Study on Properties of Cu Barrier Materials in TFT Devices

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ABSTRACT

Given the demand of stable performance, barrier materials are necessary for thin-film transistors (TFTs) to optimize the adhesion and atom diffusion of Cu layer. In this paper, we successfully demonstrate that the MoTiNi alloy (MTN) has great potential as Cu barrier layer. Notably, due to its excellent antioxidant property, MTN can also be used for bonding protection of novel displays, such as Mini-LED and Micro-LED.

1 INTRODUCTION

With the development of display technology, the demand for large-area, high resolution and high refresh rate products is growing rapidly. Copper (Cu), which has low resistivity and can obviously reduce RC delay, has been widely applied to the production of TFT devices. However, the Cu film has high peeling risk due to its poor adhesion to the substrate. And Cu ions can easily diffuse into the semiconductor layer, leading to the deterioration of electrical properties of TFT devices. Therefore, a Cu barrier layer with stable chemical properties and good adhesion is the key to guarantee the performance of TFT-LCDs. The Cu barrier materials can generally be Mo, Ti, Ta, W, Nb, as well as their alloys or metal oxides. Considering the resistivity, adhesion, etching difficulty and the ability to block Cu diffusion, it is still challenging to rational design of effective Cu barrier materials.

In this paper, we investigate properties of five Cu barrier materials, including molybdenum (Mo), Titanium(Ti), MoTi,MoTiNi alloy(MTN)、MoNbTa alloy(MNT). Then the etching and physical properties especially the ability to block Cu diffusion are explored.

2 EXPERIMENT AND RESULT

In order to characterize the physics of different metal films, there are two kinds of films with different structures are prepared by using physical vapor deposition (PVD).Firstly,the barrier monolayer film with the thickness of 150nm is deposited on the glass substrate. Secondly, composite film of barrier layer and Cu film is deposited.

The resistivity of these films were measured using the Namometer(Nano).The crystal structure and orientation were performed by using Transmission electron microscope(TEM) and X ray diffraction(XRD). Scanning electron microscope(SEM) is used to analyze etch- related properties.

1. Barrier monolayer film properties

Figure 1 shows the XRD image of the sigle barrier metal film prepared in this work.It is clear that all of these films are polycrystalline structure, growing along 111 crystal direction.The size of the gaint is smaller to ensure the denisty and the stability of the barrier layer. The grain size and resistivity are obtained by TEM and Nano, respectively. The value of these metarials are list in Table 1.It shows that all thses metal materials have excellent adhesive force and low resistivity,although the resistivity of Mo alloy is higher than Mo, they can still be used as an excellent barrier layer for TFT manufacturing.

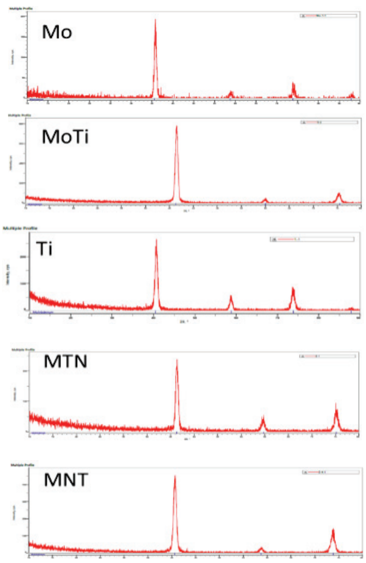


Figure 1 XRD Spectra of different barrier films

Table 1 The characteristics of barrier films

NO.	Mo	Ti	MoTi	MTN	MNT
Thickness (nm)	150	150	150	150	150
Adhesion	5B	5B	5B	5B	5B
ρ (Ω*cm)	1.6×10-3	6.3×10-3	9.1×10-3	9.9×10-3	7.1×10-3
Grain orientation	111	111	111	111	111
Grain size (nm)	14.2	14.5	13.7	14.1	12.9

2. The ability to block Cu diffusion

For the barrier layer, it is very important to block Cu diffusion into semiconductor. Hence, we focus on the ability of different metal films to prevent Cu diffusion into adjacent semiconductor. In the first step,the multi-layer film with the structure as shown in Figure 2 was fabricated.The a-Si:H active layer was deposited on the glass substrate by plasma enhanced chemical vapor deposition (PECVD) method. Then the 30nm thick barrier layer (Mo,MoTi,Ti,MTN,MNT) and Cu were continuously deposited by PVD method. Finally, a layer of ITO was deposited on top of the Cu.

