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ARTICLE

Environmentally Friendly Copper Metallization of ABS by Cu-Catalysed Electroless Process

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Abstract: An environment-friendly surface etching and activation technique for ABS surface metallization were investigated as a replacement for conventional chromic acid etching bath and palladium catalyst. After etching by H_2SO_4-MnO_2 colloid, the ABS surfaces became rough; meanwhile the carboxyl and hydroxyl groups were formed on the surface. With absorption and reduction by a sodium borohydride solution, copper particles were deposited on the ABS surface, which serve as a catalyst replacement for $SnCl_2$/$PdCl_2$ colloid. The effects of $CuSO_4$ concentration, $NaBH_4$ concentration, reduction temperature and reduction time on the adhesion strength between the ABS surface and the electroless copper film were investigated. The average adhesion strengths reaches 0.87 kN·m^{-1}.

Key words: electroless plating; reducing agent; ABS resin material; adhesion strength

Metallized ABS (acrylonitrile-butadiene-styrene) with outstanding properties of both engineering plastic and metal been widely used in electronic industry, petrolic industry and national defense field owing to its advantages. The conventional surface activation process used a solution containing $SnCl_2$ and $PdCl_2$ for sensitization and activation[1]. Because of the high price of $PdCl_2$, the cost of the surface activation occupied a high proportion in the surface metallization process. To reduce the cost in the surface metallization, Pd free surface activation process has become increasingly important.

Many studies on the activation pretreatment method for no conducted substrates have been carried out.

J. Y. Zhang et al[2], G. J. Fisanick et al[3], M. E. Gross, et al[4] and A. Gupta et al[5] fabricated some thin metal-organic precursor films by spin-coating technology. After being irradiated by excimer radiation, the thin metal-organic precursor films were decomposed to metal clusters which were used as activation layers. But the metal-organic precursors were usually expensive and dangerous.

It is reported that Cu deposition was achieved by a laser-induced chemical liquid-phase deposition (LCLD) method [6,7]. In this method, Cu seeds were formed on the substrate by a variety of laser radiations and then initiated the sequential Cu electroless deposition. Shu et al. [8] developed a chemical process consisting of adsorbing the Cu^{2+} species onto the sulfonated surface from a cupric aqueous solution and reducing Cu by dimethylamineborane solution.

R. Padiyath et al[9] reported a direct copper metallization process consist depositing a thin copper formate film by spin-coating and then reducing it by a H_2RF plasma. X. J. Tang [10] reported a new surface activation process for ABS resin. By formation film of chitosan on the ABS surface, $PdCl_2$ was adsorbed on the ABS surface for the electroless copper. However, the adhesion strength between the metal film and the substrate surface was poor.

In the conventional activation processes, noble metal palladium is usually employed as the catalyst sites to initiate the electroless plating. The cost of the palladium has increased in recent years, which raise the price of the electroless plating method. In the present, inexpensive metal copper has the catalytic property for electroless plating; economical equipment is required.

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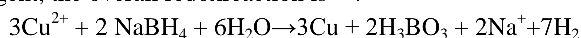
1 Experiment

The ABS substrates with a thickness of 1.0 mm and an area of 40 mm ×25 mm were used in all experiments. Before the etching, the ABS substrates were pretreated by the degreasing and swelling processes[11]. And then, ABS substrates were immersed into MnO_2-H_2SO_4 (sulfuric acid 12.3 mol/L, MnO_2 contents: 30 g·L^{-1}) colloid at 70 ℃ for about 20 min for surface etching. After that, the ABS substrates were kept in a neutralizing solution ($H_2C_2O_4$·H_2O, 0.20 mol·L^{-1}, and sulfuric acid 1.84 mol/L) at 50 ℃ for 3 min to remove residual MnO_2.

