Phase-Field Crystal Simulation of Kirkendall Void Evolution and Growth Kinetics at Interfaces and Intermetallic Compound Layers in Sn/Cu Interconnect Systems (Postprint)

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Abstract

A binary alloy phase-field model was employed to simulate and study the formation, morphology evolution, and growth process of Kirkendall voids at the Cu/Cu3Sn interface and within the intermetallic compound layer in Sn/Cu interconnect systems, analyze the microscopic mechanism of Kirkendall void growth, and simulate and analyze the effects of interfacial Cu3Sn layer thickness and impurity content on Kirkendall void morphology and growth kinetics. The study reveals that the growth process of Kirkendall voids comprises four stages: formation of numerous atomic mismatch regions at the Cu/Cu3Sn interface, rapid evolution of these mismatch regions into voids, void growth, and subsequent void coalescence. Kirkendall voids preferentially nucleate at the Cu/Cu3Sn interface, their size increases with prolonged aging time, and in the later stages of aging, void growth is accompanied by void coalescence. Both increased Cu3Sn layer thickness and higher impurity content lead to increases in Kirkendall void number, growth exponent, and size, and in both cases, the variation of void number with time exhibits an initial increase followed by a decrease.

Full Text

Phase-Field Crystal Simulation of Kirkendall Void Evolution and Growth Kinetics in the Interface and Intermetallic Compound Layer of Sn/Cu Soldering Systems

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Abstract
With the development of electronic products toward further miniaturization, multifunctionality, and high reliability, packaging density has been increasing while solder joint dimensions have been scaling down. In electronic packaging, an intermetallic compound (IMC) layer forms at the interface between molten solder and the pad (substrate) during the soldering process of Sn/Cu systems, and the interfacial microstructure plays a crucial role in the reliability of solder interconnects. Generally, numerous Kirkendall voids may form at the Cu/Cu_3Sn interface and within the Cu_3Sn layer during reflow soldering and subsequent aging. The presence of Kirkendall voids can increase the potential for brittle interfacial fracture and reduce thermal conductivity. Therefore, characterizing the formation and growth of Kirkendall voids is essential for evaluating the performance and reliability of solder interconnects. This work investigates the formation, morphological evolution, and growth kinetics of Kirkendall voids at the Cu/Cu_3Sn interface and within the Cu_3Sn layer of Sn/Cu solder systems using phase-field crystal modeling. The growth mechanism of Kirkendall voids is analyzed, and the effects of Cu_3Sn layer thickness and impurity content on void morphology and growth kinetics are discussed. Phase-field simulation results show that Kirkendall void growth exhibits four stages during thermal aging: formation of atomic mismatch zones at the Cu/Cu_3Sn interface, rapid growth of these zones leading to void formation, subsequent void growth, and finally void coalescence. Kirkendall voids nucleate preferentially at the Cu/Cu_3Sn interface, their sizes increase with aging time, and obvious void coalescence can be observed in the later aging stage. It is also shown that increasing Cu_3Sn layer thickness and impurity particle content leads to increases in both the number and size of Kirkendall voids, as well as an increased growth exponent. In both cases, the number of voids initially increases and then decreases with aging time.

KEY WORDS Kirkendall voids, intermetallic compound, growth kinetics, morphological evolution, phase-field crystal method

