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S.O. ABAKUMOV [1,*], Ch. CHEN [2,], and A.M. GUSAK [1,3,***]**

[1] Bohdan Khmelnytsky National University of Cherkasy,
Shevchenko Blvd. 81, 18031 Cherkasy, Ukraine
[2] National Yang Ming Chiao Tung University,
No. 1001, Daxue Rd., East Dist., Hsinchu City 300093, Taiwan
[3] ENSEMBLE3 Centre of Excellence,
Wolczyńska 133, 01-919 Warsaw, Poland

* abakumov.serhii.official@gmail.com, ** chihchen@nycu.edu.tw,
*** amgusak@ukr.net, andriy.gusak@ensemble3.eu

JOINING IN MICROELECTRONICS AS AN OPEN-SYSTEM PROBLEM: FROM SILICIDES TO DIRECT BONDING

Joining processes in microelectronics are traditionally analysed within separate technological frameworks, including silicide formation, soldering, intermetallic growth, direct bonding, and reliability degradation. In this review, we argue that these seemingly diverse phenomena can be understood within the unified physical framework of flux-driven transformations in open systems under geometrical and mechanical constraints. We revisit several key developments in reactive-diffusion theory relevant to microelectronics, including sequential phase formation in silicides, nucleation and growth under sharp concentration gradients, flux-driven ripening during soldering, vacancy-induced porosity evolution, and stress-assisted direct metal bonding. Particular attention is paid to the role of transport-path topology, competition between characteristic kinetic processes, and the coupling between diffusion, reaction, and defect evolution. Reactive soldering and direct bonding are interpreted as two complementary classes of non-equilibrium morphological evolution. In soldering systems, sustained atomic fluxes may generate connected porous networks and flux-driven instabilities, whereas in direct bonding, the same diffusion mechanisms progressively eliminate interfacial free volume and establish metallic continuity. Reliability degradation is further discussed as a continuation of the same open-system dynamics through electromigration, void

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coalescence, and collective damage evolution. The review emphasises that microelectronic joining phenomena are governed not only by equilibrium thermodynamics, but also by kinetic constraints imposed by external fluxes, evolving transport networks, and mechanical fields. This perspective provides a common conceptual language for understanding phase selection, morphology evolution, bonding, and failure in modern microelectronic interconnect technologies.

Keywords: diffusion, joining, reactions, soldering, wetting, direct bonding, phase selection, nucleation, cellular decomposition, flux-driven ripening, Kirkendall voiding, reliability.

1. Introduction

The continuous scaling of microelectronic devices and the transition toward three-dimensional (3*D*) integration have placed unprecedented demands on interconnection technologies. Modern packaging solutions, ranging from silicide contacts and solder microbumps to hybrid Cu–Cu bonding, must provide not only electrical continuity but also long-term mechanical and thermodynamic stability under increasingly severe geometric and thermal constraints. Despite the apparent diversity of these technologies, they share a common physical foundation: all are governed by coupled processes of diffusion, chemical reaction, and stress evolution occurring at micro- and nanoscales. Moreover, chemical reactions at the interfaces of contacting materials should be treated as phase transformations in the sharp concentration gradients and structure transformations (for example, grain growth) in contact zones, which are actually the structure transformations in open systems driven by the external fluxes.

Historically, the understanding of joining in microelectronics has evolved along several partially independent directions. Early studies of reactive diffusion in thin films and diffusion couples, notably those by Goesele and Tu, established the importance of kinetic regimes (interface-controlled, bulk-diffusion-controlled, and grain-boundary-diffusion-controlled) in determining phase growth sequences. In parallel, general theoretical approaches to phase formation in interdiffusion systems emphasised the role of flux balance and nucleation kinetics under concentration gradients in selecting intermediate phases. These developments laid the groundwork for interpreting silicide formation and related reactions as kinetic processes controlled not only by thermodynamics, but also by transport constraints.

With the advent of soldering technologies, particularly in Cu–Sn systems, attention shifted toward morphological evolution at reacting interfaces. The formation of scallop-type intermetallic compounds, their coarsening, and the associated ripening phenomena revealed that interface morphology is inherently unstable under conditions of continuous mass flux. Subsequent theoretical developments introduced the concept of flux-driven ripening, in which the evolution of microstructure is governed by the

interplay between diffusion fluxes and interface curvature, rather than by capillarity alone. These ideas demonstrated that joining processes are intrinsically open systems, where matter is continuously supplied, redistributed, and transformed.

A further level of complexity arises from the emergence of topological instabilities, such as porosity formation and discontinuous precipitation, during the later stages of interfacial reactions. In Cu–Sn interconnects, the formation of porous Cu_3Sn layers and Kirkendall voids reflects a fundamental imbalance of atomic fluxes and the competition between different types of sinks for excess vacancies. Similar flux-driven mechanisms have been identified in other systems, including the crystallisation of amorphous alloys in contact with reactive environments. These phenomena highlight that the reliability of interconnections is often governed not by average reaction rates but by localised instabilities arising from the coupling among diffusion, reaction kinetics, and defect dynamics.

In recent years, the transition toward direct metal bonding and hybrid bonding technologies has introduced an additional governing factor: mechanical constraint. In Cu/SiO_2 hybrid structures, the mismatch in thermal expansion coefficients and the geometric confinement of metallic features generate significant stress fields that, in turn, influence both mass transport and contact formation. Experimental and modelling studies have shown that parameters such as pad size, aspect ratio, and microstructure strongly affect the effective thermal expansion and the ability to achieve defect-free bonding. These findings indicate that mechanical fields are not merely a secondary effect but an active component of the joining process, capable of redistributing fluxes and modifying kinetic pathways.

The central thesis of this review is that joining in microelectronics can be understood within a unified framework of flux-driven transformations in open systems under constraint. In this perspective, all joining processes are governed by the competition and coupling between (i) diffusion fluxes driven by chemical potential gradients, (ii) reaction kinetics at moving interfaces, and (iii) mechanical fields arising from geometric and material constraints. This framework provides a common language for describing phase selection, morphology evolution, and defect formation across a wide range of technologies from silicide formation and soldering to modern hybrid bonding.

The purpose of this paper is therefore twofold. First, we revisit key developments in the physics of reactive diffusion and joining, emphasising the underlying mechanisms that unify seemingly disparate phenomena. Second, we demonstrate how these concepts can be applied to understand and control modern interconnection technologies, with particular attention to flux-driven instabilities, void formation, and stress-assisted bonding. By focusing on the fundamental interplay between transport, reaction, and mechanics, we aim to provide a coherent conceptual basis for the design of reliable microelectronic joints in next-generation devices.

Many of the ideas discussed in this review emerged, evolved, and matured through friendly competition and later through close collaboration with Professor King Ning Tu. He passed away in 2025. During his long and highly successful research career (starting in 1968 at Harvard, followed by IBM, UCLA, NCTU/NYCU, and City University of Hong Kong), he became one of the leading figures in the fields of solid-state reactions, soldering, electromigration, packaging, and reliability of microelectronic devices. This review is, to a large extent, a commemoration of his immense contributions to materials science and engineering.

2. Flux-Driven Phase Selection in Reactive Diffusion: Silicides as Model Systems

2.1. Why Phase Selection Became a Key Problem in Microelectronics

The problem of phase selection during reactive diffusion became especially important with the development of thin-film metallization technologies in microelectronics. In many metal-silicon systems, several intermetallic compounds are thermodynamically possible, yet experiments revealed that these phases do not generally grow simultaneously. Instead, phase formation often proceeds sequentially, with one phase temporarily suppressing the growth or nucleation of competing phases [1–3].

