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Basic thermo-mechanical property estimation of a 3D-crosslinked epoxy/SiO_2 interface using molecular modelling

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ABSTRACT

In this work we present a procedure for the construction of 3D networked epoxy moulding compounds and an estimation of basic thermodynamic properties by molecular dynamics simulations. Our investigations present part of general trend to extend failure analysis, reliability assessment and the development of packaging materials from the conventional discrete usage of simulation techniques to a more holistic approach of an interconnected multimethods-procedure, enabling bottom-up simulation of complex microsystems. Within that framework, the task at hand for detailed atomistic molecular modelling is to develop practical methods in order to take materials development as well as materials failure analysis to the nanoscale level. This paper reports a cross linking scheme for the construction of three dimensionally cross linked simulation packages and presents a first property analysis of an industry-oriented moulding compound material. First models and results are presented of model packages of ideal epoxy/silicon-dioxide interfaces.

1. Introduction

Advanced microelectronic packages are an integral part in many products spanning the wide range of automotives, avionics, computers and mobile applications. Increasing complexity, i.e., reduction in size while increasing functionality, to meet cost and performance demands poses a great challenge for the design of such microsystem technologies [1]. The reliability and service time of such components needs to be estimated beforehand, to avoid product recalls and ensure customer security. For this task, finite element (FE) simulations are employed to uncover weak spots of a system [2,3]. However, FE-based simulations are an approach based on continuum mechanics, and material properties need to be known.

With increasing miniaturization and complexity, structural dimensions cross over from the micro- to the nanoscale [4]. At this length scale, FE simulation methods are overtaxed: On the one hand, the ratio of surface to volume becomes large and the impact of molecular properties and structure increases – the continuum approach fails because material properties change. On the other hand the size of whole systems is too large to be simulated in atomistic detail or even coarse grained models. The key for a simulation assisted reliability assessment lies therefore in a combination of all three approaches, feeding properties calculated in atomistic detail to coarse grained and continuum models, combining the size effects with complex geometries as is required for a comprehensive evaluation procedure. This approach is being put into practice by a consortium of companies and research institutions as part of the NanoInterface project (http://www.nanointerface.eu/) with funding from the European Framework Program 7.

The capability of molecular modelling within this scheme is twofold: chemical or physical parameters of materials can be systematically varied and tendencies in property changes may be predicted. Here, the value lies in structure–property-correlation at the drawing board, avoiding time- and cost-intensive laboratory effort. Secondly, the various interfaces in complex structures can be simulated to give insight to the physics of failure through direct observation of molecular phenomena at the location where failure is likely to occur and experimental data is often hard to realize.

A typical failure mechanism occuring in microelectronic packages is the delamination of the molding compound from the chip surface. On the atomic scale, this interface is essentially that of the epoxy resin of the compound with a native silicon oxide on the chip-surface. With the numerical tool of molecular modelling it is possible to investigate bulk properties of the epoxy as well as its physical interaction with the chip-surface, that is, the contribution of the thermodynamic work of adhesion to the interfacial strength.

Some work has been reported on molecular modelling of cross linked structures in the recent past. Wu and Xu [5] developed a method to construct atomistic molecular models of cross linked polymers based on commercially important epoxy resins. In two follow-up publications [6,7] the authors investigate atomistic

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models of the same epoxy system with respect to structure and dynamics and the influence of water sorption on these. They find a tendency of the water molecules to cluster at higher concentrations and their plasticizing effects on the epoxy matrix.

Yarovsky and Evans [8] propose another methodology for constructing atomistic models of cross linked epoxy networks, making an effort of imitating the chemical curing process. Qualitative agreement with experimental results of volume reduction upon curing (and cooling) and diffusivities of water have been reported.

In an earlier work, Yarovsky provides a review on the simulation of interfaces in theory and applications [9]. In particular, she reports on structural properties and adhesive strength of interfaces influenced by water and the implications for predicting environmental stability of an interface, giving the example of the change in sign of the work of adhesion measured by contact angles in epoxy–metal oxide systems. In principle such a trend should be able to be simulated, however, the author cautions that absolute values cannot be expected to perfectly agree, in part due to the measurement of "apparent" properties in experiments.

Interfacial diffusion and adhesion of polycarbonate and silanes is investigated by molecular simulations by Deng et al. [10]. The authors report mechanical properties, surface and adhesive energy components obtained by a combination of energy minimization and molecular dynamics. Surface energies were derived from the difference in bulk models and materials with a free surface. By comparison of flow stresses, they found that the work of adhesion may not necessarily be an indication for the bi-material toughness under mechanical loading.