Introduction

In recent years, electronic products have been continuously developing toward miniaturization, multifunctionality, and high reliability, requiring increasingly higher packaging density for chips and components, with interconnect pitch and solder joint dimensions becoming ever smaller. As interconnect solder joint sizes decrease while service conditions become more complex and severe (e.g., under coupled electrical, thermal, and mechanical loading), the demands on micro-joint electrical and mechanical properties have also increased. The continuous reduction in interconnect size leads to an increasing volume fraction of the reaction interface layer formed during solder joint formation relative to the entire joint, and the interfacial microstructure has a very significant impact on joint reliability. The interfacial microstructure in micro-interconnects primarily refers to intermetallic compounds (IMCs) formed through interfacial metallurgical reactions between Sn elements in the solder and metal substrate or under-bump metallization (UBM) elements. The IMC layer formed at the solder joint interface is a hallmark of metallurgical bonding, yet it is also the weakest part of the interconnect. An appropriately thick IMC layer can improve solder wettability and joint performance; however, excessive IMC layer growth during reflow soldering can result in excessive, non-uniformly distributed IMC particles and even microscopic defects such as Kirkendall voids (sometimes referred to simply as voids). When solder joints serve at elevated temperatures (equivalent to a solid-state aging process), Kirkendall voids also appear at the interfacial region, and their size increases with temperature and time. In later stages, voids undergo coalescence, reducing the load-bearing and conductive area of the solder joint and potentially becoming sources of brittle fracture, thereby compromising joint reliability and thermal fatigue life. Different solder alloys and substrate metals form IMCs with varying types, compositions, morphologies, and nucleation sites, leading to different morphological evolution processes and growth behaviors of Kirkendall voids and resulting in different service lifetimes and failure modes. Due to their significant impact on the mechanical and electrical properties of micro-solder joints, Kirkendall voids pose serious challenges to micro-interconnect reliability and lifetime, affecting the miniaturization of electronic products. Currently, the Kirkendall void problem in solder joints has become a hot topic in theoretical and experimental research. Therefore, clarifying the morphological evolution and growth behavior of Kirkendall voids under different conditions and understanding the material, process, and service parameters that affect their formation and growth are crucial for evaluating the reliability of micro-solder joints in electronic packaging. This research holds important theoretical significance and engineering application value.

The formation process of Kirkendall voids in micro-solder joint IMC layers and Cu/Cu_3Sn interfaces is complex, comprising four stages: incubation, nucleation, growth, and coalescence. For Sn/Cu interconnect systems, Cu atoms diffuse toward the solder with relatively high mobility, leaving vacancies on the bare Cu side that are not completely filled by Sn atoms, creating atomic-scale vacancies. These vacancies accumulate at the Cu/Cu_3Sn interface and within the Cu_3Sn layer, leading to Kirkendall void formation and subsequent growth during further processing (e.g., multiple reflow cycles) or service. Additionally, thermal expansion mismatches between IMC layers or between IMC layers and the solder/substrate metal caused by temperature rise in actual solder joints lead to stress concentration at Kirkendall voids, promoting void development into crack sources and ultimately causing brittle fracture. Therefore, Kirkendall void formation significantly affects micro-solder joint reliability.

Some preliminary studies have investigated Kirkendall void formation, growth morphology, and kinetics. Ahat et al. studied aging of solder joints composed of 62Sn-36Pb-2Ag and 96.5Sn-3.5Ag solders with Cu substrates at 150 °C for various times (50–1000 h), finding that Kirkendall voids formed and grew within the Cu_3Sn layer, affecting joint shear strength. Lin and Luo found that Kirkendall void density in solder joints increased with aging time and temperature, and that void formation was the main factor causing strength and reliability degradation. Zeng et al. showed that for eutectic Sn-Pb solder reacting with electroplated Cu pads, the number of Kirkendall voids at the Cu/Cu_3Sn interface increased with aging time, while void numbers within the Cu_3Sn layer also continuously increased. Wang et al. investigated the effect of different IMC layer thicknesses on Kirkendall void growth behavior, finding that void numbers decreased with decreasing IMC layer thickness, particularly the Cu_3Sn layer. Currently, engineering approaches to controlling Kirkendall voids mainly focus on suppressing their formation through appropriate processes, such as reducing impurity introduction by modifying plating parameters or performing high-temperature annealing on electroplated Cu substrates to eliminate heterogeneous phases and suppress void nucleation and growth.

