New Etching Method of PVC Plastic for Plating by Ultrasound

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Received 16 June 1997; accepted 2 November 1997

ABSTRACT: An ultrasonic etching method is effective to pretreatment of PVC plastic for plating without chemical pollution. After being etched for 60 min by 28-kHz ultrasound, the improvement of adhesion strength of Cu–PVC can increase 13%, compared with that of chromic–sulphuric acid etching. The mechanism of adhesion improvement was studied by examination of weight loss, surface roughness, scanning electron microscopy, image analysis, and X-ray photoelectron spectroscopy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1411–1416, 1998

Key words: ultrasound; etching; PVC plastic

INTRODUCTION

Good etching effect is important for the subsequent plating on PVC plastic (polyvinyl chloride) with metal. Generally, the etching of PVC plastic was carried out in chromic–sulphuric acid solution.[1] The etching effect of chromic sulphuric acid could be improved by pretreatment with mechanical spray[2] and organic solvent swelling[3] or by modification of PVC plastic composition with inorganic filler,[4] such as alumina and calcium carbonate. In order to eliminate the pollution and health and safety problem associated with chromic–sulphuric acid etching and to improve further the etching effect, some other etching methods, such as SO_3,[5] ozone,[6] yellow phosphorus in organic solvent,[7] and plasma[8] were studied.

On the other hand, it has been known that ultrasound wave can corrode many materials due to its cavitation effect.[9] This article reports a new method to etch PVC plastic by ultrasound with better etching effect.

EXPERIMENTAL

The PVC plastic specimens were plating grade with a density of 1.63 g cm^{-3}, containing about 5.5 calcite, 1% Fe_2O_3, and 7.5% alumina powders as filler (Experiment Factory of Chinese Hefei University, Hefei, Anhui). The number-average molecular weight of the resin is about 56,000. The average diameter of the filler is 1.5–49 μm. As illustrated in Figure 1, an 28-kHz ultrasonic probe system (Wuxi Ultrasonic & Electronic Equipment Co., Wuxi, Jiangsu) was used for etching experiment. The comparative chemical etching was carried out in 825 g dm^{-3}. H_2SO_4 and 47 g dm^{-3} in $K_2Cr_2O_7$ solution at 60–70°C for 60 min according to the Liu.[10]

The cosine value of contact angle of PVC surface with distilled water was determined with an

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Contract grant sponsors: Committee of the National Natural Science Foundation of China; Yunnan Applied Fundamental Research Grants Committee.

Journal of Applied Polymer Science, Vol. 68, 1411–1416 (1998)

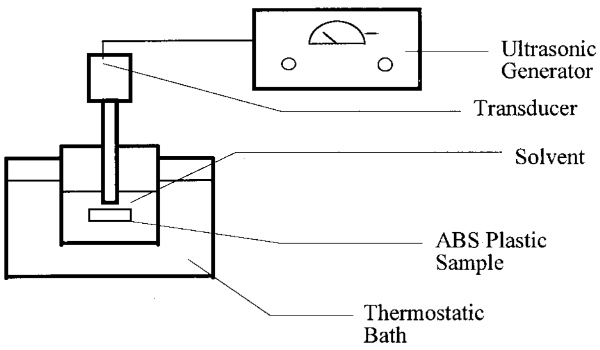

Figure 1 Experimental schematic diagram of the probe system.

O-D model precious height measurement apparatus (Shanghai Technical and Physics Institute) according to Padday.[11] Then the surface roughness R was calculated with the formula in Eick et al.,[12] where θ and Φ are the contact angles of water with PVC surface before and after etching, respectively, as follows:

$$R = \mathrm{COS}\ \Phi / \mathrm{COS}\ \theta$$

The micrographs of plastic samples surface were taken under a XJZ-6 microscope and were analyzed with a Quantimet-900 image analyzer (Cambridge, UK). X-ray photoelectron spectroscopy (XPS) analysis was done on PHI5500 ESCA (Al K_α).

After being etched, the PVC plastic specimens were electroless-plated with copper in a conventional manner.[13] Then the properties of coating were evaluated by thermal cycling test (85°C for 60 min, 20°C for 30 min, and −12°C for 60 min for 5 times) and determination of the adhesion strength on KZY-500 universal test machine.[14] The thickness of the coated Cu was measured with MeF3 Widefield metallograph.

