Adhesion of Electrodeposited Copper, Nickel and Silver Films on Copper, Nickel and Silver Substrates\textsuperscript{*1}

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The adhesion of electrodeposited Cu, Ni and Ag films on Cu, Ni and Ag substrates has been examined by the adhesion tape test. Different interfacial structures have been observed by SEM, GD-OES and TEM for the different film/substrate combinations and have been discussed in relation to the interface adhesion. Results show that the different combinations of the electrodeposited films and substrates reveal the different interface adhesive feature. Typically a strong adhesion presents in the interfaces of Ni film/Cu substrate, while a weak adhesion presents in the interfaces of Cu film/Ni substrate, Cu film/Ag substrates, Ni film/Ag substrate, Ag film/Ni substrate as well as Ag film/Cu substrate. The crystallographic coherency existing in the interface of Cu deposited film/Ni substrate suggests that the adhesion of electrodeposited films on various metal substrates is primarily determined by the crystallographic coherency rather than by the effect of voids in the interfaces.

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**Keywords:** electrodeposition, adhesion, silver, copper, nickel

1. Introduction

Proper adhesion of thin films on various substrates is one of the very important industrial factors in the engineering application for determining the mechanical behavior and performance of the coated components. A number of studies have been carried out to investigate the adhesion mechanism, and attempt to establish an effective evaluation method of adhesion.\textsuperscript{1-3} Recently, the multilayer printed wiring in the electronic industry has attracted much attention.\textsuperscript{4} Such multilayer printed wiring, generally, can be achieved by an electrodeposition process, thus inevitably introducing an important adhesion problem.

Metallic films electrodeposited on the metal substrates are commonly thought to always show a favorable adhesive strength since the electrodeposited films usually bond with substrates metallically. However, the experimental results do not always coincide with this general thinking since sometimes some electrodeposited films may exfoliate from the certain metal substrates due to the weak adhesion. Up to now, no reasonable explanation on the adhesion problem can be described, which can be accepted widely.

We propose that the adhesion of electrodeposited films with metal substrates should correlate with the thermal equilibrium phase diagrams of binary alloys. The metal-metal bond tends to form in the interface of film/substrate combination like all-proportion miscible alloy system, resulting in a favorable adhesion. Conversely, the metal-metal bond can hardly form in the interface of film/substrate combination like eutectic alloy system, thus causing a poor adhesion in the interface. Such metal-metal bond strength represents the adhesive force of the film to the substrate, generally correlates with the crystallographic coherency in the interface between the film and the substrate.

In the present study, we designed different film/substrate combinations to experimentally construct the different binary alloy systems for verifying our hypothesis. The combinations used are as follows: 1) Cu/Ni, all-proportion miscible alloy system; 2) Cu/Ag, eutectic alloy system, which separates into two phases at normal temperature state; 3) Ni/Ag peritectic alloy system, which separates into two phases at normal temperature state. Such combinations of deposited films and substrates have been practically applied in the electronic industry. For example, for achieving Ag electrodeposition on the Cu substrate, Ni thin film is always deposited on Cu substrate as an underlayer to enhance the adhesion between Cu substrate and Ag film.

2. Experimental Procedure

The different combinations of electrodeposited Cu, Ni and Ag films with such three metal film substrates deposited on Cu foils were designed to evaluate their adhesive properties. The plating baths and deposition conditions are shown in Table 1. HBO\textsubscript{3} was added to Ni plating bath as a pH buffer, while KI was added in Ag plating bath as a complex agent. All the solutions were prepared using deionized water and reagent grade chemicals. The plating cell was a beaker of 300 mL with magnetic stirrer agitation, and the bath temperature was set at 30\textdegree C.

The copper foil with the thickness of 0.035 mm was used as a substrate material. All copper foils were electrochemically polished to the mirror finishing surfaces, and immediately were used to perform the electrodeposition of Cu, Ni and Ag. Subsequently, these Cu, Ni and Ag films deposited on Cu foils were used as the new substrates to be selectively electrodeposited with Cu, Ag and Ni films. To avoid the oxidation of the deposited films in each case, all the electrodeposition processes were carried out immediately after the preparation of substrates. For all the deposition, the total thickness of deposited films was controlled as 10\textmu m, and the dimension of sample was set at 20 mm \times 10 mm. Pt plate with the dimension of 20 mm \times 20 mm was selected as the anode material or Cu and Ni electrodeposition, while Ag plate with same dimension was selected as the anode material in Ag deposition.

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The adhesive strengths were determined by adhesive tape test available to JIS H8505. The cross-section structures were observed by scanning electron microscope (SEM: JSM-6500, JEOL). The samples for cross-section observation were prepared by cross-section polisher (SM-09010, JEOL). The elemental depth profiles in the interfaces were measured by means of grow discharge-optical emission spectroscopy (GD-OES: JY-5000RF, HORIBA). The crystallographic coherency between the electrodeposited films and the substrates was determined by transmission electron microscope (TEM: JEM-2000FX, JEOL).