Although numerous experimental studies have examined Kirkendall voids, obtaining comprehensive information about their morphological evolution and growth behavior through experimental means is time-consuming and labor-intensive, and the information obtained is very limited, making it difficult to reveal the complete formation process and growth behavior. Clearly, if we can start from the material microstructure (impurity content, IMC layer thickness, etc.) and void nucleation mechanisms, and use theoretical analysis and numerical simulation to reproduce the micro-morphology and dynamic evolution of Kirkendall voids in micro-solder joints, this would complement and corroborate experimental studies and help comprehensively and deeply understand the formation process and growth behavior of Kirkendall voids in micro-solder joints. Existing simulation studies have primarily investigated vacancy formation energy and diffusion energy during Kirkendall void formation using first-principles methods, employing plane wave pseudopotential (PWP) methods based on density functional theory and quasi-Newton methods, with generalized gradient approximation (GGA) combined with ultra-soft pseudopotentials (USPP) to handle correlation terms. However, first-principles results cannot intuitively reproduce Kirkendall void morphology. The recently developed phase-field crystal (PFC) method has irreplaceable advantages in addressing atomic-scale interactions in crystalline materials. Since it can simulate microstructural evolution at the atomic scale while coupling with crystal lattice periodic structures, it offers tremendous advantages for studying crystal lattice defects including vacancies and Kirkendall voids formed by vacancy aggregation.

This work employs the PFC method to simulate and study Kirkendall void morphological evolution and growth kinetics in Sn/Cu interconnect systems (micro-solder joints), clarifying the influence mechanisms of IMC layer thickness and impurity content on Kirkendall void morphology and growth. The simulation aims to reveal the micro-morphological evolution behavior of Kirkendall voids at micro-solder joint interfaces while providing necessary growth kinetic information, to comprehensively and deeply understand the quantitative behavior of Kirkendall void morphological evolution and growth behavior and provide theoretical support for optimizing related experimental studies. Computational simulation not only helps further investigate the impact of Kirkendall voids on solder joint reliability but is also of great significance for deeply understanding the Kirkendall void formation process.

1. Establishment of the Phase-Field Model

Currently used lead-free solders are primarily high-Sn content (>95%) binary or ternary alloys, with Cu being the main substrate metal (UBM). Therefore, the Sn/Cu system can be used to represent actual micro-interconnect systems in simulations. The Kirkendall voids studied here mainly exist in the Cu_3Sn layer and Cu/Cu_3Sn interface of Sn/Cu interconnect systems. This study focuses on the IMC layer and Cu substrate in the Sn/Cu system. Since Kirkendall voids are mostly distributed in the Cu_3Sn layer, the simulation region is limited to the Cu_3Sn layer, temporarily ignoring the void-free Cu_6Sn_5 layer. Furthermore, the model does not consider orientation differences between Cu and Cu_3Sn phase grains, so the entire simulation region contains two independent solid-phase regions (the Cu_3Sn layer and Cu substrate layer) and an interface layer, as shown in [Figure 1: see original paper].

For a binary alloy composed of Cu and Sn atoms, the lowest-order free energy functional of the constructed correlation function is [21]:

$$T = \int d\mathrm{Cu}\ln(\mathrm{Sn}\ln(l) - \mathrm{Sn}] - \frac{1}{2}\int d\mathrm{CSnSn\ CCuSn\ CCuCu}$$

where F is the free energy functional, r_1 and r_2 are position correlation functions, is the atomic density of the Cu component, is the atomic density of the Sn component, representing the total atomic density of components at the interface, T represents thermodynamic temperature, k is the Boltzmann constant, δ ; CCuCu, CSnSn, and CCuSn are two-point correlation functions between two atoms, all assumed to be isotropic, i.e., CCuSn CCuSn.

