Process for plating on ABS resin using of electroless copper plating solution using saccharides as reducing agent

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We developed new electroless copper plating solution for plating on plastics as wet method, which has saccharides as reducing agent. However, this plating bath is completely different to other conventional electroless copper plating bathes, and both plating process (mainly for ABS resin) and formed plating film are also different.

In this paper, after introduction of this process, we wish to report the analysis results of the deposited plating film, and newly found information for the etching (This one is chromic acid–sulfuric acid bath as same with the conventional ones.) in development of this process.

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1. Background of Research and Development

In or around 1960, plating on plastics was industrialized by wet method. Today, it has been applying to wide ranges of various fields such as automotive parts. As the typical plastics substrate, we can introduce ABS resin (Acrylonitrile/Butadiene/Styrene). At the initial stage of application, it was developed as the substitution of zinc die-casting or copper alloys for the purpose of reducing weight and cost-down of automotive decoration parts. Recently, its application has been expanding to electric and electronics components which require various functions such as EMI shielding.1)

According to this expansion of applications, various improvements and innovations have been realized such as one rack system by catalyst–accelerator method, plating technologies on engineering plastics and others.1) 2)

And recently, for the purpose of earth environmental protection, several restrictions to plating process on plastics as wet method have been strengthened such as prohibition of throwing away of wasted materials such as wasted electroless nickel plating solution or others to ocean, strengthen of restrictions for drain of nitrogen and phosphorus to prevent formation of red tide or others by rich nutrition of water.3)

Under such a severe circumstance, new improvement for environmental protection has been requested on plating process on plastics. To solve this subject, we have developed the plating process on plastics utilizing new electroless copper plating which contains saccharides as reducing agent. 3)-7)

2. Feature of New Plating Process on Plastics

This new plating process on plastics has a future that applies electroless copper plating using a certain kind of saccharides having slight reducing effects as reducing agent in place of the conventional formalin or glyoxylic acid. We wish to introduce the feature of this process below.

1. Environmental Protection Process

As electroless copper plating solution does not contain phosphorus components and nitrogen components, and does not contain strong chelating agents such as EDTA, waste water treatment is easy. And the formation of wasted substances is few, this bath can be applied for almost semi-permanently by replenishment method after made-up fresh bath. Furthermore, this new electroless copper plating bath is stable and has never experiences of the phenomenon of off-control or off- usage, which is apt to occur on the conventional electroless copper plating bathes owing to off-balance of bath composition. For these reasons, compared with the conventional electroless copper plating solutions, the high concentration wasted solution for renewal of the bath can be reduced extremely.

2. Shortening of Number of Steps in Process

Fig. 1 shows the treatment processes of the conventional process and new process for plating on ABS resin. In this process sheet, we skipped the description of "Water Rinse" at between each step.

The process up to catalyzing step in this new process is almost same with that of the conventional process. Though there is slight difference on them, both etching solutions in Fig.1 are mixed acid of chromic acid–sulfuric acid, and catalysts are hydrochloric acid solution of palladium–tin colloid. The conducting step of this new process is electroless copper plating step using saccharides as reducing agent as stated above, and there is no accelerating step in this new process. And also, after conducting treatment, acid copper plating can be applied directly on it via water rinse.

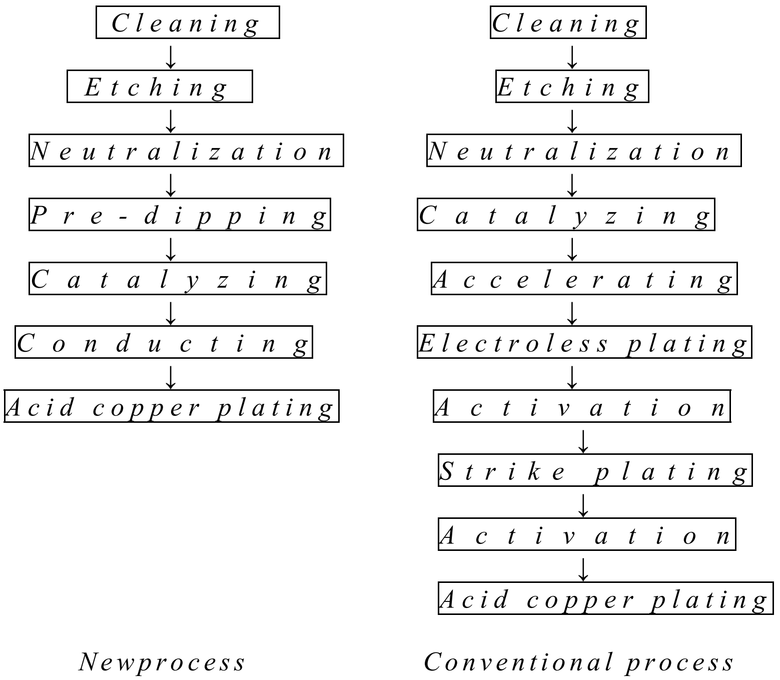
Any strike plating or acid activation are not required. Therefore, treatment step is few and reduction of installation costs and improvement of productivity can be expected.

