Pattern Formation during Interfacial Reaction in-between Liquid Sn and Cu Substrates – A Simulation Study

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Abstract

Heteroepitaxial formation of η -Cu₆Sn₅ intermetallic compound (IMC) on unidirectional Cu has been found to exhibit remarkable microstructural features and provide opportunities for microstructure control of microelectronic interconnects, but the crystallographic origin and formation mechanism of such morphological patterns are still unclear. Here we investigate pattern formation during interfacial reactions in between liquid Sn and two types of unidirectional Cu substrates, (001) and (111), by using a combination of crystallographic analysis, theory of microelasticity and phase-field simulations. The simulation results show that each symmetry-related η -Cu₆Sn₅ variant grows along the direction of best atomic site matching with the substrates. No spatial alignment can be achieved when the growth takes place without heteroepitaxial constraints. In addition, anisotropy in interfacial energy between the liquid Sn and IMC is found to lead to faceted morphology. Further, the habit planes of η -Cu₆Sn₅ precipitates and kinematic compatibility across the interfaces are analyzed theoretically and found to be consistent with the simulations. These simulation predictions demonstrate excellent agreements with experimental observations.

Keywords: solder interconnect, intermetallic compound formation, heteroepitaxial growth, phase-field method, heteroepitaxial strain

1 INTRODUCTION

Heteroepitaxial growth is an important technique to fabricate high-performance transistors and modern microelectronic interconnects. For traditional interconnects, chemical reactions between metallic substrates (such as Cu, Ag or Ni) and liquid solder alloys take place to form intermetallic compound (IMC) layers that establish metallurgical bonding between the solder and substrate [1]. Numerous studies have been carried out to investigate the formation, performance and reliability of IMCs from various perspectives, including phase stability and reactive diffusion kinetics [2-7], as well as microstructure evolution [8-12] and resistance to electric and mechanical loadings [13-19]. Recently, a promising way to enhance the properties of solder interconnects was developed by replacing the traditional polycrystalline Cu substrates with that of unidirectional Cu [20, 21]. The breakthrough opens up new opportunities for the development of novel microelectronic interconnects with significant reduction of structural defects and energy consumption.

Previous investigations [10, 22] have shown that a distinctive morphological difference arose when η -Cu₆Sn₅ formed on substrates of unidirectional or single crystal Cu as compared to that formed on polycrystalline Cu. The IMCs on unidirectional Cu were found to have highly textured patterns with regular spatial arrangement. Furthermore, possible orientation relationships (ORs) between the η -Cu₆Sn₅ precipitates and the Cu substrates have been identified. Later similar phenomena were also found at the interface of (Cu,Ni)₆Sn₅/Ni [23], Ag₃Sn/Ag [24] and Cu₂(In,Sn)/Cu [25]. In most cases, IMCs on {001} single crystal substrates grow preferentially along two perpendicular directions, whereas IMCs on {111} substrates grow along three preferred directions with an 120° angle in between. Especially, it was noted that all the preferred growth directions are the <110> directions of the substrates. These unique features were rationalized by the argument that grains of the IMCs became elongated along these crystallographic directions because they have small atomic spacing mismatch between the IMCs and substrates [10]. Nevertheless, the explanation (based on one-dimensional (1D) atomic site mismatch) may not be valid for all instances because the interfacial

pattern formation subjects to planar constraints in 2D. According to the edge-to-edge matching model [26], small atomic spacing mismatch along the close-packed direction between the matrix and IMC may indicate possible ORs that minimizes the interfacial energy. However, coherency elastic strain energy minimization plays a key role in controlling morphological pattern formation during epitaxial/heteroepitaxial growth [27, 28] as well as in solid state phase transformation [29] and should not be ignored.

In this paper, we employ a combination of crystallographic analysis, theory of microelasticity and phase-field simulations to study IMC growth in between liquid and substrate. Based on the minimization of the total free energy functional that includes chemical, interfacial and coherency elastic strain energies, the phase-field method accounts quantitatively for the heteroepitaxial strain arising from atomic site mismatch. Phase-field models that incorporate CALculation of PHase Diagrams (CALPHAD) databases [30-32] have been utilized to study interfacial reactions in the Cu-Sn solder system [33-35]. Nevertheless, most of the prior work focused on 2D morphological evolution and growth kinetics, and no attempt has been made to introduce the heteroepitaxial constraint into the model. More importantly, it is known that heteroepitaxial growth of one crystal on another crystalline substrate with higher symmetry will generate multiple orientation variants [36]. The appearance of multiple η -Cu₆Sn₅ variants (low symmetry) on unidirectional Cu substrates (high symmetry) have been identified by transmission electron microscopy (TEM) analysis [37], but the orientation relationship between the η -Cu₆Sn₅ and Cu substrate and the heteroepitaxial constraint from the substrate have never been connected to the experimentally observed morphological patterns of IMC and incorporated into simulations of Cu-Sn interfacial reactions. To fully account for this effect and characterize the growth of different orientation variants of IMCs on crystalline substrates, it is highly desirable to integrate the available phase-field model of solder system with the microelasticity theory [29] that has been applied successfully to study coherent phase transformations in solids [38-41], epitaxial/heteroepitaxial film growth [42-49], dislocation/defect

dynamics [50-52], as well as phase separation in LiFePO_4 nanoparticles [53, 54].

In the present work, we focus on pattern formation during precipitation and heteroepitaxial growth of $\eta\text{-Cu}_6\text{Sn}_5$ on unidirectional (001) and (111) Cu substrates. We choose the Cu-Sn system as the model system because it is one of the most studied and commonly-used combinations of materials for microelectronic interconnects. By taking full advantages of the microelasticity theory and phase-field approach, we simulate the pattern formation in both 2D and 3D in an attempt to provide insights into the strategies of developing IMC microstructures in a controllable manner. The paper is organized as the following. In Section 2 we present the crystallographic relation between $\eta\text{-Cu}_6\text{Sn}_5$ and two types of unidirectional Cu substrates, followed by symmetry analysis that gives quantitative descriptions of orientation variants and heteroepitaxial strain tensors. In Section 3, the construction of the phase-field model for the Cu-Sn system is presented, including the chemical free energy, anisotropic interfacial energy, multiphase-field model, and the theory of microelasticity, followed by a general description of the simulation method. In Section 4 we present 2D and 3D phase-field simulation results showing the growth and evolution of $\eta\text{-Cu}_6\text{Sn}_5$ on unidirectional (001) and (111) Cu with different heteroepitaxial constraints. The simulation results are compared with experimental observations. In Section 5 we analyze the habit plane of each $\eta\text{-Cu}_6\text{Sn}_5$ variant and the condition of kinematic compatibility across the variant boundary. Furthermore, ORs predicted by the edge-to-edge matching model are compared with experimental studies. Limitations and possible extensions of the model are also addressed. Finally, a brief conclusion is given in Section 6.

2 CRYSTALLOGRAPHIC ANALYSIS

2.1 Prediction of ORs between $\eta\text{-Cu}_6\text{Sn}_5$ and Cu

Cu possesses a cubic structure (space group: $Fm\bar{3}m$) with $a_{\text{Cu}} = 3.615 \text{ \AA}$ and $\eta\text{-Cu}_6\text{Sn}_5$ possesses a hexagonal structure (space group: $P6_3/mmc$) with $a_{\eta} = 4.190 \text{ \AA}$ and $c_{\eta} = 5.086 \text{ \AA}$ [55], as illustrated in Figure 1. According to the edge-to-edge matching model [26], energy minimization of the interface

between two phases can be achieved when close-packed (or relatively close-packed) rows of atoms and planes containing the close-packed rows are able to match across the interface. It can be shown from crystallographic analysis that the best matching close-packed row direction is $[0001]_{\eta} \parallel [110]_{\text{Cu}}$, possessing an atomic mismatch of 0.51%. The two best matching close-packed planes that contain the rows of atoms are $(1\bar{2}10)_{\eta} \parallel (1\bar{1}1)_{\text{Cu}}$ and $(0\bar{1}10)_{\eta} \parallel (100)_{\text{Cu}}$, each having a mismatch of interplanar space (d -spacing) close to 0.38%. The aforementioned matching direction and planes all suffice to the matching requirement of the edge-to-edge matching model. These ORs were mentioned with other possible ones identified by experimental work, including electron beam backscattered diffraction (EBSD), synchrotron x-ray microdiffraction, and TEM analysis [9, 10, 37, 56]. One of the predicted ORs was also identified at the $(\text{Cu,Ni})_6\text{Sn}_5/(001) \text{ Ni}$ interface in a TEM study [23]. Nevertheless, most of the previous work focused particularly on the atomic row matching without addressing the matching of planes (based on the d -spacing), which ensures that the set of planes can meet edge-to-edge at the interface and have only a small angle between them. The recent study [56] interpreted the experimental results by arbitrarily selecting the number of periodically matching atoms for finding possible minimal atomic mismatch. The interpretation led to significant underestimation of atomic mismatch along orthogonal directions and failed to realize the fact that if arbitrary selection of matching atoms can be done, then there will be no pattern formation observed in experiments. In the following crystallographic analysis of orientation variants and heteroepitaxial relations, the experimental results from Ref. [56] are utilized but we interpret them by following the edge-to-edge matching model [26].

