

Growth of intermetallic compound between indium-based thermal interface material and copper substrate: molecular dynamics simulations

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The diffusion phenomenon occurring between copper and indium was investigated by molecular dynamics simulations. The calculations were carried out in various temperatures in aging domain with the use of the commercially available Materials Studio v.6. software. The results showed that the intermetallic compound (IMC) growth followed the parabolic law, which indicated this growth to be mainly controlled by volume diffusion. The growth activation energy was estimated at $7.48 \text{ kJ} \cdot \text{mol}^{-1}$.

Keywords: *thermal interface material (TIM); molecular dynamics simulations (MD); diffusivity; intermetallic compound (IMC)*

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1. Introduction

Beyond the use of novel materials in electronics a very strong trend towards miniaturization of devices, like processors, memory etc., exists. This leads to an increase in the scale of integration (more transistors per unit area in chips), increase in frequencies of electric signals (faster devices), decrease in required voltage supply and less energy consumption. Apart from all these benefits, a large-scale integration can lead to an excessive heat generation in the semiconductor dies. This may result in overheating the integrated circuits (IC) and deterioration of their reliability.

To protect chips against overheating the heat sinks are commonly used. They are mounted on IC packages in order to enhance the efficiency of heat removal from chips to the ambient. In real terms, the use of heat sinks alone is often not enough to guarantee the sufficient cooling, due to so-called thermal contact resistance between the different materials interfaces which way the heat is transferred. Therefore, using the thermal interface materials (TIM) between the package and the heat sink

and/or inside the integrated circuit between a chip and a package (Fig. 1) would reduce the thermal resistance and improve the heat dissipation from the semiconductor die.

The role of TIM is to fill out or to reduce the micro-scale gaps between two contacting materials to enhance heat conduction via the interface (Fig. 2). There are numerous materials used as TIMs. In general terms, they can be categorized as the materials, which, apart from the thermal coupling, would additionally provide a mechanical connection, and the ones not assuring this feature. In these two classes, different types of TIMs would be specified. The first group of TIMs which also provides the mechanical joint includes solders and thermally conductive adhesives (TCA), while the other group not providing the mechanical connection includes thermal greases (TG), phase change materials (PCM), thermally conductive gels (TCG) as well as the thermally conductive tapes and foils made of soft materials [1].

In Fig. 1, as TIM "A" layer there are used the materials which do not provide mechanical connection because of reworking possibility, while inside the package as TIM "B" layer there are materials providing mechanical connection.

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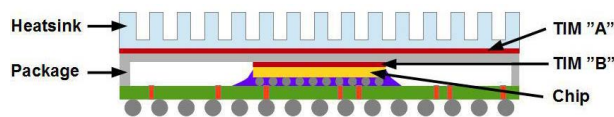


Fig. 1. Cross-section of flip-chip package.

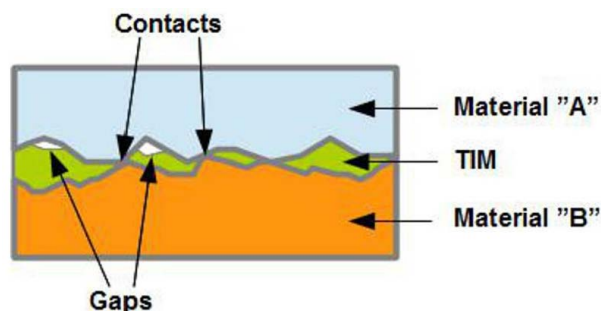


Fig. 2. The interface between two materials filled by thermal interface material (TIM) to enhance the contact area and intensify the heat flow between them.

This article describes a study on a TIM material which consists of polymer fibers with modified surface infiltrated by liquid phase indium at high pressure [2, 3]. In such TIM, the metal matrix ensures good thermal conduction and the fibers define geometry of the connection during the bonding process to the surfaces, therefore, the bonding process is carried out at an elevated temperature above the metal matrix melting point and the metal phase is in a liquid state when the connection is created. Thus, this type of thermal interface material also creates a mechanical connection between surfaces: in this case, between the chip (plated with e.g. Ti/Au) and package made of metal (e.g. copper).

