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Influence of Rare Earth on the peeling properties of Ultra-thin Copper Foil with Carrier

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Abstract: In this paper, the peeling strength between ultra-thin copper foil and carrier is improved by some rare earths used as additives during the formation of the stripping layer of H-G alloy. The effect of different rare earth and their different contents on the stripping property of ultra-thin copper foil with carrier when they are added in the H-G plating solution is investigated, and the influence of rare earth on the cathodic polarization curves and cyclic voltammetry curves of H-G alloy during its electrodeposition is analyzed too. Results show that rare earth elements of La, Sm, Y and Ce increase the peeling strength between ultra-thin copper foil and carrier to a certain extent and the peeling strength is increased from 0.13 kgf $\bullet$cm^{-1} to the range of 0.16 ~ 0.20 kgf $\bullet$cm^{-1}. Different rare earth contents also have impact on the peel strength and surface property of ultra-thin copper foil with a carrier support, in which the optimum adding amount of La is 0.1 g $\bullet$L^{-1}. Electrochemical test results show that the addition of rare earths can reduce the degree of the plating solution's polarization, accelerate the electrode reaction speed, increase the alloy reduction capacity, promote alloy's co-deposition, and improve the bonding strength between alloy layer and substrate, thus the peeling strength between ultra-thin copper foil and carrier is enhanced.

Introduction

The peelable ultra-thin copper foil with carrier foil is used widely by stacking with substrate through hot pressing process, and then strips the carrier foil (an ultra-thin copper foil remains on the substrate as circuit board using [1]). At this time, an unstable stripping phenomenon exists in the bonding interface between carrier and ultra-thin copper foil. Some carrier foil can peel off automatically in the processing because it is too easy to be stripped; some are too difficult to be stripped, even after hot pressing process. In order to solve these problems, a stripping layer needs to be formed between the carrier foil and ultra-thin copper foil to make the peeling strength exist between them, and then the carrier foil will not peel off the ultra-thin copper foil during their transportation, and can be completely stripped after the hot pressing process. At present, some scholars have studied some stripping layers between the carrier foil and ultra-thin copper foil [2, 3].

As an additive, rare earth is used widely in the field of electrodeposition. Studies have shown that the addition of rare earth can obviously improve the stability of plating solution and the property of deposit in the traditional electrodeposition [4,5]. On the other hand, rare earth ions are easy to be adsorbed on the activity position of crystal growth, which can slow down the crystal growth rate and refine the crystal structure of coating. Many documents show that adding rare earth in the plating solution can also improve the bonding strength between the alloy layer and the substrate material [6-8].

In this paper, the preparation process of the ultra-thin copper foil with carrier support is studied. In this process, an organic layer and an alloy layer as the peeling layer are used.In another words, the organic layer alloy layer are firstly formed on the carrier foil, then the ultra thin copper foil is electrodeposited on the peeling layer and the ultra-thin copper oil with carrier is obtained [9]. In this experiment, rare earth elements are added in the plating solution of H-G alloy during the formation of a peeling layer. The modification of rare earth elements on H-G alloy layer, and the effect on the peel strength are investigated; the study can further broaden the application fields of rare earths.

Experiments

(1) Preparation process of ultra-thin copper foil with carrier supporting[10]:
Carrier foil → adsorb the organic layer → electrodeposite alloy layer → electrodeposite ultra-thin copper foil.

Plating solution of H-G alloy is made up of H 20 g• L^{-1}, G 80 g• L^{-1}, $C_6H_5Na_3O_7 \cdot 2H_2O$ 50 g• L^{-1}.

(2) Electrochemical test
Electrochemical test integrated instrument of AUTOLAB P301 (Holland, Autolab scientific instrument limited company) is used for testing the cathodic polarization curves and cyclic voltammetry curves. Electrochemical workstation software of AUTOLAB and Origin7.0 are used in data processing.

Results and Discussions

Effects of different rare earths on the ultra-thin copper foil with carrier

To investigate the influence of different rare earth added to the plating solution during the electrodepositing of peeling layer on the ultra-thin copper foil with carrier support, 0.1 g •L^{-1} rare earth of lanthanum (La), cerium (Ce), samarium (Sm) and yttrium (Y) are added to the H-G alloy plating solution respectively with the optimum preparation process of ultra-thin copper foil with carrier support. The experimental results are shown in table 1.