Then, ABS substrates were kept in the $CuSO_4$ solution at 25 ℃ for 10 min, by which Cu^{2+} was adsorbed on the ABS surface. By reduction of $NaBH_4$ (sodium borohydride, $NaBH_4$) solution at 50 ℃ for 3 min, $NaBH_4$ is a powerful reducing agent, the overall redoxreaction is[12]:



$$3Cu^{2+} + 2\,NaBH_4 + 6H_2O \rightarrow 3Cu + 2H_3BO_3 + 2Na^{+} + 7H_2$$

The copper particles were deposited on the ABS surface, which were used as catalytic activation sites for electroless copper deposition.

The composition of the electroless copper plating solution was copper sulfate ($CuSO_4$·$5H_2O$, 10 g·L^{-1}) as a copper ion source, ethylenediaminetetraacetic acid disodium salt (EDTA·2Na, 30 g·L^{-1}) as a complexing agent, glyoxylic acid (CHOCOOH, 10 g·L^{-1}) as a reducing agent, and poly (ethylene glycol) (PEG, 4000 MW, 0.5 g·L^{-1}) as the surface activator. The pH of the solution was adjusted to 12.5 using NaOH (3 mol·L^{-1}) and the bath temperature was kept at 60 ℃ [13]. After electroless plating, electroplating copper was carried out at room temperature with a current density of 0.03 A·cm^2 for 60 min, which resulted in a copper thickness of 20 μm. After annealing was carried out at 110 ℃ for 2 h, the peel strength was measured by a 90° peel test at a peel rate of 25 mm/min [14]. The peel strength was reported as an average value of three times.

With an environment-friendly etching treatment, a Pd free surface activation process was investigated by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy spectra (XPS).

2 Results and Discussion

2.1 Surface adsorption and reduction of copper ions on ABS surface

Before etching, the ABS surface is very smooth (Fig.1a). With surface etching of MnO_2-H_2SO_4 colloid at 70 ℃ for 20 min, the butadiene phases on the ABS surface are oxidized, many cavities appear on the surface (Fig.1b). Meanwhile, XPS spectra measurements indicate that many -COOH and -OH groups form on the surface of ABS resins after the etching treatment, which results in the surface contact angle decrease from 94° to 36°. Because of the formation of -COOH and -OH groups on the ABS surface, copper ions are able to be adsorbed on the surface when the etched substrates are immersed into the $CuSO_4$ solution. With reduction of $NaBH_4$ solution, the copper particles are deposited on the ABS surface.

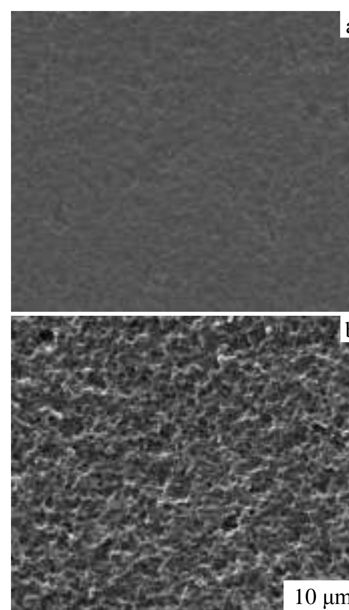


Fig.1 Surface morphology of the ABS substrates etched by 12.3 mol/L H_2SO_4-MnO_2 colloid at 70 ℃ (MnO_2: 30 g/L): (a) without etching and (b) etching treatment of 20 min

Fig.2 shows the surface morphology images of the ABS substrates after the reduction of $NaBH_4$ solution. Before the $NaBH_4$ reduction, only the rough surface is observed (Fig.2a). When the substrate is immersed in $NaBH_4$ solution for 10 s, some copper particles are formed on the surface. When the substrate is reduced for 30 s, many copper particles are deposited on the ABS surface, and the copper particles do not increase with prolonging the reduction time, which indicates that the copper ions are reduced completely by immersion in $NaBH_4$ solution for 30 s.