In this paper, the evaluation of the In/Cu compound growth rate between the TIM based on indium (whose melting point is 156 °C) and package/heat spreader made of copper, using molecular dynamics simulations, is presented. To investigate the diffusivity phenomenon between those two materials (In and Cu) the software for the modeling in nano-scale was used. The simulations aimed at obtaining the growth rate constant of In/Cu intermetallic compound (IMC) and the activation energy of diffusion process.

2. Basic model assumptions

2.1. Polymer: metal nanofibrous TIM

This material was elaborated and described by Carlberg et al. [2, 3]. A porous electrospun nanofiber network composed of temperature stable polyimide was infiltrated with liquid phase indium at a pressure of 30 MPa. This material has a relatively low melting point (for indium it is 156 °C) but higher than the work temperature of the system. Thus, during the assembly process the wetting phenomenon is occurring between TIM and surface, resulting in increasing the contact area. The polymer phase defines the composition and geometry, while the continuous metal phase provides binding to the surfaces and high thermal conductivity. The fabrication of such fiber-metal composites is schematically presented in Fig. 3.

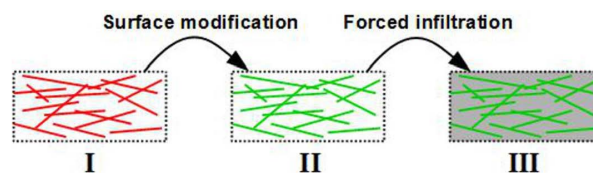


Fig. 3. Fabrication of fiber-metal nanofibrous composite: (I) electrospinning of fibers (II) surface modification of fibers (III) infiltration of metal.

2.2. Molecular dynamics

Molecular dynamics (MD) is defined as a computer simulation of atoms and molecules. They are allowed to interact with each other for a period called a time step of simulation, what makes the atoms motion view to be possible. The trajectories of atoms and molecules are determined by the Newton's equations of motion of interacting particles. Forces between the particles and their potential energy are defined by so-called force field (FF).

Force field is an expression describing the energy of molecule as a function of position of its nuclei. FF is a scalar field $V(\mathbf{R})$ of energy of interactions inside the molecules in the configuration space of the nuclei (their position is indicated by the vector $\mathbf{R}$). The forces which affect atoms are calculated as adequate components of force vector $\mathbf{F} = -\nabla V$ in 3N-dimensional space.

The shape of the function V can be described as follows (Fig. 4) [4]:

$$\begin{aligned}
 V = & \sum_{X-Y} \frac{1}{2} k_{XY} (r - r_0)^2 && \text{bonds} \\
 & + \sum_{X-Y-Z} \frac{1}{2} k_{XYZ} (\alpha - \alpha_0)^2 && \text{angles} \\
 & + \sum_{X...Y} V_{LJ}(X, Y) && \text{van der Waals's} \\
 & + \sum_{X,Y} \frac{q_X q_Y}{r} && \text{interactions} \\
 & + \sum_{\text{tors}} A_{X-Y-Z-W} (1 - \cos n\omega) && \text{electrostatic} \\
 & + \text{possible coupling members} && \text{interactions} \\
 & && \text{torsions}
 \end{aligned}$$

(1)

where: r_0 – characteristic length of a bond between atoms X and Y, r – length of a bond between atoms X and Y, other than r_0 , α_0 – characteristic angle between two bonds created by three atoms, α – an angle other than α_0 , k_{XY} , k_{XYZ} – constants for specified bonds, q_X , q_Y – charges of atoms X and Y, respectively, $A_{X-Y-Z-W}$ – constant, V_{LJ} – the Lennard-Jones potential.

As can be seen in Fig. 4, the FF is an estimation of energy in the system as a function of position of nuclei. This results in many benefits:

- less time-consuming than ab initio calculations;
- FF gives hypersurface $V(R)$ as a simple equation dependent on the positions of nuclei R, while calculations of electron energy would give the energy only for a specified position of nuclei R.