Table 1 Effect of different rare earth added to alloy plating solution on the peeling properties of ultra-thin copper foil with carrier

Rare earth	Current density of alloy layer plating ($A \cdot dm^{-2}$)	peel strength ($kgf \cdot cm^{-1}$)	Thickness of ultra-thin copper foil (μm)
La	15	0.18	3
Ce	15	0.20	3
Sm	15	0.16	3
Y	15	0.17	4
No rare earth	15	0.13	3

Table 1 shows that carrier foil can be stripped from ultra-thin copper foil after adding rare earth in H-G alloy plating solution, and the peel strength between ultra-thin copper foil and carrier have been increased in different level. The most increasing of peel strength is the solution containing some Ce, the value is increased from 0.13 kgf $\cdot cm^{-1}$ to 0.20 kgf $\cdot cm^{-1}$, followed by La, it increases to 0.18 kgf $\cdot cm^{-1}$. The experiment has also shown by observation that there is no residue remaining on the surface of ultra-thin copper foil after the carrier being stripped. That is to say, the ultra-thin copper foil surface is clean, bright and uniform. and the thickness of ultra-thin copper foil layer is also relatively uniform, all of them are under 5μm. The interesting thing is adding rare earth in H-G alloy plating process can improve the peel strength between carrier and ultra-thin copper foil and its surface quality. This main reason is because rare earth ion hinders the growth of crystals in the H-G alloy electrodeposition process, which makes the crystal nucleus formation rate be greater than the crystal growth rate, thus the alloy layer surface is more bright, smooth, density, uniform and fine. In addition, the addition of rare earth accelerates the deposition rate of metal ions in some degree [11], which also improves the adhesion strength between coatings and substrate. Therefore, the peeling strength between carrier and ultra-thin copper foil with the addition of rare earth elements has been enhanced to a certain degree when compared to the peeling strength without the addition of rare earth elements.

Effects of different rare earth contents on the ultra-thin copper foil with carrier

By the experiment, the properties of ultra-thin copper foil with carrier are not only influenced by the type of rare earth, but also by the contents of rare earth. In order to study the effects of different contents of rare earth on the peel strength of the ultra-thin copper foil with carrier, these experiments have been carried out with different content of La rare earth adding to the alloys plating solution. Effect of different content of La on the peel strength between ultra-thin copper foil and carrier is shown in Table 2.

Table 2 shows that carrier can be stripped from ultra-thin copper foil when the La content is added in range of 0.05～0.25 $g \cdot L^{-1}$ to the H-G alloy plating bath. However, carrier can be stripped because the peeling strength is too weak to be measured if the adding amount is 0.05 $g \cdot L^{-1}$. When the adding amount is ranged from 0.1 $g \cdot L^{-1}$ to 0.2 $g \cdot L^{-1}$, the peel strength can be measured. With the rare earth content being increased to 0.5 $g \cdot L^{-1}$, carrier can be partially stripped, and there are some residues on the surface of ultra-thin copper foil after carrier being stripped. At the same time, the electrolytic solution will become turbid and there is some white precipitation at the bottom of the solution, which affects the service life of electrolyte. Therefore, the best adding amount of La is 0.1 $g \cdot L^{-1}$ in alloy plating bath.

Table 2 Effects of different content of La on the stripping of ultra-thin copper foil with carrier support

content of La ($g \cdot L^{-1}$)	whether peelable	peel strength ($kgf \cdot cm^{-1}$)
0.05	peelable	/
0.1	peelable	0.19
0.15	peelable	0.18
0.2	peelable	0.18
0.25	peelable	/
0.5	part peelable	/

Effects of Rare Earth on the Electrochemical Behavior of Alloy Electrodeposition

To make a further research about the reason of rare earth affecting the peel strength of ultra-thin copper foil with carrier support, experiments test the cathodic polarization curves and cyclic voltammetry curves of H-G alloy with different rare earth (RE content is 0.1 $g \cdot L^{-1}$) in plating bath, the results are shown in figure 1 and figure 2.