To establish the connection between alloy free energy and the standard phase-field model, the total density function is typically defined using the following definition: , then the atomic density is , where c and c. Equation (1) can be transformed into:

$$= 0.5 - T = \int d\mathrm{CCuCu\ cCCuCu} + (1 - \mathrm{CSnSn} + (1-)\ln(1 - \mathrm{CSnSn})2 - \mathrm{CCuSn}$$

where, CCuCu CSnSn l)/2 + ln[CCuCu)] - CSnSn.

Typically, the atomic densities of each atom are selected to solve the dynamic equations (2). The dimensionless density functions nCu and nSn for Cu and Sn component atoms are introduced:

$$\mathrm{Cu} \equiv (\bar{\mathrm{C}}\mathrm{u})/\bar{\mathrm{S}}\mathrm{n})/$$

Simultaneously, the following density field and concentration field are introduced for extended calculation:

$$\mathrm{Sn} \equiv (\bar{\mathrm{S}}\mathrm{n} - \mathrm{Cu}) +$$

In the following calculations, δN is used instead of δc. Equation (2) is expanded at δN = 0 and n = 0 to obtain the free energy function form:

$$|\nabla\psi 2$$

where K is the gradient energy coefficient; l is the dimensionless length; R is a functional function of ; α is the expansion coefficient.

In Kirkendall void simulations, dimensionless atomic density is often used to more conveniently represent the dynamic equations, i.e., using Cu (Sn ( )/2 = to represent [22]:

$$)/2 =$$

where M is atomic mobility, its magnitude determined by atomic density. This study uses a dimensionless form to represent atomic mobility, with v representing amplitude fluctuation changes; w related to the difference between interspecies bond energy and self-bond energy; u representing atomic interactions in the system.

The two-dimensional single-mode approximate solution for the density field n in dynamic equations (15) and (16) is as follows:

$$\cos(= 0) =)/2 - \cos(qx/3(\cos(2a, qy =$$

where A has a value of 0.5, a is the lattice constant (a = 0.6927 nm). Equation (17) is also the initial condition for the simulation. qx = $2\pi/$

The simulated two-dimensional system size is y, as shown in Figure 1. In the initial simulation configuration, the system is divided along the y-direction into Cu layer, interface layer, and $\mathrm{Cu_3Sn}$ layer, where the interface layer thickness is y. The essence of the $\mathrm{Cu/Cu_3Sn}$ interface layer formation process is a relaxation process, during which the system free energy transitions from a non-equilibrium state to an equilibrium state. The following criterion is used to determine when the system free energy reaches equilibrium: when the change in system free energy between adjacent time steps is less than or equal to 10^{-6}, this moment is determined to be the initial state of $\mathrm{Cu/Cu_3Sn}$ interface layer formation.

In binary alloy systems, interface vacancies eventually form Kirkendall voids with increasing evolution time. In the early stage of void formation, the process of atomic mismatch zone formation at the interface can be approximated as a grain boundary pre-melting process [23]. In this process, small-angle interface misorientation provides individual discontinuous vacancy columns, while large-angle interface misorientation provides a continuous line of vacancies that gradually grow into voids during subsequent growth. Combining this with the void formation process in Sn/Cu alloy systems, this simulation adopts small-angle interface misorientation as the research object. According to existing research, when the alloy approaches the melting critical temperature infinitely, the relationship between wetting temperature and interface misorientation angle q can be expressed as [24,25]:

$$0(1+\nabla = 1 + (1+\nabla) = 1 + 2$$

where Bl is the dimensionless bulk modulus of the liquid phase, its magnitude is the isothermal compressibility of the liquid phase when δN = 0; Bx is proportional to crystal elastic modulus; m - 4 wet = Δ is related to wetting temperature, = 0.0217 [24]; is related to critical melting temperature, = 0.0272 [21]; E is related to dislocations, E = 0.1982 [24]. Combined with interface layer thickness, the optimal angle is approximately 4.8° [23], so the interface misorientation is initially set to 4.8° in this simulation.