3. Results

3.1 Adhesion of electrodeposited films

The adhesive strengths of deposited films to various substrates which were measured by adhesive tape testing are presented in Table 2. All the films directly electrodeposited on copper foils are not exfoliated from the substrates, showing a strong adhesion. Also the films deposited on the substrates of same kind of metal with the deposited films, are not exfoliated, indicating a strong adhesion. However, Ag films on Cu and Ni substrates, Cu and Ni films on Ag substrates and Ni film on Cu substrate are exfoliated from the substrates, showing a weak adhesion. On the other hand, Ni film on Cu substrate is not exfoliated from the substrate, showing a strong adhesion. Apparently, the adhesion of electrodeposited films changes with the different film/substrate combination.

3.2 Cross-section structural observations

Cross-section SEM samples were prepared by a cross-section polisher. Figure 1 shows the cross-section SEM images of different film/substrate combinations (a) and (a’) Cu film/Ni substrate, (b) Ni film/Cu substrate and (c) Cu film/Ag substrate.

Table 1 Plating baths and plating conditions.

<table>
<thead>
<tr>
<th>Cu bath (Anode: Pt)</th>
<th>Ni bath (Anode: Pt)</th>
<th>Ag bath (Anode: Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath composition</td>
<td>NiSO₄·6H₂O : 1 mol/L</td>
<td>AgI : 0.005 mol/L</td>
</tr>
<tr>
<td></td>
<td>CuSO₄·5H₂O : 1 mol/L</td>
<td>KI : 2 mol/L</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃ : 0.5 mol/L</td>
<td></td>
</tr>
<tr>
<td>Plating conditions</td>
<td>Current density : 150 A/m²</td>
<td>Current density : 150 A/m²</td>
</tr>
<tr>
<td></td>
<td>Temperature : 30°C</td>
<td>Temperature : 30°C</td>
</tr>
<tr>
<td></td>
<td>Agitation : Yes</td>
<td>Agitation : Yes</td>
</tr>
<tr>
<td></td>
<td>pH : 2.0</td>
<td>pH : 2.4</td>
</tr>
</tbody>
</table>

Table 2 Adhesive strength of different film/substrate combinations.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Electrodeposited film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu film</td>
</tr>
<tr>
<td>Electrodeposited copper foil (35 µm)</td>
<td>adhesive</td>
</tr>
<tr>
<td>Cu film electrodeposited on copper foil</td>
<td>adhesive</td>
</tr>
<tr>
<td>Ni film electrodeposited on copper foil</td>
<td>exfoliate</td>
</tr>
<tr>
<td>Ag film electrodeposited on copper foil</td>
<td>exfoliate</td>
</tr>
</tbody>
</table>

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Cross-section SEM samples were prepared by a cross-section polisher. Figure 1 shows the cross-section SEM images of different film/substrate combinations (a) and (a’) Cu film/Ni substrate, (b) Ni film/Cu substrate and (c) Cu film/Ag substrate. A large number of voids, approximately 30–500 nm size, are clearly observed in the interface of Cu film/Ni substrate (Figs. 1(a) and (a’)). These voids cause a decrease of the adhesion of Cu film, resulting in the exfoliation of Cu film from Ni substrate. However, the voids are not observed in the interface of Ni film/Cu substrate (Fig. 1(b)). Moreover, as shown in Fig. 1(c), many voids exist in the interface of Ag substrate/Cu foil (Fig. 1(c)) as compared to the combination Cu film/Ag substrate. The exfoliation then happens in the interface of Cu film/Ag substrate by the effect of these voids.
3.3 Elemental depth profiles

The elemental depth profiles of different film/substrate combinations were measured by GD-OES. Figure 2 illustrates the GD-OES depth profiles of (a) Cu film/Ni substrate, (b) Ni film/Cu substrate, and (c) Cu film/Ag substrate. Hydrogen with high concentration is detected in the interface of Cu film/Ni substrate (Fig. 2(a)), whereas it is not detected in the interface of Ni film/Cu substrate (Fig. 2(b)). Moreover, for the combination Cu film/Ag substrate/Cu foil (Fig. 2(c)), the hydrogen with high concentration is detected from the interface of Ag substrate/Cu foil. Since no oxygen can be detected in the interfaces of all the samples, it can be considered that the voids existing in the interfaces are due to the hydrogen evolution.