Figure 1 shows that when the H-G alloy plating solution is added with rare earth of La, Ce, Sm and Y respectively, the polarization of cathodic polarization curves is smaller than those of no rare earth, the order of polarization degree is La < Ce < Sm < Y, so the influence degree order of rare earth on alloy deposition velocity which in turn is La > Ce > Sm > Y. It can show that the polarization degree of La curve is the minimum, its current is the maximum and its deposition potential shifts positively the most, so the deposition velocity and the alloy amount with La rare earth being added are also up, and finally it affects the stripping property of the ultra-thin copper foil with carrier more obvious.

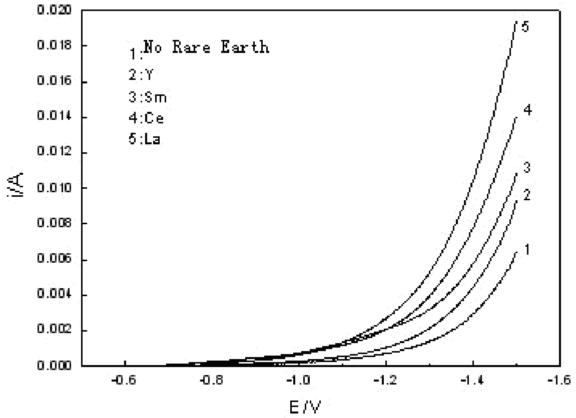

Figure 1. Cathodic polarization curves with different rare earth in alloy plating

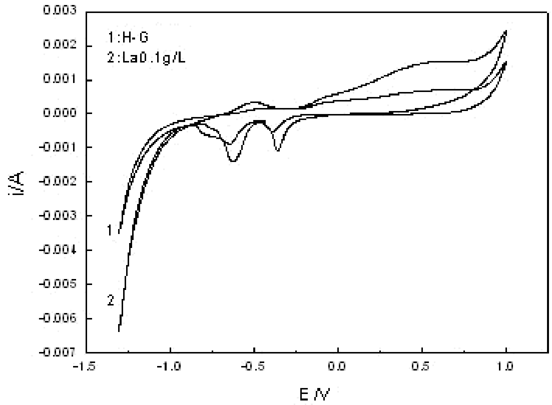

Figure 2 Cyclic voltammetry curves of alloy plating solution with rare earth and without rare earth

Figure 2 is the cyclic voltammetry curves of the alloy plating solution without rare earth adding (curve 1) and with La rare earth adding (curve 2). The scanning potential starts from 0V to -1.3V, and then scans to 1.0V. It can be seen from Figure 2, curve 1 has two smaller peaks at -0.389V and -0.645V, curve 2 has two larger reduction peaks at -0.359V and -0.622V, and two reduction peaks of curve 2 have a little more positive potential shift compared to curve 1. This fully shows that the addition of rare earth decreases the reduction potential of H-G alloy plating solution, increases the reduction capacity and promotes the alloy deposition speed. With the scanning potential shifting negatively, curve 2 has a more negative current than curve 1. That is to say, the current of hydrogen released increases with the addition of rare earth, which hinders the hydrogen evolution reaction of plating liquid. In addition, it can still be seen from Figure 2, the area of curve 2 surrounding is larger than curve 1, which further indicates that adding rare earth into the plating solution will improve the deposition speed, thereby increase the alloy deposition amount on the carrier foil, improve the bonding strength between the alloy layer and substrate and ultimately improve the peel strength between carrier support and ultra-thin copper foil.

Conclusions

(1) The peel strength between carrier and ultra-thin copper foil has various degree enhancements with different rare earths being added in alloys plating process. The peeling strength increases the most with the addition of rare earth cerium, which is changed from 0.13 kgf $\cdot cm^{-1}$ (without rare earth being added) to 0.20 kgf $\cdot cm^{-1}$, followed by La, increased to 0.18 kgf $\cdot cm^{-1}$. The thickness of ultra-thin copper foil is relatively uniform as well, and it is in the range of 1μm to 5 μm.

(2)Different rare earth contents have different effect on the peeling strength of ultra-thin copper foil with carrier, the best adding amount of La is 0.1 $g\cdot L^{-1}$.

(3)The electrochemical testing results show that the addition of rare earth elements in alloy plating bath can promote the alloy deposition on the carrier foil surface, improve the crystal nucleus formation rate and the metal's reduction capacity and accelerate the alloy deposition rate. Therefore it can increase the alloy deposition amount on the carrier foil, improve the bonding strength between alloy layer and substrate and improve the peel strength between carrier and ultra-thin copper foil ultimately.

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