3. Excellent Plating Film Properties

Some of reasons for defects in plating by the conventional process are caused by electroless plating process. In general, electroless plating is applied for about 0.2 ~ 0.5 µm. In many cases, the defects of this plating film (rough deposition, pitting, pin-holes and others) will give influences to the final finishing of products. On the contrary, the deposition film at conducting step in the new process is extremely thin at 10 ~ 20 nm as we will state later in details. So the film defects such as rough deposition are extremely small, and give less influences to the final finishing, consequently, we can expect beautiful appearance.

In case of application of the new process, the adhesion and corrosion resistance of the final plated articles are almost same degree with those for the conventional process, and there is no bad influenced to the properties. Table 1 shows the results of comparison tests for adhesion and corrosion resistance of the plated specimens with the conventional process.

As you can see above, our new process is plating process on plastics, which is easy in waste water treatment and is environmental friendly as we can expect reduction of wasted solutions. And also, this new process can provide excellent plated plastics articles at shorter treatment process than the conventional process.



Newprocess Conventional process

Fig.1 Comparing New and Conventional process of plating on ABS resin.
(Water rinse between each step are omitted.)

Table 1 Results of corrosion resistance and adhesion tests on plated ABS resin.

Tests	**Methods***	**Comparison with conventional process**
CASS test	200hr (JIS H 8502)	Better
Corrodkote test	16hr×10cycle (JIS H 8502)	Better
Nitric acid exposure test	16hr×10cycle (JIS H 8630)	Equality
Peeling test	(JIS H 8630)	Better
Thermal shock test	80°C,15min→-20°C,15min, 10cycle (JIS H 8630)	Equality

**JIS means Japanese Industrial Standards.*

3. Analysis of Deposited Film

Photo-picture 1 shows the test specimens after etching, after catalyzing, after conducting, after acid copper plating of the new process, and after catalyzing and after electroless copper plating of the conventional process. As well-known, in case of application of electeroless copper plating as pre-treatment for decorative plating in the conventional process, metallic copper film is formed for about 0.2 ~ 0.5 μm. However, in case of the new process, such a thick film does not deposit and we can see the surface of the substrate through this film.

If the deposition film has enough thickness at the conventional process, copper plating will deposit first at the higher current density areas. On the other hand, in case of the new process, as we can see in these photo-pictures, the deposition of electrolytic plating (normally, acid copper plating) will start from the contact points with jigs (We took 2 contact points with jig at top and bottom of the test specimens in these photo-pictures.)

Ono and others succeeded in TEM (Transmission electron microscope) observation on cross section of this film, and found that this deposition was composed of film of 20 ~ 50 nm by gathering of grains sized for about 2 nm.8),9)

As the deposition film is extremely thin and the surface of plastics can be observed through this film, it looks like plating without plating film, so this process is called as direct plating sometimes. However, as we can see in Fig.2, we can detect the deposition of copper. Though the degrees of increase in the deposition amounts are different by the kind of saccharides used in this test (We showed 2 kinds of saccharides of A and B in Fig.2.), both deposition amounts increased according to the plating time.

The deposition amounts of copper in Fig.2 were calculated from the measured valued of copper components in the dissolved solution by ICP (Inductively Coupled Plasma spectrometry) after copper deposition film on the test specimens treated up to conducting step was dissolved by aqua regia.

Fig.3 shows XPS (X-ray Photoelectron Spectroscopy) spectrum of specimen surfaces treated up to catalyzing step and conducting step. From the surface of specimen treated up to conducting step, copper was detected, which were not detected on the surface of specimen treated up to catalyzing step. This matter confirms the deposition of copper. In other words, the peaks of Cu2p3, CuLMM, Cu2p are detected, which are not detected on the specimen treated up to catalyzing step.