The Cu 2p XPS spectra on the ABS surface before and after reduction were also measured, and the results are shown in Fig.3. Before reduction, there are two peaks at 931.0 eV in the reference spectrum, which is attributed to Cu^{2+} $2p_{3/2}$. This indicates that copper ions are adsorbed on the ABS surface. After reduction by $NaBH_4$ solution at 50 ℃ for 30 s, two peaks, which are attributed to metal Cu $2p_{3/2}$ (930.0 eV) and $2p_{1/2}$ (950.0 eV), appear. The results reveal that the Cu(II) ions are reduced to metal copper.

2.2 Electroless copper deposition on ABS surface

When absorbed copper ions are reduced by $NaBH_4$ solution, the copper particles are deposited on the ABS surface. Because metal copper has catalyst activation for electroless copper deposition, electroless copper is able to be deposited on the ABS surface. Fig.4 is images of surface morphologies of the ABS substrates with various electroless plating times. When the substrate is dipped into the plating bath at 50 ℃ for 10 s, some bright points are found in the SEM image (Fig.4a). Energy dispersive X-ray measurement show that the bright points consist of metal copper, suggesting that the catalysis

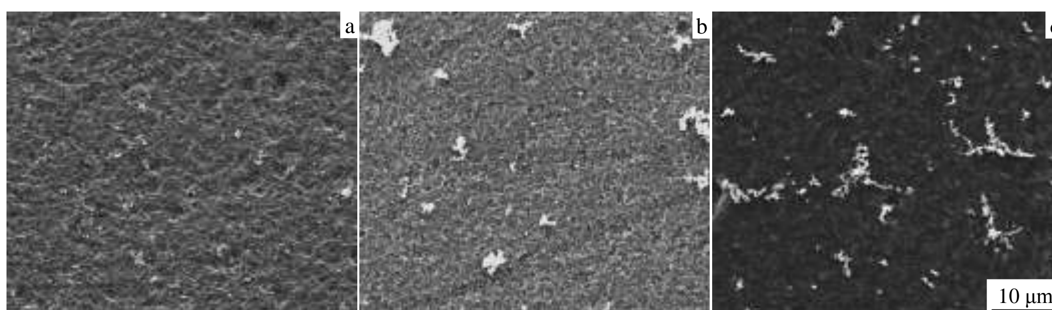


Fig.2 Surface morphology of the ABS substrates reduced by $NaBH_4$ solution with different reduction time ($NaBH_4$ concentration: 1%): (a) 5 s, (b) 15 s, and (c) 30 s

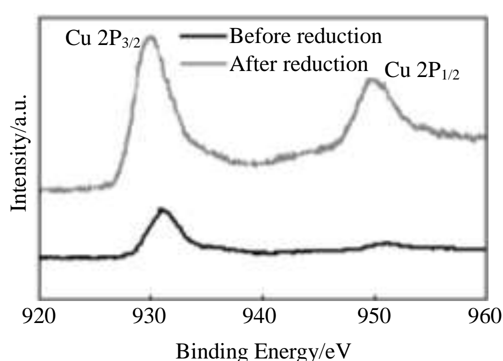


Fig.3 Cu 2p XPS spectra of ABS substrates before reduction and after reduction by $NaBH_4$ solution at 50 ℃ for 30 s

of the copper particles for electroless copper deposition is so strong that copper metals are deposited on the surface of copper particles after only 10 s. With prolonging electroless plating time, the deposited copper particles become larger and more uniform (Fig.4b and 4c). When the plating time is 60 s, almost all the surface is covered by plated copper deposits, which demonstrates that the Pd free activation technique is feasible for ABS surface metallization.