**** Material parameters used in the simulation of Sn/Cu soldering system [22]

Neumann boundary conditions are applied to the upper and lower boundaries of the simulation region, and periodic boundary conditions to the left and right boundaries. The two-dimensional system is discretized using a square grid with t = 0.001, and finite difference method is used for iterative calculations. Other parameters used in the simulation are listed in Table 1 [22].

2.1 Morphological Evolution of Kirkendall Voids

According to the simulation system set up in Figure 1, the initial Cu layer size is y, the Cu_3Sn layer size range is y, and the remainder is the Cu_3Sn/Cu interface layer (y) with randomly distributed impurity particles. Based on system free energy, the interface misorientation between Cu and Cu_3Sn layers is selected, and this study sets it to = 4.8° [23].

[**Figure 2: see original paper**] shows two-dimensional simulation results of Kirkendall void morphological evolution at the Cu/Cu_3Sn interface and within the Cu_3Sn layer of Sn/Cu interconnect systems, compared with experimental results. The simulation results reveal numerous Kirkendall voids with various shapes and non-uniform sizes distributed at the Cu/Cu_3Sn interface and within the Cu_3Sn layer (Figure 2c). The revealed Kirkendall void evolution process is as follows: (1) After the system reaches equilibrium, numerous atomic mismatch zones are randomly distributed within the Cu_3Sn layer and cover the entire Cu/Cu_3Sn interface (Figure 2a). (2) With increasing aging time, atomic mismatch zones at the Cu/Cu_3Sn interface rapidly grow into Kirkendall voids; voids at the interface quickly grow and coalesce, resulting in irregular shapes at the Cu/Cu_3Sn interface (Figure 2b). Subsequently, Kirkendall voids at the interface continue to grow, and numerous atomic mismatch zones within the Cu_3Sn layer generate Kirkendall voids with non-uniform sizes that grow rapidly. However, due to non-uniform distribution and relatively large spacing between adjacent voids, void coalescence is not obvious (Figure 2c). (3) With further aging time extension, voids continuously coalesce and grow within the Cu_3Sn layer and at the Cu/Cu_3Sn interface, forming larger, irregularly shaped Kirkendall voids. Simultaneously, the number of voids decreases with coalescence while their size increases (Figure 2d). Compared with the interfacial microstructures shown in Figures 2e and 2f for Sn-3.0Ag-0.5Cu/Cu solder joints aged at 217 °C for 120 and 240 min [3], the simulation process can well reproduce the microstructure of Kirkendall voids at the Cu/Cu_3Sn interface and within the Cu_3Sn layer, with main features of simulation results matching experimental observations. It should be noted that the phase-field crystal model used in this study cannot yet handle the Cu/Cu_3Sn interfacial reaction process, so the simulation results cannot reproduce the dynamic evolution of the Cu/Cu_3Sn interface.

With changes in aging temperature, the migration rates of Cu and Sn atoms change accordingly. Different Sn atomic mobilities (MSn = 0.05, 0.01, and 0.005) were also set in the simulation to investigate the effect of different Cu/Sn atomic mobility ratios on Kirkendall void morphology, with results shown in [**Figure 3: see original paper**]. As Sn atomic mobility decreases, void growth gradually transitions from perpendicular to the interface to parallel to the interface, and voids above the Cu_3Sn interface gradually disappear, with void morphology becoming flatter. According to literature [26], the atomic mobilities of Cu and Sn atoms in Cu_3Sn differ by 1-2 orders of magnitude at different temperatures. Considering that both Cu and Sn atomic mobilities in real systems are simultaneously affected by Cu_3Sn, Cu_6Sn_5, and the Cu_3Sn/Cu_6Sn_5 interface, the atomic mobility used in subsequent studies is M