In a paper we presented at the EuroSimE 2009 [11], structure–property correlation on a model epoxy was discussed, comparing trends obtained from molecular dynamics with experimental data. The need to accurately represent the structure was established to achieve reasonable quantitative agreement. In this work, the special challenge lies in a cross linking algorithm that produces cross links that extend the network beyond the periodic unit cell, interconnecting the latter with its virtual images. A practical procedure of cross linking will be described that adopts ideas found in the literature [5,8] but incorporates some own ideas as well, to arrive at sufficiently cross linked models within reasonable computation time. The algorithm has been applied to layered structures of epoxy and metal-oxide as well, producing two-dimensional periodic networks in an infinite sandwich layer. The last section contains some first results of these multilayered models.

2. Bulk models of epoxy phenol novolac

For the construction of detailed molecular models, the chemistry of the system under investigation has to be known. However, the complex composition of most industrially used encapsulation compounds is a safely guarded secret. For this investigation, the model epoxy system Epoxy Phenol Novolac (EPN) was chosen, which is similar to industrially used chip-encapsulation moulding compounds [12,13]. The epoxy resin and the Bisphenol-A hardener are depicted in Fig. 1.

As can be seen from the chemical formula in Fig. 1, the epoxy resin consists of a backbone of aromatic rings connected by methylene groups. The connection can be either para- or ortho-, while the fraction of meta-substitution can be neglected. For the molecular models, the exact distribution was not considered very important, and therefore an arbitrary mix of tri- and tetra-functional epoxy monomers was used. Using a monomer mixing ratio of tri:tetra:BPA = 2:3:9, the average functionality of $f = 3.6$ was met and the number of BPA hardeners allows a theoretical conversion of 100%.

In the curing reaction, the epoxy ring opens and the carbon atom connects to the oxygen of the BPA hardener, while the hydrogen of the hydroxyl group of the BPA switches to the epoxy-oxygen to form yet another hydroxyl group. At the correct curing temperature, this exothermic reaction takes place until either all epoxy groups have found a reaction partner (theoretically 100% conversion) or until, in the course of the glass transition, the mobility of reaction partners has decreased so far that further reaction is practically impossible. A typical test for the degree of conversion by DSC or other means will show that full conversion has been achieved (technically 100% conversion); however, the absolute degree of conversion remains unknown. This uncertainty has to be kept in mind when comparing experimental and simulated properties. Throughout this paper, by degree of conversion we mean the reacted fraction of the total number of epoxy groups within a model package.

3. Cross linking algorithm

The cross linking reaction as it is observed in the experiment is a complex quantum–mechanical process involving the breakage of bonds, Hydrogen transfer and the formation of bonds. Since the investigation of this process by detailed atomistic simulations is beyond the scope of this work, the challenge was to develop a cross linking algorithm which is practical and fast but still near enough to reality to lead to packing models that represent bulk behaviour of the epoxy network. On the basis of an existing cross linking-script of Accelrys that we reported before [11], the following scheme was realized:

Before packing a mixture of epoxy and BPA monomers at target density of the cross linked system in a simulation cell, with three dimensional periodic boundary conditions (3D-PBC) applied, the

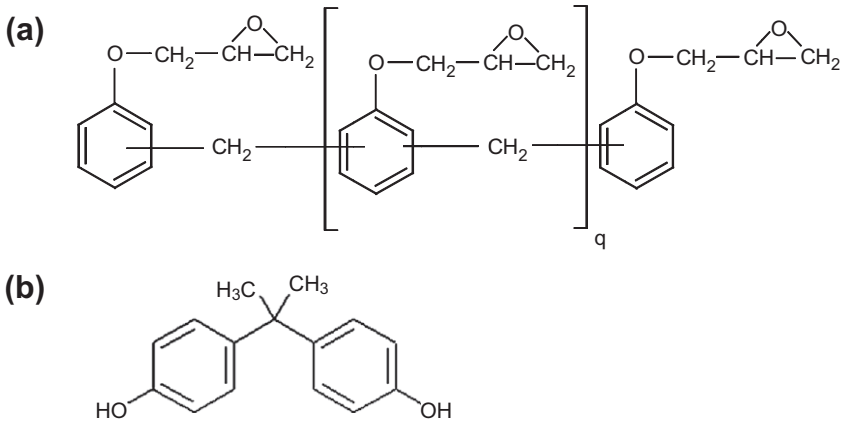

Fig. 1. (a) Epoxy resin used for this investigation. The average functionality is 3.6 ($q = 1.6$) and (b) Bisphenol-A hardener.