2.3 Effects of copper ion absorption and $NaBH_4$ reduction conditions on adhesion strength

The adhesion strength is a very important property of a electroless copper deposited film. The adhesion strength between electroless copper film and ABS substrate was measured by a 90° peel strength measurement. First, the effects of Cu^{2+} concentration, pH of $CuSO_4$ solution, absorption time and absorption temperature on the adhesion strength were investigated by peel strength measurement; the adhesion strength is found to be independent of Cu^{2+} concentration, pH of $CuSO_4$ solution, absorption time and absorption temperature, and is at a level of almost 0.44 kN m^{-1}. The effects of $NaBH_4$ concentration, reduction time and reduction temperature on the adhesion strength were also studied. Though the adhesion strength is independent of $NaBH_4$ concentration and reduction time, the adhesion strength increases with the $NaBH_4$ reduction temperature (Fig.5). When the temperature is 20 ℃, the peel strength is 0.44 kN m^{-1}, and increases quickly with temperature, and it reaches 0.87 kN m^{-1} when the temperature is 50 ℃. Upon raising temperature further, the adhesion strength decreases with increasing $NaBH_4$ reduction temperature. This result is attributed to the theory that with increasing $NaBH_4$ reduction temperature, the reduction reaction is accelerated and the copper particles are uniformly deposited on the ABS surface, which causes an increase in the adhesion strength, at least up to 50 ℃.

2.4 Effects of catalytic agent on copper deposited film

The crystallography of electroless plated Cu film deposited in the plating bath was characterized by X-ray diffraction. For the electroless plated Cu film deposited with Pd as catalyst, the peak intensity ratio $I(111):I(200)$ is 3.31 and the full width

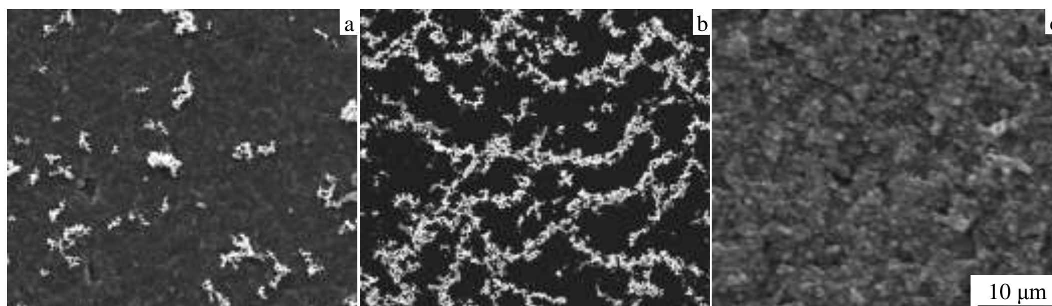


Fig.4 Surface morphology of the substrates with different electroless copper time: (a) 10 s, (b) 30 s, and (c) 60 s

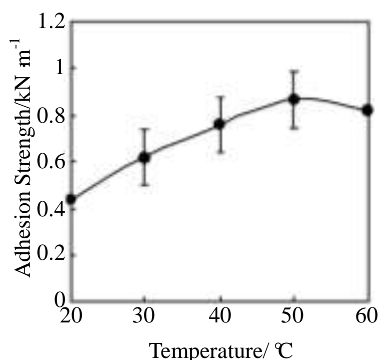


Fig.5 Effects of temperature on peeling strength

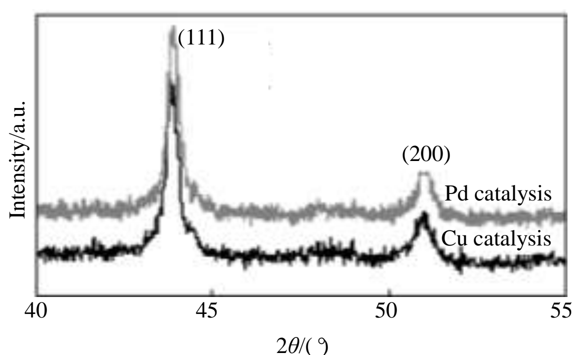


Fig.6 XRD patterns of electroless plated Cu films

at half-maximum (fwhm) of (111) for 2.2 μm thick Cu film is 0.357 ° (Fig.6). When copper is reduced on ABS substrates, the peak intensity ratio $I(111):I(200)$ is 3.23 and the fwhm of (111) for 2.2 μm thick Cu film is 0.369 ° (Fig.6). According to Scherrer's formula[15-17] the results indicate that there is no significant difference between copper catalyst and Pd catalyst on the crystallinity of electroless plated Cu film.

