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Surface Modification Using Nano-phase Structures of Epoxy/block Copolymer Blends for Electroless Copper Plating

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1. Introduction

Adhesion between electroless copper plating and polymer substrates of printed circuit boards has been an important issue. At present, the good adhesion can be achieved using the pre-formed rough surfaces in μ m-scale on the substrates¹⁾. However, considering for more-miniaturization trend with the high performance of semiconductor integrated circuit, the advanced polymer surfaces having the less-roughness were required with maintaining the good adhesion of the copper plate layer.

Several nano-phase structures of the cured epoxy/PMMA-*b*-PnBA-*b*-PMMA tri-block copolymer (BCP) blends were reported by one of the authors^{2,3)}. We have considered that the sub-micron roughness might be constructed by the selective etching of the elastomer phase in the epoxy/BCP nano-alloys. In this study, the cured epoxy/BCP blends were examined as the polymer substrates for the electroless copper plating.

2. Experimental

2.1 Materials

Diglycidyl ethers of bisphenol-A (DGEBA, epoxy equivalent weight: 189 g/eq) was utilized as the epoxy resin. Stoichiometric amount of phenol novolac (PN, hydroxyl group equivalent weight: 105 g/eq.) was used as the curing agent.

Tri-phenyl phosphine (TPP) worked as a catalyst used with the PN. The amount of the TPP was 0.5 parts per hundred resin.

The PMMA-*b*-PnBA-*b*-PMMA tri-block copolymer (BCP: weight-average molecular mass $M_w=72000$, PnBA content in the BCP was 77 wt%, $M_w/M_n=1.19$) were dissolved in the DGEBA. The blends were pre-cured using PN/TPP at 120°C for 2h, and post cured at 150°C for 2h. The content of the BCP was 10 wt% in the cured blends.

2.2 Surface treatment for substrates and the electroless copper plating

The cured epoxy/BCP blends were etched using oxygen plasma generator SAMCO PT-500S. Oxidation treatment was conducted using UV-ozone surface processor (UV wavelength: 253.7 nm, Sen Lights Corporation, UVE-200G-SSII). The cured epoxy substrates were subjected to electroless plating using the copper plating agent (OPC-750, Process-M) from Okuno Chemical.

2.3 Evaluation methods

Scanning electron microscope (SEM), atomic force microscope (AFM), and Fourier transform infrared spectroscopy (FT-IR, ATR method) were applied to examine the surface of the epoxy substrates. Peel strengths of the copper plating layer on the polymer substrates was measured using 90° peel configuration by a tensile tester (Shimadzu, sm-500n-168).

3. Results and Discussion

Fig. 1 shows a SEM image (reflection electron mode) of a surface of epoxy/BCP blend. The relatively bright

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phases consist of the PnBA stained by RuO_4 , and the dark matrix mainly consists of the epoxy thermoset. The curved lamella type nano-phase structure were observed^{2,3}. The nano-phase structure was formed by the self-assembly mechanism of the epoxy/BCP blend². The PnBA elastomer phase was expected to be etched selectively by the oxygen-plasma treatment. In fact, the curved lamellar-type concave structure was observed after the plasma etching (Fig. 2). Fig. 3 shows the effect of the plasma etching to make the surface roughness of the epoxy/BCP blends. The roughness increased with increasing the plasma treatment, although the etching was not observed on the pure epoxy substrates.

Fig. 1 “Curved lamellar” nano-phase structure of epoxy/BCP (10wt% BCP in the cured epoxy blend)

Fig. 2 Plasma-etched surface of the epoxy/BCP blend

Fig. 4 shows the effect of the surface roughness (R_{zjs}) for the peel strength of the copper plating layer on the epoxy/BCP substrates. The peel strengths of the electroless copper plating increased by the “anchor effect” of the plasma-etched epoxy/BCP substrates. However, the simple concave formation was not enough to achieve the required peel strength (more than 7 N/cm).

Therefore, UV-ozone oxidation was applied as the additional treatment, because the increased polarity was

Fig. 3 Effect of the plasma treatment on the surface roughness of the epoxy/BCP blends and pure epoxy substrates

expected to work for the wettability of the plating agent on the plasma-etched epoxy substrates. The FT-IR spectra indicated the oxidation, as evidenced by the increased absorbance ratio on C=O/benzene ring from 0.3 to 0.6. As the results, the peel strength has reached 8.1 N/cm in the best mode, with keeping the surface roughness (R_{zjs}) of 93nm, as shown in Fig. 4. It should be noted that the peel strength of the non-etched surface was only 0.3 N/cm, even after the same UV-ozone oxidation. Big synergistic effect of “nano-etching” and “oxidation” enabled the high peel strength of the copper plating. The plausible mechanism would be the increased wettability of the water-based plating agents into the nano-concaved structures on the treated substrates.

Fig. 4 Effect of the surface roughness & ozone oxidation for the peel strength of the electroless copper plating on the epoxy/BCP substrates

References

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