[Technical Paper]

High Heat Proofing Nano-Layered Film Cu Wiring Using Crystal Grain Growth Control

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Abstract

Cu is gaining a lot of attention as the main wiring material for next generation devices. However, Cu oxidizes in high-temperature heat treatments. For heat-proofing considerations, a Cr/Cu/Cr system is widely used. Currently, the required Cr layer is too thick and Cr is environmentally problematic. Therefore, we focused on the stable oxide, SnO₂, and were able to increase heat proofing by covering Cr/Cu/Cr with SnO₂. This was able to tolerate a heat treatment of 873 K for 1800 s in air. 873 K is the highest temperature in the PDP manufacturing process, which has an especially severe heat treatment for various devices. However, some oxidization along the grain boundary was observed. In order to further increase reliability, we then investigated the elucidation of an oxidation mechanism. We show clearly that Cu crystal grain growth is the most important factor for the oxidation. Based on this fact, we tried to control grain growth and improve heat proofing by inserting one or more Cr layers into the Cu layer. The result looks like a mille-feuille or Napoleon pastry. As a result, grain growth was controlled and heat proofing greatly improved.

Keywords: High Heat Proofing, Oxidation, Multi-layer, Cu/Cr/SnO₂ Thin Film, Crystal Grain Growth, Insertion Cr Layer

1. Introduction

Electronic products such as semiconductors and displays are not realized without progress in digital devices. In such digital devices, Cu is used widely as a main wiring material of the electronic circuits. However, since the adhesiveness of Cu with a surface oxide film is weak, in a high-temperature, or oxidizing atmosphere, it cannot be used independently.[1] Thus, in order to secure oxidation resistance with various heat treatments used during the manufacture of devices, protective layers, such as Cr, are used.[2] However, a very thick Cr film is needed for oxidation resistance. Also Cr may oxidize at high temperatures to hexavalent chromium, which is harmful to people (This oxidation does not happen under usual heat-treatment conditions). Therefore, it is necessary to reduce the amount of Cr used as much as possible. So realization of the high heat stability with a thin film of a nano order is desired.

For these reasons, we studied Cr/SnO₂[3–5] as a protective layer. In this case, Cr is an adhesive layer. SnO₂ is a very stable oxide and can be expected to prevent inflow of oxygen. Moreover, it is useful in PDP[6] (plasma display

panel) manufacturing, which uses a high process temperature (1800 s at 873 K in air), as it is not dissolved in a dielectric.

Cu crystal grain growth under a high-temperature heat treatment is easily predicted. The diameter of the Cu crystal grain after heat treatment is calculated by the formula[7, 8]

$$d^2 - d_0^2 = Kt \cdot \exp(-Q_{gb}/RT)$$

where d_0 is the initial grain size, t is the time, Q_{gb} is the activation energy for grain boundary diffusion, T is the heat treatment temperature, and K and R are constants. When values of $K = 3.59 \text{ m}^2/\text{s}$ and $Q = 72470 \text{ J/mol}$ are substituted into the equation,[9, 10] d is equal to $3.45 \text{ }\mu\text{m}$. Considering that the thickness of the wiring is $1 \text{ }\mu\text{m}$, protective layers will be subjected to stress. In Cu/Cr, it is thought that this stress is suppressed by the very thick Cr. In this paper, we investigated whether stress from crystal grain growth and oxidization could be suppressed by protective layers of a nano order.

2. Experimental

Cu multi layers were formed by EB (electron beam) plasma deposition. EB plasma deposition can form a continuous film with high adhesiveness.[11]

The outline of the equipment is shown in Fig. 1. The film-forming conditions are shown in Table 1. Cr and Cu of 99.99% (4Ns) purity were used to form the film.

Ultrasonic washing of the substrate was carried out in pure water and ethanol as a pretreatment of film forming, with O₂ washing in a vacuum. The basic film composition is shown in Fig. 2.