3 Conclusions

1) A Pd free surface activation technology for ABS surface metallisation has been studied. After the surface etching by an environmentally friendly MnO_2-H_2SO_4 colloid, the –COOH and –OH groups are formed on the surface of the ABS resin. With copper ion adsorption and $NaBH_4$ reduction, the copper particles are deposited on the surface of ABS resin to catalyze electroless copper deposition, and uniform electroless copper films are subsequently deposited on the ABS surface. The effects of $CuSO_4$ absorption conditions and $NaBH_4$ reduction conditions on the adhesion strength between the ABS surface and the electroless copper film are also investigated by peel strength measurement.

2) When the reduction temperature is 50 ℃, the adhesion strength between the ABS surface and the electroless copper film reaches 0.87 kN·m^{-1}, indicating that this surface activation technique may be a feasible and cost effective method for ABS surface metallization.

3) There is no significant difference between copper catalyst and Pd catalyst on the crystallinity of electroless plated Cu film.

References

1 Seeböck R, Esrom H, Charbonnier M *et al. Surface and Coating Technology*[J], 2001, 142: 455
2 Zhang J Y, Esrom H, Boyd I W. *Applied Surface Science*[J], 1996, 96: 399
3 Fisanick G J, Gross M E, Hopkins J B *et al. Journal of Applied Physics*[J], 1985, 57: 1139
4 Gross M E, Appelbaum A, Gallagher P K. *Journal of Applied Physics*[J], 1987, 61: 1628
5 Gupta A, Jagannathan R. *Applied Physics Letter*[J], 1987, 51: 2254
6 Kordás K, Békési J, Vajtai R *et al. Applied Surface Science*[J], 2001, 172: 178
7 Wang X, Zheng H, Lim G C. *Applied Surface Science*[J], 2002, 200: 165
8 Shu Zengnian, Wang Xu. *Applied Surface Science*[J], 2012, 258: 5328
9 Padiyath R, David M, Babu S V. *Metallized Plastics 2: Fundamental and Applied Aspects*[M]. New York: Plenum Press, 1991
10 Tang X, Cao M, Bi C *et al. Materials Letters*[J], 2008, 62(6-7): 1089
11 Li Z, Li N, Yin L *et al. Electrochem Solid-State Lett*[J], 2009, 12 (12): D92
12 Seita M, Kusaka M, Nawafune H *et al. Platting and Surface Finishing*[J], 1996, 83: 57
13 Jiang H, Liu Z, Wang X *et al. Transactions of the Institution Metal Finishing*[J], 2007, 85: 103
14 Wang Z, Furaya A, Yasuda K *et al. Journal of Adhesion Science Technology*[J], 2002, 16: 1027
15 Ishibashi J, Kobayashi K, Ichikawa T *et al. Journal of the Japan Institute Electronics Packaging*[J], 1998, 1: 483
16 Norkus E, Vaskelis A. *Russion Journal of Inorganic Chemistry*[J], 1987, 32: 130
17 Kim J J, Kim S K, Kim Y S. *Journal of Electroanalytical Chemistry*[J], 2004, 61: 542

环境友好的 ABS 板铜催化的铜金属化

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摘　要：采用一种新型的环境友好的 ABS 表面微蚀和活化技术以代替传统的铬酸微蚀和钯催化活化技术，经 H_2SO_4-MnO_2 微蚀后，ABS 板表面变得粗糙，在其表面出现大量的羟基和羧基。通过吸附和硼氢化钠的还原，铜粒子沉积在 ABS 板表面，以取代 $SnCl_2$/$PdCl_2$ 胶体催化活化。同时，研究了硫酸铜、硼氢化钠浓度、还原剂温度、还原时间对化学铜 ABS 板表面粘结强度的影响，最终得到的粘结强度为 0.87 kN·m^{-1}。

关键词：化学沉积；还原剂；ABS 板；粘结强度

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