Chapter 2

The basic characteristics of the plastic substrate and the hard coating layers

2.1 Introduction

Active electronic circuits on plastic substrates are attracting increasing attention for applications where light weight, non-breakability, and flexibility are required. The maximum temperature of the circuit fabrication must be lower than the glass transition temperature of the plastic substrate. Therefore, the temperature for silicon processing must be reduced, while organic material technologies already are a low temperature alternative for thin-film transistors (TFT). We have been developing an amorphous silicon (a-Si:H)-based TFT process with 100ºC maximum temperature for use on flexible plastic substrate.

Low temperature deposition of a-Si: H has been well studied by several researchers. The first report of deposition at low temperature was by Moustakas et al. [1] in studies of sputtered amorphous silicon. They noted that good quality material could be achieved by controlling the hydrogen partial pressure during reactive magnetron sputtering at low temperature , followed by a thermal anneal. Since that time, several researchers have noted similar results using various deposition methods to control bonded hydrogen content [2-15]. Most of these reports agree that when optimum material composition and structure is achieved at deposition temperatures less than ~150ºC, a thermal activation can lead to good electronic properties. He and/or H_2 dilution can be used to improve the material properties of the films deposited at low temperatures.[16]However, because of the thermal stress due to the difference of CTE (coefficient of thermal expansion) between plastic and inorganic layer, the substrate is bent considerably or the inorganic film deposited on plastic can be peeled of from the substrate [17].

In this chapter, I will introduce the basic characteristic of the plastic substrate and why I used a hard coating layer as gas barrier to reduce gas permeation into plastic and improve adhesion between metal and plastic substrate. At the next chapter, I will introduce all the fabrication of the TFT on plastic substrate. Plasma-enhanced chemical vapor deposition (PECVD) is the technique for me to fabricate the a-Si: H TFT. I improved the TFT performance using the a-Si:H and SiON layers deposited with an adequate H_2 dilution.

2.1.1 The mechanism of the PECVD

Thin films deposited by chemical vapor deposition (CVD) method usually have many advantages than physical vapor deposition (PVD). The advantages of CVD, such as high purity deposits, great variety of chemical compositions, good economy and possible process control are better than PVD.

There are two major growth mechanisms in CVD process which is showed in the figure 1-9. One is mass-transport limited deposition (High Temperature); the other is surface reaction rate limited deposition (Low Temperature). If the process conditions are situated at the high temperature region, the rate of mass-transport is only relatively weakly influenced by temperature which is respect to the diffusion constant $D \propto T^{1.5\text{-}2}$, and if the process conditions are located at the low temperature region, the reaction rate can be model by a thermally activate phenomenon according to the equation $R=R_o\, e^{-Ea/kT}$, R is represent for the reaction rate and Ea is stand for the activation energy. In order to make the process condition located at the surface reaction region, the low temperature is to demand for process. The plasma enhanced chemical vapor deposition (PECVD) has the advantage for low temperature application. The plasma generation usually has three major mechanics. As follows：

I. **Ionization** $e^- + A \rightarrow A^+ + 2e^-$

II. **Excitation-Relaxation** $e^- + A \rightarrow A^* + e^-$

$A^* \rightarrow A + h\nu$ (photon)

III. **Dissociation** $e^- + AB \rightarrow A + B + e^-$

The third mechanic is in possession of the greater part reaction, and the second mechanic could be usually used to estimate the endpoint in plasma etching process. Because of the generation of plasma, the gas molecules are more active. So the reaction energy could be lower than other high temperature process. But it still has some shortcomings, such like the loose of the film structure. In order to improve the film structure, the additional treatments like thermal annealing and so on are very effective to improve the film structure.

2.2 The Thermal stability of the plastic substrate

Plastic substrates usually have low heat resistance and serious shrinkage for thermal process. In order to realize the plastic substrate, we first employed the TDS (Thermal degas spectrum) to monitor the thermal crack of plastic substrate the various temperatures. Fig. 2.1 shows TDS (Thermal degas spectrum) of the standard plastic substrate, we mainly observe on the CO2 (44) and H2O (18) signals. From the Fig. 2.1, we observed the vapor signal at the low temperature (<80ºC). However, this signal didn't mean the decomposition of plastic substrate. The moisture which was original physically absorbed on the plastic surface contribute to it. As the temperature rises, the moisture signal is reduced gradually. Above 140ºC, the signal of H2O is increasing gradually. In addition, the CO2 signal also gradually increased with rising the temperature above 160ºC. This phenomenon shows that the C, H elements start to release from the plastic substrate above 160 ^{o}C. It also expresses the cracking of the plastic substrate. After understanding the cracked temperature of the plastic substrate, we must choose the proper temperature to fabricate the TFT to prevent the decomposing gas to participate in the fabrication process and change the composition of the deposition thin film, resulting in degradation of the device.

During the device fabrication process, we must use the photoresist to define the pattern, and chemical solutions to perform etching step. To investigate the impacts of chemical solutions, the plastic substrates were dipped with some solutions. Fig 2.2 shows that both the standard plastic substrate and hard mask covered sample soaking in the acetone. The acetone significantly destroys the sample on the both different condition. The corrosion of surface was observed to be regardless for standard and hard coating samples; they are both out of shape and twisted.