2.2 Effect of IMC Layer Thickness on Kirkendall Void Morphology and Growth Kinetics

[**Figure 4: see original paper**] shows simulation results of Kirkendall void morphological evolution with varying Cu_3Sn layer thickness. The simulation initially sets three Cu_3Sn layer size ranges: y, with Cu layer size range (103~190)Δ y, meaning the thickness ratios of Cu_3Sn layer to Cu layer in Figures 4a1–a3, b1–b3, and c1–c3 are 1:1, 9:10, and 4:5, respectively. The interface misorientation is set to 4.8° [23]. At the same evolution time ($t = 7 \times 10^5$), thicker Cu_3Sn layers correspond to more numerous and larger Kirkendall voids. From the evolution process, it can be seen that as t increases from 0 to 1 × 10^5, atoms on both sides of the interface layer continuously consume the interface, eventually forming atomic mismatch zones at the interface, as shown in Figures 4a2, b2, and c2. The number of atomic mismatch zones decreases with decreasing Cu_3Sn layer thickness, while the spacing between adjacent mismatch zones increases with decreasing Cu_3Sn layer thickness. The formed atomic mismatch zones act as pinning sites during the aging process, causing a reduction in vacancy sinks and making the vacancy concentration supersaturated in these regions [27], thereby inducing void growth. With aging time extension, Kirkendall voids formed at the interface continue to grow, with larger voids coalescing with neighboring voids during growth. In the later aging stage, void growth is dominated by coalescence, forming larger voids. Additionally, Figures 4a3, b3, and c3 clearly show that both the number and size of Kirkendall voids in the later evolution stage decrease significantly with decreasing Cu_3Sn layer thickness.

[**Figure 5: see original paper**] shows the relationship between Kirkendall void number and aging time (total aging time t = 9.95 × 10^5) for three different Cu_3Sn layer thicknesses. Clearly, Kirkendall void growth kinetics are affected by Cu_3Sn layer thickness, with void number first increasing and then decreasing, showing distinct stages: (1) In the initial stage, Kirkendall void number increases significantly with time, indicating rapid nucleation and growth at the Cu/Cu_3Sn interface. (2) In the growth stage, void number continuously decreases, indicating coalescence growth at the interface. These growth characteristics are reflected in the morphological evolution simulation results shown in Figure 4. Figure 5 also clearly shows that the duration of the initial stage of Kirkendall void growth varies with Cu_3Sn layer thickness; for example, the initial stage is longer for thicker Cu_3Sn layers (Cu_3Sn:Cu = 1:1, $t < 8 \times 10^5$) and shorter for thinner Cu_3Sn layers (Cu_3Sn:Cu = 4:5, $t < 6 \times 10^5$). Additionally, void coalescence growth is more pronounced and number reduction is faster in the growth stage for thicker Cu_3Sn layers (Cu_3Sn:Cu = 1:1), while coalescence is less pronounced and number changes more slowly for thinner Cu_3Sn layers (Cu_3Sn:Cu = 4:5). Regardless of Cu_3Sn layer thickness changes, Kirkendall void number always shows a pattern of first increasing and then decreasing during formation and growth, which more comprehensively reveals the growth behavior of Kirkendall voids compared with experimental observations [13] that found void number decreases with decreasing Cu_3Sn thickness.

[**Figure 6: see original paper**] shows Kirkendall void size versus time for three different Cu_3Sn layer thicknesses (data points) and fitting results (curves). Since Kirkendall voids become irregularly shaped due to coalescence, this study uses the average of their horizontal and vertical dimensions as the average void size. The horizontal size is the length occupied by the void along the Cu/Cu_3Sn interface direction, while the vertical size is the height occupied perpendicular to the interface. To ensure adequate statistical samples while considering computational cost, three separate simulations were performed for each case; all initial conditions (including impurity content, system size, and time step) were identical, and the sizes from the three simulations were averaged to obtain the final statistical size. Figure 6 shows that void size decreases with decreasing Cu_3Sn layer thickness. Combined with Figure 5 results, both void number and size decrease with decreasing Cu_3Sn layer thickness, consistent with experimental conclusions [12].

