Journal of Korean Institute of surface Engineering
Vol. 32, No. 3, Jun., 1999

CHARACTERISTICS OF PLATED GOLD LAYER ON ANSI 304 STAINLESS STEEL ACCORDING TO THE VARIATION OF PRETREATMENTS AND ELECTROLYSIS CONDITIONS

Dong-hun Lee and Jae-Bong Lee

School of Metallurgical and Materials Engineering
Kookmin University, Seoul 136-702, Korea

Abstract

An attempt was made to characterize the relationship between pretreatment processes, electrolysis conditions and behaviors of the plated gold layer. In order to investigate the effect of pretreatment processes on plating, rest potential measurements of various pretreated stainless steels and a.c.-impedance spectroscopy tests were carried out in the strike plating solution. Characteristics of plated gold layers and adhesions between plated gold layers and stainless steel substrates were examined by scratching tests and micro-Vickers hardness tests. The result shows that the strike plating enhanced the adhesion of interface, the cathodic electro-activation pretreatment process improving both corrosion resistance and adhesion strength. The preferred orientations of plated gold layers were examined by the X-ray diffraction technique. As the current density increases, [111] preferred orientation of plated gold layers was found to become well developed.

Key words : *pretreatment, strike plating, electrolysis, a.c.-impedance spectroscopy, rest potential, corrosion resistance, adhesion, hardness, preferred orientation.*

1. INTRODUCTION

ANSI 304 stainless steel is widely used because of its high resistance to corrosion due to the presence of passive oxide film and the excellent mechanical properties. However, in order to further improve surface property, gold is plated on its surface for decoration, dental applications and electronic interconnection purposes. The reason why gold and gold alloy plating becomes popular is that the plated gold layer improves the corrosion resistance, decreasing the electrical and the thermal resistance even in the corrosive as well as high temperatures environments$^{1)}$. It is also well known that the pretreatment processes are very important because the adhesion is poor at the interface between the gold layer and the stainless steel substrate due to the presence of passive oxide film on the substrate. Therefore, in order to thoroughly remove the passive film on the stainless steel substrate, pretreatment processes such as cleaning and activation should be applied before strike plating and main plating[2]. Since it is not easy to get completely rid of the passive oxide film on the substrate, it is very important to find out the most optimum processes among various pretreatments for obtaining the highest adhesion strength at interface[3]. Electrolysis conditions are also believed to play an important role on both the adhesion of interface and the characteristics of plated gold layers[4]. If some defects pre-exist on the plated layer resulting from inadequate pretreatments or plating conditions, there also exists the possibility of galvanic corrosion at interface between the plated gold layer and the substrate. Therefore, the objectives of this study are focussed on finding out the most optimum pretreatments and plating conditions associated with not only the highest adhesion at interface but also the electrochemical and mechanical properties of plated gold layers.

2. EXPERIMENTAL PROCEDURES

ANSI 304 stainless steel specimens (20mm wide ×20mm long×0.15mm thick) were prepared, wet-ground by using 600 grit SiC paper followed by fine polishing with suspension of 0.05㎛ particles of alumina to give a bright and smooth surface. After polishing, pretreatment processes were applied, such as ultrasonic cleaning, electro-cleaning, and activation treatments. Fig. 1 shows a block diagram for pretreatment processes of ANSI 304 stainless steel and gold plating. Ultrasonic cleaning and electro-cleaning are necessary to remove all types of grease, oil, dirt and residual alumina powder remaining after polishing. However, activation process should be still needed because of the possibility that the passive oxide film is not completely removed by ultrasonic and electro-cleaning alone. Activation treatment is the process to immerse the stainless steel in the aqueous 7 wt% sulfuric acid solution. This process was compared with the cathodic electro-activation process, in terms of the removal of the passive oxide film. The chemical solution compositions and the process conditions of various pretreatments are given in Table 1. In order to investigate the effects of various pretreatment processes on the removal of oxide passive films on stainless steel substrates, rest potentials of stainless steel specimens were monitored in the gold strike plating solutions after pretreatment processes. All potentials were measured by using a

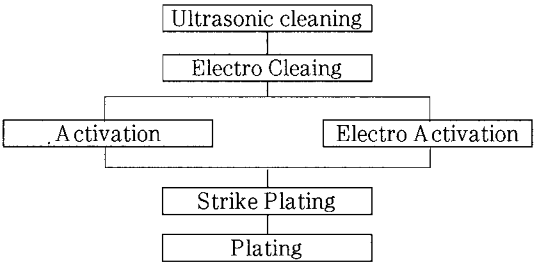


Fig. 1 Block Diagram for the pretreatment processes of ANSI 304 stainless steel and the gold plating