In order to simulate an actual manufacturing process, the created sample was held for about 1800 s after heating to 873 K, which is the softening point of the Pb-free dielectric paste in air. It was then cooled. Observation of the surface state before and after heat treatment was performed using FE-SEM (field emission scanning electron microscopy) and an optical microscope. An SEM cross-sectional observation was conducted after processing with FIB

Fig. 1 Schematic diagram of the EB Plasma Deposition apparatus.

Table 1 Condition of thin film formations by EB Plasma.

Target	Cr ₂ O ₃	Cr(4N)	Cu(4N)	Cr(4N)	SnO ₂
Deposition rate (nm/s)	0.1	0.5	0.7	0.5	0.2
Substrate heating	No heating				
RF power (W)	500

Fig. 2 Structure of Cu/Cr/SnO₂ multi-layered film.

(focused ion beam). W (tungsten) was deposited to protect the surface coat at the time of cross-sectional processing. Crystal orientation analysis was performed using EBSD (electronic backscattering diffraction pattern). Surface form and unevenness were measured and analyzed using an AFM (atomic force microscope).

3. Results and Discussion

3.1 Heat-resistance degradation mechanism

In spite of being covered by SnO₂ which is a stable oxide, the Cu thin film was oxidized after heat treatment. At this time, the Cu crystal grains were growing rapidly. Accordingly, from various examination results, the heat resistance degradation mechanism in Cu/Cr/SnO₂ system was inferred. The details are given below using the mimetic diagram of Fig. 3.

- (1) As-deposited Cu formed a detailed crystal structure of about 20 nm scale (Fig. 3(a)).
- (2) When this sample was subjected to a high-temperature heat treatment of 823 K, the surface remained flat and smooth, and the Cu crystal grains were still detailed during the time of the SEM observation. However, a stacking fault with a direction equal to the vertical section observation is seen with the SEM. Similarly, the horizontal crystal orientation analysis using EBSD shows grain growth of the internal Cu on the order of several microns (Fig. 3(b)). At this time, we see from the SEM image that the vertical grain growth of the Cu is suppressed and growing only horizontally. However, crystal grains tend to grow to a globular form, which is stable in energy. Here, since the surface protection layer prevents that, we considered that a high degree of strain occurs at the interface with the protection layer near the newly formed Cu grain boundary. Because of the strain, a diffusion path which is not observed by SEM is formed in the protection layer along the Cu crystal grains.
- (3) Oxygen flowing through the diffusion path causes a cubical expansion ($V_{Cr_2O_3}/V_{Cr} = 1.97$) by the oxidation of Cr. Moreover, when oxygen diffuses through the Cu grain boundary and is supplied to a lower layer Cr, a part of the Cu grain boundary oxidizes. Furthermore, Cu crystal grain growth is also accelerated with higher heat-treatment temperatures. More stress is put on the protective layer by this oxidation, expansion, and Cu crystal

Fig. 3 Schematic diagram of the oxidation mechanism.

grain growth advance. The protective layer changes shape under this stress causing the unevenness which follows the Cu crystal grain. Thus, the diffusion path is extended and will evolve into a visible micro crack (Fig. 3(c)).

- (4) Because the diffusion path extends to micro cracks, Cu atoms can easily diffuse to the surface. Cu diffused to the surface oxidizes and black point (Oxide) is formed (Fig. 3(d)). The wiring changes shape significantly due to the diffusion of internal Cu to the surface. The protective layer cannot maintain the original form. Oxidization advances at an accelerated pace because of the loss of the protective function of the SnO_2 film. At worst, disconnection can result.

Thus, we presumed that the predominant factor of Cu oxidation in a Cu/Cr/ SnO_2 system thin film wiring was Cu's own crystal grain growth. That is, if the crystal grain growth of Cu can be controlled, heat-resistance degradation may be prevented by the thin SnO_2 . Next, by controlling the growth of the Cu crystal grain, we verified a presumed rule factor and investigated how to raise the heat resistance.