3.4 Crystallographic coherency between films and substrates

In order to determine the crystallographic coherency of the electrodeposited films with the substrates, the deposited films and the substrates were observed simultaneously by TEM without separation. The bright-field images and their corresponding electron diffraction patterns/key diagrams of (a) (a’) Cu film/Ni substrate, (b) (b’) Ni film/Cu substrate and (c) (c’) Ni film/Ag substrate are shown in Fig. 3. It can be seen that the crystallographic coherency exists in the interfaces of Cu film/Ni substrate and Ni film/Cu substrate respectively5,6 (Figs. 3(a’) and (b’)). However, no crystallographic coherency can be observed in the interface of Cu film/Ag substrate (Fig. 3(c)). From the above, it can be considered that the metal-metal bond exists in the interface of Cu film/Ni substrate and Ni film/Cu substrate whereas it does not exist in the interface of Cu film/Ag substrate.

4. Discussion

The above results show that the adhesion of the deposited films is closely related to the interfacial structures between the deposited films and substrates. The crystallographic coherency presents in the interfaces of Cu film/Ni substrate and Ni film/Cu substrate (Figs. 3(a’) and (b’)) respectively, showing a metal-metal bond in the interface. Then a strong adhesion exists in the interface of Ni film/Cu substrate. However, the exfoliation surprisingly happens in the interface of Cu film/Ni substrate due to the existence of voids in the interface (Figs. 1(a) and (a’)) associated with the co-deposition of hydrogen during electrodeposition process. Hydrogen evolution usually takes place in the aqueous solution as a side-reaction accompanied with the metal ion reduction at the cathode. Many hydrogen atoms gradually permeate the deposited Cu film, and subsequently accumulate in the interface of Cu film/Ni substrate, finally causing the voids to generate. As described before, no hydrogen accumulates and no resulting voids occur in the interface (Fig. 2(b)) of Ni film/Cu substrate. This can be attributed to the difference in the hydrogen diffusion coefficient between Cu ($1.13 \times 10^{-7}$ m$^2$/s (723–1200 K)) and Ni ($1.8 \times 10^{-7}$ m$^2$/s (723–1200 K)). Apparently, the hydrogen atoms can diffuse more easily into Cu substrate.

On the other hand, for the combination Cu film/Ag substrate, Cu film exfoliates from the Ag substrate although no apparent voids can be observed in the interface. The TEM observation in Figs. 3(c) and (c’) clearly shows that no crystallographic coherency exists in the interface of Cu film/substrate, and then a weak adhesion appears in the interface of Cu film/Ag substrate. The reason why no apparent voids exist in the interface of Cu film/Ag substrate is that hydrogen atoms tend to diffuse into the growing Ag film rather than accumulating in the interface since the hydrogen diffusion coefficient of Ag ($10 \times 10^{-7}$ m$^2$/s) is similar to that of Cu. However, no exfoliation happens along the interface of Ag substrate/Cu foil although many voids therein exist (Fig. 1(c)). This can be explained as follows: there is a displacement reaction taking place simultaneously with the electrodeposition of Ag. The Cu foil dissolves during the displacement reaction process, and promotes the formation of voids. Meanwhile, Ag ions are substituted as the metallic state at the place in which Cu dissolution takes place. These Ag atoms spatially accumulate together and then roughen the surface of Cu foil, thereby causing the adhesion to strong by the anchor effect.
The adhesion of electrodeposited films on metal substrates generally can be considered as a result of interaction of metal atoms. As described above, the Cu/Ni combination belongs to an all-proportion miscible alloy system, and shows a favorable adhesion in the interface due to the existence of metal-metal bond. However, since both Ag/Ni and Ag/Cu combinations belong to the eutectic alloy system, the metal-metal bond does not form in their interfaces, which were confirmed by observing the crystallographic coherence in the interfaces. This is why the exfoliation happens in the interfaces of Ag/Ni and Ag/Cu.

5. Conclusions

The adhesion of Cu, Ni and Ag electrodeposited films on various metal substrates has been examined by the adhesion tape test. Different interfacial structures are observed for the different film/substrate combinations and have been discussed in relation to the interface adhesion. The results clearly indicate the followings:

1) Strong adhesion always exists in the interfaces between metals of same kind.
2) Strong adhesion exists in the Ni film/Cu substrate, while weak adhesion exists in the Cu film/Ni substrate due to the existence of voids in its interface.
3) The Ag film/Cu foil shows a strong adhesion due to the anchor effect deriving from the displacement reaction in the initial step, while the Cu film/Ag substrate shows a weak adhesion by the effect of voids.
4) Either Ni film/Ag substrate or Ag film/Ni substrate shows a weak adhesion.

The effect of voids in the interfaces and the anchor effect described herein have been examined and it was found that voids generate in the interface between the deposited films and substrates to mechanically decrease the adhesion of the films and substrates, while the anchor act as an adhesion promoter to remarkably increase the adhesion of the interface. However, such two effects as external factors do not directly connected with the inherent properties of the deposited films and substrates. Therefore, it can be considered that the adhesion of electrodeposited films on various substrates is due mostly to the crystallographic coherence between the deposited film and substrates rather than to a void effect and anchor effect in the interface. The further studies are still needed to be done in the various combinations of deposited films and substrates.

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REFERENCES