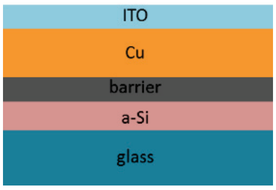


Figure 2 A schematic diagram of the multi-layer sample

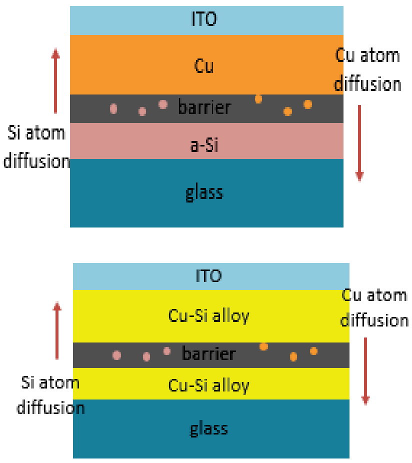
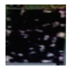
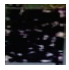
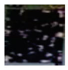
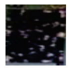
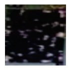
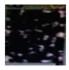


Figure 3 The schematic diagram of the Cu and Si diffusion in multi-layer film with the high temperature

Table 2 The color of the samples with different time

barrier	1h	2h	3h	4h	5h
Mo					
Ti					
MoTi					
MTN					
MNT					

In the second step, the samples were placed in oven with the temperature is 350 ℃ for 5h to deteriorate .And every hour ,to record the color of the samples.As shown in Figure 3,it is clear that with the temperature increases, without barrier layers Cu and Si diffuse with each other to form cu-si compounds. Therefore, the Cu film and a-si film become black because Cu-Si alloy is formed.When observe the sample ,not only the front of the sample but also the back of the sample are black. On the contrary , inserting a barrier layer can reduce the formation of Cu-Si, The greater the ability to resist diffusion, the less likely the sample is to be black under high temperature treatment. Therefore,to compare the affects of different barrier layer, we observed and recorded the colors of the samples with different barrier layers,which are summarized in table 2.

As can be seen from table 2, the order of the sample surface to be black is Ti→Mo→MNT→MoTi and MTN, this suggests that MoTi and MTN have the similar impact on preventing Cu diffusion,greater than MNT.Mo and Ti have the weaker effect on blocking Cu diffusion than the other barrier materials, among them Ti with the weakest impact on preventin the diffusion of Cu.

Alloy material has excellent blocking ability, because the grain size is relatively small, the grain boundary is small, and the lattice distortion is more, which is more conducive to blocking the diffusion of Cu atom.

3. Inoxidizability

In order to improve the performance of TFT devices, the performance of gate and S/D electrodes are also one kind of the focuses. Cu with low resistance can reduce Rc delay effect ,so it is widely used in industrial production. Therefore, antioxidant capacity is also one of the criteria to be considered when selecting a high-quality barrier layer.

To explore the antioxidant capacity of different barrier metals, Mo,MoTi,Ti,MoTiNi, MoNbTa,ITO and Cu films were prepared by PVD,respectively.All the films were deposited on glass substrate and the thickness are 100nm.The second, the films were placed in the oven and annealed at 250 ℃ in CDA atmosphere.Recording the resistance of films at different time. The resistances of different metal films with different processing times are shown in the figure 4. As the annealing time increases, the resistance of Cu,MNT and Mo change obviously,.Especially, after annealing for 0.5h, Cu has been transformed from the low-resistance conductor to an insulator. Mo and MNT exhibit insulation in annealing for 2 hours and 1 hour respectively, which mean complete oxidation occurs.

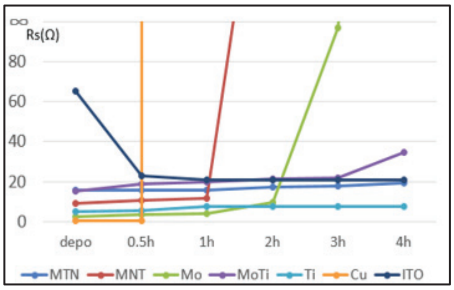


Figure 4 Film resistance at different annealing times

However, the annealing treatment has little effect on changing the resistance of the other metal films. It is interesting that, the resistance of ITO films decreases firstly and then remains stable under annealing conditions. This is due to the the crystal structure of ITO change from amorphous structure to polycrystalline. The films with low resistance after annealing show that these materials such as MTN、MoTi、Ti、ITO are good at resisting oxidation.As a result, these materials can be sputtered over Cu as a protective layer to avoid Cu oxidation when manufacture the TFT devices.

Ti,MTN,MoTi have excellent resisting oxidation because of the anti-oxidation materials such as Ti and Ni in the film.

4. Etch-related properties

As we all know, the material used as the barrier layer must be etched by the same acid with the Cu.Hence the indexs related to etching such taper angle,CD loss,undercut,tail, etched residual tip and so on are very important for choosing barrier layer.In this paper, under the same etching condition, the response of different barrier layers to etching are compared directly by SEM cross section.Figure 5 display cross section morphologys of the barrier/Cu duallayer films,5(a) is the SEM image of Mo/Cu,it is clearly shown that when Mo is used as barrier layer,there will exist undercut after etching. And the step coverage of upper dielectric layer is poor, consequently,proning to form crack increase the risk of ESD. On the contrary,the other metal barrier layer films like Ti,MoTi,MTN and MNT show good etching characteristic, namely there is no undercut phenomenon. At the same time, the step coverage of the upper dielectric layer is better than Mo/Cu due to the subsistent tail of the barrier layers after etching. Therefore, the probability of ESD in gate insulation layer can be reduced. In addition, we measured the taper angle of these five samples with the process of etching,th`are summrized in Table 3.As shown in table 3, both Ti and Mo alloys can be barrier layers applied to TFT devices.

