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

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Key words: Epoxy, Block copolymer, Phase structure, Electroless plating, Peel strength

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 μm-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 authors²,³. 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 Mw=72000, PnBA content in the BCP was 77 wt%, Mw/Mn=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
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 ob-
served$^{2,3}$. The nano-phase structure was formed by the
self-assembly mechanism of the epoxy/BCP blend$^2$.
The PnBA elastomer phase was expected to be etched se-
lectively by the oxygen-plasma treatment. In fact, the
curved lamellar-type concave structure was observed af-
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 sub-
strates.

![Fig. 1](image1)

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

![Fig. 2](image2)

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

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 (Rzjis) 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 mecha-
nism would be the increased wettability of the water-
based plating agents into the nano-concaved structures
on the treated substrates.

![Fig. 3](image3)

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

![Fig. 4](image4)

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

References