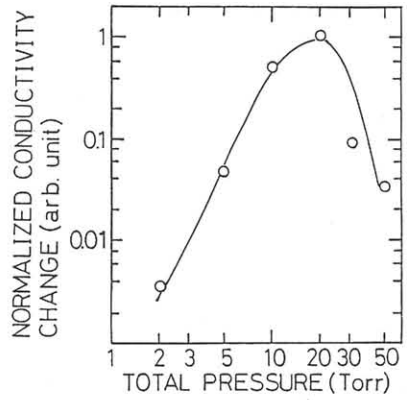

Fig. 4 Conductivity change γ as a function of H_2 pressure. The γ value was normalized by its peak value.

have only a small chance to transfer its energy to hydrogen to excite it. The γ value took a maximum value at 20 Torr and the γ value was twenty times higher than that in standard condition.

2.5 Optimization Annealing Conditions

The H_2 annealing time after HRA was chosen equal to the same the HRA time. The γ value was almost saturated after 10 minutes annealing.

The optimum annealing conditions are tabulated in Table II. It should be mentioned that, there should be a simple scaling rule, namely the Hg partial pressure and H_2 pressure should be inversely proportional to the spacing between window and samples.

Table II The optimum HRA conditions.

H_2 flow rate with Hg	8 sccm
H_2 flow rate without Hg	32 sccm
Total chamber pressure	20 Torr
Time	10 min

2.6 Annealing Effects on TFT Characteristics

Figure 5 shows the semi-logarithmic drain current, $\log(|I_D|)$, as a function of the gate voltage V_G for n channel and for p channel operations, respectively. Source and drain electrodes were biased to -5V and 5V, respectively, in order to keep symmetry. The dashed and solid lines represent the characteristics before and after HRA under standard conditions, respectively. After HRA, field-effect mobilities μ_{FE}, threshold voltages and subthreshold swings for both n and p channel modes were clearly improved. After HRA the electron and hole mobility were increased from $0.80cm^2/Vs$ and $0.12cm^2/Vs$ up to $1.2cm^2/Vs$ and $0.15cm^2/Vs$, respectively.

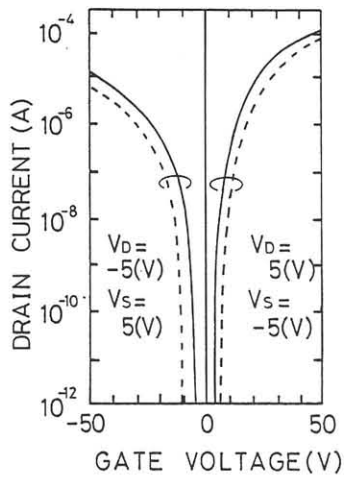

Fig. 5 Semi-logarithmic current, $\log(|I_D|)$, as a function of gate voltage V_G. The dashed lines and solid lines represent before and after HR annealing, respectively.

3. Discussion and Conclusion

The origin of drastic improvement by HRA is not clear yet. We are speculating, however, that hydrogen radicals will enhance drastically their sticking probability at the a-Si surface and that hydrogen will diffuse to the a-Si/SiO_2 interface. Since the flux density of diffusion is approximately proportional to the density of atoms near the surface, the interface properties can be quickly improved by HRA.

The HRA is a very powerful method for applying the CVD a-Si films into electronic devices.

4. References

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