In some sense, sequential phase formation at the interface is very similar to Ostwald's rule of steps, for example, sequential polymorphic transformations as a chain of transitions from higher (by energy) metastable states to lower metastable states [4–6] (Fig. 1, *a*).

The sequential formation and growth of silicides during reactive diffusion may also be partially related to the different nucleation barriers of different silicides, but the main reason we see this is the kinetic con-

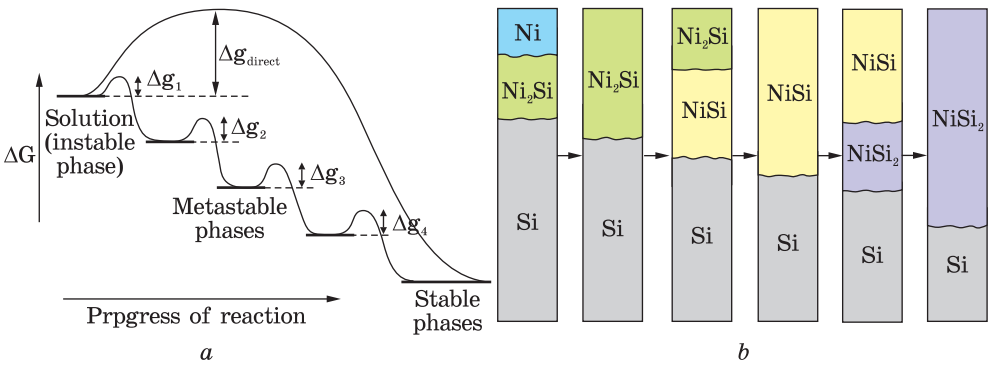

Fig. 1. (*a*, *b*) Two mechanisms of sequential phase formation. (*a*) Ostwald-type sequence controlled mainly by nucleation barriers between metastable states. (*b*) Sequential silicide formation in reactive diffusion controlled primarily by transport constraints and flux divergence in an open system

straints (even in the case of successful nucleation) imposed by the divergence of external fluxes (see below). A classic example is the reaction between Ni thin films and Si substrates [1, 7]. Although several silicides (Ni_2Si, NiSi, $NiSi_2$ are stable in the Ni–Si phase diagram, their formation occurs in a distinct sequence. First, Ni_2Si nucleates and grows until the Ni film is exhausted. Only afterwards does NiSi form through the reaction between Ni_2Si and Si, and finally $NiSi_2$ may appear at higher temperatures. Similar sequential behaviour was later observed in many other systems relevant to microelectronics.

Sequential silicide formation during reactive diffusion proceeds through a chain of intermediate phases (Fig. 1, *b*). However, the underlying mechanism is fundamentally different. In this case, even successfully nucleated phases may remain kinetically suppressed because continued growth requires transport through already-formed layers and satisfaction of flux-balance conditions at moving interfaces.

Thus, the sequential formation of silicides should be viewed not simply as an Ostwald-like nucleation sequence, but rather as an open-system kinetic evolution controlled by divergence of external atomic fluxes and competition between growing phases. Although differences in nucleation barriers may contribute, the dominant effect appears to arise from the kinetic suppression of already-nucleated phases under conditions of constrained flux balance.

This distinction between closed-system nucleation sequences and open-system flux-controlled evolution will repeatedly reappear throughout the present review in the context of soldering, porosity formation, and direct bonding.

Observations of the sequential silicide formation contradicted earlier diffusion-zone theories based on simultaneous parabolic growth of all equilibrium phases. As a result, the question emerged: What determines which phase appears first, which phases are suppressed, and when suppressed phases become active? Two partially independent theoretical approaches were subsequently developed to answer this question [8–13].

2.2. Sequential Growth and Diffusion Suppression of Competing Phases

One of the earliest explanations of sequential phase formation was proposed by Geguzin *et al.* [8] and co-workers and later independently developed in greater detail by Goesele and Tu [9–10].

The central idea was that phase selection may arise not from equilibrium thermodynamics alone, but from kinetic competition between growing layers. In reactive diffusion couples, the product phase forms an intermediate layer separating the original reactants. Continued reaction therefore requires atomic transport through already-formed phases and transfer across moving interfaces.

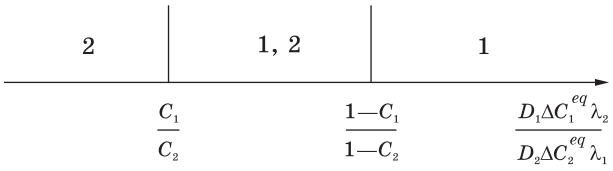

Fig. 2. Growth/suppression criteria according to Goesele and Tu [9]. Actually, this form of representation was introduced in Ref. [11] with a critical nucleus size ratio $l_{cr}^{(2)}/l_{cr}^{(1)}$ instead of λ_2/λ_1

For a phase layer of thickness ΔX_i, the atomic flux can be represented schematically as

$$j_i \propto -\frac{D_i \Delta C_i}{\Delta X_i + \lambda_i} \tag{1}$$

that characterises the kinetic resistance associated with interface transfer. In the limit $\Delta X_i \ll \lambda_i$, growth is interface controlled, whereas for $\Delta X_i \gg \lambda_i$, diffusion through the phase becomes rate limiting.

A key consequence is that the growth rate of a phase depends not only on its own transport properties, but also on the flux balance through neighbouring phases,

$$\frac{d\Delta X_1}{dt} = \frac{1}{C_2 - C_1}\left(\frac{C_2}{C_1}\frac{D_1\Delta C_1^{\text{eq}}}{\Delta X_1 + \lambda_1} - \frac{D_2\Delta C_2^{\text{eq}}}{\Delta X_2 + \lambda_2}\right), \tag{2a}$$

$$\frac{d\Delta X_2}{dt} = \frac{1}{C_2 - C_1}\left(-\frac{D_1\Delta C_1^{\text{eq}}}{\Delta X_1 + \lambda_1} + \frac{1 - C_1}{1 - C_2}\frac{D_2\Delta C_2^{\text{eq}}}{\Delta X_2 + \lambda_2}\right). \tag{2b}$$

Under certain conditions, the effective growth rate of one phase becomes negative during the initial stage, meaning that the phase is kinetically suppressed by faster-growing competitors.

In the simplest case of two competing intermediate phases, one obtains criteria separating three regimes, as shown in Fig. 2:

• suppression of phase 2 by phase 1,

$$r \equiv \frac{D_1\Delta C_1^{\text{eq}}}{D_2\Delta C_2^{\text{eq}}}\frac{\lambda_2}{\lambda_1} > \frac{1 - C_1}{1 - C_2} \Rightarrow \left.\frac{d\Delta X_1}{dt}\right|_{\Delta X_1 = 0} > 0\,, \quad \left.\frac{d\Delta X_2}{dt}\right|_{\Delta X_2 = 0} < 0\,; \tag{3a}$$

• simultaneous growth of both phases,

$$\frac{C_1}{C_2} < r \equiv \frac{D_1\Delta C_1^{\text{eq}}}{D_2\Delta C_2^{\text{eq}}}\frac{\lambda_2}{\lambda_1} < \frac{1 - C_1}{1 - C_2} \Rightarrow \left.\frac{d\Delta X_1}{dt}\right|_{\Delta X_1 = 0} > 0\,, \left.\frac{d\Delta X_2}{dt}\right|_{\Delta X_2 = 0} > 0\,; \tag{3b}$$

• suppression of phase 1 by phase 2,

$$\frac{C_1}{C_2} > r \equiv \frac{D_1\Delta C_1^{\text{eq}}}{D_2\Delta C_2^{\text{eq}}}\frac{\lambda_2}{\lambda_1} \Rightarrow \left.\frac{d\Delta X_1}{dt}\right|_{\Delta X_1 = 0} < 0\,, \left.\frac{d\Delta X_2}{dt}\right|_{\Delta X_2 = 0} > 0\,. \tag{3c}$$

If, *e.g.*, phase 2 is suppressed initially (case 1), it will start growing after the suppressing growing phase 1 will reach some critical thickness [7].