2.2 Orientation variants and heteroepitaxial strain of η -Cu₆Sn₅ on (001) Cu

According to the experimental results [37, 56], the 2D atomic site correspondence or heteroepitaxial relationship at the η -Cu₆Sn₅/(001)Cu interface was obtained as

$$\frac{3}{2}[110]_{(001)\text{Cu}} \leftrightarrow [\bar{1}100]_{(11\bar{2}0)_\eta}, [1\bar{1}0]_{(001)\text{Cu}} \leftrightarrow [0001]_{(11\bar{2}0)_\eta}$$

where the subscript indicates the specific lattice plane. Figure 1(a) shows the schematic illustrations of atomic site matching at the interface (001) Cu and (11 $\bar{2}$ 0) η -Cu₆Sn₅ according to the correspondence. Basically, an equivalent variant can be generated by a symmetry operation that is present in the substrate but absent in the product phase. By following the symmetry analysis [36, 57, 58] at the lattice plane of contact interface, the number of equivalent orientation variants can be determined. Considering the 2D symmetry on a particular plane in a lattice, the 2D crystallographic point group of (001) Cu surface is $4mm$ and that of (11 $\bar{2}$ 0) η -Cu₆Sn₅ is $2mm$. It can be demonstrated that the intersection group is $2mm$ according to the heteroepitaxial relationship. The number of orientation variants arising from symmetry breaking is determined by $P(4mm)/P(2mm) = 2$, where P is the order of symmetry group. We note that the number of variants predicted by the symmetry analysis is in accord with the TEM result [37] showing a simultaneous appearance of two sets of η -Cu₆Sn₅ diffraction patterns when the zone axis was $[11\bar{2}0]_\eta \parallel [001]_{\text{Cu}}$.

The transformation matrix $\mathbf{F}$ can be obtained by the relation that associates the lattice vectors of the product phase with those of the substrate phase at the η -Cu₆Sn₅/(001) Cu interface. Here we consider the atomic site matching or heteroepitaxial constraint at the interface, instead of the lattice correspondence that is considered frequently in solid-state phase transformations in bulk. Such a determination of $\mathbf{F}$ has been utilized to describe the orientation and strain in heteroepitaxial growth [59], as well as epitaxial conditions of molecular organization on crystalline substrates [60, 61]. It is calculated that when the reference coordinate L_1 is linked to the cubic axes of the substrate lattice structure ($x_1 \parallel [100]_{\text{Cu}}$, $x_2 \parallel [010]_{\text{Cu}}$), the correspondence can be described by considering a uniform deformation from substrate to product, and the transformation matrix of the first variant is given by

$$\mathbf{F}_1 = \begin{pmatrix} c_\eta/2\sqrt{2}a_{\text{Cu}} + a_\eta/\sqrt{6}a_{\text{Cu}} & c_\eta/2\sqrt{2}a_{\text{Cu}} - a_\eta/\sqrt{6}a_{\text{Cu}} \\ c_\eta/2\sqrt{2}a_{\text{Cu}} - a_\eta/\sqrt{6}a_{\text{Cu}} & c_\eta/2\sqrt{2}a_{\text{Cu}} + a_\eta/\sqrt{6}a_{\text{Cu}} \end{pmatrix} \quad (1)$$

Generally, the transformation matrices of other variants can be determined by symmetry operations associated with the contact lattice planes. In this case the operation is just the change of sign of the off-diagonal components of $\mathbf{F}_1$. The stress-free epitaxial transformation strain tensor of each variant is calculated directly from the transformation matrix via Lagrange strain formula

$$\boldsymbol{\varepsilon}^{00}(p) = \frac{1}{2} [\mathbf{F}_p^T \mathbf{F}_p - \mathbf{I}] \quad (2)$$

where p indicates the number of η -Cu₆Sn₅ variants, the superscript T indicates transpose of the matrix, and $\mathbf{I}$ is the identity matrix. The two heteroepitaxial strain tensors are calculated as

$$\boldsymbol{\varepsilon}^{00}(1) = \begin{pmatrix} -0.0287 & 0.0235 \\ 0.0235 & -0.0287 \end{pmatrix}, \boldsymbol{\varepsilon}^{00}(2) = \begin{pmatrix} -0.0287 & -0.0235 \\ -0.0235 & -0.0287 \end{pmatrix} \quad (3)$$

Since η -Cu₆Sn₅ may possess different heteroepitaxial relationships with Cu substrates of different oriented directions, the results of crystallographic analysis in Section 2.2 should only be applicable for the heteroepitaxial growth on (001) Cu.

2.3 Orientation variants and heteroepitaxial strain of η -Cu₆Sn₅ on (111) Cu

The orientation variants and their heteroepitaxial strain on (111) Cu can be obtained in a similar manner. The 2D heteroepitaxial relationship was shown by a recent TEM study [56] as

$$[11\bar{2}]_{(111)\text{Cu}} \leftrightarrow [1\bar{2}10]_{(10\bar{1}0)\eta}, [1\bar{1}0]_{(111)\text{Cu}} \leftrightarrow [0001]_{(10\bar{1}0)\eta}$$

Figure 1(b) shows the schematic illustrations of atomic site matching at the interface. It is noted that the first part of this heteroepitaxial relationship is different from the previous work [37], but here we adopt the recent result because it was analyzed based on the local cross-sectional microstructure showing the interfacial characteristic. The 2D crystallographic point group of the (111) Cu and (10 $\bar{1}$ 0) η -Cu₆Sn₅ planes are $6mm$ and $2mm$, respectively. Based on the identified relationship, the number of η -Cu₆Sn₅ variants that form on (111) Cu can be determined to be $P(6mm)/P(2mm) = 3$. The result is

also consistent with the previous TEM analysis [37] which showed a simultaneous appearance of three sets of η -Cu₆Sn₅ diffraction patterns when the zone axis was $[11\bar{2}0]_{\eta} \parallel [\bar{1}11]_{\text{Cu}}$.