RESULTS AND DISCUSSION

The Effects of Various Parameters on Ultrasonic Etching

Surface roughness R, the mean values of roughness of surface in two runs, is used to characterize the effects of ultrasonic etching in terms of solvents, irradiation time, acoustic power, and temperature.

Figure 2 shows the effects of five solvents on the roughness of PVC surface after being etched ultrasonically. The best etching effect is obtained in acetone, and the worst solvent for etching of PVC plastic is 95% alcohol under our experimental conditions. These results could be explained through a consideration of the combination of the vapor pressure of these solvents and also the solubility of PVC resin in these solvents. Acoustic cavitation, which is the motivation of etching, is more violent in solvents with a lower vapor pressure because less vapor enters the cavitation bubble so that the cushion effect of vapor on bubble collapse is smaller. The sequence of these solvents in the order of decrease in vapor pressure is as follows: acetone, 95% alcohol, water, 1,4-dioxane, and toluene. On the other hand, the solubility of PVC plastic in acetone is greatest among the five solvents. The fact that ultrasonic etching can achieve largest effect in acetone means that although the acetone is a bad solvent to cause cavitation, the solubility of PVC plastic in it dominates for ultrasonic etching. However, water is a more reasonable solvent for ultrasonic etching, although the etching effect in acetone is 1.6 times greater as that in water, considering the price and toxicity of organic solvents.

The effects of temperature on the roughness of PVC surface after being etched by ultrasound are shown in Figure 3. It can be seen that there is no large variation in surface roughness at different temperatures in our experimental range. The greatest roughness was obtained at 29°C and is only 1.13 times greater than the lowest surface roughness, obtained at 18°C. The fact means that temperature has little effect on the etching of PVC plastic in our experimental range.

Figure 4 indicates that the surface roughness of PVC plastic increases along with the increase of ultrasonic irradiation time. Figure 5 shows that the surface roughness of PVC plastic increases as the increase in ultrasonic power entering the etching system. After being etched at 42.4 W, the roughness of PVC surface is 1.9 times greater than before etching.

Therefore, the largest etching effect can been achieved in water at 42-W power and 29°C for 80 min in the range of our experiments. The larger surface roughness must be of benefit to the wettability of PVC surface to various treating solutions in subsequent processes, which is probably one of the reasons why ultrasonic etching can produce a better adhesion between copper and PVC than chromic acid etching.

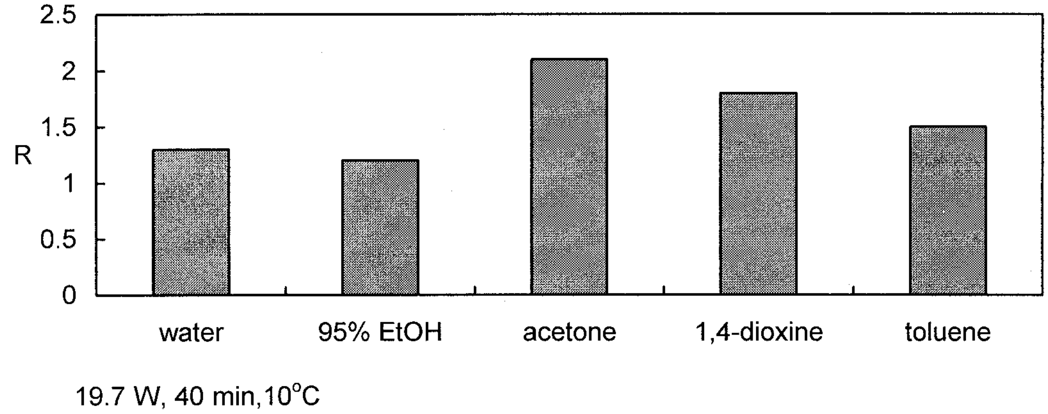

Figure 2 Effects of solvent on roughness.

The weight loss per square meter of PVC plastic caused by ultrasonic etching is shown in Figure 6. It can be seen that the weight of PVC decreases along with an increase in the etching time. This phenomenon is in coincidence with that of the relationship between roughness and irradiation time. This weight loss could be the result that the acoustic cavitation that happened on the PVC surface removes the inorganic fillers and PVC resin from the PVC surface continuously and selectively.

