A STUDY OF ADHESION AT THE E-GLASS/FR4 INTERFACE

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ABSTRACT

The goal of this work is to investigate mechanisms for the loss of adhesive strength between E-glass and FR4 epoxy upon humidity and temperature conditioning. In this paper we discuss the distribution of moisture between the interface region and the bulk epoxy examined by neutron reflection, and the relationship of this data to adhesive strength.

KEY WORDS: Adhesives, Primers, Laminates

1. INTRODUCTION

The majority of printed circuit boards are copper clad laminates composed of fiberglass cloth impregnated with FR4 epoxy. An important factor affecting the reliability of these assemblies is the integrity of the epoxy/glass fiber interface. Delaminations can lead to copper ion migration and ultimately, to shorts in the circuit. In addition, delaminations can cause visual defects such as measling which contribute to a loss in yield for the board manufacturer. Delaminations are most significant after high temperature and high humidity conditioning and in additive copper processes which involve alkaline etches. Expensive and time consuming baking cycles are common practice to avoid delamination during soldering. The goal of this work is to investigate mechanisms for the loss of

adhesive strength between FR4 and fiberglass cloth after moisture and temperature conditioning.

Our program involves four key elements: i) characterization of the distribution of moisture between the interface region and the bulk epoxy by neutron reflection; ii) characterization of the topology and the degree of wetting of adhesion promoting finishes on E-glass by atomic force microscopy, scanning electron microscopy, and Auger spectroscopy; and iii) characterization of contamination on the glass surface resulting from processing; and iv) development of a quantitative adhesion test which is sensitive to variations in interfacial strength. In this paper we focus on the moisture distribution and the correlation with adhesive strength.

EXPERIMENTAL

Moisture distribution by neutron reflectivity

Determining the moisture profile at a buried interface *in situ* is a challenging experimental problem. However, some success has been achieved recently through the use of neutron reflectivity[1,2] and FTIR-multiple internal reflection (FTIR-MIR) spectroscopy.[3] Neutron reflection has been used to study the profile of adsorbed D_2O at the interface between a polyimide and a silicon wafer[1] and between a polyurethane and molybdenum.[2] The primary advantage of this technique is excellent depth resolution (5Å). This allows examination of the degree of penetration of moisture into particular interfacial layers, such as silane or metal oxide layers. This information is critical for understanding mechanisms of moisture induced adhesive failure. The main disadvantage of this technique is that only a few sources of high flux, low wavelength neutrons exist and the available beam time is limited. The advantages of FTIR-MIR spectroscopy are that i) like neutron reflectivity, it has good sensitivity such that a low level of moisture can be detected, and ii) it can be performed in-house. An important disadvantage is that the depth resolution is limited by the penetration depth of the incident radiation, typically thousands of angstroms. Thus, with this technique only the integrated excess of moisture can be determined and not the detailed moisture profile.

In this work we have examined the distribution of moisture between interfacial silane layers and the bulk epoxy. The samples were prepared by exposing the polished surface of silicon wafers to silane finishes for 30 sec., and then spinning off the excess with a photo resist spinner. This typically resulted in a silane layer 200-400 Å thick, with ~ 50-100 Å peak to valley roughness, as observed by atomic force microscopy. The samples were cured at 90 °C for 1 hr to drive off water, and then roll coated with ~2 μm of deuterated epoxy, which was specially synthesized for this work. The epoxy was cured at 177 °C for 2 hrs. The samples were then desiccated until the reflectivity experiments were performed. The reflectivity was obtained first from the samples in the desiccated state, then after exposure to a saturated D_2O atmosphere at 23 °C for 18 days, and then once again after exposure to a saturated D_2O atmosphere at 80 °C for 2 days. Based on measurements of the diffusion of moisture in epoxies reported in the literature,[4] an exposure time of 18 days should be sufficient to allow the moisture to

diffuse entirely through the 2 μm epoxy layer and reach a quasi-steady state in the system. Two proprietary commercial silane finishes were examined which will be referred to as A and B. The samples will also be referred to by these designations.

Figure 1a shows the reflectivity from sample A in the desiccated state, and then after exposure to a saturated D_2O atmosphere at 23 °C for 18 days. The solid curve through the data corresponds to a 200 Å layer of silane with 70 Å roughness. The reflectivity at q values greater than the critical q for total reflection (~0.012 Å^{-1}) is sensitive to moisture in the interfacial region. No change in the reflectivity is observed after conditioning. The minimum moisture level in the silane layer which would be detectable in this experiment is roughly 3 % by volume. Therefore, we conclude that the steady state moisture content for samples conditioned in 100 % relative humidity at 23 °C is less than 3 %. Furthermore, since the equilibrium uptake of moisture in bulk FR4 epoxy is known to be roughly 1-2%,[4] we can conclude that there is not a large excess of moisture at the interface relative to the bulk of the epoxy under these conditions.

