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Improved ABS plastic activating treatment for electroless copper plating

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A new method is described for the electroless deposition of copper onto acrylonitrile–butadiene–styrene (ABS) plastic. Etched ABS plastic was dipped directly into $PdSO_4$ solution instead of the usual sensitization followed by activation. Experimental results show that the Pd^{2+} ions from $PdSO_4$ solution are coordinated to the polar groups (i.e. –COOH, $-SO_3H\cdots$, etc.) on the surface of the etched ABS, resulting in the formation of ABS–Pd^{2+} complex. In an electroless copper bath containing a formaldehyde (HCHO) reducing agent, the ABS–Pd^{2+} complex is reduced to product Pd^0 atoms, which then act as catalysts and initiate the deposition of copper metal. Initially, the copper deposition rate was slow; however, it rose to that for conventional methods in about 10 min.

(Keywords: electroless plating; activation; etching)

Introduction

Electroless plating cannot be performed on an acrylonitrile–butadiene–styrene (ABS) substrate without first depositing a catalyst onto the ABS surface. Usually the etched ABS is dipped into an aqueous colloidal suspension of palladium (Pd), resulting in the deposition of about 1–2 nm diameter particles of Pd^0 on the ABS surface[1–5]. The process is fairly simple, but it has some problems. Because the colloid is prepared by reduction of Pd^{2+} to Pd^0 by $SnCl_2$, the Pd particles are surrounded by a tin chloride shell[6,7]. Tin chloride is not an active catalyst for electroless copper deposition (ECD). It inhibits the activity of the Pd catalyst. The shell can be dissolved away by an 'acceleration step', which typically involves immersion of the coated ABS in aqueous HCl or NaOH[1–5]. Acceleration must be carried out soon after applying the colloid, however, since the shell oxidizes in air to form tin oxides that are very difficult to remove. The acceleration step also causes agglomeration of Pd particles on the ABS surface[1–5].

Recently, some authors showed that functional polymers can coordinate with noble metal ions (e.g. Pd^{2+}) through complex formation[8–10]. The polymer–Pd^{2+} complex is reduced to Pd^0 in an electroless plating bath (EPB) prior to the electroless deposition of metal.

ABS does not possess any polar groups which can form a complex with Pd^{2+}. The etching of ABS will produce polar groups such as –COOH, $-SO_3H$ or $-CONH_2$ on the surface of the substrate. In this paper, a new method for initiating ECD onto ABS is described. The etched ABS is immersed into $PdSO_4$ solution. The polar groups will coordinate with the Pd^{2+} ions resulting in an ABS–Pd^{2+} complex. No acceleration step is required. Immersion of this modified ABS into an EPB spontaneously reduces the Pd^{2+} to Pd^0, which is an active catalyst for ECD. We have compared our process with the colloidal palladium process.

Experimental

In typical experiments, ABS (22% acrylonitrile, 15% butadiene, 63% styrene) was cleaned by washing in 2 wt% NaOH solution, rinsing in water, then immersing in 30 wt% HNO_3, and rinsing in water. After chromic acid etching, the substrate was dried and weighed.

The etched ABS was immersed into 0.01 M $PdSO_4$ solution for 30 min to form ABS–Pd^{2+} complex. Then the ABS–Pd^{2+} complex was examined by X-ray photoelectron spectroscopy (XPS). ECD was performed in two ways: (1) ABS–Pd^{2+} complex was reduced first to Pd^0 with reductant solution (10 wt% HCHO) and subsequently treated in the EPB (*Table 1*) to produce a metallized ABS; and (2) ABS–Pd^{2+} complex was directly immersed into the EPB to produce metallized ABS. After it was rinsed and dried, we weighed it and calculated the amount deposited.