Thus, phase selection emerges as a dynamic consequence of flux competition in an open diffusion system rather than as a direct reflection of equilibrium stability. This approach successfully explained many experimentally observed sequences of silicide formation in thin-film systems and became one of the foundations of modern reactive-diffusion theory in microelectronics.

2.3. Nucleation in Sharp Concentration Gradients

An alternative but closely related approach emerged from considering the nucleation stage itself under conditions of strong concentration gradients. In contrast to classical nucleation theory, where the parent phase is assumed spatially homogeneous, reactive diffusion couples represent strongly non-equilibrium systems with continuously evolving chemical-potential gradients.

Within this framework, intermediate phases nucleate not in a uniform environment, but inside narrow diffusion zones where concentrations, fluxes, and local thermodynamic driving forces vary sharply with position, as shown in Fig. 3. As a result, the probability of nucleation becomes spatially selective and strongly coupled to mass transport.

The key insight was that a phase can remain absent not because its bulk free energy is unfavourable, but because the conditions required for the formation of a critical nucleus are not achieved within the evolving concentration profile. In this sense, suppression becomes a nucleation phenomenon rather than merely a growth phenomenon.

The very first (we now call it 'naïve') approach based on synergy of nucleation barriers and divergence of fluxes at the moving interfaces of emerging nuclei was initially suggested [11] the same year as approach of Ref. [9] and gave very similar growth/suppression criteria, except that initial thickness of any phase was taken as it's critical nucleus size except of zero (as in Ref. [9]). Kinetically, any phase could grow only after its critical nucleus was not kinetically suppressed by a neighbouring compe-

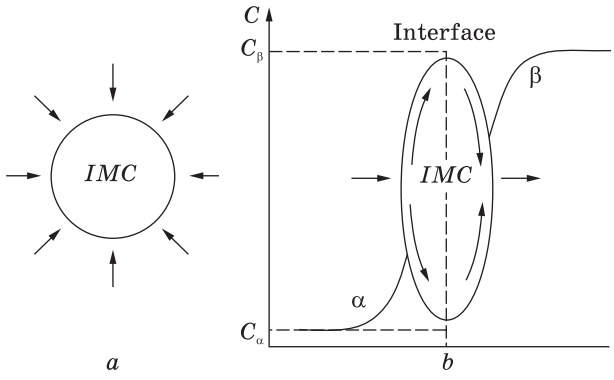

Fig. 3. (*a*, *b*) Difference between traditional nucleation and precipitation in the closed system (supersaturated solution) (*a*) and flux-driven nucleation in an open system at the moving interface under divergence of external fluxes and in the sharp concentration gradient (*b*)

ting phase. In the simplest case of one suppressed phase 2 and growing suppressing phase 1, the critical thickness of suppressing phase 1 beyond which phase 2 is allowed to grow is

$$\Delta X_1^{\text{threshold}} = \frac{D_1 \Delta C_1}{D_2 \Delta C_2} l_{\text{cr}}^{(2)} . \quad (4)$$

This approach naturally introduced the concept of:

• flux-driven nucleation — influence of external flux divergence on the kinetics and size distributions of nuclei; the idea can be described by a general equation for the number of atoms (or monomers) $n(t)$ in the emerging nucleus [20]:

$$(dn/dt)^{\text{open system}} = (dn/dt)^{\text{closed system}} - \text{div}(J^{\text{diffusion}}) \cdot \Omega \cdot n ; \quad (5)$$

• thermodynamic constraints of nucleation by the concentration gradient (for example, dependence of the nucleation barrier on the concentration gradient, including total thermodynamic suppression of nucleation by a sharp enough (over some threshold value) concentration gradient) [14–17]:

$$\Delta G(n) = -\alpha \cdot R^3 + \beta \cdot R^2 + \gamma \cdot (\nabla C)^2 \cdot R^5 \quad (6)$$

(in some cases, the order of the gradient term is 4 instead of 5 [18]), characteristic dependences $\Delta G(R)$ at various concentration gradients are shown in Fig. 4;

• metastable suppression of intermediate phases (case *b* in Fig. 4).

An especially important result was the realisation that diffusion fluxes themselves modify nucleation barriers and can even stabilise or destabilise particular phases depending on the local gradient structure.

The two approaches, namely, diffusion suppression of growing layers [8–10] and nucleation suppression in concentration gradients [11–15], were initially developed independently. However, they are now understood as complementary manifestations of the same open-system behaviour [16–18]: the competition between characteristic times of transport, interface reaction, and structural transformation.

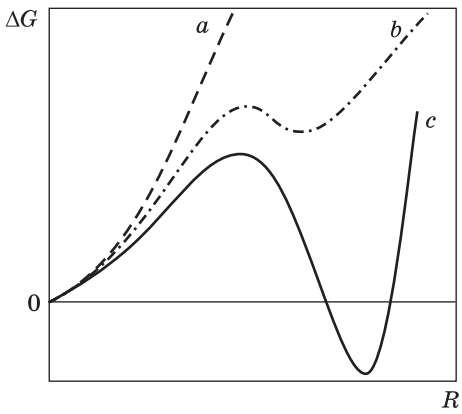

Fig. 4. Dependence of the Gibbs thermodynamic potential change on the size of a spherical nucleus in the concentration gradient field: (*a*) nucleation is for-bidden; (*b*) a metastable nucleus can be formed; and (*c*) nucleation is possible

2.4. Toward a Unified Open-System Description

From the viewpoint of non-equilibrium thermodynamics, both approaches describe the same fundamental phenomenon: phase selection in open systems driven by external fluxes.

In classical equilibrium thermodynamics, phase sequences are determined primarily by free-energy minimisation. In contrast, reactive diffusion systems continuously exchange matter through diffusion fluxes and therefore evolve under kinetic constraints that may temporarily override equilibrium preferences.

The resulting microstructure is governed by competition between several characteristic processes:

(1) diffusion through existing phases,
(2) interface attachment kinetics,
(3) nucleation of new phases,
(4) relaxation of stresses and defects.

As a consequence, transiently suppressed phases, metastable phases, or unusual morphologies may appear naturally during joining reactions in microelectronics. This open-system perspective later proved essential not only for silicide formation but also for understanding soldering reactions, flux-driven ripening, Kirkendall porosity, and eventually stress-assisted direct bonding.

3. Flux-Driven Morphology Evolution during Soldering

3.1. Why Soldering is Fundamentally Different from Classical Reactive Diffusion

Reactive diffusion during soldering differs fundamentally from classical solid-state phase growth [21, 22]. In conventional diffusion couples, intermediate phases typically form compact planar layers through which diffusion becomes progressively slower with time. In contrast, during wetting reactions between molten Sn-based solders and Cu, the dominant intermetallic compound Cu_6Sn_5 develops a highly non-planar scallop-type morphology protruding into the liquid solder. This morphology is not a secondary geometric feature but a direct consequence of the open character of the reacting system. The presence of the liquid phase continuously supplies reactants to the interface and prevents the establishment of closed diffusion geometry typical for solid-state reactions [20].

