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Description	

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Advantage of Plasma-Less Deposition in Cat-CVD to the Performance of Electronic Devices

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Abstract

Advantage of plasma-less deposition in catalytic chemical vapor deposition (Cat-CVD) is demonstrated in performance of amorphous-silicon (a-Si) thin-film transistors (TFTs), by comparing with a-Si TFTs fabricated by plasma-enhanced CVD (PECVD). Cat-CVD a-Si TFTs show 2 or 3 orders of magnitude lower off-current than PECVD ones. Exposure of Cat-CVD TFTs to an argon or a hydrogen plasma severely increases their off-current, while the off-current recovers by chemically etching the plasma-damaged surface layer. It is concluded that PECVD damages the a-Si surface to a depth of several tens of nm, whereas Cat-CVD induces no serious damage to the film surface and therefore induces no deterioration of electrical properties.

Keywords

Cat-CVD, PECVD, Thin Film Transistor (TFT), Amorphous Silicon (a-Si), Silicon Nitride (SiN_x), Plasma damage, Plasma treatment

1. Introduction

Among various advantages of catalytic chemical vapor deposition (Cat-CVD) over the conventional plasma-enhanced CVD (PECVD), a feature of plasma-damage-less deposition is one of the most expectable ones. Actually, the deposition of silicon-nitride (SiN_x) films by Cat-CVD demonstrates much better performance in compound semiconductor devices than that of PECVD SiN_x films. Due to this advantage, Cat-CVD has been already industrially implemented in the fabrication of electronic devices such as semiconductor lasers and high frequency transistors [1,2]. This plasma-damage-less feature is even clearer in the performance of amorphous-silicon (a-Si) thin-film transistors (TFTs).

In this paper, we study how a plasma damages the surface of substrates or films, by observing the change of performance of a-Si TFTs after exposure to a plasma. In addition, it is also demonstrated that the plasma-damage-less feature of Cat-CVD is effective to realize much lower off-currents in Cat-CVD a-Si TFTs than PECVD ones, keeping the on-current of both TFTs at a same level [3]. This may open a new feasibility of Cat-CVD a-Si TFTs. The superiority of Cat-CVD to PECVD is demonstrated in TFT performance.

2. Fundamental for Experiment

The structure of the a-Si TFT used in the present experiment is schematically illustrated in Fig. 1, and the conditions to prepare a SiN_x gate insulator, an a-Si active layer, and an n-type a-Si layer by Cat-CVD are summarized in Table I. PECVD a-Si TFTs with the same structure as that shown in Fig. 1 are also provided by a company making liquid-crystal displays for comparison. The performance of PECVD a-Si TFTs

appears equivalent to that of other TFTs ever reported [4]. Thus, we believe that the present PECVD a-Si TFT shows typical characteristics.

The transfer characteristics of both Cat-CVD and PECVD a-Si TFTs are shown in Fig. 2. It is seen that Cat-CVD and PECVD a-Si TFTs show almost equivalent on-current, while the off-currents in the Cat-CVD TFT is 2 or 3 orders of magnitude lower than that of the PECVD TFT. In this case, when the ratio of channel width W to channel length L is increased in Cat-CVD a-Si TFTs, the on-current of a-Si TFTs can be increased up to similar level to the on-current of polycrystalline silicon (poly-Si) TFTs, keeping the off-current low enough. That is, TFTs with a similar current drivability as poly-Si TFTs can be obtained even by using a-Si, if Cat-CVD is used instead of PECVD for the deposition of the thin films. In the figure, the expected imaginary performance of a Cat-CVD a-Si TFT for W/L of 40 is also demonstrated with typical results of a poly-Si TFT formed by laser-annealing of a-Si [3], although the structure of a poly-Si TFT is different from that shown in Fig. 1.

The off-current is determined by the leakage current between source and drain of a TFT. Since the dark conductivity of a Cat-CVD a-Si is often lower than that of a PECVD one, this lower off-current might be understood. However, if the surface of an underlayer is damaged during the deposition of an overlayer, and if such a damaged layer provides another current path through defects, the off-current cannot be kept low. For a study on the off-current of TFTs it is of great significance to know the effect of a plasma.

3. Experimental Procedure and Results

The method to know the effect of a plasma is to observe the change of off-current

after a plasma exposure. After fabricating the TFTs, they were set inside a plasma treatment chamber, and the back channel of the TFT was exposed to a plasma. The conditions of the plasma treatment are summarized in Table II. The apparatus for the plasma treatment is a diode type with two parallel electrodes. The diameter of the electrodes is 8 cm and the plasma power is fixed to as low as 5 W, which is almost the minimum power to maintain plasma discharge. In the chamber, a radio frequency plasma of 13.56 MHz is generated. Argon (Ar) or hydrogen (H_2) gas is introduced into the plasma chamber.