Fig.4 shows the details peak of Cu2p3 of the specimen surface after conducting step. The binding energy of this peak is around 932eV, and the deposition seems to be metallic copper. Consequently, we could confirm the deposition of copper.

However, we also can observe that the deposition effects of acid copper plating decreases if the adsorption amount of catalyst is few at catalyzing step. Therefore, we think that palladium and tin, especially palladium which are adsorbed on plastics surface at catalyzing step act as conductive film. In case of the conventional process also, palladium and tin are adsorbed on the plastics surface by similar palladium – tin colloid catalytic solution. However, palladium of this case is just only initiator of plating, and it is not considered in general to have function as conductive film.

As the deposition effects of acid copper plating will decrease if the adsorption amount of catalyst at catalyzing step is few in case of the new process, at present, it is required to give much amounts of palladium and tin, especially palladium on the plastics surface to gain good deposition of electrolytic copper plating, compared with the conventional process. So catalyzing solution in the new process required higher concentration of palladium for few times than that in the conventional process. As palladium is higher value metal, and it has been increasing production costs of plating, this matter has been suppressing the expansion of this new process.

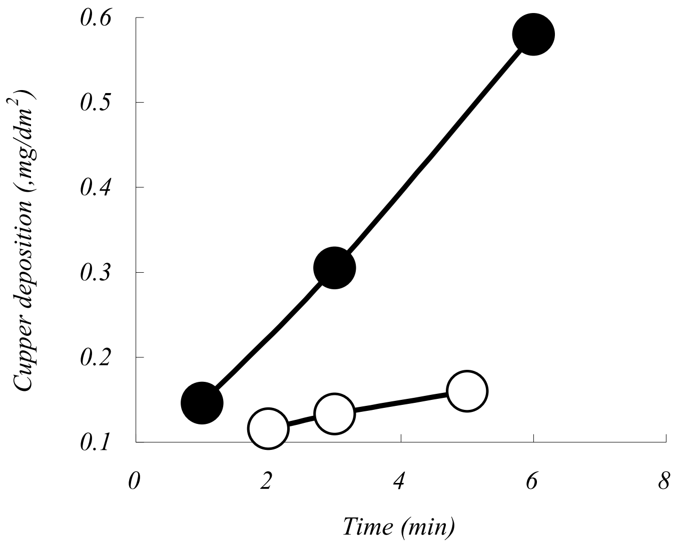


Fig.2 Cupper deposition from Conducting, electroless cupper plating solution using saccharide as reduction agent. There are two sort of solution including sascchardes A(□) and B(□).

