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Theoretical and experimental investigations of microstructural changes in lead-free solders

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Abstract

Experiments show that the microstructure of solders changes over time. From a materials science point-of-view this phenomenon considerably affects the reliability and lifetime of microelectronic products. It is, therefore, important to quantitatively predict the amount of microstructural change. In the present paper we concentrate on a theoretical and experimental description of spinodal decomposition as well as subsequent phase growth in binary solder alloys. We present experimental results and a theoretical description, which is based on an extended diffusion equation of the phase field type, and which can be interpreted as an generalization of the CAHN–HILLIARD equation. Moreover, it takes diffusion of the FICKian type, surface tensions along the phase boundaries as well as local thermo-mechanical stresses into account. In particular we turn our attention to the determination of the required material parameters, which can all be obtained consistently from atomistic models or adopted from literature. As an example the FCC-structured lead-free solder alloy Ag–Cu is considered and numerical results are presented.
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1. Introduction

There is an ongoing miniaturization in the area of microelectronics driven by an increasing requirement for mobility and more complex functionalities (e.g., automotive or portable industry). The minimal feature size within semiconductors continuously decreases whereas the number of transistors rapidly grows (cf., Fig. 1). As a consequence the demands on strength and lifetime of the used materials considerably rise while the material size is continuously reduced.

In addition to these technological trends *environmental initiatives* become increasingly important. The purpose of these activities is the reduction of electronic waste and/or the hazardous substances within (e.g., Pb). One example in this context is the lead-free legislation initiative started by July of 2006 in the EU according to RoHS, [4]. From the materials science point-of-view this directive leads to new tasks and problems. In particular it is necessary to, first, evaluate adequate lead-free materials and, second, investigate their material properties experimentally as well as theoretically.

A central issue that considerably affects the joining capability of microelectronics is the micromorphological development within the solder materials during use. In what follows we want to turn the attention to special kind of phase separation process, namely *spinodal decomposition* (SD) and *coarsening* (C). We briefly show some experimental results and present an approach allowing for the quantification of these processes from the theoretical point-of-view.

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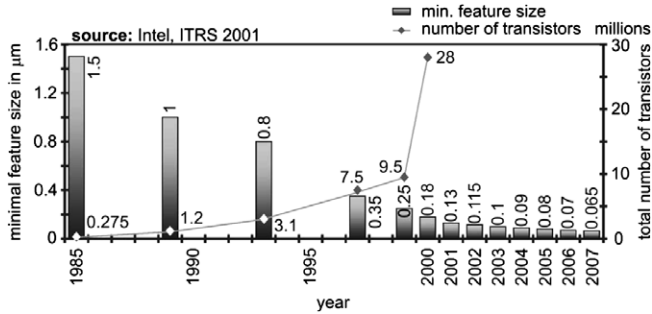[1] Tel.: +49 30 314 27682; fax: +49 30 314 24499.

Fig. 1. The development of the minimal feature size and the number of transistors in microelectronics.

2. Microstructures in solders

2.1. General remarks

In modern electronic packaging, e.g., flip-chips, solder balls (or bumps) play an important role, cf., Fig. 2. On the one hand side they guarantee the electrical connection between the chips and the electronic circuits, on the other hand they provide the mechanical connection of the different electronic components on the printed circuit board.

From a microscopic point-of-view these solder balls are basically exposed to two different micromorphological changes, cf., Fig. 3: (a) the formation of scallop-shaped intermetallic compounds (IMCs) at the interface solder/ substrate and (b) spinodal decomposition and coarsening in the bulk.
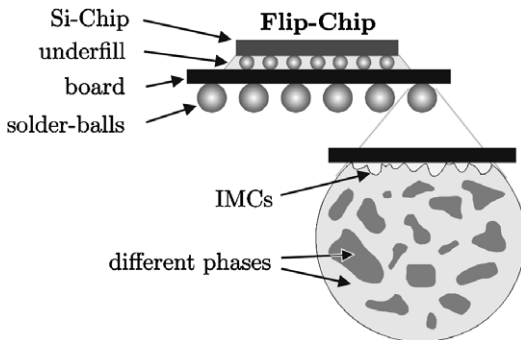