Experimentally (as shown in Fig. 5), the Cu_6Sn_5 scallops were found to grow larger but fewer with time, indicating simultaneous grain growth and interfacial reaction. Between neighbouring scallops, narrow liquid channels extend almost to the Cu substrate and provide rapid transport paths for Cu atoms dissolved into the molten solder. At the same time, the second intermetallic compound, Cu_3Sn, forms only as a thin intermediate

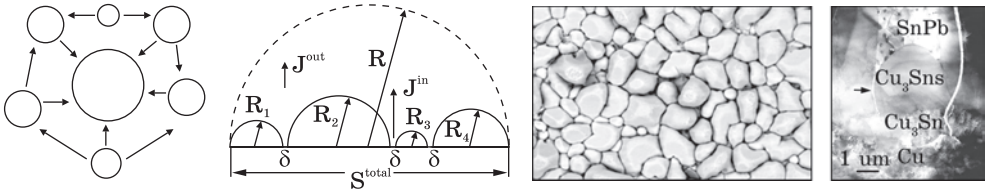

Fig. 5. (*a*) Traditional ripening in closed system — redistribution of the almost constant new phase volume; (*b*) scheme of flux-driven ripening — redistribution of incoming flux (or divergence of incoming minus outgoing fluxes) between scallops at the constant-area substrate; (*c*) plan-view; (*d*) liquid channel view. Figures *b*, *c*, and *d* were originally published by one of the authors in Ref. [25]

layer adjacent to Cu and contributes comparatively little to the mechanical formation of the solder joint itself. Instead, Cu_3Sn becomes important mainly during long-term ageing and reliability degradation because Kirkendall voiding preferentially develops near the Cu_3Sn/Cu interface.

Thus, the essential physics of soldering is governed primarily by the morphology, growth, and collective evolution of Cu_6Sn_5 scallops and the associated liquid-channel network.

3.2. Scallop Morphology and the Liquid-Channel Network

The existence of liquid channels between neighbouring Cu_6Sn_5 scallops is the key structural feature controlling the kinetics of soldering reactions.

These channels provide rapid pathways for:

(1) dissolution of Cu from the substrate,
(2) transport of Cu through molten solder,
(3) redistribution of matter between neighbouring scallops,
(4) and later grain coarsening and morphology evolution.

The channels effectively transform the reacting interface into a dynamically evolving transport network. As long as the channels remain open, Cu atoms can bypass slow diffusion through solid intermetallic compounds and reach the reaction front through the liquid phase. This explains why soldering reactions proceed surprisingly rapidly even at temperatures near 200 °C. The importance of the channels becomes especially evident from the morphology itself. If neighbouring scallops fully merged into a continuous compact layer, the liquid transport paths would disappear and the kinetics would become much slower, approaching ordinary diffusion-controlled layer growth.

Thus, scallop morphology is self-preserving in a kinetic sense: the persistence of channels sustains rapid transport, while rapid transport sustains scallop growth.

3.3. Coupled Growth and Ripening: from Coexistence to Synergy

The early kinetic treatment by Kim and Tu [23] (see also [24]) correctly recognized that scallop growth is accompanied by ripening phenomena. However, growth and ripening were initially treated largely as two parallel processes superimposed on each other. Subsequent analysis suggested a stronger coupling between them. The ripening process is not merely concurrent with growth; rather, both processes are kinetically interdependent. Ripening modifies the number and geometry of liquid channels between scallops. Since these channels control Cu supply to the interface, ripening directly influences the reaction rate. Conversely, the continued influx of Cu through the channels continuously feeds scallop growth and alters the ripening dynamics itself.

Therefore, growth and ripening form a feedback loop:

(1) growth changes morphology,
(2) morphology changes transport,
(3) transport changes ripening,
(4) ripening changes morphology again.

The reacting interface thus behaves as a self-organising open system.

3.4. Flux-Driven Ripening as a Transformation in an Open System

Classical Lifshitz–Slyozov–Wagner (LSW) ripening describes coarsening in closed systems, where the total volume of the growing phase remains constant while the total interfacial area decreases [25–29]. In contrast, soldering reactions represent an open system supplied continuously by external atomic fluxes from the Cu substrate. Under these conditions, the

Table 1. **Comparison of classical ripening and flux-driven ripening [25]**

LSW	FDR
Closed system	Flux-driven system
Constant volume, decreasing surface	Constant surface, increasing volume
Driving force — reduction of surface energy	Driving force — gain of bulk free energy
One constraint (almost constant total volume)	Two constraints (almost constant total surface area, total volume growth rate proportional to influx)
The number of grains decreases as t^{-1}	The number of grains decreases as $t^{-2/3}$
$\langle R\rangle^3 = k^{\mathrm{LSW}}t$, the rate constant k^{LSW} is proportional	$\langle R^3\rangle = kt$, the rate constant k is independent of surface tension
to surface tension $k^{\mathrm{LSW}} = \frac{4}{9}\frac{n}{n_i}\frac{D\alpha}{C_i}$	$\langle R\rangle^3 = (0.913)^3\, kt, k = \frac{9}{2}\frac{n}{n_i}\frac{D(C^b - C^e)\delta}{C_i}$

total volume of Cu_6Sn_5 scallops increases with time while the total interfacial area between scallops and solder remains approximately constant.

This unusual constraint leads to a fundamentally different ripening regime termed flux-driven ripening (FDR). The essential geometric constraint can be written schematically as $S_{total} \approx \text{const}$ while the total volume continues to increase $V(t)\uparrow$. As a result, the mean scallop radius follows approximately the time law $t^{1/3}$ despite the fundamentally different physical mechanism compared with classical LSW coarsening. The driving force is no longer the reduction of total surface energy alone. Instead, capillarity-driven redistribution acts together with a continuous external supply of Cu through liquid channels.

Comparison of LSW and FDR is summarised in Table 1.

3.5. Grain Agglomerates, Wetting Transitions, and Ultrafast Grain Growth

An important unresolved question concerns the topology of the liquid-channel network and its relation to crystallographic correlations between neighbouring scallops. Experimental observations suggest that not all interfaces between neighbouring Cu_6Sn_5 grains are equally wetted by liquid solder. High-angle boundaries appear more likely to remain wetted, whereas low-angle or crystallographically correlated boundaries may become effectively dry. This raises the possibility that neighbouring scallops nucleated on the same Cu grain inherit related crystallographic orientations and therefore form low-energy interfaces between each other. Such grains may evolve into agglomerates separated from other agglomerates by wetted liquid channels. Within this picture, the reacting interface does not consist of independent scallops, but consists of dynamically evolving grain clusters connected by selective liquid pathways.

Recent observations in microbump solder joints revealed extremely rapid grain growth when opposing scallops come into contact across thin solder layers [27]. The proposed explanation involves liquid-channel wetting of grain boundaries and extremely fast atomic transport across nanometer-scale liquid interlayers. The estimated channel widths are remarkably small, of the order of 1–2 nm.

3.6. Cu_3Sn as a Parasitic Reliability Phase

From the viewpoint of joint formation, Cu_3Sn plays a comparatively secondary role. The mechanical and metallurgical joining during soldering is achieved primarily through the formation of Cu_6Sn_5. However, during long-term ageing and operation, Cu_3Sn becomes increasingly important because it is closely associated with Kirkendall void formation near the Cu/Cu_3Sn interface. The dominant diffusion of Cu through Cu_3Sn generates vacancy fluxes toward the Cu side, where vacancies may condense into pores if not efficiently absorbed by defect sinks.

Thus, the same flux-driven mechanisms that initially enable rapid joining later contribute to the degradation and failure of the interconnection. This transition from beneficial flux-assisted joining to destructive flux-induced instability represents one of the central paradoxes of microelectronic packaging physics.

4. Flux-Driven Porosity Formation and Reliability Degradation

4.1. Vacancy Fluxes and the Origin of Porosity in Cu–Sn Interconnects

Porosity formation is one of the major reliability problems in Cu–Sn interconnects because pores strongly facilitate crack initiation and propagation along brittle intermetallic interfaces. Although porosity in solder joints is often discussed as a single phenomenon, experimentally observed void structures can be divided into two fundamentally different classes [32–39].