By choosing the reference coordinate L₂ as $x_1 \parallel [\bar{2}11]_{\text{Cu}}$ and $x_2 \parallel [0\bar{1}1]_{\text{Cu}}$ on the (111) Cu plane, the transformation matrix of the first variant is calculated as

$$\mathbf{F}_1 = \begin{pmatrix} \sqrt{6}a_{\eta}/3a_{\text{Cu}} & 0 \\ 0 & \sqrt{2}c_{\eta}/3a_{\text{Cu}} \end{pmatrix} \quad (4)$$

$\mathbf{F}_2$ and $\mathbf{F}_3$ can be determined by symmetry operations.

$$\mathbf{F}_2 = \begin{pmatrix} \sqrt{6}a_{\eta}/12a_{\text{Cu}} + 3\sqrt{2}c_{\eta}/8a_{\text{Cu}} & \sqrt{2}a_{\eta}/4a_{\text{Cu}} - \sqrt{6}c_{\eta}/8a_{\text{Cu}} \\ \sqrt{2}a_{\eta}/4a_{\text{Cu}} - \sqrt{6}c_{\eta}/8a_{\text{Cu}} & \sqrt{6}a_{\eta}/4a_{\text{Cu}} + \sqrt{2}c_{\eta}/8a_{\text{Cu}} \end{pmatrix} \quad (5)$$

$$\mathbf{F}_3 = \begin{pmatrix} \sqrt{6}a_{\eta}/12a_{\text{Cu}} + 3\sqrt{2}c_{\eta}/8a_{\text{Cu}} & \sqrt{6}c_{\eta}/8a_{\text{Cu}} - \sqrt{2}a_{\eta}/4a_{\text{Cu}} \\ \sqrt{6}c_{\eta}/8a_{\text{Cu}} - \sqrt{2}a_{\eta}/4a_{\text{Cu}} & \sqrt{6}a_{\eta}/4a_{\text{Cu}} + \sqrt{2}c_{\eta}/8a_{\text{Cu}} \end{pmatrix} \quad (6)$$

The three heteroepitaxial strain tensors are then obtained.

$$\boldsymbol{\varepsilon}^{00}(1) = \begin{pmatrix} -0.0522 & 0 \\ 0 & -0.0051 \end{pmatrix}, \boldsymbol{\varepsilon}^{00}(2) = \begin{pmatrix} -0.0169 & 0.0204 \\ 0.0204 & -0.0404 \end{pmatrix}, \boldsymbol{\varepsilon}^{00}(3) = \begin{pmatrix} -0.0169 & -0.0204 \\ -0.0204 & -0.0404 \end{pmatrix} \quad (7)$$

3 MODEL

We employ the multiphase-field model developed by Steinbach *et al.* [62, 63] to study the evolution of microstructures involving three phases, Cu(α), liquid Sn(L), and η -Cu₆Sn₅ with multiple variants, whose structures are characterized by a set of non-conserved order parameters. The model has been applied not only to the fundamental studies of IMC nucleation and growth [34], but to more advanced processes such as transient liquid state bonding [64] and electromigration [35] as well. It should be noted that although both η -Cu₆Sn₅ and ε -Cu₃Sn IMCs form during interfacial reactions according to the Cu-Sn binary phase diagram and experiments, η -Cu₆Sn₅ has been shown to nucleate first at the early stage and possess a specific OR with the Cu substrate [1, 56]. Therefore, the present study focuses on the formation of η -Cu₆Sn₅ and neglects that of ε -Cu₃Sn. The chemical free energy of

each phase is formulated using the CALPHAD thermodynamic database for solder alloys. In particular, we introduce a two-sublattice model to calculate the chemical free energy of the stoichiometric compound (η -Cu₆Sn₅). As determined by the bi-crystallography and symmetry argument, two orientation variants of η -Cu₆Sn₅ are generated on (001) Cu and three variants on (111) Cu. Accordingly, we choose the correct order parameters to reflect the degeneracy of the orientation variants in our phase-field formulation. Those non-conserved order parameters are introduced in the model to characterize the spatial distribution of each orientation variant with prescribed stress-free heteroepitaxial strain, and the elastic strain energy is calculated by the microelasticity theory.

3.1 Chemical free energy

The chemical free energy density of Cu and liquid Sn are available in the binary CALPHAD database [65] and can be expressed as

$$f_{\text{ch}}^{\rho} = \sum_{i=\text{Cu,Sn}} x_i {}^0G_i^{\rho} + RT \sum_{i=\text{Cu,Sn}} x_i \ln x_i + {}^E G^{\rho} \quad (8)$$

where x_i is the conserved order parameter or atomic fraction of species i , ${}^0G_i^{\rho}$ is the Gibbs energy of the pure element i in the chemical phase ρ . The last term corresponds to the excess Gibbs energy, which can be written by the Redlich-Kister polynomial:

$${}^E G^{\rho} = x_{\text{Cu}} x_{\text{Sn}} \sum_{r=0}^n \left[{}^r L_{\text{Cu,Sn}}^{\rho} (x_{\text{Cu}} - x_{\text{Sn}})^r \right] \quad (9)$$

where ${}^r L_{\text{Cu,Sn}}^{\rho}$ is the temperature-dependent interaction parameters in the binary system. Because of the stoichiometric nature of η -Cu₆Sn₅, the chemical free energy was described as a temperature-dependent single value instead of a continuous function of composition [65]. The description causes a difficulty for any phase-field model because the variational derivative of free energy functional with respect to composition is not available. To resolve the issue, we follow the work of Moelans [66] by treating η -Cu₆Sn₅ as a chemical compound with small solubility and

adopting a two-sublattice model $(\text{Cu},\text{Sn})_{\text{m}}(\text{Sn},\text{Cu})_{\text{n}}$. The chemical free energy of $\eta\text{-Cu}_6\text{Sn}_5$ is expressed based on the compound energy formulation:

$$f_{\text{ch}}^{\eta} = \sum_{i,j=\text{Cu},\text{Sn}} y_i^{\text{I}} y_j^{\text{II}} {}^0G_{i,j}^{\eta} + RT \left(m \sum_{i=\text{Cu},\text{Sn}} y_i^{\text{I}} \ln y_i^{\text{I}} + n \sum_{i=\text{Cu},\text{Sn}} y_i^{\text{II}} \ln y_i^{\text{II}} \right) + {}^E G^{\eta} \quad (10)$$

where y_i^{I} and y_i^{II} are site fractions of species i in sublattice I and II, respectively. ${}^0G_{i,j}^{\eta}$ is the Gibbs energy of formation of the compound $i_{\text{m}}j_{\text{n}}$ or the so-called end member phases, and m and n give the ratio of sites on the two sublattice, which are 0.545 and 0.455, respectively. The last term is the excess Gibbs energy, which was neglected in the study [66].

Figure 2 shows the Gibbs energy plots of $\text{Cu}(\alpha)$, liquid $\text{Sn}(\text{L})$, and $\eta\text{-Cu}_6\text{Sn}_5$ chemical phases at 523 K. The energy curve of $\eta\text{-Cu}_6\text{Sn}_5$ with large curvature at $x_{\text{Cu}} = 0.545$ clearly reflects its stoichiometric feature. Detailed thermodynamic parameters used in the present study are summarized in the Supplementary material (Table S1).

3.2 Multiphase-field description

The multiphase-field approach combined with the diffusion equation was applied in the studies of Cu-Sn soldering reactions. Among them, Park and Arroyave [33] carried out extensive evaluation of parameters in the multiphase-field model of Cu-Sn binary system. In the present study, a set of non-conserved order parameters ϕ_i ($i = 1$ to n_p) are introduced to describe the nucleation and growth of $\eta\text{-Cu}_6\text{Sn}_5$ at the liquid Sn/Cu interface and characterize the evolution of each phase. $\phi_i = 1$ ($\phi_{j \neq i} = 0$) represents the existence of the phase i . ϕ_1 and ϕ_2 correspond respectively to the Cu and liquid Sn phases, while ϕ_j ($j = 3$ to n_p) corresponds to the $(j-2)$ th orientation variant of $\eta\text{-Cu}_6\text{Sn}_5$. For $\eta\text{-Cu}_6\text{Sn}_5$ formed on (001) Cu, two non-conserved order parameters are introduced to characterize the structural non-uniformities associated with the orientation variants, whereas for that on (111) Cu, three non-conserved order parameters are introduced. The region in which non-conserved order parameters vary continuously between 0 and 1 corresponds to the interface or grain boundary.

Following the multiphase-field description, a non-conserved order parameter can be taken as an interpolation function connecting the chemical free energy and phase composition of each chemical phase. The order parameters are constrained by $\sum_i \phi_i = 1$. The total free energy functional is represented as

$$F^{\text{tot}} = \int_V \left\{ \sum_{i,j(i < j)} \left[\frac{\kappa_{ij} a_{ij}^2}{2} (\phi_j \nabla \phi_i - \phi_i \nabla \phi_j)^2 + \omega_{ij} \phi_i \phi_j \right] + \sum_i \phi_i \frac{f_{\text{ch}}^i(x_{\text{Cu}}^i)}{V_m} \right\} dV + F^{\text{elas}} \quad (11)$$

where κ_{ij} is the gradient energy coefficient of the interface between phases i and j , a_{ij} is an anisotropic function which will be defined in Section 3.4, ω_{ij} is the energy barrier of the double-well potential, V_m is the molar volume, F^{elas} is the elastic strain energy, which is calculated according to the theory of microelasticity and is presented in Section 3.3. x_{Cu}^i is the phase composition of Cu in the phase i , which is related to atomic fraction via $x_{\text{Cu}} = \sum_i \phi_i x_{\text{Cu}}^i$. The Kim-Kim-Suzuki (KKS) model [67] was employed in the phase-field model by considering the interface as a mixture of phases with equal chemical potentials. It is noted that the gradient energy term $(\phi_j \nabla \phi_i - \phi_i \nabla \phi_j)^2$ is different from some phase-field models of soldering reactions [33, 34]. If we consider the interface or boundary between phase i and j , the gradient energy term reduces to the general expression $(\nabla \phi_i)^2$. Mathematical details were presented by Steinbach *et al.* [62].