Table 1. Chemical solution compositions and process conditions of various pretreatment processes

Bath	Ultrasonic cleaning	Electrocleaning	Activation
Composition (wt%)	Na_2SiO_3 45 $C_{18}H_{20}O_3SNa$ 5	NaOH 12 Na_2CO_3 43 Na_2SiO_3 19	H_2SO_4 7
Solution Temperature (℃)	55	25	25
Current density (A/dm^2)		5	22
Preatreatment Time (min)	15	5	2

Table 2. Summary of types of samples pretreated by a series of various pretreatment processes

Sample	U.C	C.C	A	C.A	S.P	P
A	○	○	–	–	–	○
B	○	○	–	–	○	○
C	○	○	○	–	○	○
D	○	○	–	○	○	○

U.C:Ultrasonic Cleaning, C.C:Cathodic electro-Cleaning
A :Activation, C.A :Cathodic electro-Activation
S.P :Strike Plating , P :Plating

saturated calomel electrode (SCE : 0.242 volts vs the standard hydrogen electrode). After applying a series of various pretreatment processes to four types of samples as shown in Table 2, electrochemical characteristics of plated gold layers were examined by a.c.-impedance spectroscopy at rest potentials in both 0.1N HCl and 0.1N NaCl solutions deaerated by flowing nitrogen prior to and during the experiments. The applied alternating current (AC) signal was 10 mV in a frequency range of 0.1 Hz to 10,000 Hz. The electrolytic plating cell consists of pretreated ANSI 304 stainless steels as cathodes, and platinized titanium meshes as anodes. Two kinds of cyanide gold plating solutions were chosen for the strike plating (pH=1.2) and the electroplating (pH=4.2) solutions respectively. Gold was electroplated at 10 cm distance between a cathode and an anode with the variation of electrolysis conditions such as current density, bath temperature and agitation velocity. The thickness of gold deposit layer is about 3㎛. The effect of pretreatment processes on adhesion at interface was investigated by a SCEM Model CH-2007 Neuchatel automatic scratch tester in which loads were applied from 0 N up to 80 N. Critical loads were determined by acoustic emission analyses[5)] and gold deposit failure modes around scratches were examined by SEM. In order to examine mechanical characteristics of the plated gold layer with the change of the electrolysis conditions, Micro-Vickers hardness tests were conducted on deposited surfaces under a load of 5 grams. The surface morphology and microstructures of cross sections of the gold deposits were observed by using both OM (Optical Microscope) and SEM (Scanning Electron Microscope). Preferred orientations of gold deposits depending on electrolysis conditions were determined using X-ray diffractometer, which were expressed with texture coefficients.

3. RESULTS AND DISCUSSION

3. 1 Rest Potential

The presence of the passive oxide film on the surface of the stainless steel makes plating difficult. Since the passive oxide film which is not completely removed on the substrate causes the decrease in the adhesion strength at interface, pretreatment processes have much to do with the adhesion at interface and the quality of the gold layer in plating. Fig. 2 shows the anodic polariza-

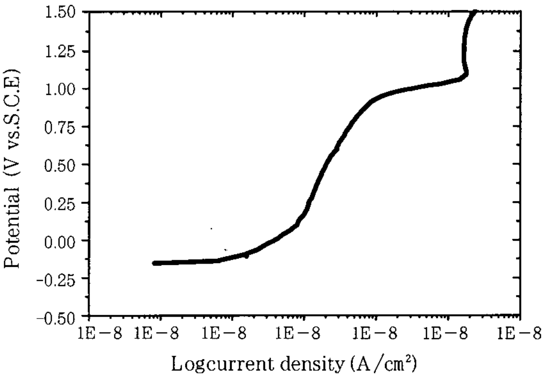


Fig. 2 Anodic polarization curve of the pretreated ANSI 304 stainless steel in strike plating solution.

tion curve of the pretreated ANSI 304 stainless steel in the strike plating solution open to air. The rest potential is around -0.1 volts (SCE). In order to investigate effects of various pretreatment processes on the passive film removal, rest potentials were monitored in the strike plating solution after finishing various pretreatment processes (Fig. 3). As shown in Fig. 3, rest potentials of stainless steel specimens vary with various pretreatments such as ultrasonic cleaning, cathodic electrocleaning, activation treatment, and cathodic electroactivation treatment, depending on how much the passive film is removed. Fig. 3 shows that ultrasonic cleaning has the highest rest potential while cathodic electroactivation represents the lowest rest potential with the elapse of time. Activation and cathodic activation treatments show much lower rest potentials than the other else processes do, by 200 mV, indicating the extent of effectiveness of film removal. As compared activation with cathodic activation, since the latter has the lower potential than the former, cathodic activation treatment process seems to be the more effective process than activation treatment. The rest potential monitoring results show that ultrasonic cleaning or cathodic electrocleaning process alone is not be sufficient for the complete removal of the passive film.