The first class corresponds to classical Kirkendall (or Frenkel) voiding associated with vacancy supersaturation generated by unequal atomic fluxes during interdiffusion. These pores form predominantly near the Cu_3Sn/Cu interface during solid-state ageing.

The second class corresponds to porous interconnected structures formed during complete consumption of solder in microbump or SLID systems. In this case, porosity emerges not merely as isolated vacancy condensates but as a self-organised percolating network accompanying phase transformation itself, as shown in Fig. 6.

The distinction between these two regimes is important because they differ not only morphologically but also kinetically and conceptually.

4.2. Classical Kirkendall Voiding at the Cu_3Sn/Cu Interface

In Cu–Sn interconnects, Kirkendall voiding develops primarily near the Cu/Cu_3Sn interface because Cu diffuses through Cu_3Sn substantially faster

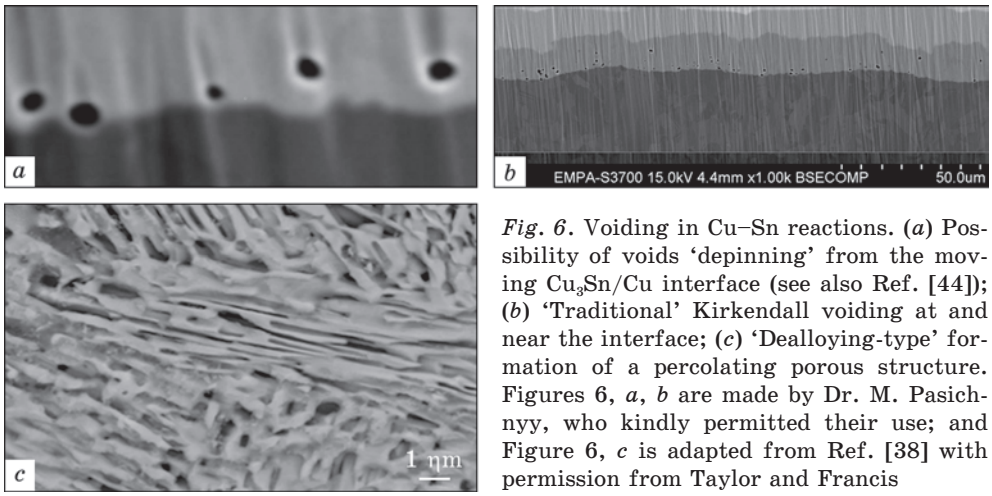

Fig. 6. Voiding in Cu–Sn reactions. (*a*) Possibility of voids 'depinning' from the moving Cu_3Sn/Cu interface (see also Ref. [44]); (*b*) 'Traditional' Kirkendall voiding at and near the interface; (*c*) 'Dealloying-type' formation of a percolating porous structure. Figures 6, *a*, *b* are made by Dr. M. Pasichnyy, who kindly permitted their use; and Figure 6, *c* is adapted from Ref. [38] with permission from Taylor and Francis

than Sn. This imbalance generates a net vacancy flux toward the Cu side:

$$J_{\mathrm{v}} = J_{\mathrm{Cu}} - J_{\mathrm{Sn}} . \quad (7)$$

If vacancy sinks are insufficient to absorb the incoming excess vacancies, vacancies condense into pores. Historically, Soviet literature often referred to this process as the Frenkel effect, whereas Western literature adopted the term Kirkendall voiding. In reality, both describe different manifestations of the same underlying vacancy imbalance phenomenon. The resulting pores frequently remain attached to the moving Cu/Cu_3Sn interface, producing chains of interfacial voids that strongly weaken mechanical reliability.

4.3. Competition of Vacancy Sinks: Kirkendall Shift vs. Frenkel Voiding

Vacancy supersaturation can relax through two competing mechanisms. The first mechanism involves annihilation of vacancies at dislocations, grain boundaries, and other extended defects (*K*-sinks in the terminology of Geguzin). This pathway produces a lattice shift and manifests itself as the classical Kirkendall effect. The second mechanism involves condensation of vacancies into pores (F-sinks), producing Frenkel voiding.

Thus, Kirkendall shift and Kirkendall voiding should not be viewed as unrelated phenomena. They are competing relaxation pathways for the same vacancy flux. This competition explains why porosity is highly sensitive to the defect structure of copper.

4.4. Flux-Driven Cellular Decomposition and Porous Cu_3Sn Formation

A qualitatively different type of porosity formation was later observed in small SLID and microbump interconnects after complete consumption of the solder phase. Instead of isolated Kirkendall voids near a planar interface, a sponge-like interconnected porous structure formed throughout the transforming Cu_6Sn_5 region. Experimentally, the porous region propagated from the periphery toward the centre of the joint while the remaining Cu_6Sn_5 continuously disappeared, as shown in Fig. 7.

This phenomenon resembles dealloying, but differs fundamentally from classical dealloying because the driving force is not selective dissolution into an electrolyte. Instead, Sn atoms are continuously withdrawn from Cu_6Sn_5 through a dynamically formed percolating network of internal pore surfaces.

The transformation can be represented schematically as

$$Cu_6Sn_5 - 3Sn \rightarrow 2Cu_3Sn + \text{voids} , \quad (8)$$

where the outflow of Sn simultaneously produces:

(1) vacancy supersaturation,
(2) Cu supersaturation in the remaining phase,
(3) formation of Cu_3Sn,
(4) and growth of pores.

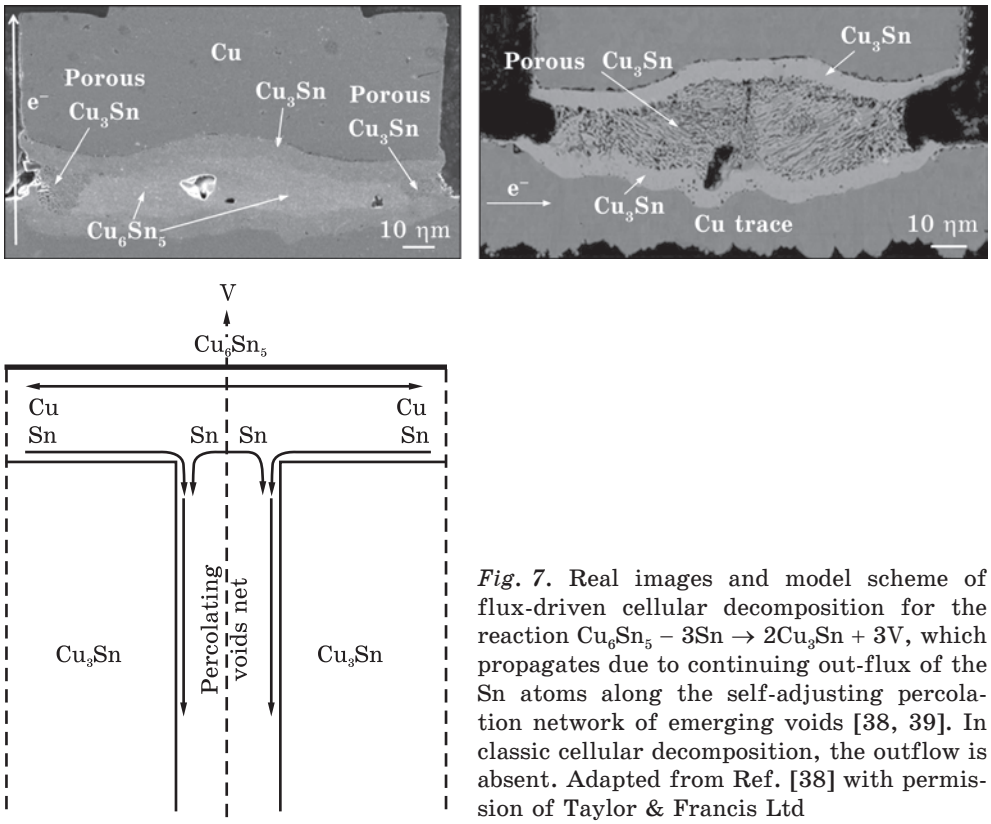

Fig. 7. Real images and model scheme of flux-driven cellular decomposition for the reaction $Cu_6Sn_5 - 3Sn \rightarrow 2Cu_3Sn + 3V$, which propagates due to continuing out-flux of the Sn atoms along the self-adjusting percolation network of emerging voids [38, 39]. In classic cellular decomposition, the outflow is absent. Adapted from Ref. [38] with permission of Taylor & Francis Ltd

Thus, porosity here is not a secondary defect but one of the transformation products itself. For this reason, the process was interpreted as flux-driven cellular decomposition in an open system.