Results and discussion

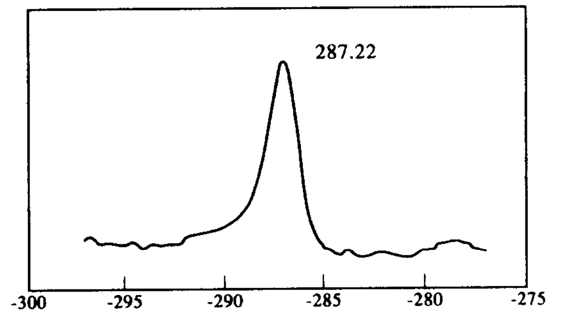
In *Figure 1* we anchored the energy scale to the C (1s) peak at 284.6 eV (ref. 11), and the Pd ($3d_{5/2}$) peak was found at 337.6 eV. This is close to the literature value of 336.1 eV given for Pd^{2+} in a predominantly covalently bonded species (Pd^0, ref. 11). The data reported here suggest that Pd^{2+} ions are captured by the polar groups to form a complex compound on the etched ABS surface.

While Pd^0 is a well known catalyst that initiates ECD, it is not known that Pd^{2+} is a catalyst as well. It appears, however, that the ABS–Pd^{2+} complex is reduced to Pd^0 in the EPB. This was shown by the prompt colour change of the ABS surface, from ivory to black, observed upon immersion of the ABS–Pd^{2+} complex in the EPB.

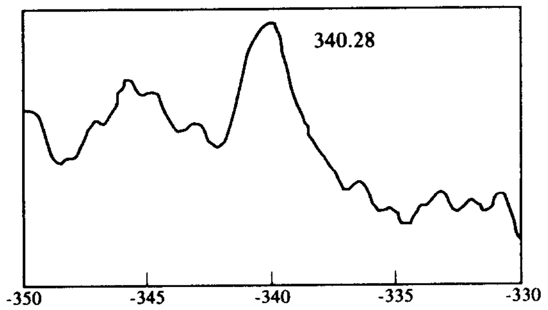
Figure 2 shows the deposition amount *versus* time. The ABS–Pd^{2+} complex was immersed into the EPB directly. Initially, the copper deposition rate was slow, but after a while approached that for the conventional method. The

Table 1 Formulation of the electroless copper plating bath used in this work. The bath was used at room temperature during plating

Component	Concentration ($g l^{-1}$)
A	
HCHO	150
$CuSO_4$	90
B	
Na_2EDTA	150
NaOH	80
Na_2CO_3	30
$A:B:H_2O = 1:1:4$	



(a) C 1s Spectra



(b) Pd 3d Spectra

Figure 1 XPS spectra of ABS–Pd^{2+} complex: (a) C 1s spectrum; (b) Pd 3d spectrum

time delay is about 10 min. If ABS–Pd^{2+} complex is reduced first with HCHO solution before immersion in the EPB, then there is no significant difference in deposition amount and rate between the two methods.

Conclusion

A new method for initiating the electroless deposition of copper onto ABS has been described. The etched ABS formed a complex with Pd^{2+} and consequently catalysed the deposition of copper onto ABS. This method is comparable in simplicity to the colloidal palladium method of initiating ECD on ABS. No acceleration step is required and the agglomeration of palladium particles on the ABS surface was minimized. Directly applying $PdSO_4$ solution to catalyse ABS can result in better efficiency in ABS electroless plating since it omits not only the sensitization step but also the acceleration treatment.

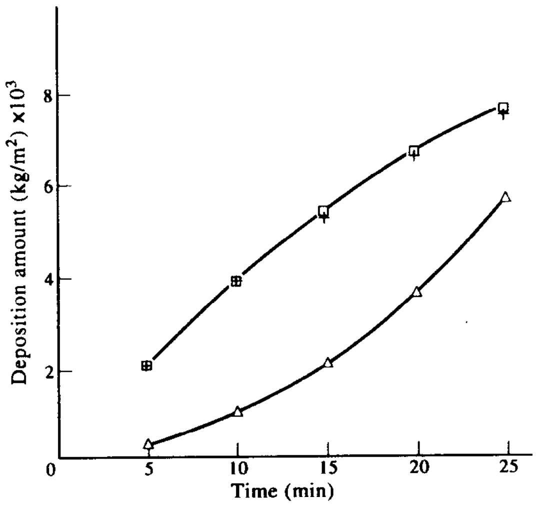


Figure 2 Deposition amount *versus* time: □, conventional method; △, ABS–Pd^{2+} complex immersed directly in the EPB; +, ABS–Pd^{2+} complex first reduced then immersed in the EPB

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