2.3 The Hard Coating Layers

2.3.1 The reason why we use the additional layers

One of the difficulties associated with processing plastic substrates is gas out-diffusion from the plastic during heating process and subsequent gas absorption during cooling step. Associated with this out-diffusion and subsequent absorption of gas is an undesirable change in substrate dimension once it has been heated and cooled [18]. High gas permeability of the substrate can lead to instability of the TFT over time. Because the surface of the plastic is rough and the plastic substrate is easy to be damaged by chemical attacking. To prevent the gas absorption of the plastic substrate, an inorganic gas-barrier film, such as SiN or SiCN deposited by PECVD, can be used. So to deposit the additional layer (called it the hard coating layers) to served as gas barrier to reduce gas permeation into plastic substrate and to improve adhesion between metal and plastic substrate.

I have tried several kinds of films to serve as the hard coating layers, such as SiCN, SiON, SiN, TiO2 and Al2O3. These not only protect the plastic from gas adsorption, but also can improve the adhesion of metal to the substrate.

Fig. 2-3 shows the comparison of the weight losses after annealing at various temperatures. The difference in two samples is that one sample was covered with SiN on the both sides and the other was not. We find that there is a cracked state after annealing at 150 for the standard sample, and caused the loss of quality. But the sample with SiN hard coating is improving a lot.

2.3.2 Experiment Process

The hard coating layer was deposited by the dual electron gun evaporation system and PECVD method. SiCN, SiON and SiN were deposited by the PECVD method and the process temperature is 100 degree Centigrade. TiO2 and Al2O3 are deposited by the dual e-gun system at room temperature. The refractive index and thickness of the PECVD deposited thin films are measured with an n&k analyzer. The infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer calibrated to an unprocessed wafer, for determining the chemical structure of the thin films. Electrical characterization is performed on metal oxide semiconductor (MOS) structure formed on the p-type silicon wafer with a resistively of 15-25 Ω-cm. These PECVD deposited thin films of about 30 nm were deposited as an insulator. Al electrodes were evaporated on the front surface of the films and the back surface of the substrate. The area of the gate electrode is 0.00503 cm^2 for C-V analysis. MOS capacitors are used for the determination and evaluation of the permittivity of these thin films; the dielectric measurements are done using a Keithley Model 82 CV meter. The capacitor was measured at 1 MHz with an AC bias. And current voltage (I-V) characteristics were also measured using MOS structure with the HP 4156C Precision Semiconductor Parameter analyzer. The area of the gate electrode was 0.001244 cm^2 for I-V analysis.

2.3.3 Results and Discussion

First, we used the PECVD to deposit the SiN layer at 100ºC. From Fig 2-4, it shows SiN films were deposited for various periods. We found that the thick SiN exhibit to be red and purple. As a consequence, we should control the thickness of SiN to own optimized transmittance. After adjusting the thickness of the film the transmittance is improved. We can obviously compare the difference of the two samples in Fig. 2-4. Although the thinning SiN layer is transparent, the adhesion between the SiN layer and plastic substrate is poor. Moreover, the plastic substrate is bended after SiN hard coating. So we try to serve other films to be more suitable for hard coating layers.

Because the mainly composition of the plastic base plate is C-H bonding, we tried to deposit the SiCN film as the hard coating layer. We expect that the adhesion between the plastic substrate and the SiCN layer can be improved, and the SiCN layer is suitable to serve as the buffer layer between the substrate and the thin film transistor. We deposited various thicknesses of the SiCN hard coating layers by using PECVD method. The thickness of the film is controlled by the deposition time, so we try three different conditions, such as 5min, 8min and 10min. Notably, we observe that the vacuum during deposition process is improved due to the hard coating layers. It obviously evidence that the hard coating layer had obvious dandified and restrained the out-gas from the plastic substrate. Moreover, there is no peeling off the film even under 10 min ultrasonic wave shocks which is used to remove the photoresist. Although SiCN can be a good hard coating layer, the transmittance for light is poor. Fig.2-5 shows the transmittances of SiCN samples for various deposition periods. With increasing the depositing time, the color is become dark. We also use the PECVD method to deposit the SiON layer. Nether less, the SiON layers are not transparent.

Although SiCN films have poor penetrability of light, it is a good candidate to be the hard coating layer as a adhesion layer. On the other side, the SiN film has the good penetrability of light, but has the poor adhesion ability with plastic substrate. For these reasons, it's the advantage to adopt the combination of both SiCN and SiN films to form the multilayer coating layer. The penetrability and adhesion ability with the plastic substrate are improved by using the multilayer. Fig.2-6 shows the penetrability of the SiN and multilayer. The penetrability of the multilayer is very approach to the standard plastic substrate.

Instead of the hard coating layers deposited by PECVD, the TiO2 and Al2O3 films deposited by dual e-gun are candidates for hard-coating layers. Fig.2-7 shows that the TiO2 film is lightly blue and the Al2O3 is transparent. However, a lot of cracks appear in the Al2O3 film in the view of microscope, as Fig 2-8 shown. As a result, the Al2O3 hard coating layer is not suitable for plastic substrate.

2.4 Summary

In order to prevent the moisture or degas molecular diffuse through the plastic substrate during the deposition, the SiCN thin film capped on plastic substrate must be adopted. We focus on the SiCN film deposited at low temperature. We coated the SiCN films with PECVD system and then deposited the TFT device on plastic substrate. After the SiCN hard coating layer deposited on plastic substrate, the vacuum of chamber become better. By using the multilayer as hard coating layer, we will have the advantages of adhesion and transmittance. Table 2-1 is the summary of the multilayer.