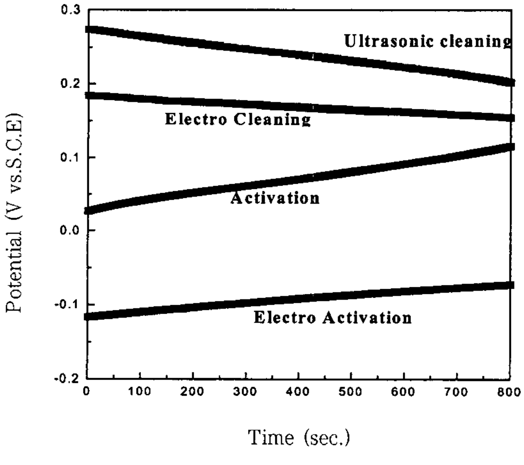


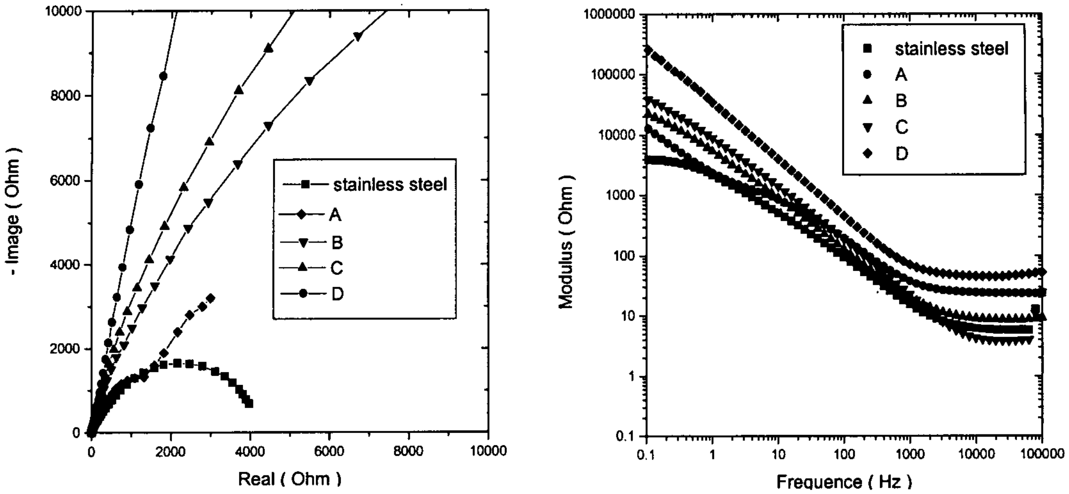
Fig. 3 Rest potential variations monitored in the strike plating solution after applying pretreatment processes.

3. 2 Corrosion Resistance

In order to understand effects of pretreatment processes on corrosion resistance to galvanic corrosion between the plated gold layer and the stainless steel substrate, a.c.-impedance spectroscopy tests for four types of samples were carried out in the deaerated 0.1 N NaCl and 0.1 N HCl solutions respectively. Fig. 4 and 5 show that sample B pretreated with ultrasonic cleaning, cathodic electrocleaning and strike plating processes has the much higher polarization resistance than sample A pretreated with ultrasonic cleaning and cathodic electrocleaning processes alone does in both 0.1 N HCl and 0.1 N NaCl solutions. This result indicates that strike plating plays an important role on the increase in the resistance to galvanic corrosion.