The process combines features of:

(1) cellular precipitation,
(2) eutectoid decomposition,
(3) dealloying,
(4) and Kirkendall instability.

Yet this process differs from all of them because the transformation is sustained by continuous external fluxes through an open transport network.

4.5. Generalisation to Other Open-System Transformations: Amorphous Ni–P

The concept of flux-driven decomposition is not limited to Cu–Sn systems. A closely related transformation was later observed during the reaction of amorphous Ni–P coatings with Sn-containing solder. In this case, outflow of Ni toward the solder interface induced simultaneous crystallisation of

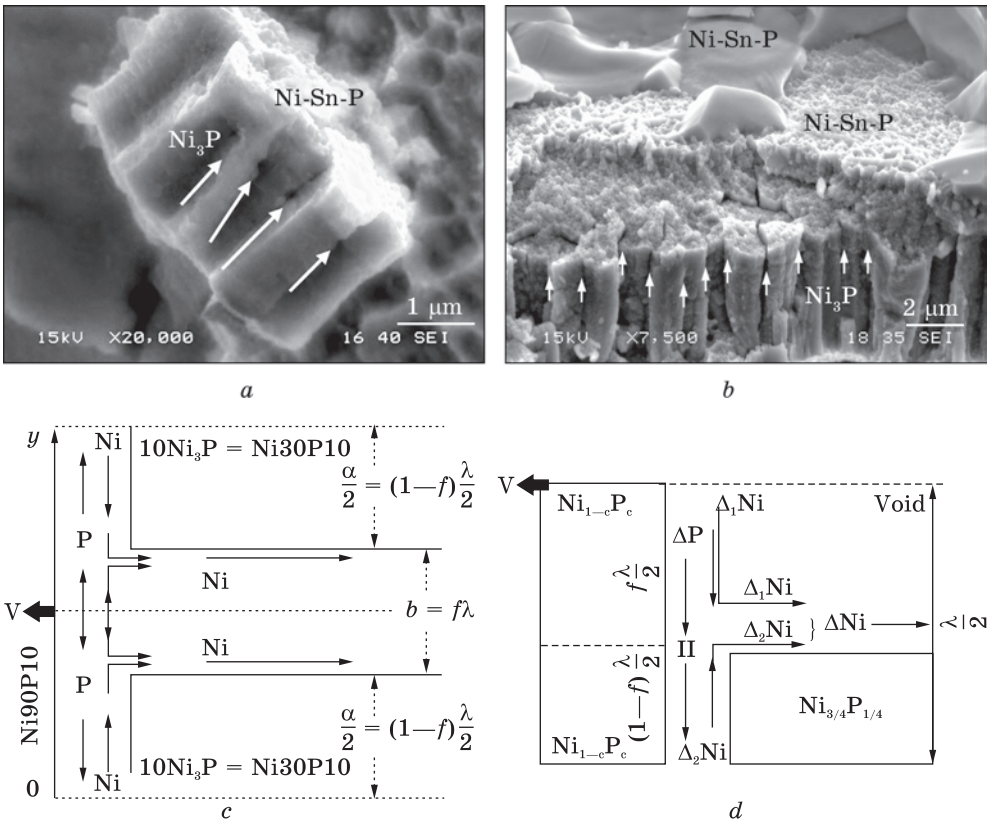

Fig. 8. Flux-driven crystallisation of amorphous Ni–P with simultaneous flux-driven decomposition into Ni_3P plus voids at and near the interface. Reproduced from Ref. [42] with permission from Elsevier

amorphous Ni–P into crystalline Ni_3P together with pore formation, as shown in Fig. 8.

Again, the transformation was driven not by spontaneous instability of the parent phase itself, but by externally sustained atomic fluxes associated with the interfacial reaction. These observations suggest that flux-driven transformations in open systems may represent a broader class of non-equilibrium phase-evolution phenomena.

4.6. Controlling Void Formation through Microstructure Engineering

Since vacancy relaxation strongly depends on the availability of sinks, substantial effort has been devoted to controlling porosity through engineering of Cu microstructure. A natural idea is to increase the density of vacancy sinks by increasing dislocation density or grain-boundary density in Cu. However, this approach leads to competing effects. Additional defects may indeed increase vacancy absorption, but simultaneously increase

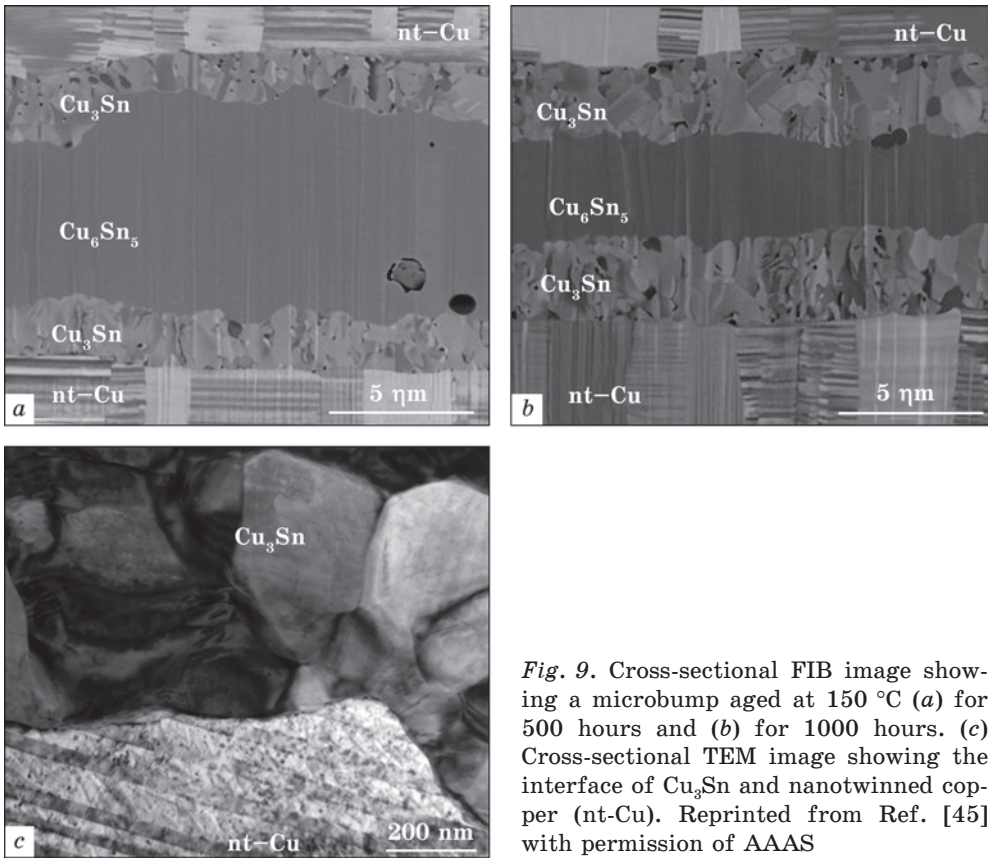

Fig. 9. Cross-sectional FIB image showing a microbump aged at 150 °C (*a*) for 500 hours and (*b*) for 1000 hours. (*c*) Cross-sectional TEM image showing the interface of Cu_3Sn and nanotwinned copper (nt-Cu). Reprinted from Ref. [45] with permission of AAAS

the density of heterogeneous pore nucleation sites, especially grain-boundary triple junctions. Experiments with differently pre-treated Cu substrates demonstrated that increased defect density does not necessarily suppress porosity and may instead redistribute pore nucleation spatially [43, 44].