2.3. Molecular model of indium and copper interface and simulation procedure

At the first stage, a three-dimensional model with periodic boundary conditions was created. To simplify the calculations the microfibrers were omitted in the TIM structure. It was assumed that the structure was made of indium and copper crystals. Indium had tetragonal structure with lattice parameters $a = b = 3.252 \text{ \AA}$, $c = 4.945 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ (I4/mmm space group no. 139) [4] and copper had cubic close-packed structure with parameters $a = b = c = 3.614 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ (Fm-3m space group no. 225) [5].

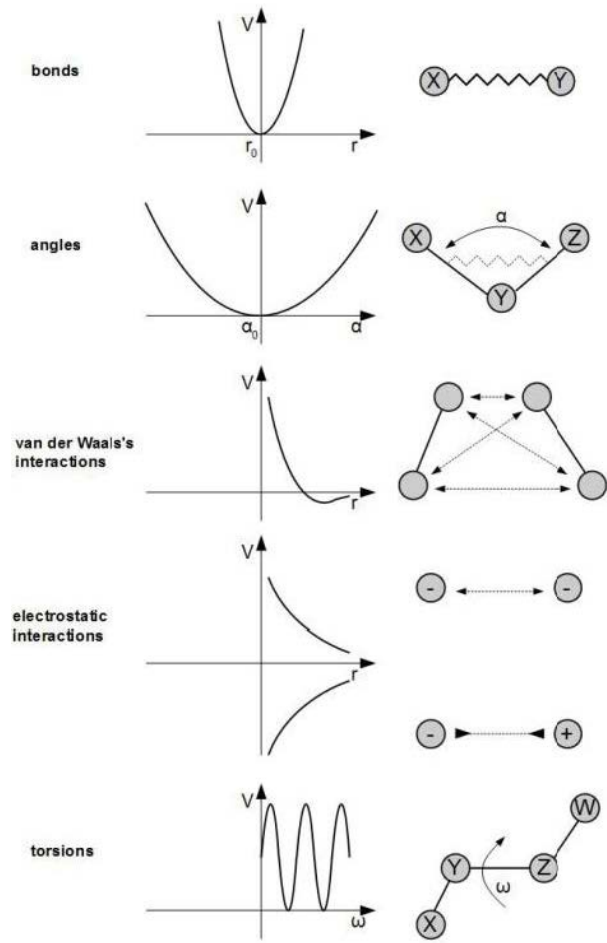


Fig. 4. Graphical representation of the components of force field.

Crystal layers of In and Cu had dimensions $50 \text{ \AA} \times 50 \text{ \AA} \times 100 \text{ \AA}$, therefore, the whole model was $200 \text{ \AA}$ long with an interface in the middle of the structure and consisted of over 33,000 atoms. The model used in the calculations with specified In and Cu lattices was presented in Fig. 5. The structure was built up as a supercell, it means that it was treated as a single cell in the crystals (Fig. 6).

Next, the structure was geometrically optimized to achieve relaxed interface layer. It was an iterative process with the atoms coordinates adjusted to bring the energy of the structure to a stationary point, where the forces exerted on the atoms were zero to achieve zero stress relaxation. Simulations

were carried out in various constant temperatures of aging (298 K, 350 K, 400 K) in time domain (up to 260 ps) with a time step of simulation 1 fs, to make the intermetallic compound growth possible to be observed (Fig. 7).

The temperature did not exceed the melting point of In (429 K). To control temperature the Berendsen's thermostat was used with decay constant of 0.1 ps [6]. Atoms and interactions between them were described by the Universal Force Field [7] with the Ewald technique as the method for the computation of non-bond energies. The conditions applied to the simulations were determined by the NVT thermodynamic ensemble (N – constant number of atoms, V – constant volume of the model and T – constant temperature dynamics). The aim of this research was reconstruction of

real conditions during the aging process so the thermostat permanently affected the structure together with force field. The calculations were performed with a commercially available software: Material Studio v.6 (produced by Accelrys, Inc.) in Forcite module.

3. Results

Fig. 8 shows the growth of intermetallic compound between In and Cu for various “time of” aging simulations at a temperature of 350 K. After 260 ps the atoms of In and Cu were counted in the interface layer; there were 222 atoms of indium and 453 atoms of copper. This allowed us to presume that the most possible composition of IMC in this case was Cu_2In . The result achieved conforms to the research performed by Kao [8] who found that in addition to Cu_2In , the Cu_7In_3 and $\text{Cu}_{11}\text{In}_9$ compositions could be formed, as well.