Figure 3 shows the transfer characteristics of Cat-CVD a-Si TFTs before and after exposure to the Ar and the H_2 plasma for 30 and 180 s. The H_2 plasma degrades the performance of TFTs more seriously than the Ar plasma. It is also found that the off-current is so sensitive to plasma exposure particularly in the H_2 plasma.

If this increase of off-current is due to the creation of a new leakage path through defects generated by the plasma, the off-current should recover after removing the damaged layer by chemical etching. Thus, the back channel of a plasma-exposed TFT was etched by a mixture of hydro-fluoric acid and nitric acid diluted by water. A layer of a thickness of about 3 to 5 nm from the a-SI surface was etched in a single-step etching process.

Figure 4 demonstrates the transfer characteristics of Cat-CVD a-Si TFTs exposed to a H_2 plasma for 180 s and those after etching. The etching depth of the back channel was estimated from the etching depth of an a-Si film placed close to the TFT samples during plasma exposure. The etching depth of the reference a-Si samples was measured with a stylus surface profiler. It is clearly confirmed that the off-current is likely to recover after the etching of proper depth of an a-Si layer. That is, the thickness of

plasma damage formed by exposure to a H_2 plasma for 180 s is about 16 nm in these plasma conditions. Similar results under exposure to H_2 plasma for 30 s demonstrate that the depth of the damaged layer is only 5 nm for this case, since the transfer characteristics after 5 nm thick etching show the complete recovery of the off-current.

The similar experiments were carried out using an Ar plasma. Figure 5 shows the transfer characteristics of Cat-CVD a-Si TFTs before and after 180 s exposure to the Ar plasma, taking the etching depth as a parameter. It is seen that the performance recovers after the removal of a 9 nm thick damaged layer. The damaged layer thickness is estimated to be roughly half of those of H_2-plasma-exposed TFTs.

4. Discussions

The above experimental results clearly show that a plasma degrades TFT performance. The performance of TFTs is more sensitive to a H_2 plasma, and a plasma-affected layer by a H_2 plasma is apparently deeper than that by an Ar plasma. The reason why a H_2 plasma affects more strongly the degradation of TFT performance than an Ar plasma has not been clearly understood at the moment. Even if the plasma is generated under equivalent electric power condition, the ionization ratio usually varies according to the kind of gas molecules. It is not so simple to estimate the density ratio of ionized Ar to ionized H_2. If we are allowed to say that the density of ionized H_2 is larger than ionized Ar, it would simply help to understand the results shown in Fig. 3.

However, one may also wonder how H atoms affect chemically the surface of a-Si films. When H atoms generated catalytically in a Cat-CVD apparatus sometimes etches even the surface of crystalline Si (c-Si). According to our previous work [5], when a c-Si surface is exposed for 60 s to H atoms with a density lager than 5×10^{12} cm^{-3}, the

surface of c-Si is etched to a depth of about 2 nm, measured by AFM, while no detectable etching is observed when the H atom density is lower than 10^{12} cm^{-3}. In a weak plasma like the present experiment, the density of H atoms generated by the plasma is estimated to be on the order of 10^{11} cm^{-3} or less [6]. Thus, the effect of etching by H atoms does not appear a major reason to explain the results of Fig. 3.

If H_2 ions and Ar ions are accelerated by the same plasma voltage, the penetration depth of H_2 in a-Si should be larger than that of Ar. If theory of ion-implantation is simply adopted as the first order approximation, the penetration depth of H_2 in a Si substrate is at least 5 times larger than that of Ar for accelerated voltages lower than 1000 V. The defects are commonly created following trajectory of species. Thus, H_2 makes a deeper damaged region than Ar.

Of course, the damage density is related with the mass number of colliding particles. The mass number of Ar atom is 40 and that of a H_2 molecule is only 2. If ionized species are accelerated by the same plasma voltage, such species should have same kinetic energy. If the mass of the element of substrate is M_2 and that of the colliding species M_1, it is known that the energy transferred from the colliding species to the substrate atoms is roughly proportional to $M_1M_2/(M_1+M_2)^2$. Here, the substrate atom is Si and its mass number is about 28. Therefore, the energy transferred from Ar to Si is about 4 times larger than that from H_2 to Si. Of course, the creation process of defects by the collision of species is not so simple. However, the defect density is very roughly proportional to the energy transferred to substrate atoms.

As mentioned above, if it is allowed to think that the density of H_2 ions generated in a plasma is larger than that of Ar, the density of defects generated by a plasma in an a-Si layer may not be so different between H_2 and Ar plasma, and only the depth of the

defect layer is different. This may be the explanation of the results shown in Figs. 4 and 5.