Changes of Surface Morphology of PVC Plastic After Being Etched Ultrasonically

It has been reported that chromic acid etching can produce a lot of cavities on the surface of PVC plastic.[1] From the scanning electron microscopy (SEM) and microphotos of PVC surface before and after being etched ultrasonically (Figs. 7 and 8) it can be seen that ultrasonic etching can also produce a similar effect. By means of image analysis technology, it has been quantitatively determined that the surface morphology of PVC etched ultrasonically in water at 42-W power and at 10°C for 60 minutes. The results are summarized in Table I.

From Table I, it can be seen that for ultrasonic etching the total area of cavities on the PVC surface is 33.3%, their average diameter is 5.21 μm, and the number of these cavities on per square centimeter is 2.82×10^6, versus 27.6%, 4.99, and 2.48×10^6 for chromic acid etching, respectively. It can be seen that ultrasonic etching can produce more cavities whose sizes are larger than that of chemical etching.

The cavities into which copper is subsequently anchored are necessary for good bonding between copper and PVC. According to the report,[15] substrate surface with cavities whose radius are between 0.03–20 μm and density is above $10^6/cm^2$ toward a good interlocking bonding mechanism. The fact that the surface morphology of PVC etched ultrasonically is in this range probably is another reason why ultrasonic etching can produce a better adhesion between copper and PVC.

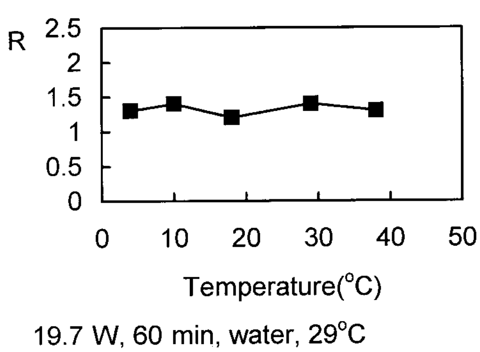

Figure 3 Effects of temperature on roughness.

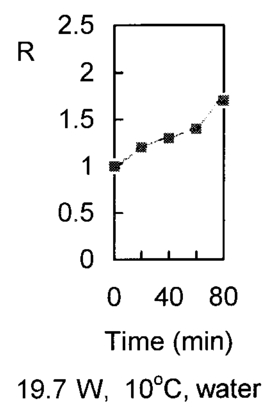

Figure 4 Effects of time on roughness.

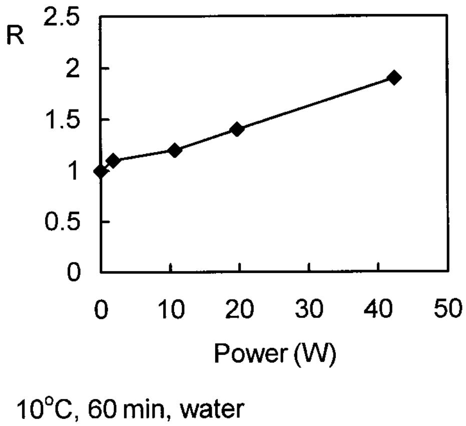

Figure 5 Effects of power on roughness.

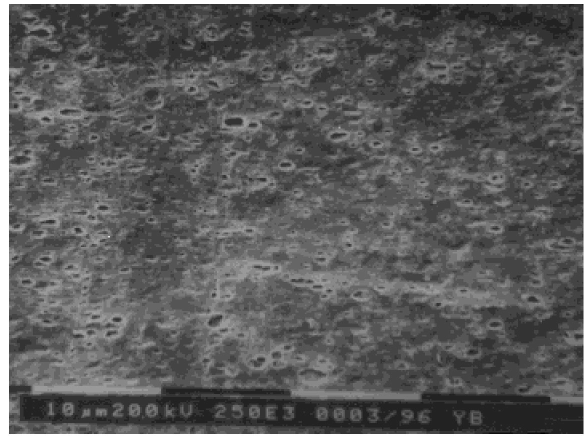

Figure 7 SEM of PVC surface after ultrasonic etching.