These results are consistent with the results of Nguyen, et al,[5] obtained by FTIR-MIR. In that work, no uptake of moisture in the interfacial region was detectable for epoxy/silane/silicon samples which were exposed to 45 % rel. humidity at 24 °C for 12 days.
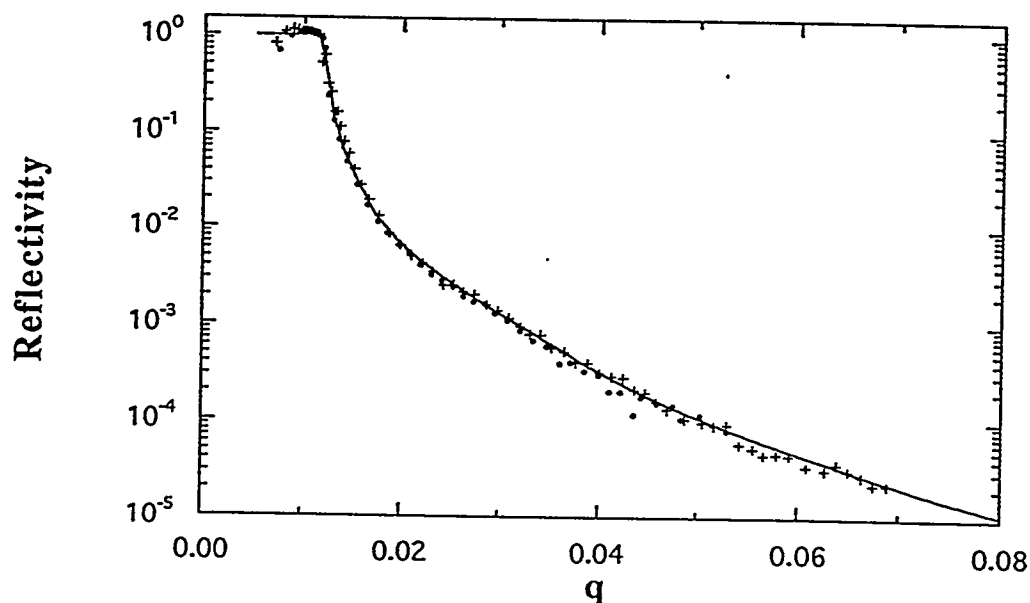

Figure 1a. Neutron reflectivity from sample A desiccated (+), and after 18 days in an atmosphere of sat. D_2O at 23 °C (filled circles)

Figure 2 compares the reflectivity obtained from sample A after 2 days exposure to a saturated D_2O atmosphere at 80 °C, with that obtained in the desiccated state. Whereas

there was no difference after conditioning at room temperature, there is a very significant difference in the reflectivity after conditioning at 80 °C. The curve through the data for samples conditioned at 80 °C corresponds to ~ 18 % D_2O in the interfacial silane layer. This is considerably higher than the ~ 2% moisture content in the bulk of the epoxy. The reflectivity from sample B after conditioning for 2 days at 80 °C is shown in Figure 2. We again observe a noticeable increase relative to the reflectivity in the desiccated state, however, the effect is much weaker than that observed for sample A.

Adhesion testing

Tensile test specimens were machined from E-glass rods. Each end of the rods were polished. One end of each rod was dipped into a bath of silane finish for 30 seconds, and then the rods were placed into an oven at 90 °C for 1 hr. Following this, the samples were placed into a mold and FR4 epoxy was injected into the 0.5 mm gap. After curing, the specimens were inspected visually for bubbles or other defects. The cured specimens where then exposed to 100% relative humidity at 80 °C for 72 hours, followed immediately by submersion in molten solder (260 °C) for 40 seconds. The average tensile forces required to break the bonds after this conditioning treatment are given in Table 1. The data points represent the average of at least 4 samples. Occasionally, the samples broke in the glass rather than in the bond line due to defects in the glass. Only samples which broke in the bond line were included. As a control, we examined samples for which no silane finish was applied to the rods. These specimens all broke when submersed into molten solder after humidity conditioning.