That is, when samples are exposed to a plasma, the surface of a few tens of nm thick is simply damaged by ionic species accelerated by the plasma voltage. In case of Cat-CVD, we are able to avoid this. One may claim that the experiment is too much exaggerated because in case of plasma deposition the surface is immediately covered with a depositing film. It might be true. However, even in such a case, just before the first layer is formed, the naked surface is still damaged in some parts.

5. Conclusions

The off-current of Cat-CVD a-Si TFTs is 2 or 3 orders of magnitude lower than that of PECVD a-Si TFTs. To explain the reason of it, we studied on the effect of plasma exposure to TFTs. Then, it is known that the surface of a-Si with a thickness of a few to several tens of nm is likely to be damaged by a plasma if the surface is simply exposed to a plasma. This plasma exposure also degrades the off-current of TFTs, and the off-current increases some orders of magnitude by the plasma. The feature of plasma-damage-less deposition of Cat-CVD appears to contribute to the better performance of a-Si TFTs than PECVD ones.

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List of Tables and Figure Captions

Table I Cat-CVD conditions of SiN_x, a-Si and n^+-a-Si layers used in a-Si TFTs.

Table II Conditions for plasma treatment.

Figure 1 Schematic cross-sectional view of an a-Si TFT used in the present experiment.

Figure 2 Transfer characteristics of a Cat-CVD a-Si TFT and a PECVD one for W/L of 23 μm/4 μm=5.75. Expected imaginary characteristics of Cat-CVD a-Si TFT for larger W/L=40 are also drawn for comparison with a laser-crystallized poly-Si TFT with a mobility of 210 cm^2/Vs.

Figure 3 Transfer characteristics of Cat-CVD a-Si TFTs before and after exposure to Ar and H_2 plasma for 30 and 180 s.

Figure 4 Transfer characteristics of Cat-CVD a-Si TFTs before and after exposure to H_2 plasma for 180 s, and those after the chemical etching of the surface of a-Si damaged layer, taking etching depth as a parameter.

Figure 5 Transfer characteristics of Cat-CVD a-Si TFTs before and after exposure to Ar plasma for 180 s, and those after the chemical etching of the surface of a-Si damaged layer, taking etching depth as a parameter.

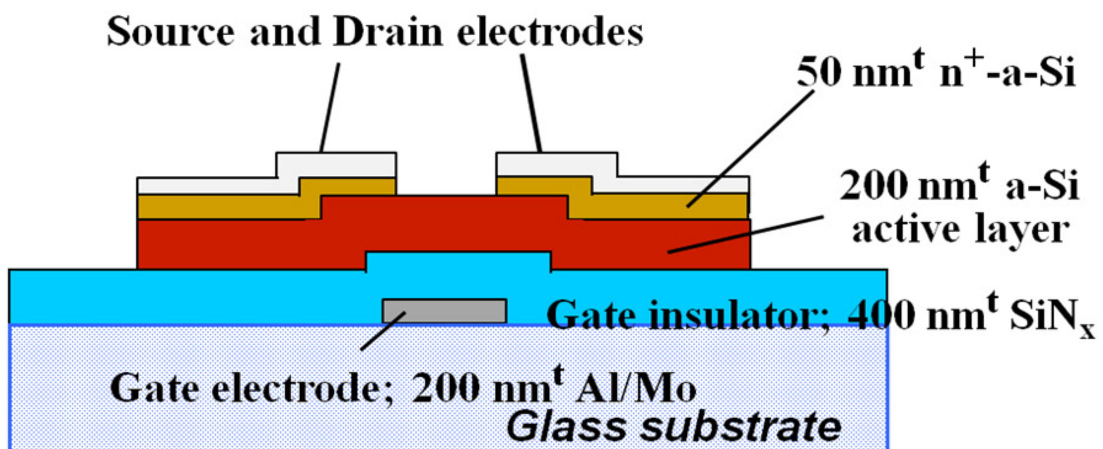
Table I H. Matsumura *et al*.

	SiN_x	a-Si	n^+-a-Si
SiH_4 flow rate	6 sccm	50 sccm	20 sccm
H_2 flow rate	----	10 sccm	200 sccm
NH_3 flow rate	300 sccm	----	----
PH_3 flow rate	----	----	10 sccm
Gas pressure (P_g)	15 Pa	1.1 Pa	1.0 Pa
Catalyzer temperature (T_{cat})	1750 ^oC	1750 ^oC	1800 ^oC
Substrate temperature (T_s)	330 ^oC	330 ^oC	330 ^oC
Distance between catalyzer and substrate (D_{cs})	14 cm	12 cm	12 cm

Table II H. Matsumura *et al*.