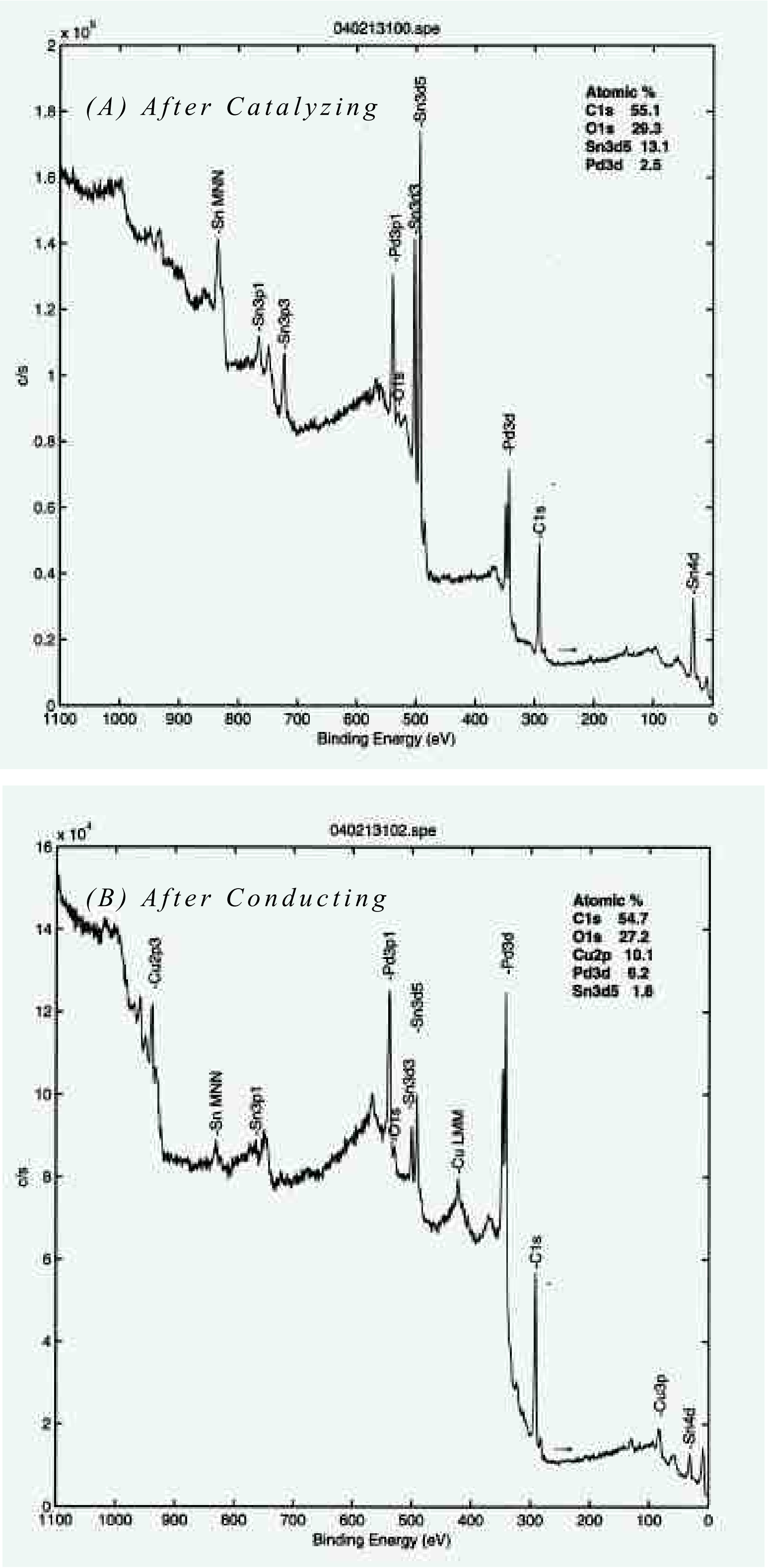


Fig.3 XPS spectral chart of ABS resin surface after Catalyzing(A) and Conducting(B).