Chemical Changes of PVC Plastic Surface After Being Etched Ultrasonically: XPS Analysis

By comparison of the spectra for C_{1S} and O_{1S} core level of PVC samples before and after chemical and ultrasonic etching, it can be seen that after being etched new peaks at E_b = 288.1 and 534.3 eV appears in both samples of chemical and ultrasonic etching, corresponding to the formation of new carboxyl groups[16]; and, in the case of chromic acid etching, the peak intensity is larger. This means that ultrasonic etching can produce a similar chemical change as chemical etching, although the amount of carboxyl groups formed is less (Fig. 9).

It has been reported by Decker[17] that PVC plastic is easy to be degraded and produces some polar organic functional groups, such as R—OH, R—CO_2H, and R—CHO, on PVC surface initiated by heat, light, or X-ray. It has been known that ultrasonic cavitation can produce a high local temperature and pressure (around 5000°C and 1000 atm) in some hot spots in liquid.[9] In the extreme high-energy environment of these hot spots, the water molecular is deformed in $^{\bullet}$H and $^{\bullet}$OH radicals.[18] It is supposed that the C—Cl and C—H bond of PVC plastic would react with $^{\bullet}$OH and formed alkoxyl radicals, which would further decomposed into some organic groups, such as R—OH, R—CO_2H, and R—CHO, through a similar mechanism as that in Decker.[17] It has been reported[14] that the R—OH, R—CO_2H, and R—CHO on substrate surface can form chemical

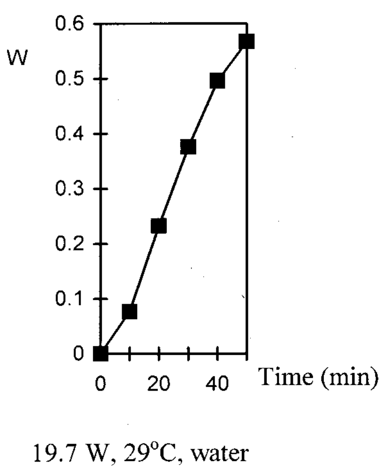

Figure 6 Effect of etching time on weight loss (g/m^2) of PVC.

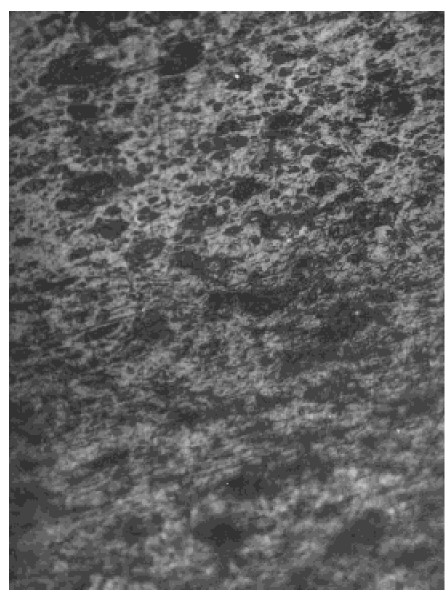

Figure 8 Micrograph of the PVC surface after ultrasonic etching (×350).

Table I Image Analysis of Micropores on PVC Surface Etched Ultrasonically and Chemically

Micropore	Total Area (%)	Average Diameter (μm)	Standard Deviation	Density $\times 10^6$ cm^{-2}
Unetched	7.5	2.11	1.36	2.53
Ultrasonically etched	33.3	5.21	6.19	2.82
Chemically etched	27.6	4.99	5.68	2.48

bonds with coating metal and result in good adhesion. This may be another reason why ultrasonic etching can produce an improved adhesion between copper and PVC.

Adhesion Strength Test

Our results of adhesion strength test show that the adhesion strength between copper coating and