The total thickness of the intermetallic compound can be expressed by the following equation [8]:

$$l = kt^n + l_0 \quad (2)$$

where: l – the thickness of the intermetallic layer, k – the growth rate constant, t – the reaction time (time of simulation), n – the time exponent, l_0 – a fitting constant.

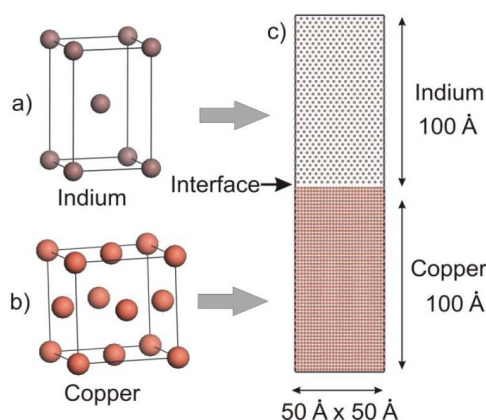


Fig. 5. Model of the investigated structure, (a) lattice of indium, (b) lattice of copper and (c) the model structure.

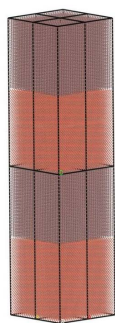


Fig. 6. Representation of the structure as the supercell with periodicity as that presented in crystals.



Fig. 7. Schematic view of the growth of intermetallic compound (IMC) in the model in time domain for one constant temperature during a single simulation (three simulation processes were carried out for temperatures 298 K, 350 K and 400 K).

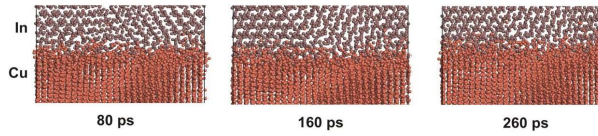


Fig. 8. The IMC growth between In and Cu in time domain of molecular dynamics simulation at a temperature of 350 K.

Basically, the growth of IMC can have kinetics of linear or parabolic nature. The growth rate is limited by the reaction rate when the growth of IMC is linear. When the parabolic growth is observed it means that the growth of IMC is limited by the volume diffusion. In this case the growth of IMC layer should follow the square root time law. It is empirically confirmed that when the time exponent n in equation 2 has the value of 0.5, diffusion in interface layer is controlled by volume diffusion.

In Fig. 9, the comparison of a linear and a parabolic fit for IMC thickness obtained from MD simulations at the temperature of 350 K is presented. As can be seen, the growth of IMC follows a parabolic law. It means that the growth of the layer is diffusion-controlled. The growth rate constant was estimated from a linear fitting of l vs. $t^{0.5}$, where the slope is a square root of k (Fig. 10). The growth rate constants (k) for various temperatures have the following values: $3.86 \times 10^{-6} \text{ m}^2/\text{s}$ for 298 K, $6.99 \times 10^{-6} \text{ m}^2/\text{s}$ for 350 K and $8.20 \times 10^{-6} \text{ m}^2/\text{s}$ for 400 K, respectively. The linear correlation coefficients (R^2) for these linear fittings were higher than 0.93. Thus, it is the confirmation that the growth of the IMC is diffusion-controlled over the temperature range in this investigation.

To determine the activation energy for IMC growth the Arrhenius relationship was used:

$$k = k_0 e^{\frac{-Q}{RT}} \quad (3)$$

where: k – the growth rate constant, k_0 – the constant, Q – activation energy, R – the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T – the aging temperature (absolute unit).