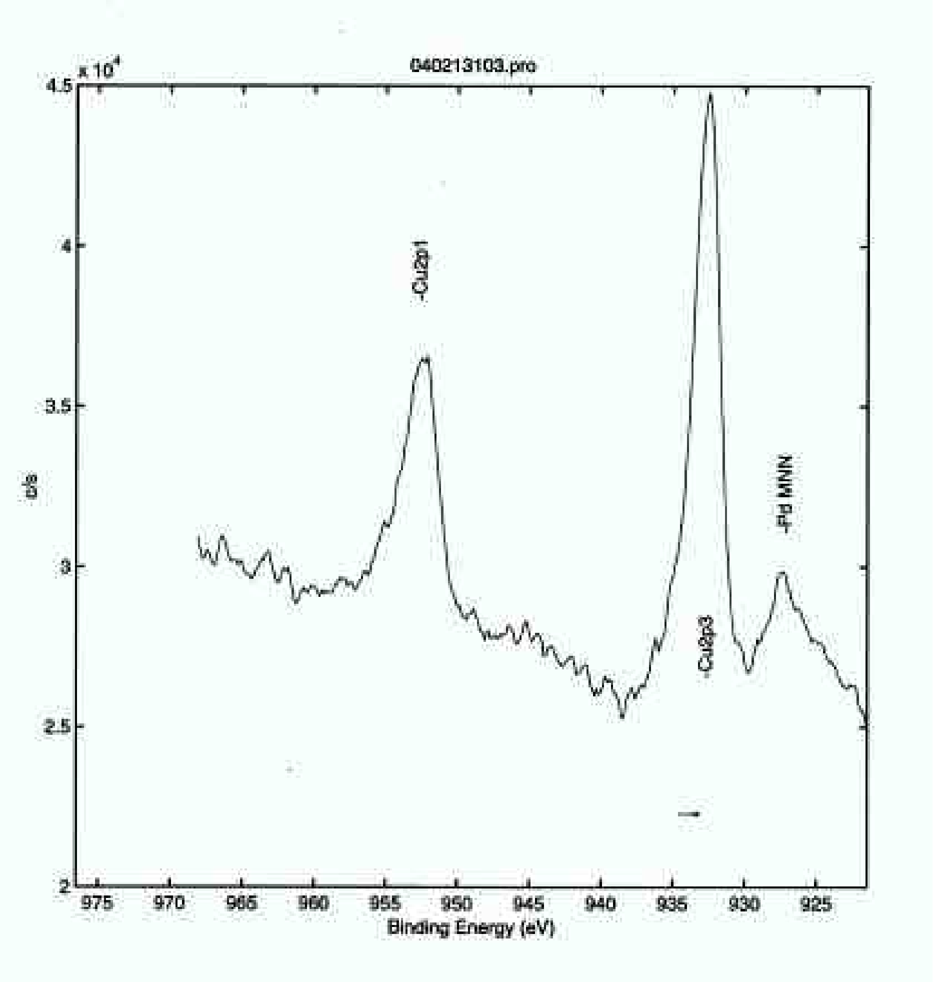


Fig.4 XPS peak of Cu2p3 after Conducting.

4. Study of Etching Bath

To adsorb palladium on the plastics surface as much amount as possible by the catalyzing bath containing palladium as lower concentration as possible, we found that the etching step as the former step was important. Etching step is the step for treatment which dips the plastics into chromic acid–sulfuric acid mixed solution at 60 ~ 70. By this treatment, the plastics surface is strongly oxidized, forms polar radical and has hydrophilicity, and on the plastics surface, fine pores called as anchor form by dissolving of butadiene rubber in ABS Resin preferentially and they make the plastics surface rough. By adding of trace amount of palladium into this etching bath, we found that we could reduce the concentration of palladium in catalyzing bath widely. Fig.5 shows this effects. By adding of 5 mg/L of palladium into etching bath, the palladium adsorption amount after conducting step increased from 0.30 mg/dm^2 to over 0.45 mg/dm^2. It was an increase for over 50%. As we can see in Fig.6, the deposition effects of acid copper plating was improved. In case of application of etching bath without addition of palladium, the required palladium concentration in catalyzing bath to gain good deposition was 155 mg/L. On the other hand, in case of the etching bath containing palladium for 10 mg/L, we could gain good deposition by catalyzing bath of 95 mg/L of palladium concentration. This difference (reduction of palladium) was 60 mg/L, and this figure is 6 times of palladium we added to the etching bath.

We analyzed this effects by applying of XPS. We wish to show our consideration for change in surface condition of etched plastics and adsorption mechanism by XPS measurement below.

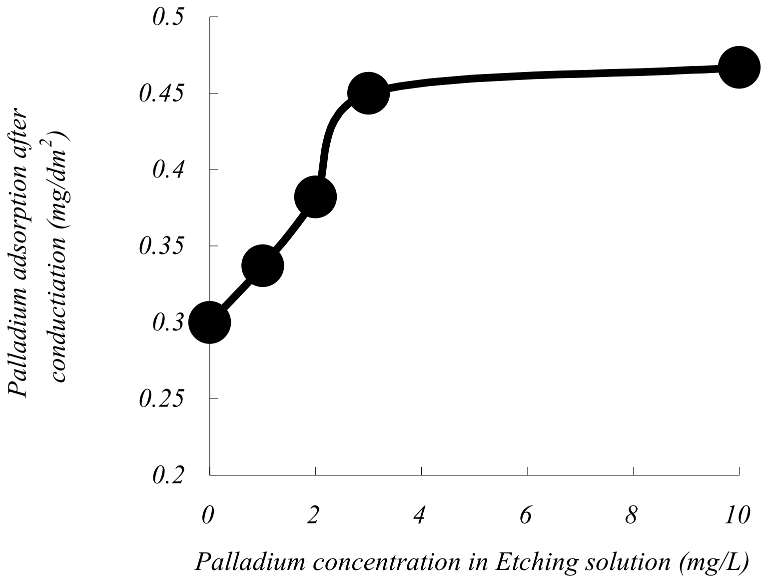


Fig. 5 Palladium concentration in Etching solution to the adsorpion on ABS resin surface after conducting. Palladium concentration in Catalyzing solution is 190mg/L.