A much more successful approach employed highly (111)-oriented nanotwinned Cu. The dense network of nanotwins' boundaries acted as highly efficient vacancy sinks and dramatically reduced Kirkendall voiding during Cu–Sn reactions [45], as shown in Fig. 9. The effectiveness of nanotwinned Cu may originate not only from ideal coherent twin boundaries themselves, but also from associated imperfect defects and junctions acting as additional vacancy sinks.

4.7. Pinning, Depinning, and Spatial Redistribution of Voids

For mechanical reliability, not only the total porosity but also its spatial distribution is critically important. Voids remaining attached to the moving Cu/Cu_3Sn interface are especially dangerous because interfacial pores

strongly facilitate crack propagation. In contrast, pores detached into the bulk of the intermetallic layer are generally less detrimental. Therefore, the problem of void pinning at moving interfaces becomes central.

Traditionally, pinning has been discussed in terms of capillary (Zener-type) interactions between pores and moving interfaces. However, reactive diffusion systems may also exhibit kinetic pinning associated with vacancy concentration gradients near non-ideal vacancy sinks. In this picture, vacancy fluxes themselves generate effective forces tending to keep ('pin') voids near moving interfaces.

The competition between capillary pinning, kinetic pinning, and depinning determines whether porosity remains localised at dangerous interfacial regions or redistributes into the bulk of the growing phase. Overall, porosity formation in reactive interconnect systems appears not as a secondary imperfection but as an intrinsic manifestation of flux-driven instability in open systems.

Depending on the topology of transport paths, vacancy relaxation mechanisms, and availability of sinks, the system may evolve toward:

(1) isolated Kirkendall voids,
(2) interfacial pore chains,
(3) or fully percolating porous structures.

Thus, reliability degradation emerges as a natural continuation of the same flux-driven processes that initially enable rapid joining.

5. Direct Metal Bonding as Inverse Porosity Evolution

5.1. Direct Bonding versus Reactive Soldering

Direct Cu–Cu bonding represents an alternative route toward ultrafine-pitch interconnect formation without intermediate solder layers [46–49]. From a physical viewpoint, direct bonding differs fundamentally from reactive soldering discussed in previous sections. In reactive soldering systems, diffusion fluxes tend to generate porosity through vacancy supersaturation, Kirkendall imbalance, or flux-driven decomposition. In contrast, direct bonding starts from an initially disconnected system containing substantial interfacial free volume associated with surface roughness and incomplete contact.

The bonding process therefore requires elimination of this free volume through diffusion-mediated mass transport and progressive formation of metallic continuity across the interface. Thus, direct bonding can be viewed as an inverse problem of porosity evolution.

5.2. Surface Creep and Stress-Driven Elimination of Interfacial Free Volume

Under thermal compression, the initial contact between two rough Cu surfaces occurs only at isolated asperities. The remaining interface forms a connected network of nanoscale void space. External pressure generates

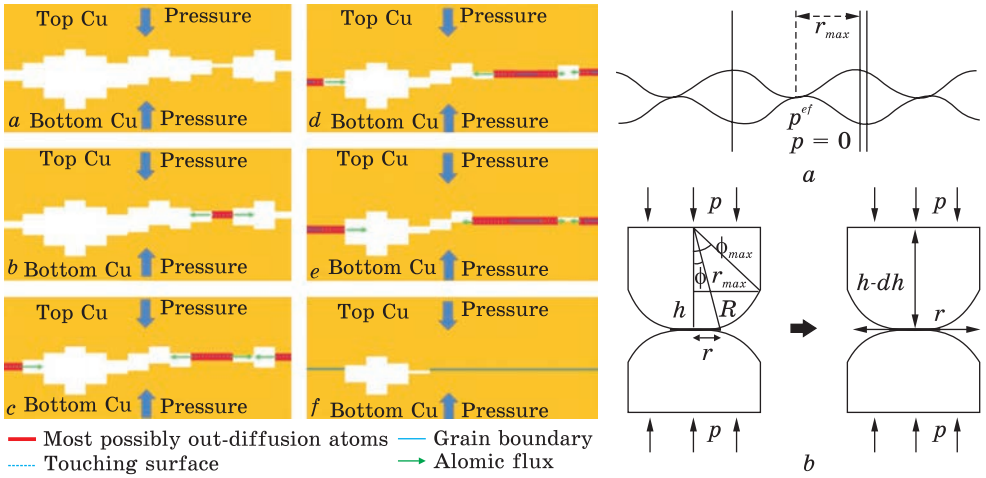

Fig. 10. (Left) Illustration of the bonding mechanism. Since the surface roughness is at the order of nanometers, the steps can be represented as atomic layers. (*a*) Before the contact of two Cu surfaces. (*b*) Once the hill of the surface is touching, the layers of atoms at that touching point or surface will be squeezed out by surface diffusion, and (*c*) the touching area expands continuously. (*d*) Some touching surfaces change into a grain boundary, and grain boundary diffusion joins the bonding mechanism. (*e*) More and more surface becomes a grain boundary. (*f*) Pressure-induced bonding stops, and most of the contact area converts into a grain boundary. (Right) direct bonding as a surface creep [49]

strong stress gradients near contact regions, producing diffusion fluxes directed away from compressed asperities toward adjacent free surfaces. The resulting atomic transport progressively fills interfacial gaps and increases bonded area, as shown in Fig. 10.

The driving force can be represented schematically as

$$J = \frac{D}{kT}\nabla\sigma, \tag{9}$$

where the stress gradient drives surface and grain-boundary diffusion.

In this picture, bonding proceeds through a surface-creep-like mechanism in which atoms are effectively squeezed from highly stressed contact regions into neighbouring void space. The thermodynamic driving force of bonding contains two coupled contributions. The first contribution is associated with the reduction of the free volume between contacting surfaces under external pressure:

$$\Delta G_{\mathrm{p}} = p\Delta V. \tag{10}$$

The second contribution originates from the replacement of two free surfaces by a grain boundary:

$$\Delta G_{\gamma} = (\gamma_{\mathrm{GB}} - 2\gamma_{\mathrm{S}}) \cdot \Delta A. \tag{11}$$

Since grain-boundary energy is typically smaller than the energy of two free surfaces, grain-boundary formation further stabilises bonded regions.

In contrast to Kirkendall voiding discussed previously, vacancies here are not generated by flux imbalance. Instead, the dominant process is redistribution and elimination of pre-existing free volume.

Consequently, the interface evolves from:

(1) isolated contact points,

(2) to interconnected bonded regions with isolated voids,

(3) and eventually toward complete elimination of the interface by grain growth.

