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Self-diffusion in intermetallic $AlAu_4$: Molecular dynamics study down to temperatures relevant to wire bonding

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ABSTRACT

We demonstrate the ability of long time (~1 μs) molecular dynamics modeling to provide quantitative diffusion coefficients for the compound $AlAu_4$ (β-Mn type), down to temperatures (~200 °C) that are relevant to Al—Au wire bonding. Concerning Au diffusion, our results agree quite well with DFT calculations of the vacancy-formation energy, the activation energy, and the diffusion mechanisms. Our model underestimates, however, the vacancy-formation energy of Al, whose diffusivity is found to be at least 10 orders of magnitude slower than Au one. The van Hove correlation-function analysis shows that Au diffusion takes place mainly on the Wyckoff **b** sublattice. Moreover, we shed light on the high-temperature region, as the stability limit $T^{\star}$ of $AlAu_4$ is approached and unfavorable jumps contribute to the diffusivity. This concerns, for instance, jumps generating antisites defects. The latter lead to a massive disorder which ends up in a phase change to a distorted fcc structure at $T^{\star}$. Including the melting temperature in the potential-fitting procedure seems to be an effective way to gauge the temperature scale and properly capture the order of magnitude of diffusion.

1. Introduction

Wire bonding is a key interconnect technology widely used in microelectronics to provide electrical paths for power and signal distribution between integrated circuit chips and their packages [1]. The commonly used process in wire bonding is thermosonic attachment of Au or Cu wire to Al bond pad. This method consists of combining ultrasonic energy, pressure (~140 MPa) and heat (150–250 °C). During the wire bonding process and the device usage, thermally activated reactive diffusion leads to the nucleation and growth of various intermetallic compounds (IMCs) at the Au/Al and Cu/Al interfaces. The IMCs are essential to form a strong bond of wire and pad. But excessive IMCs formation is associated with the generation of voids, microcracks, a higher electrical resistivity and finally failure of the bonding. IMCs formation is still an active research field and many issues remain controversially discussed [2–4]. This concerns the following for instance: (1) Which of the IMCs predicted by the phase diagram are formed and in which sequence do they appear? which is a complex question in view of polymorphism and metastability of the phases; and (2) how thermodynamics, thermomechanics, kinetics, and crystalline symmetry interplay in the question above? There are also distinct lines of reasoning regarding the generation of voids. The most popular approach is the unbalanced diffusion of atoms from and to wire (Au or Cu) and pad (Al). This is the so-called Kirkendall effect, due to a high disparity in the atom-species diffusivities through the IMCs. However, Xu et al. [2] support the suggestion [5] that the specific volumina of the IMCs could change upon phase transformations.

The controversies above point out that the complex interplay of distinct phenomena occurring in wire bonding remains poorly understood. Many crystallographic and thermodynamic data, like the structures and heats of formation of Al—Cu and Al—Au IMCs, are available in the literature. However, crucial diffusion data are still manifestly lacking, due to the non-availability of appropriate tracer isotopes for these compounds. This lack explains why empirical rules are mostly used to rationalize kinetic phenomena in wire bonding [1]. For instance, the conclusion that Au (Cu) is the dominant diffusion species in Au (Cu) rich Al—Au (Al—Cu) compounds relies on the empirical Cu_3Au rule [6]. The latter, due to d'Heurle, states that in compounds of the form A_mB_n with $m/n \geqslant 2$, the majority element A diffuses faster than B. This correlates the higher diffusion of an atom species with its larger connectivity on its sublattice.

Our study is aimed at showing the ability of molecular dynamics (MD) modeling to provide quantitative diffusion coefficients for Al—Au compounds down to temperatures that are relevant to wire bonding processes. This ability is illustrated for $AlAu_4$ and Al_3Au_8.

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Ab initio methods - such as the density functional theory (DFT) - and semi-empirical atomistic modeling methods - such as MD and kinetic Monte Carlo (kMC) - are recently playing a more and more significant role in understanding and calculating diffusivities of metal alloys and compounds [7]. The continuous increase of MD capabilities is due to the growing computer power, on the one hand, and to the elaboration of more reliable interatomic potentials, on the other hand. The use of semi-empirical potential is expected to remain the main stream of diffusion modeling. MD simulations do not only offer the possibility to calculate diffusion coefficients, but they also represent a valuable tool for the exploration of unknown diffusion mechanisms in complex structures, which is the case of Al—Au and Al—Cu IMCs. For instance, Al_3Au_8 and Al_4Cu_9 have 44 and 52 atoms per unit cell. This complexity and the resulting large list of jumps make very difficult the use of the more accurate DFT and kMC methods. This difficulty has been illustrated by Ulrich et al. [8] in a DFT study of diffusion and its mechanisms in the compound $AlAu_4$ (20 atoms per unit cell).

Our diffusion study is also aimed at providing physical insights and data that are needed for the construction of macroscopic approaches of wire-bonding processes. We mention, in this context, the phenomenological DIffusion Controlled TRAnsformation (DICTRA) method [9] and the model by Svoboda et al. [10] relying on the Onsager's thermodynamic extremal principle. A strong impact on modeling reaction kinetics of layered interfaces is expected from the multiphase-field model [11–13], which is a powerful technique for studying microstructure evolution during phase transformation. These continuum methods, when coupled to atomistic approaches, are predestinated to advance our understanding of the complex interplay of thermodynamics, kinetics and thermomechanics in wire-bonding systems.