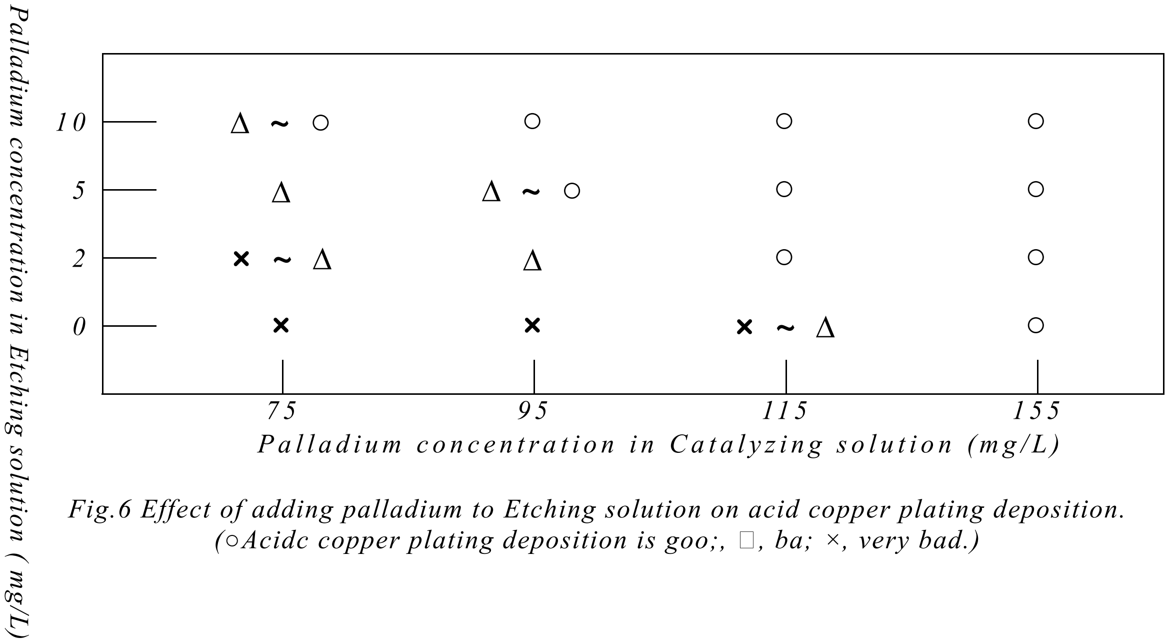


Fig.6 Effect of adding palladium to Etching solution on acid copper plating deposition. (○Acidc copper plating deposition is goo;, □, ba; ×, very bad.)

5. Influence of Etching Treatment to Chemical Bond Status of ABS Resin Surface

Fig.7 shows XPS spectrum of 3 different kinds of substrate: ABS Resin substrate, substrate etched by etching bath containing palladium and substrate etched by etching bath without addition of palladium. On the ABS Resin surface before etching treatment, we measured photoelectric spectrum of Cr2p, O1s, N1s and C1s. The peaks were detected at O1s, N1s and C1s respectively. We think that the peak detected at C1s is by –CH bond or –C≡N bond on the ABS Resin surface from their binding energy values.

We applied same measurement on the ABS resin surface after etching treatment. However, in this measurement, we did not measure N1s, but measured Pd3d in place of it. From this result, we could detect the peak at Cr2p spectrum, and found the remaining of slight amount of chromium by etching treatment. And we could confirm the clear change in peak profile of C1s spectrum. Before etching, we can find only the peak showing –CH bond (–C≡N bond). On the other hand, clear shoulder was observed at around 288eV on the surface after etching. From data sheets, we think that the energy value at this shoulder part is by C=O bond and C–O bond. And in corresponding to formation of shoulder of C1s spectrum, the increase in strength of O1s peak was detected.

Furthermore, in case of application of etching bath containing palladium, the shoulder at around 288eV became more clear and O1s peak increased further. Beside above, we could also detect the adsorption of slight amount of palladium.

We think that C=O bond and C–O bond which were detected by XPS measurement are caused by formation of carboxyl group (–COOH) or carbonyl group (>C=O) at ABS resin surface. And the increase in the strength of O1s peak is considered by the formation of many functional groups on the resin surface. Carboxyl group is well known as a functional group which form strong coordinate bond with metals. We can consider that carboxyl group (or carbonyl group) will act as the adsorption sites of Sn-Pd catalyst. As the main reason for increase in the deposition effects of plating by adding trace amount of palladium into etching solution, we think the increase in catalyst adsorption amount owing to formation of much amount of catalyst adsorption sites on the plastics surface except palladium adsorption at etching treatment.