There is a strong correlation between Kirkendall voids and IMCs in micro-interconnect interfaces. Voids commonly appear at the Cu/Cu_3Sn interface and within the Cu_3Sn layer, rarely in the Cu_6Sn_5 layer, and their size decreases with the Cu_3Sn layer. Numerous experimental studies and theoretical analyses of Kirkendall void nucleation and growth in micro-solder joints have established relationships between interfacial nucleation free energy, interfacial energy, and stress [28], and developed constitutive models for Kirkendall void nucleation and growth in micro-solder joints [29], linking void growth rate to diffusion energy for quantitative characterization. Stress analysis [30] suggests that void growth is proportional to atomic mobility at void surfaces. Research also indicates that void size quantification can be performed using IMC layer quantification methods [31], described by the exponential function shown in Equation (19):

$$Y = Y_0 + K_t t^{n_Y}$$

where Y represents Kirkendall void size at reaction time t, nY is the initial IMC layer thickness, Kt is the void growth exponent, and Y is the growth rate constant.

The Kt and nY values obtained through curve fitting are listed in ****. The results show that nY decreases with decreasing Cu_3Sn layer thickness. When Cu_3Sn:Cu = 1:1, nY = 1.126, while when Cu_3Sn:Cu = 4:5, nY = 0.312. According to existing research conclusions [32], nY values between 0.3 and 1.5 indicate interfacial nucleation, meaning that for all selected Cu_3Sn thickness cases in this study, voids can be considered to nucleate at the interface. Thus, Kirkendall void nucleation location is independent of Cu_3Sn layer thickness.

2.3 Effect of Impurity Content on Kirkendall Void Morphology and Growth Kinetics

Studies [13-15] have found that various impurities (S, Cl, N, C, etc.) present in Cu pad plating layers can enter the IMC layer during solder joint formation. Impurities act as heterogeneous nucleation sites in the Cu_3Sn layer, causing non-uniform nucleation and segregation of Kirkendall voids, reducing void formation energy at interfaces, inducing local stress concentration and pinning of vacancy sinks, causing vacancy concentration supersaturation, and thus forming Kirkendall voids. To investigate Kirkendall void morphological evolution under different impurity content conditions, the model shown in [**Figure 7:**

see original paper] is used. The simulation employs a two-dimensional system size of y. The initial simulation configuration divides the system along the y-direction into Cu layer, interface layer, and Cu_3Sn layer. The interface layer thickness is y, and both Cu and Cu_3Sn layer thicknesses are y. Due to different impurity particle aggregation modes, occurrence locations, and particle sizes, different contents (concentrations) and sizes of impurity particles are randomly distributed within the Cu_3Sn layer during simulation.

Atoms on both sides of the interface continuously consume the interface, eventually forming atomic mismatch zones at the interface, as shown in [Figure 8: see original paper] (a2, b2, and c2). The number of atomic mismatch zones increases with impurity content, while the spacing between adjacent mismatch zones decreases with increasing impurity content. When impurity content is high, numerous atomic mismatch zones are already distributed within the Cu_3Sn layer in the early evolution stage. These act as pinning sites during aging, causing vacancy sink reduction and vacancy concentration supersaturation [27], thereby inducing void growth. With increasing impurity content, atomic mismatch zone density increases, and both the number and size of voids formed in later aging stages increase. Additionally, due to the uncertain distribution of impurity particles, void occurrence locations become uncertain, manifested in simulations as irregular Kirkendall voids appearing simultaneously inside and at the top of the Cu_3Sn layer. With aging time extension, Kirkendall voids formed at the interface continue to grow, with larger voids coalescing with neighboring voids during growth. In later evolution stages, coalescence between voids intensifies growth, forming larger voids. Figures 8a3, b3, and c3 clearly show that both the number and size of Kirkendall voids in later evolution stages increase significantly with impurity content.