The paper is organized as follows: Section 2 describes the modeling methods and the fitting procedure to obtain the potential parameters with respect to the compound $AlAu_4$. Before calculating the self-diffusion coefficients for Au and Al in Section 3.3, an insight into the diffusion correlations is provided by the van Hove functions in Section 3.2. In Section 3.4, we address a polymorph phase change of $AlAu_4$ that takes place during annealing slightly below the melting temperature. Subsequently, we consider this phase change within a layers system Au/$AlAu_4$/Al. This MD experiment mimics the conditions of reaction kinetics in wire-bonding systems. Finally, concluding remarks and outlook are given in Section 4.

2. Model

2.1. Simulation methods

We perform MD simulations for an isothermal-isobaric (N, T, p) ensemble of N atoms, zero pressure p, and periodic boundary conditions. For cubic $AlAu_4$, the simulation box has an orthorhombic geometry (cubic for diffusion simulations and tetragonal when modeling solid-liquid interfaces). In the case of rhombohedral Al_3Au_8, we use hexagonal axes which are commonly preferred to rhombohedral ones because they are easier to describe mathematically and to visualize. The hexagonal setting is in fact a supercell with three primitive rhombohedral units. More details can be found in Refs. [14,15] regarding the hexagonal supercell considered and how to convert hexagonal Bravais lattices to rhombohedral ones and vice versa. Crystallographic data of both compounds are listed in Table 1. The unit cell of $AlAu_4$ with its Wyckoff sublattices is represented in Fig. 1. Ref. [14] offers an interactive 3D view of the structure.

Table 1
Crystallographic data of the IMCs $AlAu_4$ and Al_3Au_8. We give the space group and the number of atoms per unit cell (first column). The Wyckoff positions are shown in the third column. The reduced coordinates are results of relaxation using DFT, taken from [8]. For Al_3Au_8, the coordinates are given in rhombohedral axes. Conversion to hexagonal axes is straightforward [14].

Compound	Lattice parameters	Positions	Coordinates
$AlAu_4$	$a = b = c = 6.9227$ Å	Al 4**a**	(0.6875, 0.6875, 0.6875)
$P2_13$ (198)	$\alpha = \beta = \gamma = 90°$	Au 4**a**	(0.0671, 0.0671, 0.0671)
20 atoms	[17]	Au 12**b**	(0.1342, 0.1999, 0.4632)
Al_3Au_8	$a = b = c = 14.72$ Å	Al 2**b**	(0.0, 0.0, 0.0)
R-3c (167)	$\alpha = \beta = \gamma = 30.42°$	Al 4**c**	(0.1557, 0.1557, 0.1557)
44 atoms	[18]	Al 6**e**	(0.9339, 0.5661, 0.25)
		Au 4**c**	(0.2173, 0.2173, 0.2173)
		Au 4**c**	(0.0638, 0.0638, 0.0638)
		Au 12**f**	(0.0035, 0.6490, 0.2962)
		Au 12**f**	(0.1205, 0.6516, 0.3840)

We determine melting temperatures T_m by using the standard method that consists of analyzing the velocity V_I of a solid-liquid interface versus T (more details in Ref. [13] and references therein). T_m is defined as the temperature at which V_I vanishes. A linear fit of the relation $V_I = \mu(T - T_m)$ yields the kinetic coefficient μ. As discussed in Ref. [16], a special care has to be taken when determining interface velocities by means of MD methods. The application of a global thermostat leads to the formation of temperature gradients at the interface during growth and melting. In MD methods, the electronic contribution to the thermal conductivity is absent, making the dissipation of the latent heat abnormally slow in metallic systems. We remedy this problem by using the layered thermostat approach presented in Ref. [16] for planar interfaces. We divide the simulation cell into layers parallel to the interface. Each layer, of thickness 15 Å, has its own thermostat maintained at the same undercooling by a simple velocity rescaling after every MD step.

Diffusion in intermetallics is expected to take place, principally, via a vacancy mechanism. Therefore, we carry out diffusion simulations with samples that contain one single vacancy created by removing one atom from a perfect $AlAu_4$ crystal (N = 11520 atoms). We distinguish three cases: the vacancy is on Au **a**, Au **b**, or Al Wyckoff sublattice. By considering one single vacancy, we model the case of low vacancy concentrations where the vacancies do not interact with one another. MD runs for times between 50 ns and 1 μs are performed, depending on the temperature. For system sizes in the range of 10^4 atoms, μs simulations are today at the reach of relatively small computer clusters using a computing capacity of about 100 processors running for one week. The produced simulation data are used in the van Hove correlation analysis in Section 3.2 and in the diffusion calculations in Section 3.3. The Au-diffusion coefficients are averaged over the cases of one Au **a** and one Au **b** vacancy. In addition, each simulation is repeated twice starting with different initial configurations.

2.2. Interatomic interaction potentials

To the best of our knowledge, interatomic potentials for Al—Au compounds have not been reported so far in the literature. Peng et al. [19] constructed a potential for Al—Au melts based on existing models for pure Al and Au. Since this potential has been fitted only to liquid-state properties, we estimate that it is not appropriate for Al—Au IMCs. In the following, we develop a cross-term Al—Au potential suitable to capture the available thermophysical properties of crystalline $AlAu_4$. The latter is the compound we focus on in the present study.

We start with Gupta interaction potentials that have been developed on the basis of a second-moment approximation of a