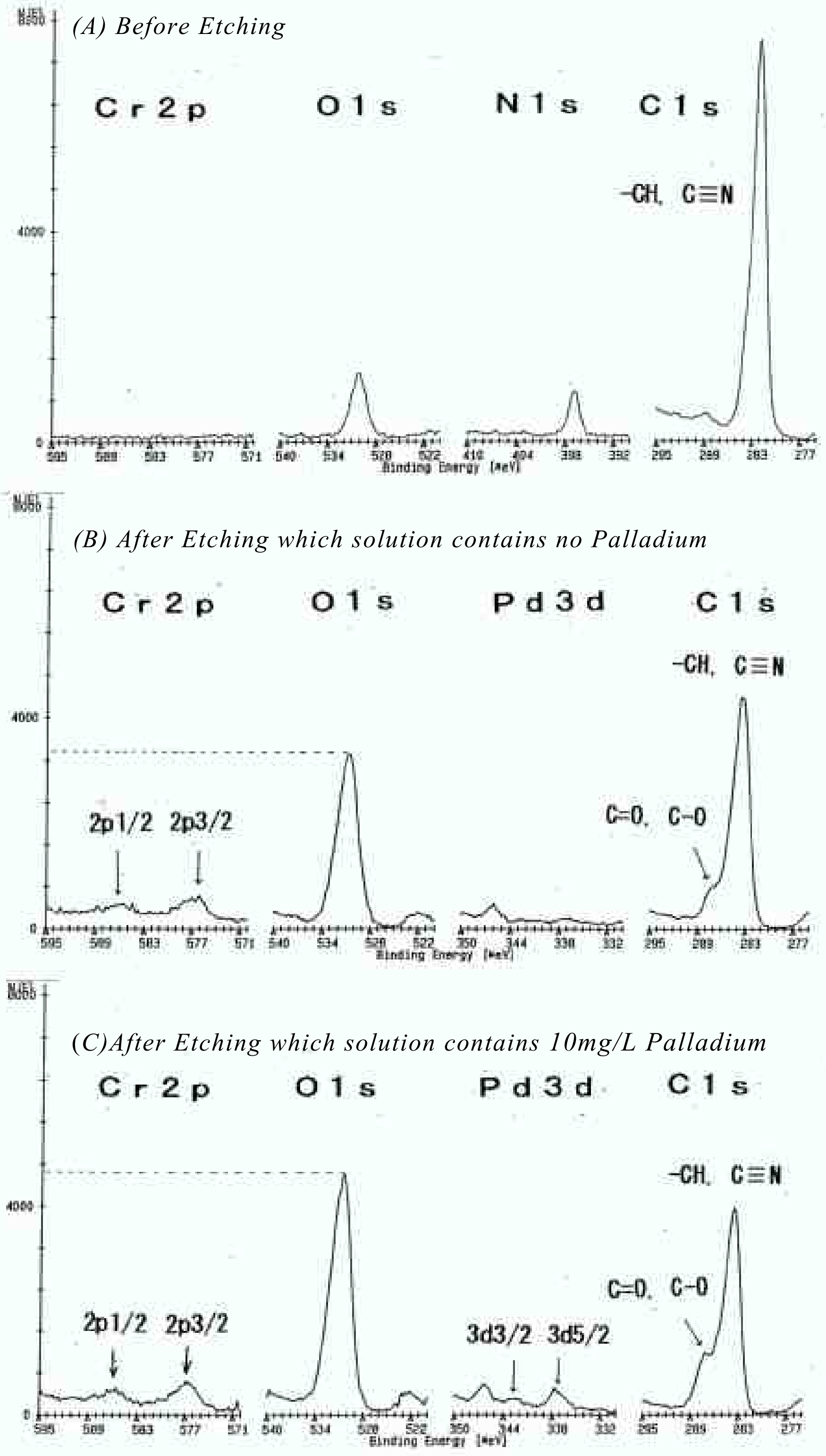


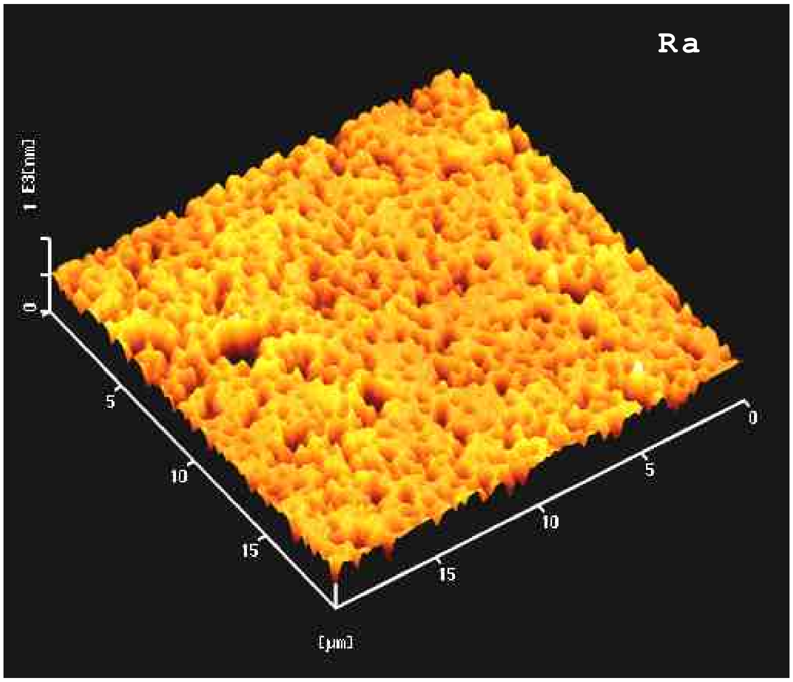
Fig.7 XPS spectral peaks of ABS resin surface.

6. Influence of Etching Treatment to Surface Roughness of ABS Resin Surface

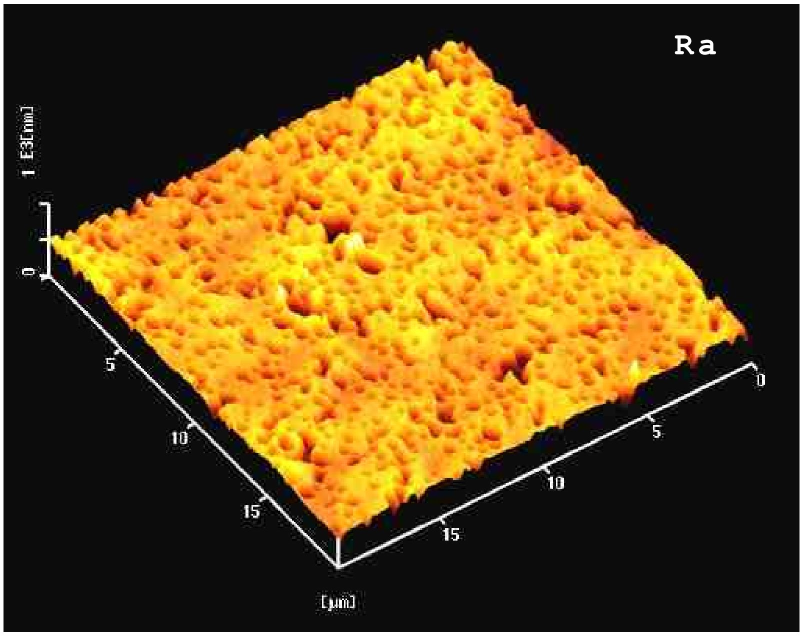
As we stated above, by adding palladium into etching solution, we found the formation of functional groups on the plastics surface was accelerated. We wish to report our results of influence of addition of palladium to roughening power which is another function of etching.

Fig.8 shows AFM (Atomic Force Microscopy) images of plastics surface which were treated by etching solutions having no addition of palladium and having 10 mg/L of palladium addition. On these images, we show the average surface roughness (Ra). We found from these figures that the roughening degree of plastics surface was suppressed slightly by adding of palladium to etching bath. However, even by this suppression of surface roughening, the adhesion between plastics specimen and plating film did not decrease.

From this result, we think that functions of etching of giving hydrophilicity and roughening are different reactions. And we think that, by adding of palladium to etching bath, the former function is accelerated and the latter function is suppressed.



(A) Treated with etching solution containing no palladium



(B) Treated with etching solution containing 10mg/L palladium

Fig.7 AFM image of ABS resin surface after etching.

7. Conclusion

In electroless copper plating having saccharides as reducing agent, palladium-tin colloid adsorbed on plastics surface at catalyzing step acts as conductive film. So it is required to adsorb it at higher amount compared with the conventional process, and the concentration of palladium in catalyzing bath is required to be higher concentration by few times.

By adding of palladium to etching bath, the concentration of palladium in catalyzing bath can be reduced remarkably.

By adding of palladium to etching bath, the adsorption amount of palladium at catalyzing step increases. This is supposed that the formation of function groups is accelerated.

By adding of palladium to etching bath, the formation of function groups is accelerated, and roughening of plastics surface is suppressed. From these results, we suppose that the functions of formation of function groups and roughening by etching are different mechanism.

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