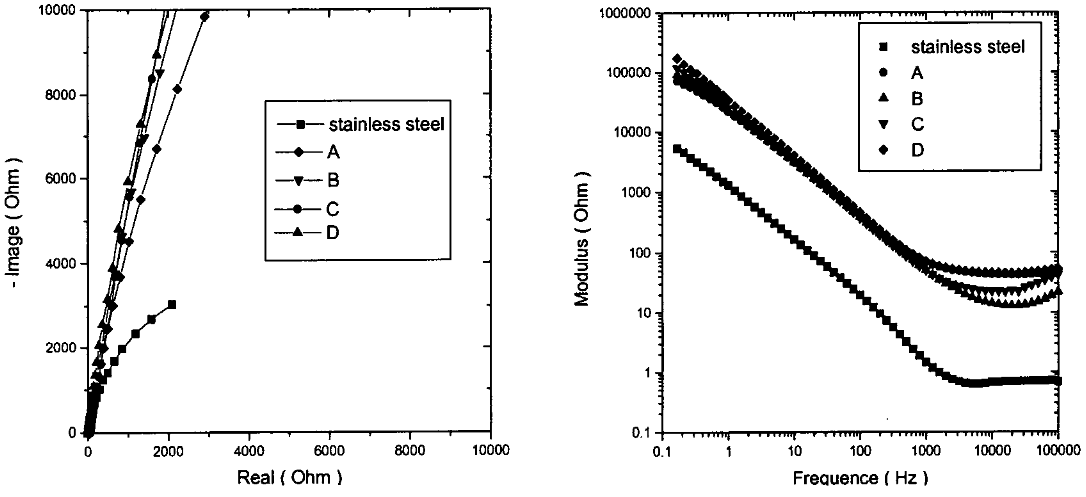
3. 3 Adhesion

In order to understand effects of pretreatment processes on the adhesion strength at interface, scratch tests were carried out. Loads were applied from 0 N up to 80 N during scratching. Critical loads for samples pretreated were determined by acoustic emission analyses[4] and compared for among pretreatment conditions. Fig. 6 represent effects of pretreatments on adhesion through the comparison of critical loads obtained



(a) (b)

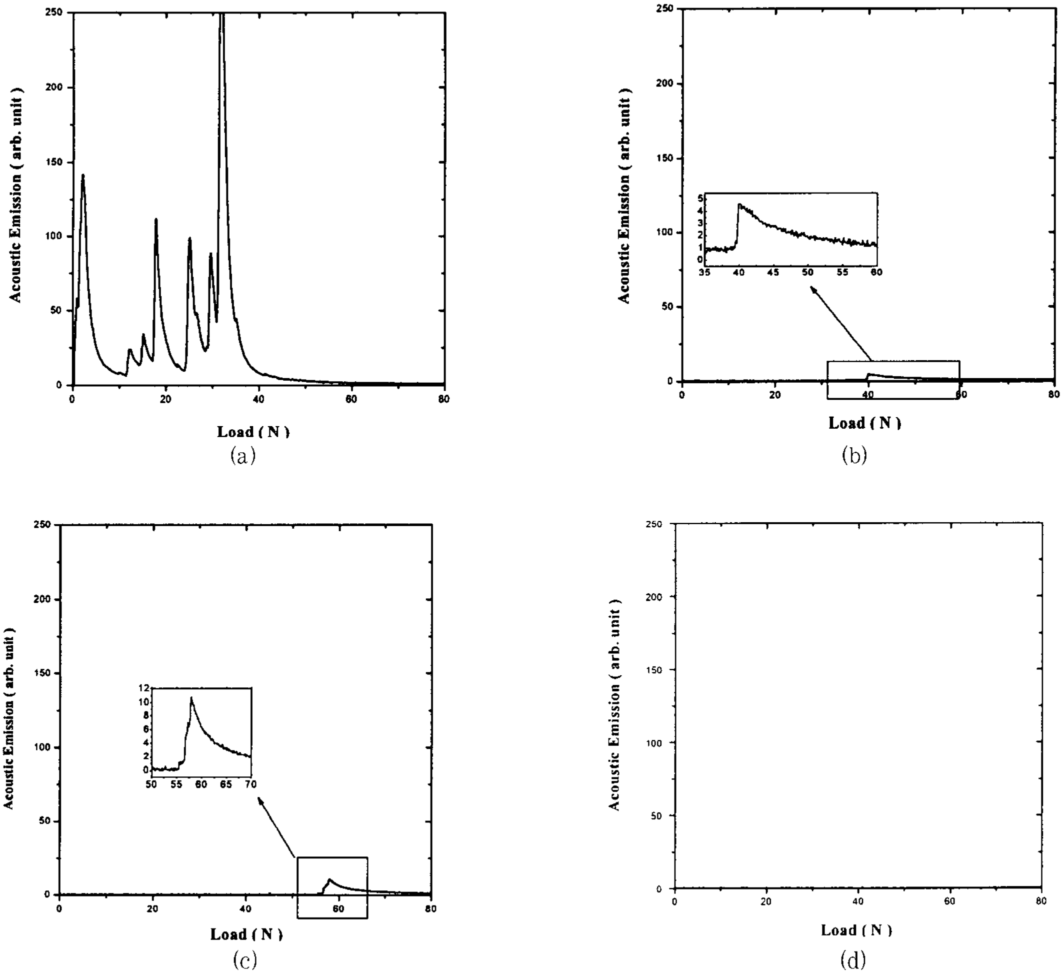
Fig. 4 (a) Nyquist plot and (b) Bode plot according to the types of samples in 0.1N HCl.