The Arrhenius plot for Cu–In IMC obtained by the linear fit is presented in Fig. 11. The activation

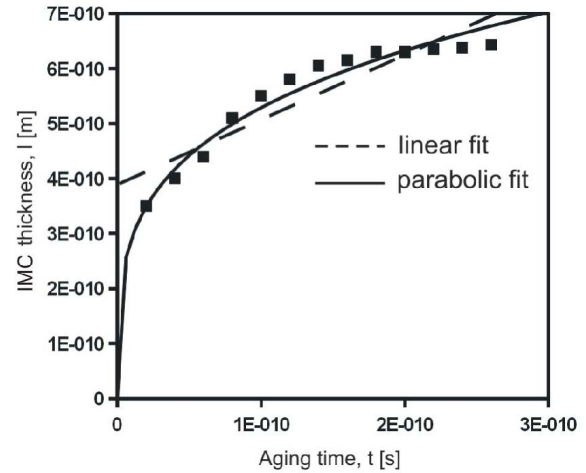


Fig. 9. The comparison of a linear and a parabolic fit for IMC thickness obtained from MD simulations at a temperature of 350 K.

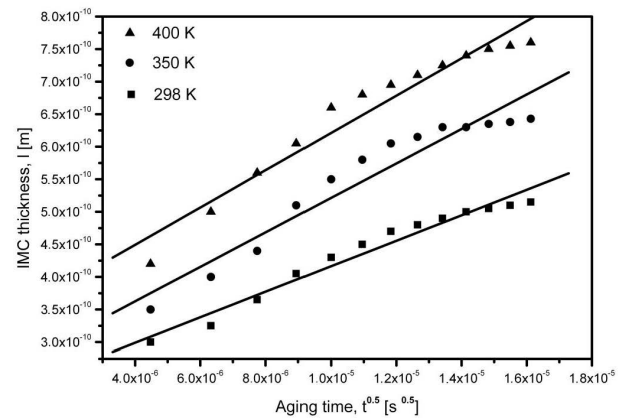


Fig. 10. Thickness of the IMC layer in time domain.

energy is $7.48 \text{ kJ}\cdot\text{mol}^{-1}$. According to the literature [9, 10] the activation energy obtained in experiments for intermetallic compound of copper and indium is in the range of $20 \text{ kJ}\cdot\text{mol}^{-1}$ to almost $37 \text{ kJ}\cdot\text{mol}^{-1}$. It is presumed that the relatively low value of activation energy obtained in this study is caused by the fact that the very early stage of IMC formation with an ideal interface at the beginning was investigated.

4. Conclusion

In this study the intermetallic compound growth between pure copper and indium was investigated

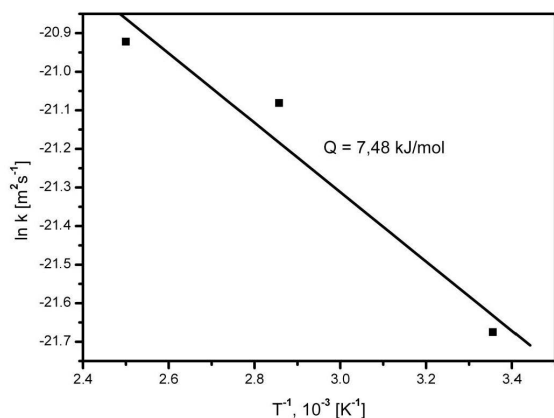


Fig. 11. Arrhenius plot of the IMC layer growth.

using molecular dynamics simulations. The aging temperatures were 298 K, 350 K and 400 K. The time of simulations ranged from 0 to 260 ps. The analysis of the layer thickness of the intermetallic compound as a function of time and temperature was presented. The parabolic relationship between the growth of IMC and aging time was observed. The results showed that the growth was mainly controlled by the volume diffusion. The obtained value of activation energy for indium and copper IMC was $7.48 \text{ kJ} \cdot \text{mol}^{-1}$. The value of activation energy was different from the value obtained experimentally, reported in the literature. It could be caused by the fact that the investigation on formation of IMC was done in very early stage of diffusion process: the ideal interface and short time of formation of IMC were assumed in the simulations.

Acknowledgements

This work was partially supported by The National Center for Research and Development (NCBiR), Grant No. MNT/NanoTIM/2012. The works were partially financed by statutory Grant No. S40050 at Wrocław University of Technology. Authors acknowledge Wrocław Center for Networking and Supercomputing (WCSS) for the possibility of using modelling software and hardware.

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Received 2014-01-30

Accepted 2015-02-27