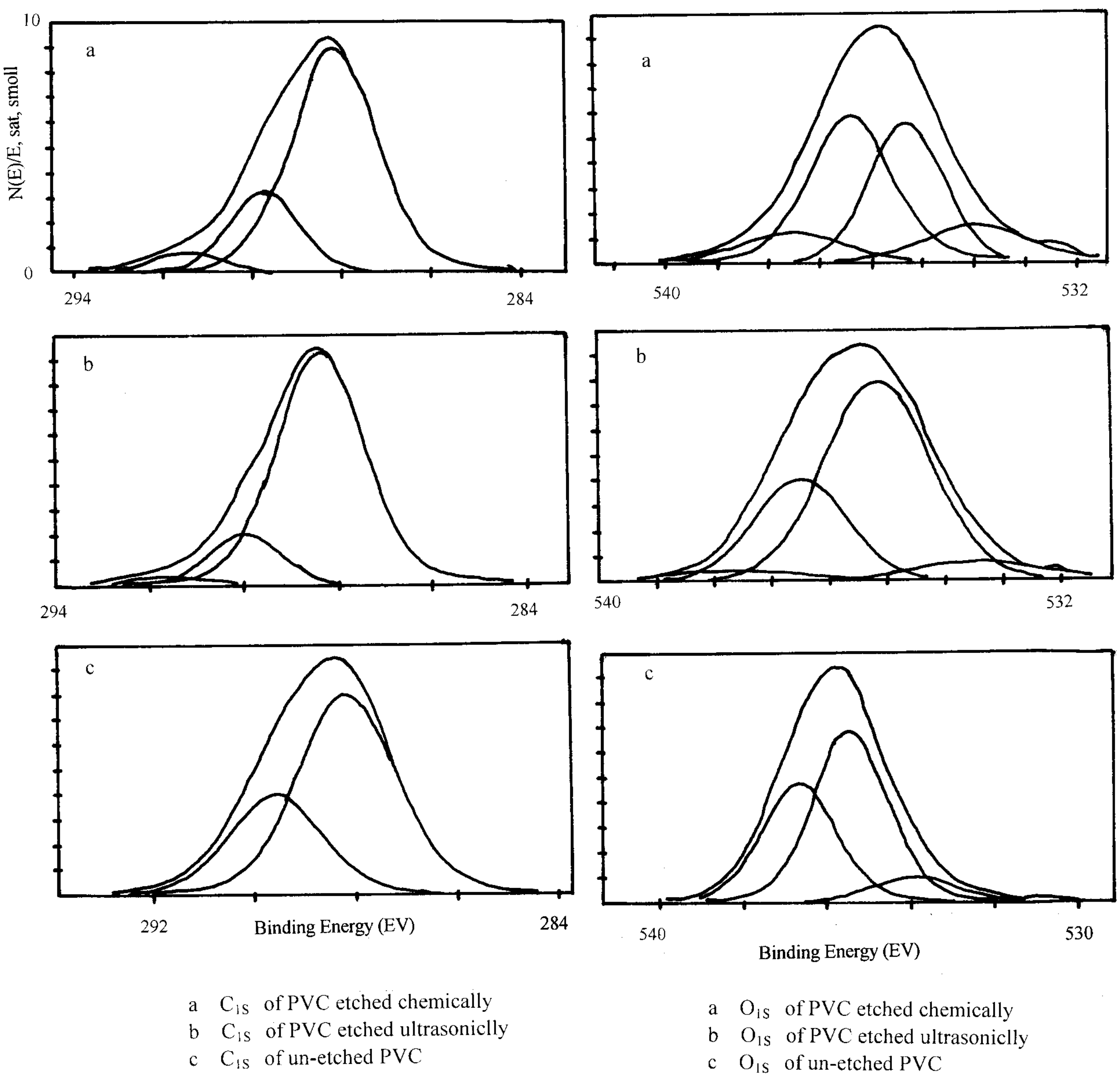

Figure 9 Spectrum of C1S core level of PVC surface after ultrasonic etching.

PVC surface etched ultrasonically is larger than that of chromic–sulphuric acid etching under the same conditions for electroless plating and adhesion determining. For the sample etched under 28-kHz and 19.7-W ultrasound at 29°C in water for 60 min, the mean adhesion is 51 kg/cm^{-2} (the thickness of Cu is 46 ± 3 μm), compared with 44 kg/cm^{-2} (the thickness of Cu is 45 ± 4 μm) for chemical etching.

Thermal Cycling Test

After 5 times of thermal cycling, no adhesion failure is found between copper–PVC etched ultrasonically, as well as the samples etched with chromic acid. The fact means that the adhesion strength is good for the sample etched ultrasonically.

CONCLUSION

In conclusion, ultrasonic irradiation can etch PVC plastic surface for electroless plating Cu on it with larger adhesion strength and without chemical pollution. The mechanism of adhesion improvement should be that ultrasonic etching produces rougher PVC surface.

The authors thank the Committee of the National Natural Science Foundation of China and the Yunnan Applied Fundamental Research Grants Committee for the financial support on this work.

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