Cu Wiring Process for TFTs
- Improved Hydrogen Plasma Resistance with a New Cu Alloy -

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1. Introduction

As flat-screen TVs become larger and their resolution higher for digital broadcasting, 40-inch screens with 1920 by 1080 pixels (full HD) have become popular in recent years. And as a result of changes in the way audiences watch TV programs brought about by the spread of digital home appliances and high-speed Internet systems, 4000-by-2000 (4K-by-2K) TFT-LCD panels with four times as many pixels as current digital broadcasting TV screens are being developed. In order to develop 4K-by-2K panels, however, it is necessary to solve problems regarding signal delays and increases in circuit costs. While Al alloy wires are widely used for driver circuits at present, high-speed driving for large-size screens causes signal delays as a result of higher wire resistance. Panels provided with driver ICs on both sides and divided into several sections for operation are used to resolve this difficulty. However, these panels involve increases in the number and complexity of parts, causing increases in manufacturing costs. Therefore, in order to achieve high-speed driving and reductions in costs, the use of Cu alloy materials, which have a lower resistance than Al alloy materials, is preferred.

Cu films have problems regarding adhesion to underlayers as well as the same problems with counter diffusion with Si underlayers as Al films. Current Al alloy wiring requires Mo or Ti barrier layers, increasing panel costs. We have reported that while Cu wiring also requires similar barrier layers, forming a Cu alloy oxidized layer on the interface with the underlayer by oxygen mix sputtering improves the adhesion and barrier capabilities of film layers.

However, in recent TFT manufacturing processes, hydrogen plasma treatment is sometimes performed after forming source/drain electrodes. It has been confirmed that this treatment deoxidizes the oxidized Cu alloy layers, thereby decreasing film adhesion. Our examination of Cu alloy materials and treatment processes led us to discover that Cu alloy oxidized layers with Ca or Mg-Al added show high resistance to hydrogen plasma treatment.

2. Reduction in TFT Manufacturing Costs

As large-screen LCD TVs have become more popular, the price of TFT-LCD panels has fallen, leading to reductions in material costs and cuts in the number of processes.

TFT arrays are created by deposition (sputtering or CVD (chemical vapor deposition)) followed by a series of processes—masking (resist coating, light exposure and development), etching (wet or dry) and resist stripping—that are repeated several times. Ordinarily, one pattern is formed and etched in one masking process. The manufacture of TFT arrays, which are composed of a number of thin layers, requires several masking processes, causing a considerable increase in manufacturing costs.

A process using half-tone masks that allow consecutive etching of several types of thin films with a single masking process has been developed and commercialized in recent years. This process, which reduces the high number of masking processes required for the manufacturing of TFT arrays and makes it possible to downsize facilities, is being developed by various panel manufacturers as a low-cost process.

A photomask normally etches a pattern by the transmission and blocking of light. Positive photoresist exposed to transmitted light is removed through development, while...
photoresist unexposed to light remains intact after development. Half-tone masks have narrow slits (approximately 1 μm) on some parts of their surface so as to allow partial transmission of light, which is half-way between light transmission and light-blocking. Areas of photoresist that are exposed to partial transmission of light form a film thinner than areas not exposed to light. Figure 1 shows the structure of a TFT array, and Figure 2 an example of a low-cost TFT manufacturing process using half-tone masks.

(1) Deposition

In a low-cost TFT manufacturing process, a series of layers is successively deposited—a gate dielectric film (SiNx), a semiconductor layer (a-Si) and a contact layer (n’a-Si) by CVD and source/drain electrodes (metal) by sputtering—after gate electrodes have been formed.

(2) Resist patterning

Photoresist is patterned using half-tone masks. Light to TFT source/drain electrode areas is blocked by these masks, while light to channel areas is half-transmitted. Photoresist films thinner than those formed on source/drain electrode areas are formed on channel areas through this process.

(3) Metal layer wet etching

Source/drain electrodes are formed by wet etching.

(4) n’a-Si/a-Si layer dry etching

Si layers exposed after (3) are removed by dry etching.

(5) Ashing -1-

Photoresist is uniformly etched in the direction of film thickness by ashing. In consequence, photoresist on channel areas coated with thinner films is removed, leaving photoresist only on source/drain electrode areas.

(6) Channel formation -1- (metal layer wet etching)

Metal films on TFT channel areas are removed by wet etching.

(7) Channel formation -2- (n’a-Si layer dry etching)

n’a-Si on channel areas is removed by dry etching.

(8) Ashing -2-

Residual photoresist is removed.

The half-tone mask process makes it possible to perform the dry etching of Si layers and the wet etching of metal layers successively in a single masking process. It also makes it possible to perform dry etching to remove the contact layer (n’a-Si) on channel areas without a new photo-masking process, thereby greatly shortening the manufacturing process compared with traditional photo masking.

