Mechanism of Moisture Diffusion, Hygroscopic Swelling and Adhesion Degradation in Epoxy Molding Compounds

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Abstract
Epoxy Molding Compounds (EMCs) are widely used as encapsulation materials in semiconductor industry for protecting the IC's/MEMS against the environment. Despite their advantages like low-cost and good mechanical behavior, an important disadvantage of these materials is moisture absorption from the environment. This causes many reliability problems, including interface delamination and 'popcorn' effect during soldering reflow process. In this paper a systematic approach was conducted to investigate the mechanisms of Fickian and non-Fickian moisture absorption in EMCs. Different sample geometries were produced and their mass uptake/loss due to moisture absorption/desorption were investigated. Results reveal a dual-stage moisture uptake during absorption and irreversible residual moisture content upon complete desorption, indicating that some EMCs retain moisture for long time even at elevated temperatures. This residual content is a complex function of sample geometry, baking temperature and sample sorption history.
The hygroscopic swelling was investigated by the means of warpage measurement of Cu/EMC bimaterial beams. A significant permanent change of the dimension of EMCs due to irreversible residual moisture content was observed. This indicates that not all the swelling of samples can be recovered when they are baked in dry conditions.
The adhesion of Cu/EMC was also measured for dry and moist samples. The interfacial fracture toughness was obtained using the end-notched flexure (ENF) tests based on interface fracture mechanics. Two mechanisms of adhesion losses were observed. Some of the adhesion loss due to small amount of moisture content was recovered via a proper annealing. However, upon activation of the second saturation phase, none of the adhesion loss was recovered after baking the moist samples.

Key words
Moisture, Absorption and Desorption, swelling, Adhesion, Epoxy Molding Compound (EMC)

1. Introduction
In spite of many advantages like smaller size, lower weight, good performance, and lower-cost of Plastic Encapsulated Microcircuits (PEMs), an important disadvantage is that the molding compound absorbs moisture when exposed to a humid environment [1-8].
Epoxy molding compounds (EMC) compose of a polymer matrix, silica fillers and other additives. Moisture behavior of EMC is mainly dominated by the diffusion of water through epoxy resin. However, the amount of filler and its shape can influence the moisture diffusivity [9].

dependency to the time exposed to moisture [6]. Moisture content in a material can be analyzed using the so-called thermal-moisture analogy [2-4]. The method can be also developed to overcome the discontinuity problem of moisture concentration across the bi-material interfaces [3]. More recently, a direct concentration approach (DCA) has been developed to study the moisture diffusion with varying temperature and humidity conditions such as in soldering reflow [10].
Water molecules in polymeric materials have been identified to have two distinct states. "Free" or "unbound" state of water is attributed to water molecules that are present in voids and nanopores of the material [11-13], while "bounded" water molecules react with the polymer chains via hydrogen bonding or some chemical reactions. This identification is further supported by measurement of the ratio of hygroscopic volume expansion to the volume of

absorbed water which is less than unity, indicating that some of the absorbed water does not contribute to swelling.
Interfacial adhesion is of important concern for multilayered structures such as microelectronic packages [14-17, 25]. Moisture can influence the interfacial adhesion through three mechanisms. The first mechanism is the intrinsic aggregating effect of water molecules upon direct presence at the interfaces and degrading the interfacial adhesion by bonding to the polymer chains [14]. The second mechanism is that the absorbed moisture changes the mechanical properties of polymeric materials [15-17, 22]. For example moisture can change the elastic modulus and shift the glass transition temperature of polymers to lower values. This mechanism leads normally to a slight difference in the mode mixity of the measured fracture toughness of moist sample when compared to that of dry sample [16]. The third mechanism is the swelling of polymeric materials upon exposure to moist environments and causing an additional mismatch between volumetric expansions of substrate and adhesives [6, 18, and 19]. This is even more pronounced when the joint between a polymer and metal is investigated. Since the metallic substrate is impermeable to moisture, only the polymeric adhesive absorbs moisture and causes mismatch in hygroscopic strains. In order to measure the intrinsic fracture toughness of a moisture preconditioned sample, the influence of hygroscopic swelling which induces an apparent change in the measured fracture toughness should be isolated.
In this work, we first investigated the non-Fickian behavior of moisture absorption and desorption. The residual moisture content upon the desorption of the EMC was investigated by comparing the results of moisture desorption of different sample geometries at different baking temperatures. In addition, the first run of moisture absorption was compared to the second run after baking in different conditions. Secondly, the hygroscopic swelling of the molding compound was investigated by a bimaterial beam which was exposed to humid environment and its warpage was documented periodically. Finally, the influence of aging in humid conditions on the adhesion between EMC and copper was studied.

2. Moisture Diffusion

2.1 Fickian Moisture Diffusion

Fick's second law can be applied to describe the moisture diffusion process in polymeric materials [1-4]:

The moisture absorption in some molding compounds can be characterized by linearly decreasing diffusivity as a function of average moisture content [4], while for highly non-Fickian diffusion of some organic substrates a power-

desorption process. Two points from moisture absorption diagram were selected. Point A represents a virtual

absorption/desorption cycle would be even more complicated. Samples were initially placed in a humid chamber to reach a virtual saturation (two weeks for thin samples and four weeks for the thick samples). They were then removed from humid chamber and placed in an infrared dry oven at two temperatures of 110°C and 160°C to release their moisture at a constant temperature. After reaching a ‘virtual dry state’ (the plateau value in Fig.2 and

desorption is the same. However, similar to the residual moisture content upon desorption of the molding compounds a residual hygroscopic strain may also exist. In other words, not all the swelling during the moisture uptake may be recovered after the desorption. In this work the swelling of the EMC's was investigated by measuring the deflection of a bi-material beam during the moisture absorption. A bi-material beam of Copper/EMC was designed and manufactured. The samples were used later for the characterization of interfacial fracture toughness between EMC and copper leadframe [16 and 25]. Copper substrates were machined into $50\times10\times0.4$ mm^3 strips. After cleaning with acetone the substrates were placed in the cavity of a molding machine. Pellets of the same EMC were introduced into the cavity of a pre-heated mold at about 175 °C and kept under a pressure of 60-80 MPa for 120 s; the molding compound was dispensed automatically on the copper surface at 175°C. After molding, the samples were placed in an environmental chamber for post-mold curing at 175°C for six hours to complete the polymerization process of the epoxy molding compound. Fig.6 shows the dimension of the bimaterial beam.

Fig.6 Bi-material beam designed for the measurement of hygroscopic swelling of EMC and its adhesion to Cu.

The initial warpage of the sample due to chemical cure shrinkage and mismatch between coefficients of thermal expansions (CTEs) was measured at room temperature by a chromatic sensor. Some samples were later placed in a humid chamber and were removed periodically from the moisture chamber and their warpage was measured at room temperature. During the moisture absorption, the warpage changed from concave to the convex shape (see Fig.7). The convex shape increased and reached a constant value of approximately 150 micrometers after 3 weeks. Further exposure to moisture did not affect the warpage.

Some samples were removed from moisture chamber after the saturation and were placed in a dry infrared oven at 110°C. The Warpage of the samples was measured at room temperature after 10 Days desorption. This was done to investigate, if the hygroscopic swelling of the sample is reversible. As it was expected, not all the moisture-induced warpage due to moisture absorption was recovered. This suggests that the measurement of the hygroscopic swelling by any method that deals with-6(the m)7()6(ch)k me

J/m^2 in dry condition reduced to 26.3 J/m^2 when the virtual saturation level was achieved at interface.