3.3 Strain energy calculation

The elastic strain energy functional is formulated by the microelasticity theory [29] :

$$E^{\text{elas}} = \frac{1}{2} \int C_{ijkl} \varepsilon_{ij}^* \varepsilon_{kl}^* dV + \frac{V}{2} C_{ijkl} \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl} - \bar{\varepsilon}_{ij} \int C_{ijkl} \varepsilon_{kl}^* dV - \frac{1}{2} \oint \frac{d^3 g}{(2\pi)^3} n_i \tilde{\sigma}_{ij}^* \Omega_{jk}^0 \tilde{\sigma}_{kl}^* n_l \quad (12)$$

where C_{ijkl} is the elastic stiffness tensor, ε_{ij}^* is the eigenstrain, which can be expressed as a linear combination of the order parameters of η -Cu₆Sn₅ variants and their stress-free heteroepitaxial strain tensors:

$$\varepsilon_{ij}^* = \sum_{k=3}^{n_p} \phi_k \varepsilon_{ij}^{00} (k-2) \quad (13)$$

$\bar{\varepsilon}_{ij}$ is the prescribed macroscopic strain if the strain-controlled boundary condition is employed, $\Omega_{ik}^{0-1} = C_{ijkl} n_l n_j$, $n_i = g_i / |g_i|$, and g_i is a vector in the reciprocal space. $\tilde{\sigma}_{ij}^* = C_{ijkl} \tilde{\varepsilon}_{kl}^*$, where $\tilde{\varepsilon}_{kl}^*$ is the Fourier transform of ε_{kl}^* . The last integral in the reciprocal space excludes the point at $g = 0$.

We note that because the effect of in-plane heteroepitaxial strain at the interface between Cu and η -Cu₆Sn₅ is known to be the dominant source of heteroepitaxial constraints affecting the pattern formation at the interface, the out-of-plane strain incompatibility is not taken into account by making the out-of-plane components of eigenstrain zero. In other words, the treatment excludes any elastic constraint along the direction normal to the interface.

3.4 Anisotropic interfacial energy

The η -Cu₆Sn₅ crystal in liquid Sn was found to exhibit a highly anisotropic shape and faceted interface with six-fold symmetry on the basal plane [1]. However, the γ -plot of η -Cu₆Sn₅ characterizing the hexagonal anisotropy of interfacial energy has not been evaluated and identified. To take the interfacial anisotropy into account in an approximated but quantitative manner, we follow the treatment developed by Wendler *et al.* [68] and introduce an anisotropic function a_{ij} in a piecewise-defined form by using the maximum condition:

$$a_{ij} = \max_{1 \leq k \leq n} \left\{ \frac{\phi_j \nabla \phi_i - \phi_i \nabla \phi_j}{|\phi_j \nabla \phi_i - \phi_i \nabla \phi_j|} \cdot \bar{\eta}_{k,ij} \right\} \quad (13)$$

where the first term in the braces characterizes the unit vector of interface normal, the second term denotes the set of vertex vectors for the corresponding Wulff construction, and n indicates the number of defined vertex vectors. The interfacial energy is isotropic if the anisotropic function is a constant. We consider only the η -Cu₆Sn₅/Sn interface to be anisotropic and assume that the anisotropic function is equal to 1 for each other phase boundaries. For the interface between hexagonal

η -Cu₆Sn₅ and Sn, we define 12 vertex vectors by letting two of them be parallel to the $[1, 1.732, \pm 1.5]$ directions (based on a Cartesian coordinate with the third component normal to the basal plane) while keeping the magnitude of the vectors equal to unity, and then six-fold rotations are applied about the $[001]$ direction to obtain the other 10 vertex vectors. It is noted that a rotation matrix has to be imposed on each η -Cu₆Sn₅ variant to align the Cartesian coordinate with respect to the computational coordinate and let the $[0001]_\eta$ direction follow the crystallographic relation.

3.5 Kinetic equations

In the phase-field model, the time-evolution of non-conserved order parameters is governed by the time-dependent Ginzburg-Landau equation. Steinbach *et al.* [63] derived the governing equation for the multiphase-field theory as a superposition of pairwise interaction between phase i and other coexisting phases. The pairwise interaction is weighted by the mobility of each pair of phases. The governing equation of non-conserved order parameters was derived as [63]

$$\frac{\partial \phi_i}{\partial t} = -\frac{2}{N_p} \sum_{j(j \neq i)} s_i s_j a_{ij}^2 L_{ij} \left(\frac{\delta F^{\text{tot}}}{\delta \phi_i} - \frac{\delta F^{\text{tot}}}{\delta \phi_j} \right) + \zeta(\mathbf{r}, t) \quad (14)$$

where N_p is the local number of coexisting phases, s_i is a step function which is equal to 1 when the phase i exists and is 0 otherwise, L_{ij} is the mobility of the interface between phases i and j , and ζ is the Langevin-noise terms describing thermal fluctuations of the order parameters [69]. The time-evolution of the conserved order parameter or atomic fraction is governed by the Cahn-Hilliard equation [70]:

$$\frac{\partial x_{\text{Cu}}}{\partial t} = V_m^2 \nabla \cdot \left[\tilde{M} \nabla \left(\frac{\delta F^{\text{tot}}}{\delta x_{\text{Cu}}} \right) \right] \quad (15)$$

The term in square brackets represents the negative atomic flux of Cu defined in the laboratory frame of reference and $\tilde{M}$ is the corresponding chemical mobility.

3.6 Description of simulations

The model is first demonstrated by 2D simulations of η -Cu₆Sn₅ growth on (001) and (111) Cu, followed by simulations in 3D. The 2D work was carried out by considering the nucleation and growth of η -Cu₆Sn₅ in Cu-supersaturated liquid Sn on a unidirectional substrate which maintains continuous growth of η -Cu₆Sn₅. The 2D computational supercell was discretized into a system of 192×192 grids. Initial nucleation was only allowed at the center of the computational supercell for local nucleation. The anisotropic interfacial energy was temporarily not considered in the 2D work for better demonstration of the effect of heteroepitaxial constraints, stress fields, and coherency elastic strain energy, which will be analyzed and quantified more precisely in Section 5.

Figure 3 shows the schematic illustration of the initial 3D computational supercell in this study. All the energy contributions were considered in 3D simulations. The mesh spacing was 2 nm and the interfacial width consisted of 5 mesh grids (in both 2D and 3D work). The 3D computational supercell was discretized into a system of $128 \times 128 \times 48$ grids. Periodic boundary conditions were assumed along the x- and y-directions, and a no-flux boundary condition was enforced explicitly at the bottom and top surfaces. Under the initial condition, liquid Sn and unidirectional (001) or (111) Cu contacted with each other at a planar interface without initial formation of η -Cu₆Sn₅. Langevin-noise terms describing thermal fluctuations of the order parameters were introduced in the last term of Eq. (15) during the initial stage in order to induce the nucleation of η -Cu₆Sn₅. In addition to the modeling of η -Cu₆Sn₅ formation on (001) and (111) Cu, we also presents the simulation without considering heteroepitaxial constraint or elastic strain energy for comparison. It has been shown in the EBSD study by Kumar *et al.* [71] that no preferred orientation relationship was found between η -Cu₆Sn₅ and polycrystalline Cu at the interface. Therefore, the simulation without heteroepitaxial relationship can be regarded as an approximated case of IMC formation on traditional electroplating or polycrystalline Cu where no specific heteroepitaxial relationship with Cu can be

achieved for each η -Cu₆Sn₅ grain. All the simulation results are compared with experiments of interfacial reactions.