[**Figure 9: see original paper**] shows the relationship between Kirkendall void number and aging time for three different impurity contents in the Cu_3Sn layer. Clearly, impurity content has a significant effect on Kirkendall void growth kinetics. When impurity contents are 22.26% and 35.56%, Kirkendall void number shows distinct stages with time: (1) In the initial stage, void number increases significantly with time, indicating rapid nucleation and growth at the interface. (2) In the growth stage, void number continuously decreases, indicating coalescence growth at the interface. Notably, when impurity content is 12.98%, the number change during Kirkendall void growth is more complex. As shown in Figure 9, void number peaks appear at $t = 4.5 \times 10^5$ and $t = 7 \times 10^5$, but the overall trend still shows decreasing void number. To verify this phenomenon, three simulation statistics were performed for Kirkendall void numbers at impurity contents of 5.12%, 8.16%, 11.23%, and 14.56%, all showing two void number peaks. Analysis suggests that in the early growth stage, voids preferentially nucleate and grow at the interface. Since impurity content in the Cu_3Sn layer is relatively low, longer time is required for void nucleation and growth. Before void formation inside the Cu_3Sn layer, number changes mainly result from nucleation/growth and coalescence at the interface, causing the first increase-then-decrease change in void number. With aging time extension, the increase in void number formed inside the Cu_3Sn layer exceeds the decrease due to coalescence at the interface, causing a second increase in void number. With further aging time extension, extensive void coalescence leads to a sharp decrease in void number. Regardless of impurity content, Kirkendall void number always shows an initial increase followed by a decrease during formation and growth.

[**Figure 10: see original paper**] shows Kirkendall void size versus aging time (data points) and fitting results (curves) for three different impurity contents in the Cu_3Sn layer. Clearly, Kirkendall void size continuously increases throughout the evolution process, but the size growth rate is slower at 12.98% impurity content and faster at 22.26% and 35.56% impurity contents. This indicates that different impurity contents affect not only void size but also size growth rate. Additionally, Kirkendall void size increases with impurity content, consistent with experimental observations that impurity presence in plating layers can promote vacancy nucleation [13–15]. However, regardless of impurity content, Kirkendall void size increases with aging time.

The Kt and nY values obtained through curve fitting are listed in ****. The results show that nY increases with impurity content, with values between 0.385 and 0.899. According to research [32], nY values between 0.3 and 1.5 indicate interfacial nucleation, so Kirkendall voids in all selected impurity content cases in this study can be considered to nucleate at the interface, meaning nucleation location has no obvious relationship with impurity content.

Conclusions

(1) Kirkendall voids preferentially form and grow at the Cu/Cu_3Sn interface. In the early aging stage, numerous atomic mismatch zones rapidly generate at the Cu/Cu_3Sn interface and evolve into Kirkendall voids. In the intermediate aging stage, void size and growth rate are larger at the Cu/Cu_3Sn interface with obvious coalescence, while void size and growth rate are smaller within the Cu_3Sn layer with less obvious coalescence. In the later aging stage, void spacing decreases at both the Cu/Cu_3Sn interface and within the Cu_3Sn layer, and coalescence occurs, leading to increased void size and decreased void number.

(2) Both Kirkendall void number and size increase with increasing Cu_3Sn layer thickness, while the growth exponent decreases with decreasing Cu_3Sn layer thickness. Cu_3Sn layer thickness does not significantly affect Kirkendall void nucleation location or growth behavior, and void number shows an initial increase followed by a decrease with time.

(3) Kirkendall void number, size, and size growth rate all increase with increasing impurity content, and the growth exponent also increases with impurity content. Throughout the aging process, impurity content does

not significantly affect Kirkendall void nucleation location or growth behavior, and void number shows an initial increase followed by a decrease with time.

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Note: Figure translations are in progress. See original paper for figures.