(a) (b)

Fig. 5 (a) Nyquist plot and (b) Bode plot according to the types of samples in 0.1N NaCl.

from acoustic emission signals resulting from scratching. The effect of strike plating on adhesion was examined in Fig. 6(a), (b), indicating that sample B with strike plating has the much higher critical load than sample A without strike plating does. Based on this result, strike plating seems to be the most important process, in terms of the increase in adhesion strength. Activation and cathodic electroactivation were compared in Fig. 6(c), (d) in terms of adhesion, showing that sample D with cathodic electroactivation has the higher adhesion strength than sample C with



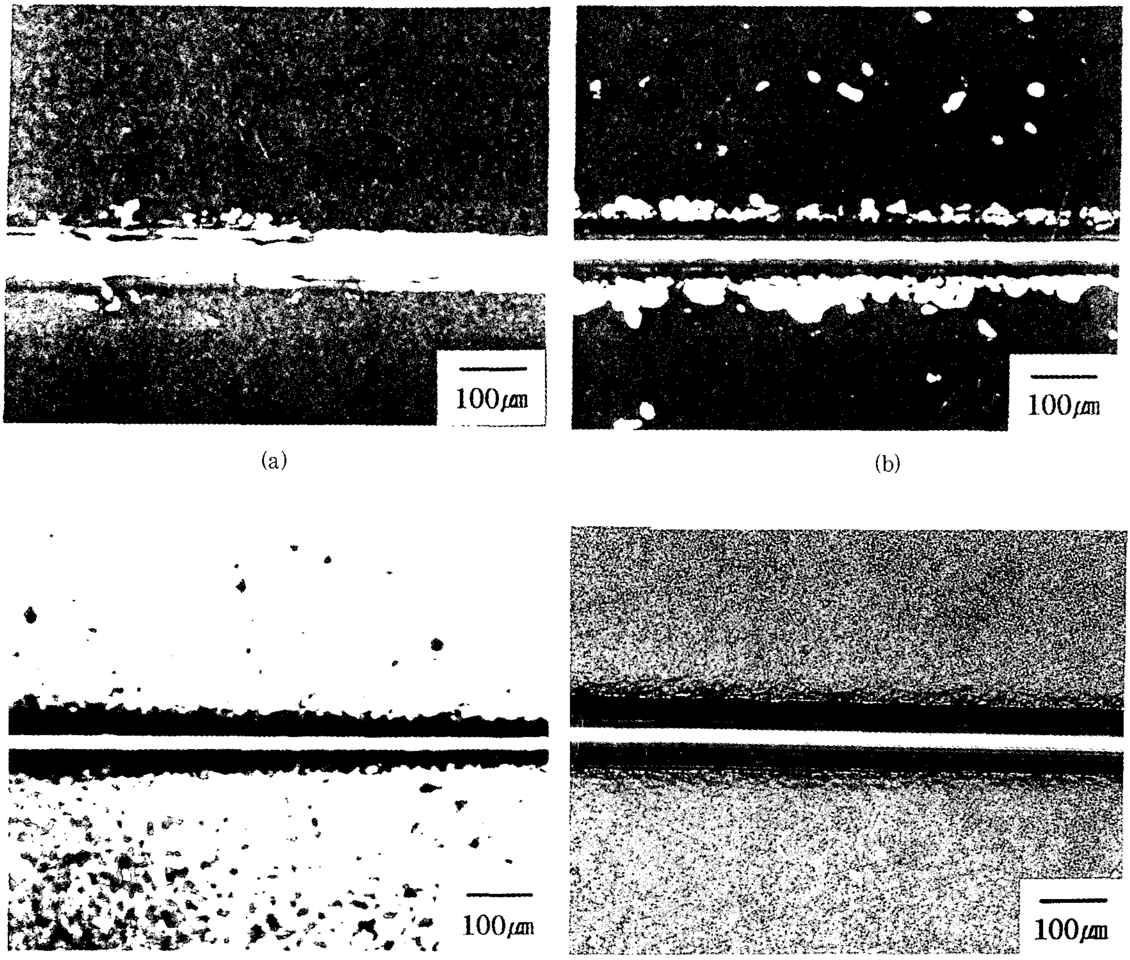
(a) (b) (c) (d)