The Cu-substrate and η -Cu₆Sn₅–precipitate system was treated to be elastically homogeneous for simplicity. A stress-free boundary condition was employed along the z-direction, whereas a clamp or zero-strain boundary condition was prescribed along the x- and y-directions. Elastic properties of η -Cu₆Sn₅ were taken from the experimentally measured Young's modulus, shear modulus, and Poisson's ratio, which were 9.69×10^{10} N m⁻², 3.70×10^{10} N m⁻² and 0.309 respectively [17].

We adopted the kinetic parameters assessed by Park and Arroyave [33] in the phase-field model of soldering reactions. Due to the lack of reliable experimental data, the interfacial energies of Cu(α)/ η -Cu₆Sn₅, η -Cu₆Sn₅/Sn(L), and interphase boundaries (or grain boundaries) of η -Cu₆Sn₅ with respect to temperature and orientation are difficult to be determined and verified. For simplicity, we followed the previous work by assuming all the interfacial energies to be isotropic and constant, except that the η -Cu₆Sn₅/Sn interface was treated to be anisotropic by following Section 3.4. The interfacial energies of Cu/ η -Cu₆Sn₅, η -Cu₆Sn₅/Sn, Cu/Sn interfaces, and η -Cu₆Sn₅ interphase boundaries were considered to be 0.30, 0.10, 0.35, and 0.30 J m⁻², respectively. The widths of all the interfaces or interphase boundaries were assumed to be 10 nm. It is noted that a relatively large interfacial width is required for the length scale considered in the current study. Because the key interfacial properties that control the kinetics of the microstructure evolution are the interfacial energy and mobility (diffusion-controlled growth has been ensured in the simulations) and they are independent of the interfacial width in the current model, the effect of boundary width on the kinetics can be ignored. According to the gradient thermodynamics, the gradient energy coefficient and energy barrier height in Eq. (11) can be obtained as

$$\kappa_{ij} = \frac{8w_{ij}\sigma_{ij}^{\text{int}}}{\pi^2} \quad \text{and} \quad \omega_{ij} = \frac{4\sigma_{ij}^{\text{int}}}{w_{ij}} \quad (16)$$

where w_{ij} and σ_{ij}^{int} are the width and interfacial energy of the interface between phases i and j , respectively.

4 RESULTS

4.1 2D simulation of η -Cu₆Sn₅ formation on (001) Cu

Figure 4(a) - (c) shows the time-evolution of the η -Cu₆Sn₅ variants (dash line) with the distributions of coherency stress field (σ_{11} , σ_{22} , and $\sigma_{11} + \sigma_{22}$) on (001) Cu. The calculations of stress on (001) plane of Cu was based on the L_1 coordinate. The blue and orange dash lines correspond to the boundaries of variant 1 and variant 2, respectively. Shortly after the nucleation of η -Cu₆Sn₅, tensile stress was generated around the center of the nucleus. Because of the negative trace of each heteroepitaxial strain tensor and the imposed clamp boundary condition, it is expected that tensile stress can be generated macroscopically by the nucleation and growth of η -Cu₆Sn₅. Nevertheless, slight local compression can be seen close to the tips of variants during the initial stage, while at the later stage the compressive stress gradually decreased with time. The tensile area was found to increase with the growth of η -Cu₆Sn₅, and the magnitude of tensile stress also increased. Particularly, the strong tensile stress was produced at the grooves of two variants, as shown by the plot of the invariant ($\sigma_{11} + \sigma_{22}$) in Figure 4(c). It can be seen that local and concentrated compressive stress is generated at the inner tip of the boundary of two variants. The stress field distribution indicates that the grooves with high tensile stress will be elastically unfavorable for further growth of IMC or formation of multi-variant configurations. The new nucleation process will be more preferred to take place at the tips of variants.

The pattern in Figure 4 demonstrates pronounced preferred growth and elongation along two perpendicular directions. The preferred directions were not evident initially because of the strong chemical driving force of nucleation, but became more pronounced afterward as the growth of η -Cu₆Sn₅ increased the overall contribution of elastic strain energy. Based on the L_1 coordinate, it can

be shown that the two aligned directions perpendicular to each other belong to the $\langle 110 \rangle$ direction of Cu and exhibit a windmill pattern. The 2D pattern formation is in good agreement with that characterized by SEM and EBSD analysis [72]. Most importantly, the simulation shows that the elongated directions of variant 1 and variant 2 correspond to the principal directions of the heteroepitaxial strain tensors (Eq. (3)) with minimal eigenvalues, which are $[110]$ and $[1\bar{1}0]$ of Cu, respectively. The minimal eigenvalue is -0.51% and it reflects the minimum atomic mismatch between η -Cu₆Sn₅ and Cu.

4.2 2D simulation of η -Cu₆Sn₅ formation on (111) Cu

Figure 5(a) - (c) shows the time-evolution of the η -Cu₆Sn₅ variants (dash line) accompanied with the distributions of coherency stress field (σ_{11} , σ_{22} , and $\sigma_{11} + \sigma_{22}$) on (111) Cu based on the L_2 coordinate. The blue, orange, and red dash lines correspond to the boundaries of variant 1, variant 2, and variant 3, respectively. After initial nucleation, tensile stress was produced around the nucleus, but compressive stress was also generated at the center. The nucleation and growth of η -Cu₆Sn₅ overall produced macroscopic tensile stress and its magnitude increased with the IMC growth. Similar to the previous section, it can also be found that pronounce tensile stress occurred at the grooves of two variants but slight compressive stress at the tips. The pattern of η -Cu₆Sn₅ displayed in Figure 5 seems to exhibit different alignments compared to that on (001) Cu. The three variants align to three directions with an intersection angle of 120° (or 60°) between each other. According to the L_2 coordinate, it can be shown that the three directions correspond to the $[0\bar{1}1]$, $[10\bar{1}]$, and $[\bar{1}10]$ directions of Cu, which is actually analogous to the growth on (001) Cu. It can be further demonstrated that each direction also respectively reflects the principal direction of each heteroepitaxial strain tensor (Eq. (7)) with a minimal eigenvalue or atomic site mismatch. The growth directions of variant 1, 2, and 3 respectively follow the $[0\bar{1}1]$, $[10\bar{1}]$, and $[\bar{1}10]$ directions of Cu. Because the best-matching direction can offer minimization of both interfacial energy and elastic

strain energy, each variant can be energetically more favored to grow along the $\langle 110 \rangle$ direction on both (001) and (111) Cu.

4.3 3D simulation of η -Cu₆Sn₅ formation on (001) Cu

Figure 6(a) - (e) shows the time-evolution of η -Cu₆Sn₅ precipitated at the Sn/(001) Cu interface. The distributions of Cu and liquid Sn phases are omitted in the figure for better demonstration. Because no η -Cu₆Sn₅ layer formed initially and worked as a diffusion barrier prior to interfacial reaction, the Cu atoms dissolved into liquid Sn rapidly and caused supersaturation of Cu, especially for those close to the interface of Cu and liquid Sn. The supersaturation provided a large chemical driving force for the precipitation of η -Cu₆Sn₅, as indicated in Figure 6(a). The magnitude of chemical driving force gradually decreased with the formation of η -Cu₆Sn₅ and the contribution of elastic energy became more significant, as pointed out by the stress field distribution in the 2D simulation. This situation was reflected by the specific pattern and alignment of η -Cu₆Sn₅ grains which gradually appeared during the latter stage of chemical reaction, as shown in Figure 6(b) - (e). The two directions correspond to the [110] and $[1\bar{1}0]$ directions of Cu, according to the L_1 coordinates chosen in the simulation on (001) Cu. The result is consistent with the 2D simulation in Section 4.1. In addition to the preferred alignment, the coarsening phenomenon appeared at the same time, by which small grains were consumed gradually, as shown in Figure 6(b) - (e). The introduction of anisotropic interfacial energy (Section 3.4) results in the formation of faceted η -Cu₆Sn₅/Sn interface. Figure 6(f) is the experimental observation showing the top-view SEM (scanning electron microscopy) image of η -Cu₆Sn₅ on (001) single-crystal Cu [10]. The pattern and preferred growth directions predicted by the simulation exhibit excellent agreement with Figure 6(f).