Table 1 Results of tensile test

Tensile strength (lbf/in^2)	Finish A	Finish B
	2690 +/- 620	4280 +/- 1043

DISCUSSION

In Table 1 we observe that the bond strength for samples with silane finish A is significantly weaker than that for the samples with silane finish B. This appears to correlate with the larger increase in reflectivity upon elevated temperature conditioning for sample A. We suspect that the large uptake of deuterium in the interface region after elevated temperature conditioning is due to hydrolysis of siloxane bonds, which weakens the interface. Hydrolysis apparently does not occur at room temperature on the time scale of 18 days. Further work is in progress to clarify this and to investigate methods for improving the durability of this interface.
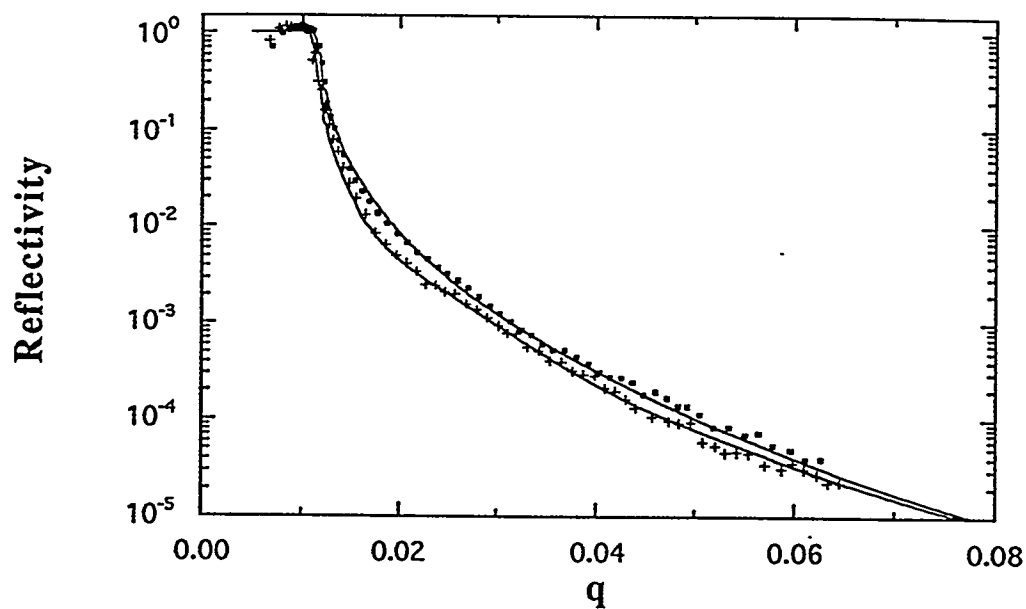
Figure 1b. Neutron reflectivity from sample A desiccated (+), and after 2 days in an atmosphere of sat. D_2O at 80 °C (filled circles)
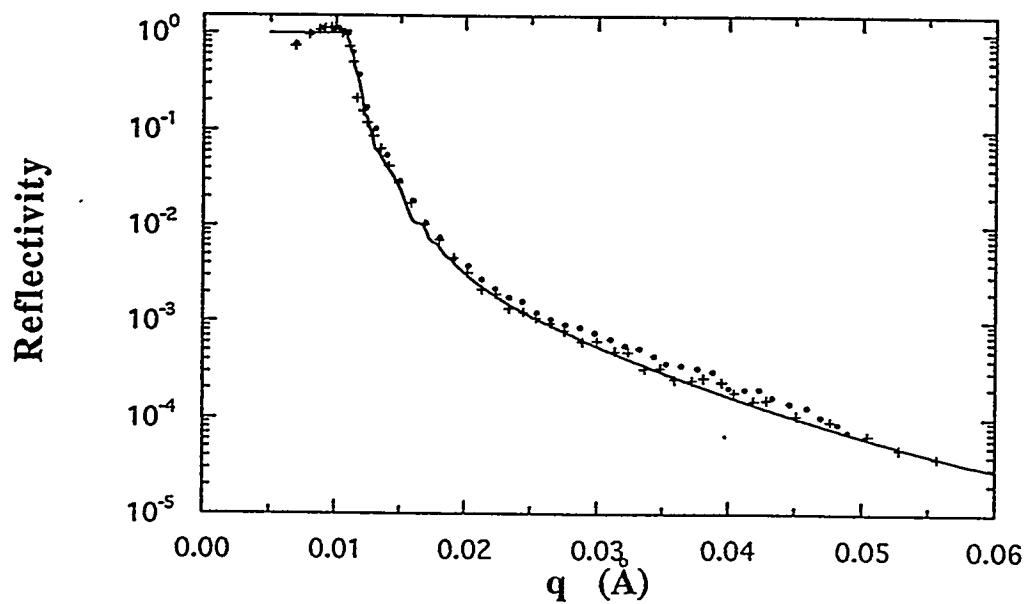

Figure 2. Neutron reflectivity from sample B desiccated (+), and after 2 days in an atmosphere of sat. D_2O at 80 °C (filled circles)

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