Fig. 6 Effect of pretreatment processes on critical loads obtained from acoustic emission:(a) sample A (b) sample B (c) sample C (d) sample D (plating condition: 40℃, 400 rpm, 1.0 A/dm^2)

activation does. Fig. 7 show optical micrographs of regions scratched with 40 N applied loads for the previous four types of samples A, B, C, and D respectively. It is observed that samples A and B have a lot of debris and fragments of plated gold layer around scratches while samples C and D have sound scratches without any debris, indicating that samples C and D have the sound adhesion at interface.

3. 4 Hardness

Micro-Vickers hardness tests[6] were performed in order to investigate mechanical characteristics of plated gold layers according to the electrolysis conditions. Hardness values are averaged after measuring in 5 times for each sample under a load of 5 grams. Fig. 8 show the variation of hardness values of plated gold layers with varying current densities, agitation speeds, and solu-



(a) (b)

(c) (d)

Fig. 7 Optical micrographs of scratches on plated gold layers: (a) sample A (b) sample B (c) sample C (d) sample D (plating condition: 40℃, 400 rpm, 1.0 A/dm^2)

tion temperatures. Hardness values tend to increase with current density as shown in Fig. 8 (a). However, agitation speed as well as solution temperature seems to have little influence on the increase of hardness, compared with current density. Fig. 9 shows the surface morphology of plated gold layers with the increase of current density. As current density increases, grains of gold deposits are found to become smaller and smoother[7]. This result is in good agreement with the hardness increase tendency shown as in Fig. 8 (a).

3. 5 Preferred Orientation

Electrodeposited samples were examined with an X-ray diffractometer in order to determine preferred orientations. The orientation of the deposit is expressed in terms of a texture coefficie-

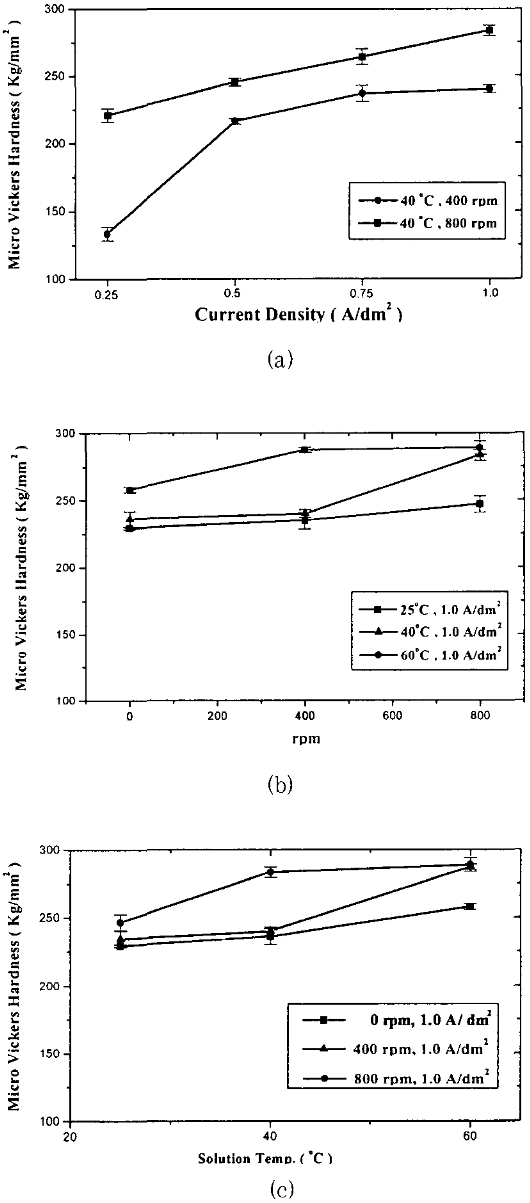


Fig. 8 Hardness variation with varying (a) current density, (b) agitation speed, and (c) solution temperature.