Nevertheless, slight differences can be seen from the comparison of Figure 6(e) and 6(f). Although the simulated microstructure shows the faceted η -Cu₆Sn₅/Sn interface, the interface observed in experiment exhibited sharper edges and some of them grew more outward and normal

from the surface. On the contrary, the simulated η -Cu₆Sn₅ was found to be more attached to the interface. This discrepancy may be caused by the simplified nucleation process and phenomenological treatment of anisotropic interfacial energy for accommodating the lack of experimental evaluations. Additionally, in the experimental work [10, 22], the samples had experienced a cooling process (to room temperature) after soldering reactions. The process produced even more precipitation of IMC on the interface due to the significantly lower solubility limit of Cu in Sn at room temperature. The current simulation work is not able to reflect the thermo-kinetic process of solidification, which is beyond the scope of this simulation study.

Figure 7 shows the pattern of η -Cu₆Sn₅ with each variant identified by different colors for visualizing each arrangement and distribution. It is readily seen again that the elongation of variant 1 aligns to the [110] direction of Cu lattice whereas that of variant 2 aligns the [1 $\bar{1}$ 0] direction. The simulation result with symmetry analysis of orientation variants is able to fully account for the speculation from experiments which showed η -Cu₆Sn₅ grains became elongated along the directions of small atomic spacing mismatch. The volume ratio of variant 1 and variant 2 shown in Figure 7 was calculated to be close to 1:1 since the two variants are both chemically and crystallographically equivalent. The zero-strain boundary condition prescribed at the x-y plane also favors the 1:1 ratio of the two variants by canceling the off-diagonal or shear components of the heteroepitaxial strain tensors in Eq. (3). The cancelation makes the microstructure more compatible with the clamp boundary constraint.

4.4 3D simulation of η -Cu₆Sn₅ formation on (111) Cu

The time-evolution of η -Cu₆Sn₅ formation on (111) Cu is shown in Figure 8(a) - (e). Figure 8(a) shows the early-stage nucleation without evident patterns or elongation, and Figure 8(b) shows the pattern formation and elongation of variants to three directions at the later stage, with several small grains formed in between those elongated variants. Some of the η -Cu₆Sn₅ grains were smaller than

those found in the simulation on (001) Cu at the early stage. Similar to the previous section, coarsening of each η -Cu₆Sn₅ precipitates occurred and simultaneously the aligned growth of each variant was maintained. It can be demonstrated in Figure 8 that the preferred directions of the elongated η -Cu₆Sn₅ variants align closely to the $[0\bar{1}1]$, $[10\bar{1}]$, and $[\bar{1}10]$ directions on (111) Cu. The distribution of each variant is displayed in Figure 9, which shows that the aligned directions of variant 1, 2, and 3 correspond to $[0\bar{1}1]$, $[10\bar{1}]$, and $[\bar{1}10]$, respectively. The result is consistent with the 2D simulation (Section 4.2). Analogous to the previous section, each direction also respectively reflects the principal direction of each heteroepitaxial strain tensor (Eq. (7)) with a minimal eigenvalue or atomic site mismatch. Figure 8(f) shows the top-view SEM image of η -Cu₆Sn₅ on (111) single-crystal Cu [22]. The overall pattern and preferred growth directions in the simulation demonstrate consistency with that of the SEM result, though slight discrepancies as described in Section 4.3 were also found in the simulated growth of η -Cu₆Sn₅ on (111) Cu.

From the comparison between Figure 7 and Figure 9 as well as in the experimental studies, it is shown that the interfacial reactions on (001) and (111) Cu demonstrate analogous pattern formations: All the elongated directions of η -Cu₆Sn₅ variants follow the dense $\langle 110 \rangle$ rows on the Cu lattice planes, and accordingly the patterns can be determined basically by the directions those rows align with on the unidirectional surface of Cu. It is worth noting that although the first part of the heteroepitaxial relationships on (001) Cu and η -Cu₆Sn₅ on (111) Cu are crystallographically different, the principal values of the total five heteroepitaxial strain tensors in Eq. (3) and Eq. (7) are exactly identical, which are -0.51% and -5.2%, respectively. It is caused by the fact that the values of atomic site mismatch along the directions of $[110]_{\text{Cu}} \parallel [\bar{1}100]_{\eta}$ and $[11\bar{2}]_{\text{Cu}} \parallel [1\bar{2}10]_{\eta}$ are the same. In other words, the orientation variants of η -Cu₆Sn₅ on (001) and (111) Cu are mathematically equivalent, albeit based on nonequivalent crystallographic relationship, and thus the pattern formation on the two types of surface can operate in such a similar way.

4.5 3D simulation of η -Cu₆Sn₅ formation without heteroepitaxial constraint

Figure 10(a) - (e) shows the time evolution of η -Cu₆Sn₅ formation without elastic strain energy calculations in an attempt to reveal the effects of unidirectional Cu substrates and heteroepitaxial constraint shown in the previous sections. It is found that after initial nucleation, η -Cu₆Sn₅ grains are demonstrated to be of scalloped morphology without elongation along any specific direction. The scalloped shape of η -Cu₆Sn₅ grains with deep grooves at η -Cu₆Sn₅ grain boundaries was attributed to the smaller interfacial energy of η -Cu₆Sn₅/Sn compared to that of η -Cu₆Sn₅ grain boundaries [1]. From the energetic perspective, the deep grooves of η -Cu₆Sn₅ grains increased the area of the η -Cu₆Sn₅/Sn interface with lower interfacial energy. The evolution of microstructures was solely controlled by the interfacial-energy-driven ripening or coarsening process. The result is similar to the 3D phase-field simulation work of IMC layer growth by Kim *et al.* [73]. Figure 10(f) shows the experimental observation of η -Cu₆Sn₅ grain morphology and it can be found that the simulation is consistent with the previous phase-field simulation [73] and experiment [22].

5 DISCUSSION

5.1 Analysis of habit planes

Our simulation results have successfully reproduced the pattern formation of η -Cu₆Sn₅ precipitates on (001) and (111) planes of Cu in both two and three dimensions. In this section, we analyze some of the detailed morphological characteristics of the patterns. We will start with calculating quantitatively the habit plane normal of each variant using the microelasticity theory.

The habit plane normal can be determined by searching for a unit vector $\mathbf{n} = \mathbf{n}_0$ in reciprocal space, which corresponds to the normal of the precipitate habit plane in real space, such that the function $B_{pq}(\mathbf{n}_0)$ reaches the minimum value. $B_{pq}(\mathbf{n})$, defined by Eq. (12), characterizes the coherency strain energy density (in reciprocal space) and is expressed as [29]

$$E^{\text{elas}} = \frac{1}{2} \sum_{p,q} \int \frac{d^3 g}{(2\pi)^3} B_{pq}(\mathbf{n}) \tilde{\phi}_p(\mathbf{g}) \tilde{\phi}_q^*(\mathbf{g}) \quad (17)$$

and

$$B_{pq}(\mathbf{n}) = \begin{cases} C_{ijkl} \varepsilon_{ij}^{00}(p) \varepsilon_{kl}^{00}(q) & \mathbf{n} = 0 \\ C_{ijkl} \varepsilon_{ij}^{00}(p) \varepsilon_{kl}^{00}(q) - n_i \tilde{\sigma}_{ij}^{00}(p) \Omega_{jk}^0 \tilde{\sigma}_{kl}^{00}(q) n_l & \mathbf{n} \neq 0 \end{cases} \quad (18)$$

for the clamp boundary condition, where p and q specify the orientation variants, $\tilde{\phi}_q^*$ is the complex conjugate of $\tilde{\phi}_q$, and $\tilde{\sigma}_{ij}^{00} = C_{ijkl} \tilde{\varepsilon}_{kl}^{00}$.