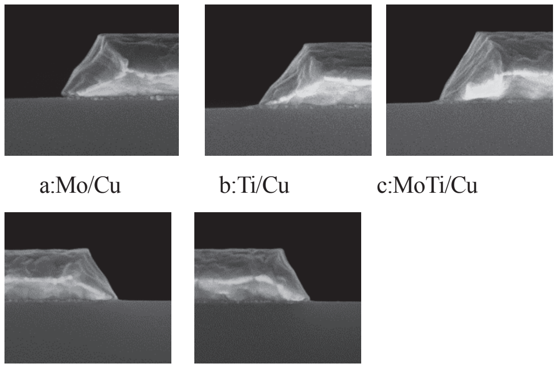


Figure 5 SEM cross section images of barrier/Cu duallayers.

Table 3 Physical properties of barrier/Cu duallayers after etching

structure	Taper angle	Undercut	Tail
Mo/Cu	55°	Yes	No
Ti/Cu	52°	No	0.2um
MoTi/Cu	56°	No	0.1um
MTN/Cu	57°	No	0.07um
MNT/Cu	49°	No	0.07um

With the increasing demand for display devices, Micro - LED gradually become the main focus areas of current research and development. In the current Micro-LED manufacturing process,Cu is still used as LED-chip bonding pad and cof bonding line. Because it is in the outside of the panel ,so it’s easy to be oxidized resulting in poor panel quality.To reduce the influnence of oxidation,ITO is deposited above the Cu electrode to protect Cu from being affected by external environment.But this add a mask to the process.Therefore, replacing ITO with barrier layer can not only protect Cu but also maintain the number of masks, which is conducive to the reduction of cost.Figure 6 is the schematic diagram of barrier layer replaies ITO as Cu protection layer.

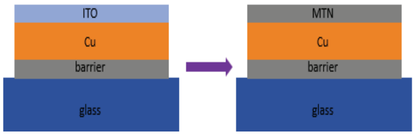
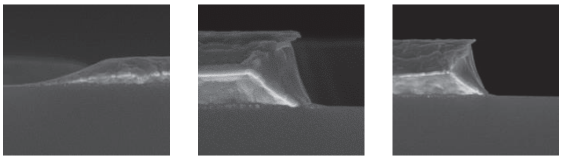
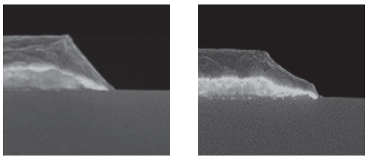


Figure 6 schematic diagram of barrier layer replaies ITO as Cu protection layer.



a:Mo/Cu/Mo b:Ti/Cu/Ti c:MoTi/Cu/MoTi



d:MTN/Cu/MTN e:MNT/Cu/MNT

Figure 7 SEM cross section images of barrier/Cu/barrier triplelayers.

Table 4 Physical properties of barrier/Cu/barrier trilayer after etching

structure	Taper angle	Undercut	Tail	Tip
Mo/Cu/Mo	15	No	No	No
Ti/Cu/Ti	68	No	0.2um	Yes
MoTi/Cu/MoTi	65	No	0.1um	Yes
MTN/Cu/MTN	47	No	0.07um	No
MNT/Cu/MNT	41	No	0.07um	No

From this figure, it is known that the metal layer not only need to contact with the semiconductor layer but also with the insulating layer. For barrier/Cu double layer,on side of Cu is not protected so that oxidation reaction occurred to affect profermance of the TFT device.In order to further reduce the influence of Cu diffusion or oxidation.The barrier/Cu/barrier triple layer is analyzed too. Physical properties of these films are displayed in following table 4 and the morphologys are described in figure 7.

According to the data in the table 4 and the corresponding SEM image, it can be known that the taper angle of Mo/Cu/Mo is too small to be used as electrode in TFT structure.Although Ti/Cu/Ti and MoTi/Cu/MoTi with the good taper angle,but a tip will generate at the edge of the films, which will affect the coverage effect of the upper insulation layer and lead to ESD. Therefore,the MTN/Cu/MTN and MNT/Cu/MNT are good choice for acting barrier layer , because of the good taper angle and the property of no tip after etching. The difference in etch rate of MTN, MNT and Cu is relatively small, so no tip is generated.

3 CONCLUSION

In summary，we have fabricated the simple to verify the practical of different barrier layer in TFT devices. The Mo,Ti,MoTi,MTN and MNT are selected as research objects and characterized their physical properties by XRD,SEM,etc. All of these barrier layers show excellent adhesion about 5B, the ability to block Cu diffusion into other layers is pretty good and resistivity of these barrier materials is low. Among them, MoTi,Ti and MTN exhibit more excellent antioxidant capacity, that can substitude ITO as Cu barrier layer in Micro-LED. In the meantime, considering the adaptation of the etching process,based on our results,MTN as barrier material is combined into MTN/Cu and MTN/Cu/MTN barrier layer,there are no undercut and tip condition under the deal with etching.The taper Angle of about 40° also meets the design requirements of the product. From what has been discussed above, MTN as Cu barrier has the potential for the application of high quality TFT devices.

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