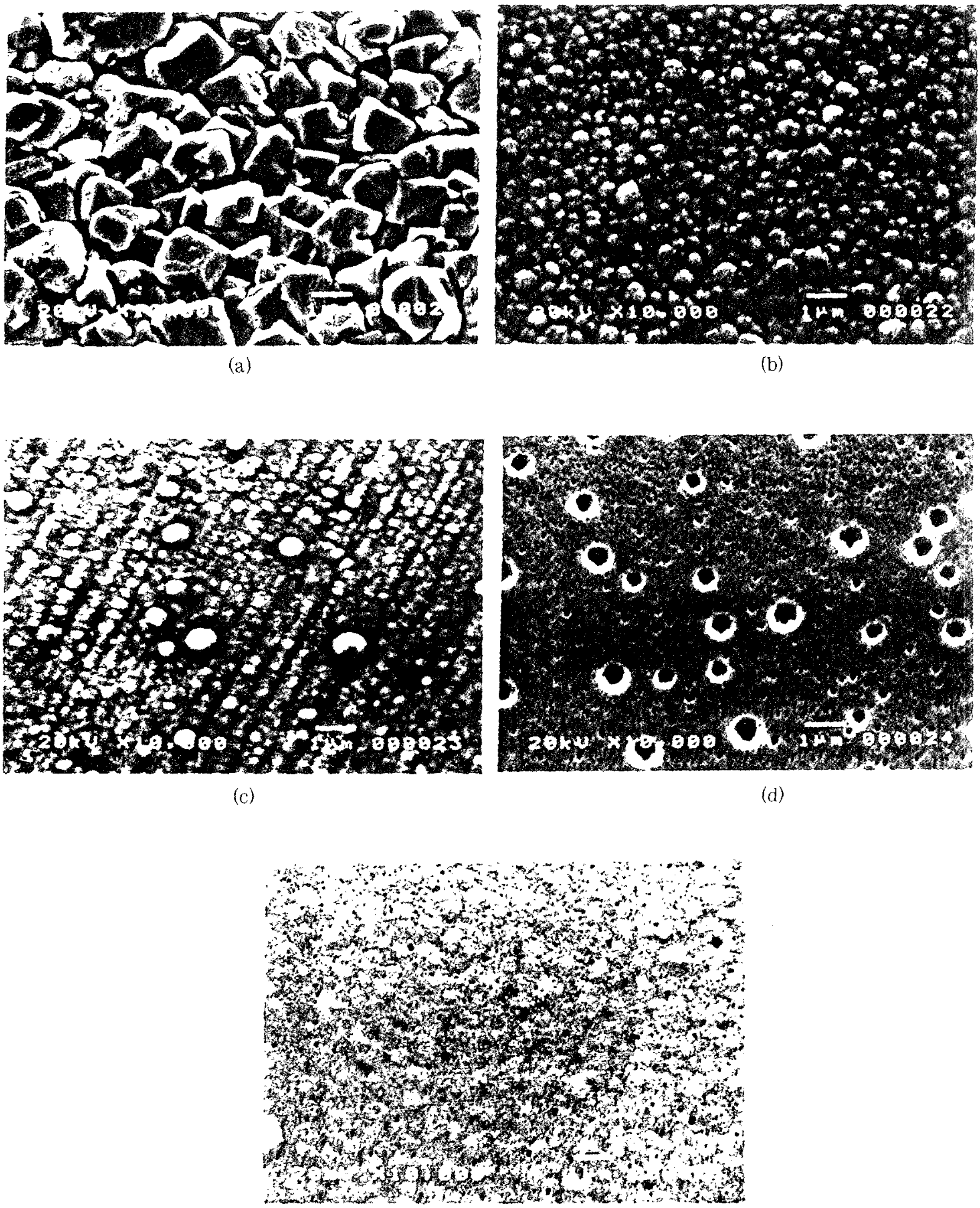
nt known as TC. TC is defined as the following equation.

$$TC=(I_{hkl}/I^{o}_{hkl})/\{(1/n)\ \Sigma(I_{hkl}/I^{o}_{hkl})\}$$

where I_{hkl} and I^{o}_{hkl} are the integrated intensities of (hkl) reflections measured for experimental samples and standard powder samples, respectively, and n is the total number of reflection planes. When TC of all reflection planes is unity, the distribution of crystal orientation is random. When TC of any (hkl) plane is larger than unity, a preferred orientation is developed where grains are oriented with their (hkl) planes parallel to the surface. The larger the value of TC, the greater the degree of preferred orientation. In this study, any sample for which TC is equal to four is determined to have all grains oriented with (hkl) planes parallel to the surface, because four reflection planes are used to calculate TC. Fig. 10 shows the variation of the preferred orientation with changes in current density. As current density increses, the preferred orientation tends to change from the random distribution of crystals to the [111] texture having the lamella microstructure parallel to surface[8]. Compared with the effect of current densities on the texture, solution temperature as well as agitation speed is not quite noticeable, suggesting that current density may be the most important factor affecting the texture of plated gold layers. Fig. 11 shows the SEM micrograph of cross section consisting of gold layer by strike plating, plated gold layer, and ANSI 304 stainless steel substrate. The plated gold layer with lamella microstructure has approximately 3 ㎛ thickness.