Figure 11(a) and 11(b) show the polar plots of $B_{pp}(\mathbf{n})$ projected on the (001) and (111) planes of Cu based on L_1 and L_2 coordinates, respectively. It is seen that for the two variants on (001) Cu, B_{11} and B_{22} reach minimum when the habit plane normal $\mathbf{n}_0$ of each variant corresponds to the $[1\bar{1}0]$ and $[110]$ directions, respectively, as indicated by the arrows. Similarly, B_{11} , B_{22} , and B_{33} of the three variants on (111) Cu reach minimum when $\mathbf{n}_0$ corresponds to $[\bar{2}11]$, $[1\bar{2}1]$, and $[11\bar{2}]$, respectively. Thus for all the η -Cu₆Sn₅ variants on the (001) and (111) planes of Cu, their growth along the $\langle 110 \rangle_{\text{Cu}}$ $\parallel [0001]_{\eta}$ directions will yield habit planes of each variant as predicted by the analysis of $B_{pp}(\mathbf{n})$. If variant 1 on (111) Cu is considered, for example, its growth along the $[0\bar{1}1]$ direction results in a $(\bar{2}11)$ habit plane, which is exactly the habit plane predicted by the minimization of B_{11} . It can be shown in Section 4.1 and 4.2 that the habit planes on both the (001) and (111) planes are consistent with those predicted by the minimization of $B_{pp}(\mathbf{n})$. This analysis indicates that the observed patterns in the simulations are dominated by the minimization of the coherency elastic strain energy.

5.2 Analysis of kinematic compatibility

In addition to the habit planes and directions of growth, it is also important to analyze the lattice continuity across the interface between two η -Cu₆Sn₅ variants on a unidirectional Cu substrate. The condition was described mathematically by the condition of kinematic or rank-one compatibility [74].

$$\mathbf{Q}\mathbf{F}_i - \mathbf{F}_j = \mathbf{a} \otimes \hat{\mathbf{n}} \quad (19)$$

where $\mathbf{Q}$ is a rigid body rotation matrix of variant i with respect to variant j , $\mathbf{a}$ is a shear vector, $\hat{\mathbf{n}}$ is the normal unit vector of the interface between variants i and j , and $\otimes$ is a dyadic product. Since the heteroepitaxial descriptions in Section 2.2 and 2.3 are formulated in 2D at the η -Cu₆Sn₅/Cu interface, the compatibility condition is examined in 2D as well. The solution of Eq. (20) has been given by Ball and James [74].

For the growth of two η -Cu₆Sn₅ variants on (001) Cu, if i and j correspond respectively to variant 1 and variant 2, there exists a set of two solutions, $\hat{\mathbf{n}} = [0, 1]_{L1}$ or $\hat{\mathbf{n}} = [1, 0]_{L1}$ with respect to the L_1 coordinate. The normal direction of the variant 1/variant 2 interface has to be either along the [001] or [010] direction to keep the η -Cu₆Sn₅ lattices continuous across the interface. It is noted that the same set of solution can also be given by the geometrically linear theory based on strain compatibility [75]:

$$\boldsymbol{\varepsilon}^{00}(1) - \boldsymbol{\varepsilon}^{00}(2) = \frac{1}{2}(\mathbf{a} \otimes \hat{\mathbf{n}} + \hat{\mathbf{n}} \otimes \mathbf{a}) \quad (20)$$

or precisely,

$$\begin{aligned} \boldsymbol{\varepsilon}^{00}(1) - \boldsymbol{\varepsilon}^{00}(2) &= \frac{1}{2} \{ [0.094, 0] \otimes [0, 1] + [0, 1] \otimes [0.094, 0] \} \\ &= \frac{1}{2} \{ [0, 0.094] \otimes [1, 0] + [1, 0] \otimes [0, 0.094] \} \end{aligned} \quad (21)$$

The solution can be validated by the 2D simulations of growth on (001) Cu, as shown by the dash lines in Figure 4. The normal direction of the variant 1/variant 2 interface gradually approaches to the $[0, 1]_{L1}$ or $[1, 0]_{L1}$ direction. This characteristic is in excellent agreement with the prediction of the kinematic compatibility.

It is also straightforward to solve the compatibility condition of the three η -Cu₆Sn₅ variants on (111) Cu with respect to the L_2 coordinate. For the interface of variant 1 / variant 2, variant 2 / variant 3, and variant 1 / variant 3, the solutions give $\hat{\mathbf{n}} = [0.866, -0.500]_{L2}$ or $\hat{\mathbf{n}} = [0.500, 0.866]_{L2}$, $\hat{\mathbf{n}} = [0, 1]_{L2}$ or $\hat{\mathbf{n}} = [1, 0]_{L2}$, and $\hat{\mathbf{n}} = [0.866, 0.500]_{L2}$ or $\hat{\mathbf{n}} = [-0.500, 0.866]_{L2}$, respectively. The common feature of the solutions on (001) and (111) Cu is that the bisector direction of any two preferred

growth directions ($\langle 110 \rangle_{\text{Cu}}$) on (001) or (111) Cu is able to align on one of the interfaces predicted by kinematic compatibility. If considering the interface of variant 1 / variant 2, the solution of compatibility reflects the interface with a normal vector $\hat{n} = [\bar{1}10]$ or $\hat{n} = [\bar{1}\bar{1}2]$ of Cu. The two bisector directions of variant 1 and variant 2 can be found to align on these two interfaces. The coherent interfacial characteristic has not been identified by experiments, but it can be found in good agreement with 2D simulations, as demonstrated by the variant boundaries in Figure 4 and Figure 5.

5.3 Comparison of OR predictions and recent experiments

As described in Section 2.1, the edge-to-edge matching model predicts two types of OR, $[0001]_{\eta} \parallel [110]_{\text{Cu}}$, $(1\bar{2}10)_{\eta} \parallel (1\bar{1}1)_{\text{Cu}}$ (Type I), and $[0001]_{\eta} \parallel [110]_{\text{Cu}}$, $(0\bar{1}10)_{\eta} \parallel (100)_{\text{Cu}}$ (Type II), both of which share the same directional relation. The crystallographic relationship between η -Cu₆Sn₅ and Cu was studied recently by a combined analysis of EBSD and TEM [56], though not explicitly addressed and pointed out by the authors, both Type I and II ORs can actually be observed by the SAED (selected area electron diffraction) images. For the η -Cu₆Sn₅ growth on (001) Cu, the SAED pattern from the zone axis $[0001]_{\eta} \parallel [110]_{\text{Cu}}$ showed that the $(1\bar{2}10)_{\eta}$ plane was in near parallel to $(1\bar{1}1)_{\text{Cu}}$ with a rotation angle of 5.26° about the matching direction $[0001]_{\eta} \parallel [110]_{\text{Cu}}$. Similarly for the η -Cu₆Sn₅ growth on (111) Cu, the SAED pattern from the same zone axis showed that the $(0\bar{1}10)_{\eta}$ plane was in near parallel to $(100)_{\text{Cu}}$ with a rotation of 5.26° . It is noted that from the viewpoint of the edge-to-edge matching model, the small rotation angle is required to let the interface of two phases meeting edge-to-edge and possess a maximum matching of atomic rows and a lower interfacial energy. The SAED images indicate that the η -Cu₆Sn₅ growth on (001) Cu follows Type I OR, whereas that on (111) Cu follows Type II OR. The SAED result from another previous study also showed that the η -(Cu,Ni)₆Sn₅ growth on (001) Ni followed Type I OR, in accord with the growth on (001) Cu. It is possible that the OR on a specific surface of the substrate is chosen in a way to release the in-plane heteroepitaxial constraint or have a lowest possible strain of the initial layer [59]. Nevertheless,

fundamental rationales behind the differently chosen ORs between the IMCs and Cu substrate of different orientations still remain ambiguous and require further experimental and theoretical investigations. The work should be essential for understanding and predictions of IMC pattern formation.