Another characteristic of the TFT array structure presented in this article is that no protective films are needed to protect channel layers. Protective films are formed in order to improve the etching selectivity of n’a-Si and a-Si layers during the dry etching of the channel formation process and to protect the a-Si layer from plasma damage. However, forming protective films requires additional de-
position, resist patterning, and etching processes, causing a considerable increase in manufacturing costs.

Recently, TFT array structures that do not need protective films are being used. The etching selectivity of n’a-Si and a-Si layers has been improved by the optimization of the dry etching process. However, there is a risk of plasma damage to the a-Si layer, causing deterioration in TFT capabilities. To protect the layer from plasma damage, hydrogen plasma treatment is performed in processes subsequent to channel formation. Hydrogen plasma treatment terminates the Si dangling bonds on the a-Si layer and resolves the problem of deterioration in TFT capabilities.

Hydrogen plasma treatment is performed after the formation of channels and before the deposition of the passivation layer (SiNx) by CVD. Source/drain electrodes (metal wiring) are exposed to hydrogen plasma along with the a-Si layer. Therefore, in a low-cost TFT manufacturing process, the hydrogen plasma resistance of metal wires must be improved.

3. Cu Wiring Process for TFTs Using Oxygen Mix Sputtering

3.1 Film Composition of the Cu Wiring and Effects of Adding Oxygen Gas

Forming a Cu alloy oxidized layer on the interface with the underlayer by oxygen mix sputtering provides film layers with high levels of adhesion and good barrier capabilities. A Cu alloy oxidized layer produces oxides of Cu and alloy elements on the interface with the underlayer, thereby improving the adhesion and barrier capabilities of film layers. Figure 3 shows the film composition of Cu wiring for TFTs.

3.2 Development for Low-cost TFT Manufacturing Processes

In the low-cost TFT manufacturing process described in the preceding section, source/drain electrodes are exposed to hydrogen plasma without protection as a result of the use of half-tone masks and the elimination of the protective film formation process. We have confirmed that

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sub. [Glass, n’a-Si, SiNx]</th>
<th>After H2 Plasma</th>
<th>After H2 Plasma + SiNx depo.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as depo.</td>
<td>Power density [W/cm²]</td>
<td>Power density [W/cm²]</td>
</tr>
<tr>
<td>Cu/Mo/sub.</td>
<td>OK</td>
<td>0.6 0.8 1.0</td>
<td>0.6 0.8 1.0</td>
</tr>
<tr>
<td>Cu/Cu-Mg-O/sub.</td>
<td>NG</td>
<td>NG  NG  NG</td>
<td>NG  NG  NG</td>
</tr>
<tr>
<td>Cu/Cu-Ca-O/sub.</td>
<td>OK</td>
<td>OK  OK  OK</td>
<td>OK  OK  OK</td>
</tr>
<tr>
<td>Cu/Cu-Mg-Al-O/sub.</td>
<td>OK</td>
<td>OK  OK  OK</td>
<td>OK  OK  OK</td>
</tr>
</tbody>
</table>

Evaluated by tape tests (OK: no peeling in any grid; NG: peeling in any of the grids)
if Cu alloy oxidized films are used in combination with adhesion and barrier layers, hydrogen plasma treatment causes deterioration in the adhesion and barrier capabilities of film layers. Figure 4 shows a model to explain the deterioration in adhesion caused by hydrogen plasma exposure. It has been confirmed that hydrogen plasma exposure causes hydrogen ions to pass through the upper metal Cu film layer, thereby deoxidizing the lower Cu alloy oxidized film layer. Our experiments lead us to assume that this phenomenon causes oxides of Cu and alloy elements formed on the interface with the underlayer to deoxidize, which in turn causes deterioration in the adhesion of film layers.

4. Improvement in Hydrogen Plasma Resistance by Cu-Ca Alloy and Cu-Mg-Al Alloy

Hydrogen plasma resistance is considered to be an essential requirement for the low-cost TFT manufacturing process that is being developed by various companies. In order to improve the hydrogen plasma resistance of film layers, we searched for alloy elements that produce oxides more stable than those of traditionally used alloy elements. Our search led us to discover that Cu alloy oxidized films formed with Ca or Mg-Al added show high hydrogen plasma resistance.

4.1 Adhesion after Hydrogen Plasma Treatment

Table 1 presents the results of adhesion tests of Cu-Ca alloy and Cu-Mg-Al alloy after hydrogen plasma treatment. They were evaluated by tape tests using glass substrates, n’a-Si films, and SiNx films as underlayers for Cu alloy. We compared Mo films and Cu-Mg-O films that are traditionally used as Cu alloy oxidized films. Hydrogen plasma treatment was performed under the following conditions:

- H$_2$ pressure: 200Pa
- Power density: 0.6, 0.8 and 1.0 W/cm$^2$
- Tsub.: 250°C
- Time: 60 sec.