3.2 Controlling Cu crystal grain growth

To control Cu crystal grain growth, we investigated lamination wiring with Cr layers inserted into the Cu layer, as shown in Fig. 4. From this structure, we expected to mitigate stress on the protective layer by controlling crystal grain growth, maintaining low resistance. Fig. 5 shows the SEM verticality section image of these samples after heat treatment. This result shows that Cr clearly exists in layers after the heat treatment and the laminated structure is maintained.

Next, we investigated the heat-resistance effect of a lam-

Fig. 4 Structure of Cu multi-layered film which Cr inserted.

Fig. 5 The cross section of Cu/Cr multi-layer after heat treatment.

	Single layer (1μm)	Multi layer (500nm × 2)	Multi layer (100nm × 10)
As depo
Ω/cm	1.2	1.5	2.0
873K
Ω/cm	1.5	1.4	2.0

Fig. 6 The surface oxidation and asperity observation before and after heat treatment.

inated structure. Observations of the surface changes of a single layer (= 1 μm for Cu layers) and laminated layers are shown in Fig. 6, and the measurement result of surface

	As depo.	Single layer (1 μ m) annealed	2 multi-layer (500nm x 2)annealed	10 multi-layer (100nm x 10) annealed
3D image
Surface roughness (nm)	2.4	66.6	48.8	34.9

Fig. 7 Surface average roughness after heat treatment under each thin film circuit structure.

Fig. 8 The observation of control effect of Cu horizontal crystal grain growth by multi layered.

coarseness is shown in Fig. 7. From these results, it can be seen that the surface of the single layer wiring oxidized and the black point (Oxide) was increased after the heat treatment. On the other hand, in lamination wiring, generation of a surface oxide is suppressed as the number of divisions increases. Moreover, the irregularity of the surface, which is probably based on Cu crystal grain growth, was also suppressed. We consider that these results were clearly due to the influence of the inserted Cr layers.

Next, we investigated the influence of the inserted Cr layers on the Cu crystal grain growth suppression. Each sample was processed using FIB and the comparison of the substrate Cu crystal grain size in the horizontal direction after heat treatment is shown in Fig. 8. From this result, it can be seen that the approximately 20 nm initial particle diameter has grown to the order of 1–2 μ m after heat treatment in the single layer. On the other hand, in the ten division layers, growth could then be controlled to about 100–200 nm, and grain growth could be held down to about 500–800 nm in the 2 division layers. The Cr layer inserted into the layers played the role of a growth suppression factor for Cu crystal grains.

The average particle diameter after heat treatment and its relation to the film thickness of the Cu layer are shown in Fig. 9. This result also shows that particle diameter is dependent on film thickness. We also clarified that crystal grain size can be controlled by varying the number of layers in the Cu lamination structure. These results show the possibility of realizing highly heat-resistant Cu-system

Fig. 9 The relationship between film thickness and grain size after heat treatment.

thin-film wiring by controlling the Cu crystal grain growth. One proof that the factor which degrades the heat resistance of Cu/Cr/SnO₂ system wiring is growth of Cu crystal grain could be shown.

However, in the laminated structure which we investigated here, not only the direction of film thickness but horizontal crystal grain growth was controlled. Thus, we are concerned about an increase in specific resistance. In the future, we plan to investigate the proper film thickness of the Cu and Cr layer in consideration of the trade-off between heat proofing and resistance, as well as the proper number of Cr layers, etc., in a laminated structure.

4. Conclusion

This paper investigated the oxidization and crystal grain growth of Cu in Cu/Cr/SnO₂ system multi-layers. We conclude that

1. The grain growth of Cu is the dominant factor affecting Cu oxidization in Cu/Cr/SnO₂.
2. Control of grain growth is possible by inserting Cr layers into the Cu layer, and grain size is dependent on the Cu film thickness. By controlling the grain growth, heat resistance was greatly improved.

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