5.4 *Potential applications and limitations of the model*

One of the most important advantages of the present model is its ability to be extended to simulate the growth of materials on other substrates of any oriented direction as long as the heteroepitaxial relationship or correspondence is identified. It should be pointed out that the number of variants and their growth patterns are not pre-assumed in this model. Instead, the variant is determined by following the principle that multiple variants will be generated when the material is grown on a unidirectional substrate of higher symmetry [36], and the heteroepitaxial strain of each variant is characterized by the lattice correspondence suggested by the experimentally observed OR. Finally, the overall precipitate patterns are controlled by the heteroepitaxial constraint on the unidirectional substrates as compared to the IMC formed on polycrystalline Cu without the elastic strain energy considered. The successful application and agreement with experimental observations on both (001) and (111) Cu clearly demonstrate its applicability. It should be a straightforward exercise to apply the model to other solder systems such as Ni-Sn and Ag-Sn. Experiments have shown that IMC growth on unidirectional Ag or Ni produced distinctive morphological features as well [24, 76], including the growth of Ni_3Sn_4 (monoclinic, $C2/m$ [77]) on Ni and Ag_3Sn (orthorhombic, $Pmmn$ [78]) on Ag. Because of the different crystal structures of the IMCs, the orientation variants on a unidirectional substrate, their ORs and heteroepitaxial correspondence are required to be re-determined and re-evaluated by following Section 2. The methodology developed in this study also provides a robust approach to model pattern formations on heteroepitaxial or epitaxial thin films and offer insights into the establishment of structure-morphology relationships.

Nevertheless, the current model has some limitations. As mentioned in Section 3.6, homogeneous and isotropic elastic modulus of η -Cu₆Sn₅ is assumed for simplicity. The nucleation process was simulated by the Langevin-noise terms introduced at the liquid and substrate interface, which is qualitative in nature but may be sufficient for the study of the strain-induced pattern formation. Additionally, only the interfacial energy of the η -Cu₆Sn₅/Sn interface is treated to be anisotropic, whereas those of the other interfaces are assumed isotropic. Since the present work is aimed to establish a general model for heteroepitaxial IMC growth and focuses on the effect of heteroepitaxial strain on IMC pattern formation, we leave the consideration of anisotropic and inhomogeneous elasticity for future development of more accurate models. Despite these limitations, the present simulation results are in excellent agreement with the pattern formations observed in experiments, which are essentially strain-induced. The application of this approach is not limited to interfacial reactions in solder interconnects, but can be extended to any heteroepitaxial growth of materials in an analogous manner.

6 CONCLUSION

Pattern formation and heteroepitaxial growth of η -Cu₆Sn₅ during chemical reactions between Sn and unidirectional (001) and (111) Cu are investigated by using a combination of crystallographic analysis, microelasticity analysis and phase-field simulations in both 2D and 3D. The symmetry-related orientation variants determined by the crystallographic analysis are characterized by a set of non-conserved order parameters in the phase-field model. According to the analysis, two and three η -Cu₆Sn₅ variants can be generated on (001) and (111)-oriented Cu single crystal substrates, respectively. For each variant, the stress-free heteroepitaxial strain is calculated quantitatively based on the identified heteroepitaxial relationship and symmetry operations.

The η -Cu₆Sn₅ domain patterns on both (001) and (111) Cu obtained from the phase-field simulations show excellent agreements with the experimental observations. The results on (001) Cu

show that the η -Cu₆Sn₅ grains grow along two perpendicular directions, while the results on (111) Cu show that the η -Cu₆Sn₅ grains growth along three directions with an intersection angles of 120° or 60°. It can be seen that each η -Cu₆Sn₅ variant, either on (001) or (111) Cu, grows along the principal direction of heteroepitaxial strain with the minimum eigenvalue, which in all the cases corresponds to the $\langle 110 \rangle_{\text{Cu}}$ direction. In contrast, η -Cu₆Sn₅ grains grown without the heteroepitaxial constraints (e.g., grown on a polycrystalline substrate) do not exhibit any alignment. Additionally, the consideration of anisotropic interfacial energy correctly predicts faceted η -Cu₆Sn₅/Sn interface as observed in experiments.

The alignment along $\langle 110 \rangle_{\text{Cu}}$ found in the phase-field simulations is further elucidated by the microelasticity analysis, which is shown to minimize $B_{pp}(\mathbf{n})$, the characteristic coherency elastic energy density. The interface normal of any two η -Cu₆Sn₅ variants observed in the simulations as well as in the experiments is found to obey the kinematic compatibility condition. The stress field calculations based on 2D simulations show that strong tensile stress can be generated at the grooves of the η -Cu₆Sn₅ variant boundaries.

Two types of orientation relationships (ORs) between η -Cu₆Sn₅ and Cu substrates are predicted by the edge-to-edge matching model, which are actually appeared in the SAED pattern from a recent study. The ORs for η -Cu₆Sn₅ growth on (001) and (111) Cu are identified to be $[0001]_{\eta} \parallel [110]_{\text{Cu}}$, $(\bar{1}210)_{\eta} \parallel (1\bar{1}1)_{\text{Cu}}$ and $[0001]_{\eta} \parallel [110]_{\text{Cu}}$, $(0\bar{1}10)_{\eta} \parallel (100)_{\text{Cu}}$, respectively.

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FIGURE CAPTION

- Fig. 1. (Color online) Schematic illustrations showing the 2D atomic site correspondence or heteroepitaxial relationship at the interface between (a) η -Cu₆Sn₅ and (001) Cu. (b) η -Cu₆Sn₅ and (111) Cu. The shaded area in the hexagonal lattice η -Cu₆Sn₅ shows the lattice plane in parallel with the Cu surface. The circles of dash line in (b) represent the atomic sites that are not in the same atomic layer with the other atoms.
- Fig. 2. (Color online) Plots showing the chemical free energy of Cu(α), liquid Sn(L), and η -Cu₆Sn₅ as a function of composition at 523 K.
- Fig. 3. Schematic drawing showing the simulation supercell with initial distribution of the Cu substrate and liquid Sn.
- Fig. 4. (Color online) Time-evolution of the stress fields of (a) σ_{11} , (b) σ_{22} , and (c) $\sigma_{11} + \sigma_{22}$, with the dash lines outlining the growth of η -Cu₆Sn₅ (blue for variant 1 and orange for variant 2) on (001) Cu. The stress fields are calculated based on the L_1 coordinate.
- Fig. 5. (Color online) Time-evolution of the stress field distributions of (a) σ_{11} , (b) σ_{22} , and (c) $\sigma_{11} + \sigma_{22}$ with the dash lines outlining the growth η -Cu₆Sn₅ (blue for variant 1, orange for variant 2 and red for variant 3) on (111) Cu. The stress fields are calculated based on the L_2 coordinate.
- Fig. 6. (a)-(e) 3D phase-field simulation results showing the time-evolution of the heteroepitaxial growth of η -Cu₆Sn₅ on a (001) Cu substrate. (f) Top-view of a scanning electron

microscope (SEM) image showing the pattern and morphology of η -Cu₆Sn₅ on a (001) Cu substrate. (Courtesy of Prof. K. N. Tu [10])

Fig. 7. (Color online) 3D phase-field simulation result (same as what shown in Figure 6(e)) showing spatial distribution of the two η -Cu₆Sn₅ variants (represented by two different colors) on (001) Cu.

Fig. 8. (a)-(e) 3D phase-field simulation results showing heteroepitaxial growth of η -Cu₆Sn₅ on a (111) Cu substrate. (f) Top-view of a scanning electron microscope (SEM) image showing the pattern and morphology of η -Cu₆Sn₅ on a (111) Cu substrate. (Courtesy of Prof. Z. F. Zhang [22])

Fig. 9. (Color online) 3D simulation result (the same as what shown in Figure 8(e)) showing spatial distribution of the three η -Cu₆Sn₅ variants (represented by three different colors) on (111) Cu.

Fig. 10. (a)-(e) 3D phase-field simulation results showing growth of η -Cu₆Sn₅ on a Cu substrate without heteroepitaxial constraints. (f) Top-view of a scanning electron microscope (SEM) image showing the scalloped grains of η -Cu₆Sn₅ on a polycrystalline substrate. (Courtesy of Prof. Z. F. Zhang [22])

Fig. 11. (Color online) Polar plots of $B_{pp}(\mathbf{n})$ showing the density of coherency elastic strain energy of each η -Cu₆Sn₅ variant projected on (a) (001) plane and (b) (111) plane of Cu. The calculations of (a) and (b) are based on the L_1 and L_2 coordinates, respectively. The arrows indicate the habit plane normal direction of each variant.

fig1

fig2

fig3

fig4

fig5

fig6

fig 7

fig 8

fig 9

fig10

graphical abstract