4. CONCLUSIONS

In order to investigate effects on pretreatment processes on adhesion, rest potentials were measured after performing various pretreatments.



(a)

(b)

(c)

(d)

(e)

Fig. 9 Surface morphology of plated gold layers with the increase of the current density (a) 0.25A/dm² (b) 0.5A/dm² (c) 0.75A/dm² (d) 1.0A/dm² (e) 2.0A/dm² (plating condition: 40℃, 400 rpm)

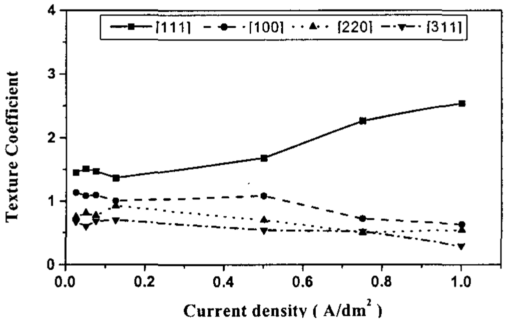


Fig. 10 Variation of preferred orientation with changes of current density (plating condition: 40℃, 400 rpm)

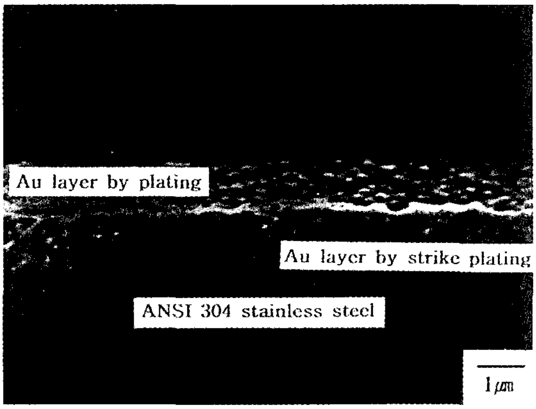


Fig. 11 SEM micrograph of cross section of plated gold layer

The sample pretreated by cathodic electroactivation has the lowest potential among pretreatment processes while samples with ultrasonic cleanig process alone has the highest potential. The variations of rest potentials depend on the extent of the passive film removal. The a.c.-impedance spectroscopy results show that the plated gold layer sample with strike plating is superior to that which has not been strike plated in terms of corrosion resistance. Cathodic electroactivation also increases the corrosion resistance of samples more than activation does. Scratching results demonstrate that strike plating makes the most noticeble contribution to the increase in adhesion strength at interface among pretreatment processes. Based on the critical load analyses, samples pretreated by cathodic electroactivation have the higher adhesion strength than those done by activation.

In order to examine the effects of plating conditions on mechanical properties of plated gold layers, hardness tests were carried out. Hardness values are found to increase with the increase in current density. On the other hand, agitation speeds and solution temperature do not have the noticeable influence on the hardness value increase, indicating that current density is the most important factor as to increasing the hardness of plated gold layers. The surface morphology of plated gold layers shows that, as current density increases, grains of gold deposits become smaller and smoother. This result is consistent with the hardness tendency. The orientation of the deposit is analyzed by the X-ray diffraction technique in terms of texture coefficient known as TC. As the current density increases, the [111] texture with lamella microstructure is found to become well developed.

REFERENCES

1. C. S. Back, H. G. Jang, and H. J. Kim, J. Korean Inst. of Surf. Eng. 25 (1992) 107.
2. Y. Iwaki and T. Yamashita, 表面技術, 41 (1990) 218.
3. B. S. Han and H. K. Chang, J. Korean Inst. of Surf. Eng. 28 (1995) 24.
4. R. J. Blazek and W. A. Piper, Proceeding of 28th Electronic Components Conference

(1978) 373.

5. J. Sekler, P. A. Steinmann and H. E. Hintermann, Surface and Coating Technology, 36 (1988) 519
6. ASTM B578-87 "Standard Test Method for Microhardness of Electroplated Coating"
7. T. Osaka, A. Kodera, T. Misato, T. Homma, and Y. Okinaka, J Electrochem. Soc. 144 (1997) 3463.
8. D. N. Lee and Y. W. Chang, J. Kor. Inst. Met. & Mater., 12 (1974) 247