Assuming the deposition of a passivation (SiNx) layer, we also evaluated the adhesion of SiNx film layers successively formed after hydrogen plasma treatment.

Using Cu-Mg-O films in combination with adhesion layers provided high adhesion as depo., but hydrogen plasma treatment caused the film adhesion to deteriorate.

Meanwhile, when Cu-Ca-O films and Cu-Mg-Al-O films were used in combination with adhesion layers, hydrogen plasma treatment did not cause deterioration in film adhesion in the subsequent deposition of SiNx films. Similar results were obtained for different types of underlayers (glass substrates, n’a-Si films and SiNx films). These results lead us to conclude that oxides containing Ca or Mg-Al formed on the interface with underlayers remain without being deoxidized by hydrogen plasma, maintaining high film adhesion.

4.2 Barrier Capabilities after Hydrogen Plasma Treatment

Assuming the application of our technology to source/drain electrodes in low-cost TFT manufacturing processes, we evaluated the barrier capabilities of film layers. We first formed an a-Si film (300 nm) on a glass substrate by
CVD and successively deposited a Cu-Ca oxidized layer (50 nm) by oxygen mix sputtering and a low-resistance pure Cu layer (300 nm) by pure Ar gas sputtering. We then exposed these film layers to hydrogen plasma under the same conditions as described above. We then annealed the material at 350°C in a vacuum for an hour and studied its layer composition in the direction of film thickness by AES analysis. The results of the AES analysis presented in Figure 5 show that there is no Cu diffusion into the a-Si film layer, confirming that oxides containing Ca formed on the interface improve the hydrogen plasma resistance and barrier capabilities of film layers.

4.3 Contact Capabilities with n’a-Si Films

Assuming the application of our technology to source/drain electrodes, we also measured electric contact capabilities with an n’a-Si layer. We created a measurement sample by forming an n’a-Si film (300 nm) on an n’Si wafer by CVD and by successively forming a Cu-Ca or Cu-Mg-Al oxidized layer (50 nm) by oxygen mix sputtering and a low-resistance pure Cu layer (300 nm) by pure Ar gas sputtering. Figure 6 shows the element structure of our evaluation sample.

Evaluations were made both as depo. and after annealing the material at 350°C in a vacuum for an hour. We also performed evaluations of a sample created using Mo for the upper Cu barrier layer in order to make comparisons.

Figure 7 (a) presents results obtained using Mo for the barrier layer. These results show the same V-I properties as depo. as after annealing.

Meanwhile, Figures 7 (b) and (c) present results obtained with Cu-Ca-O films and Cu-Mg-Al-O films used as barrier layers. These results lead us to conclude that these Cu alloys have contact capabilities with n’a-Si films equivalent to the Mo film. They have the same V-I properties as depo. as after annealing, leading us to conclude that heat treatment causes no deterioration in these properties.

4.4 Application of Cu-Mg-Al Adhesion Layers for Gate Electrodes

In this article, we presented a Cu wiring process using Cu-Ca alloy and Cu-Mg-Al alloy as a technology that can be used for low-cost TFT manufacturing processes. We also showed that the Cu-Mg-Al alloy has characteristics that other Cu alloys do not have. Cu-Mg-Al alloy has high adhesion levels to glass even without using oxygen mix sputtering. In other words, in processes using Cu-Mg-Al alloy, it is possible to use films sputtered with Ar gas alone for the adhesion layer.

Figure 8 shows an SEM photo showing a cross-section of film layers after wet etching, which were formed consecutively by depositing a Cu-Mg-Al film with Ar gas and then forming a low resistance Cu film. The photo shows a good cross-sectional shape produced by a single solu-
tion etching. If low-resistance Cu is used in combination with other materials for the adhesion layer, the wet etching of deposition layers sometimes causes a cell reaction (galvanic corrosion). This can cause a difference in the etching speed between the low-resistance layer and the adhesion layer, preventing a smooth tapered shape from being formed. It is known that materials such as Mo have particularly strong effects on the cell reaction with Cu. The deposition film formed using Cu-Mg-Al alloy for the adhesion layer can be easily processed by etching.

5. Summary

In this paper, we presented Cu wiring technology using Cu alloy material, which can replace the Al alloys currently used for TFT wiring. The Cu wiring process presented in this paper can be used for the low-cost TFT manufacturing processes that are currently being developed by various companies. Our technology, which does not require the use of barrier metals, can help reduce the materials costs and manufacturing costs of large-size TFT panels. It is also expected to play an important role in the development of 4k-by-2k high-density panels and high-speed drives that can be operated at two or four times current operation speeds.

Cu alloy oxidized films and Cu-Mg-Al alloy metal films have high levels of adhesion to underlayers. Since these films improve adhesion, one of the problems with Cu films, they are also expected to be used for the development of electronic devices apart from TFTs.

References

6) S.Takasawa,et al.: IDW ’08 Digest P95, 2008