Fig. 2. Schematic illustration of a flip-chip assembly and the various kinds of microstructures occurring in the solder ball.
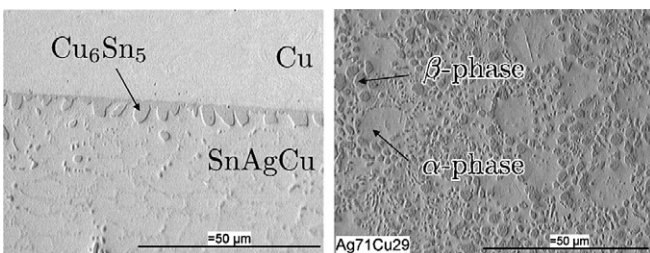

Fig. 3. Left: scallop-shaped Cu_6Sn_5-IMCs at the interface solder (SnAg-Cu)/substrate (polished Cu). Right: SD and C in eutectic Ag–Cu after 20 h heat treatment at 1000 K.

IMCs are formed and grow due to an interfacial reaction. In the case of a Cu substrate and an Sn-containing solder (e.g., Sn–Ag–Cu) this reaction takes place between Cu and Sn and necessitates a mass transport from the substrate to the solder, cf., Fig. 3 (left) and [6]. However, the resulting expanding "scallops" can have a positive influence on the strength and lifetime of the solder joints, because they guarantee a "dovetail connection". On the other hand there are stress peaks around the IMCs, leading to crack initiation in this region. Consequently it is reasonable that the positive effects are limited by a critical size.

In contrast to IMC-formation SD and C are diffusion processes exclusively driven by aspects of thermodynamical stability and interfacial energy minimization, cf., Section 2.2 and [2]. The resulting "composite" of different phases can be interpreted as a "particle reinforced material" in which the stiffer phase acts as the reinforcement. Unfortunately mechanical failure, such as cracks, favorably grow along the phase boundary which result, among other reasons, from thermal mismatching. Thus the benefit of phase dispersion is also limited by a critical phase size.

However, there is a considerable interest in predicting the micro-morphological temporal development, which is the basic requirement for further failure analysis of the heterogeneous material. In the following we focus on spinodal decomposition and on the coarsening process. The binary alloy Ag–Cu is investigated, in which SD results in two equilibrium phases, the α-phase (Ag-rich) and the β-phase (Cu-rich), cf., Fig. 3 (right). It has qualitatively a similar miscibility gap (phase stability data) as the previously used Sn–Pb solders, and all required material parameters can easily be obtained.

2.2. Spinodal decomposition and coarsening

From a thermodynamical point-of-view a binary alloy A–B decomposes into two equilibrium phases α and β due to a gain of the GIBBS free energy $G(c, T)$, which is a function of mass concentration $c \equiv c_B (c_A + c_B = 1)$ and temperature T. Without loss of generality we put $T_{melt} \equiv T_{eut}$ where T_{eut} denotes the eutectic temperature. In Fig. 4 two different
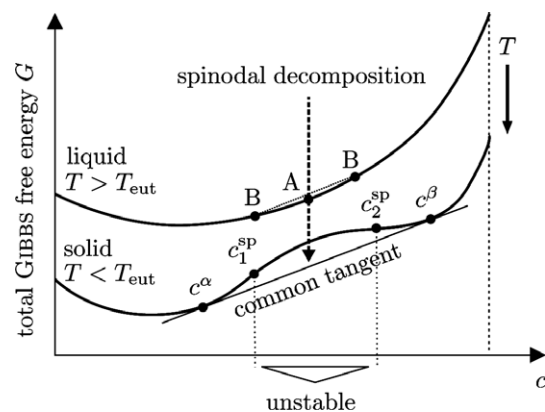

Fig. 4. Schematic GIBBS free energy curves for two different temperatures.