Parameters	Conditions
Electrode size	Diode type, 8 cm$^{\phi}$
Power for glow discharge	5 W
Frequency of discharge	13.56 MHz
Gas pressure	27 Pa
H_2 flow rate	50 sccm
Ar flow rate	50 sccm
Substrate temperature	250 ^{o}C
Process time	30 s, 180 s

Figure 1 H. Matsumura *et al*.



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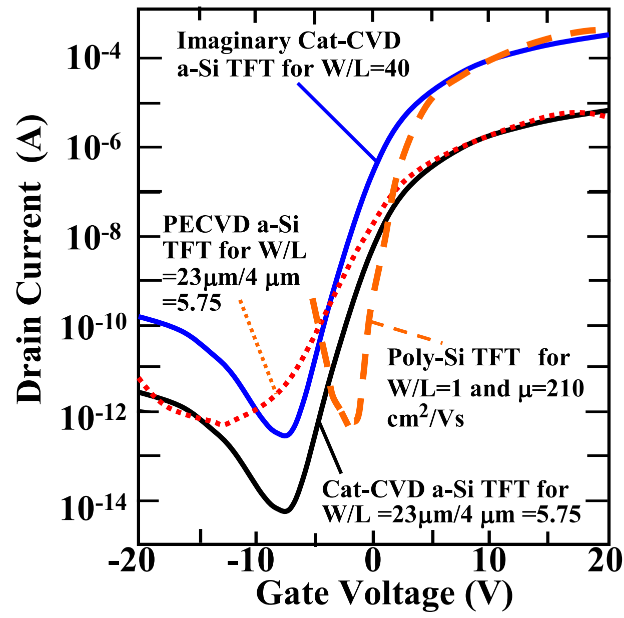


Figure 3 H. Matsumura *et al*.

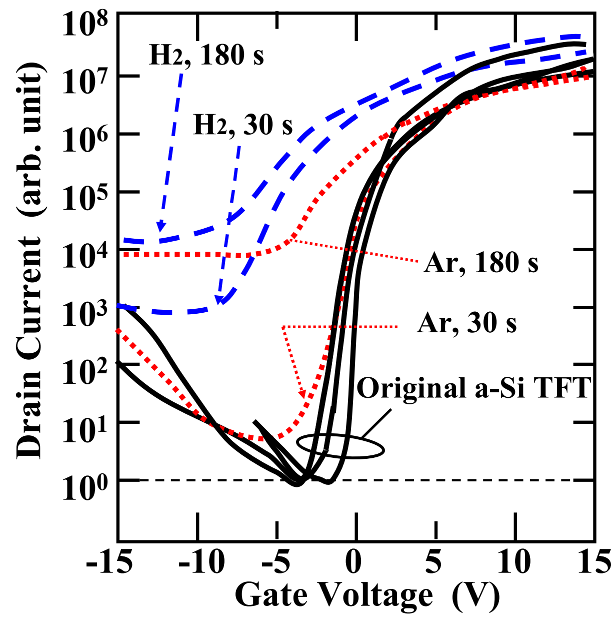
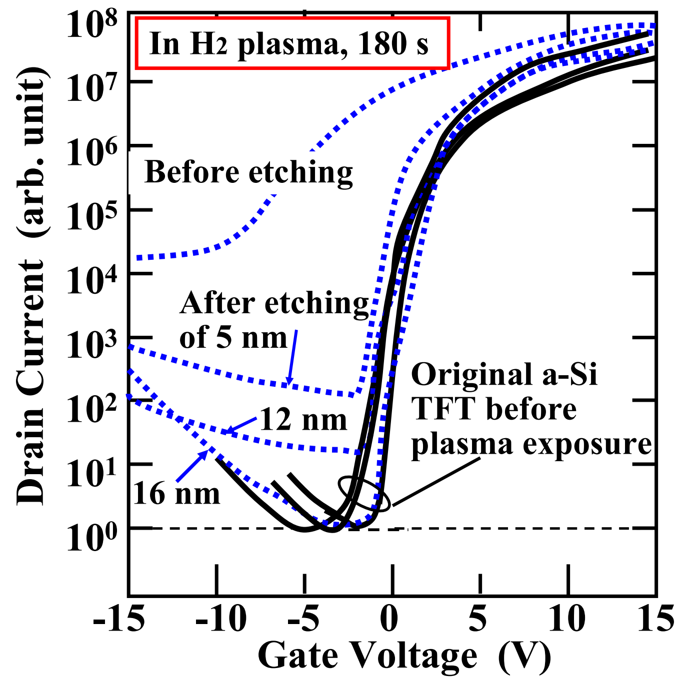


Figure 4 H. Matsumura *et al*.



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