5.3. Evolution and Ripening of Residual Interfacial Voids

Even after substantial bonding is achieved, nanoscale interfacial voids frequently remain trapped near the original bonding interface. Their subsequent evolution is governed by diffusion-driven ripening analogous to classical Ostwald ripening, although constrained by the quasi-two-dimensional geometry of the bonding interface. TEM observations revealed a systematic increase of average void size accompanied by a decrease in void number during annealing, as shown in Fig. 11. This behaviour indicates coarsening through vacancy exchange mediated predominantly by grain-boundary diffusion at early stages.

5.4. Competition between Grain-Boundary Diffusion and Lattice Diffusion

A particularly important transition occurs when grain growth starts to eliminate the original bonding interface. Before interfacial elimination, residual voids remain connected to fast grain-boundary diffusion paths, enabling rapid ripening kinetics.

After grain growth crosses the interface, however, the dominant transport path changes from grain-boundary diffusion to much slower lattice diffusion. As a consequence, void coarsening slows dramatically once the original interface disappears.

5.5. Nanotwinned Copper and Low-Temperature Bonding

Highly (111)-oriented nanotwinned Cu plays a special role in both reactive soldering and direct bonding technologies. In soldering systems, nanotwins' boundaries act as efficient vacancy sinks and suppress Kirkendall voiding. In direct bonding systems, the same microstructure promotes rapid bonding due to the exceptionally high diffusivity of Cu (111) surfaces.

Thus, nanotwinned Cu simultaneously:

(1) suppresses harmful porosity formation,

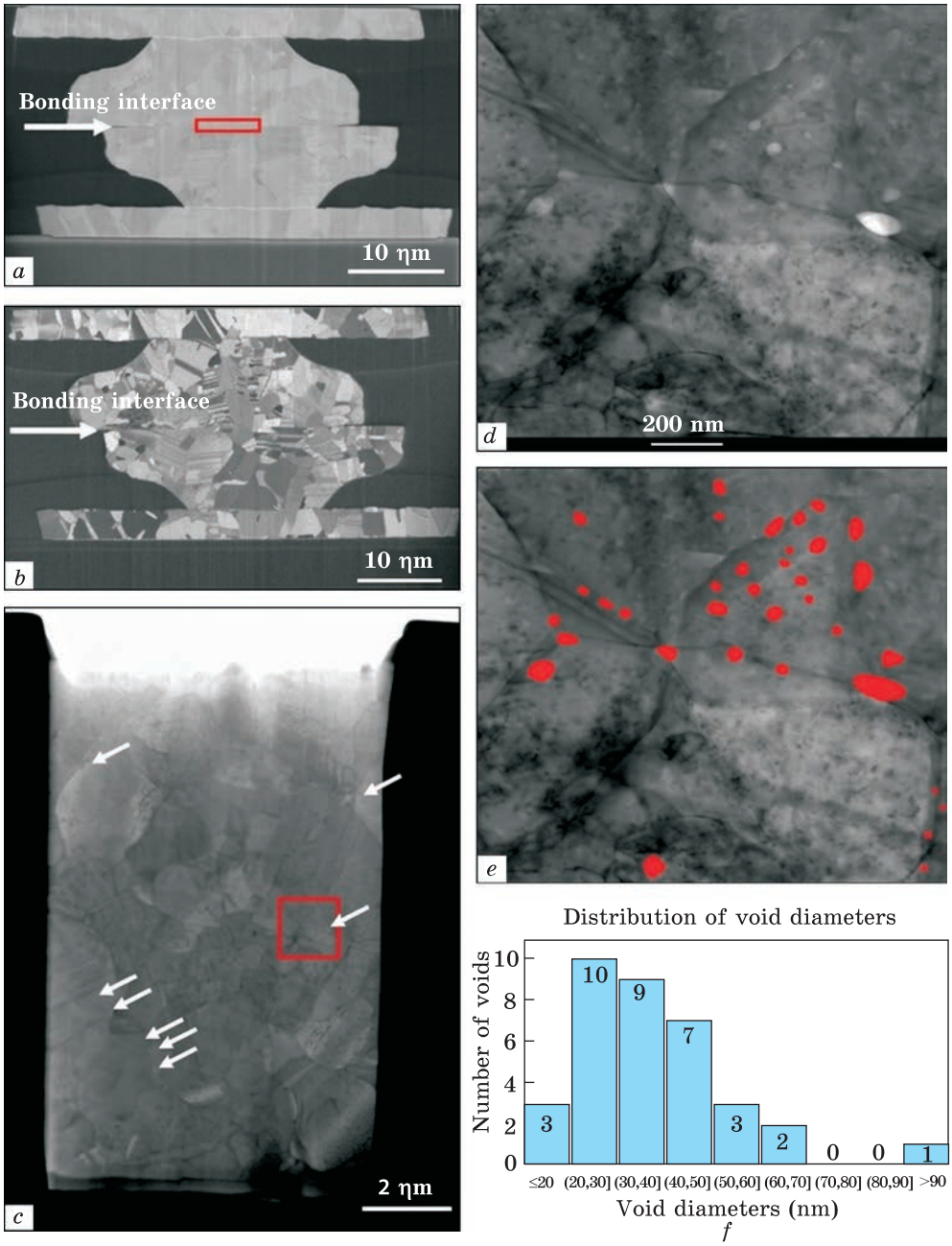

Fig. 11. Morphology of direct bonding of the nanotwinned copper. The bonding condition was. (*a*) Electron and (*b*) ion images of the cross-section of Cu microbump. (*c*) The TEM sample of the bonding interface, which was cut at the red rectangle of (*a*). White arrows point out voids in the bonding interface. (*d*) The enlarged image of the red square in *c*. (*e*) Voids in image (*d*) are emphasised by red marks. (*f*) Distribution of void diameters in image *d*. Figure 11 was originally published by two of the current authors in Ref. [49]

Table 2. **Flux-driven morphology evolution**

Soldering	Bonding
pore-network formation connected liquid channels emergence of connectivity	pore-network elimination disconnected residual pores destruction of connectivity

(2) and accelerates porosity elimination during bonding.

This dual functionality makes nanotwinned Cu particularly attractive for next-generation ultrafine-pitch interconnect technologies.

Reactive soldering and direct bonding represent two opposite directions of evolution of free-volume topology, as shown in Table 2.

In soldering:

disconnected free volume → connected porous network.

In bonding:

connected free volume → isolated pores → disappearance.

From this viewpoint, reactive soldering and direct bonding may be regarded as two opposite classes of non-equilibrium morphological evolution driven by diffusion fluxes: one generates free-volume connectivity, whereas the other progressively destroys it.

6. From Joining to Failure: Flux-Driven Degradation and Statistical Kinetics

6.1. Reliability as Continuation of Joining Kinetics

The previous sections considered various joining phenomena in microelectronic systems from the viewpoint of flux-driven evolution in open systems [50, 51]. However, the same diffusion fluxes that initially enable phase formation, soldering, porosity evolution, and direct bonding eventually continue to operate during service conditions and gradually transform the joined structure itself. From this viewpoint, reliability degradation is not a fundamentally separate phenomenon but rather a continuation of the same non-equilibrium evolution at later stages.

Electromigration, thermomigration, stress migration, interfacial voiding, and diffusion-driven coarsening all involve sustained atomic fluxes, defect redistribution, and progressive accumulation of structural damage. The distinction between joining and degradation is therefore not qualitative but kinetic and temporal:

(1) joining initially creates functional connectivity,

(2) whereas prolonged flux-driven evolution progressively destroys it.

Thus, joining and failure may be regarded as two complementary stages of the same open-system dynamics.

6.2. Weibull's Statistics and Avrami-Type Transformation Kinetics

A striking empirical feature of reliability phenomena in microelectronics is the frequent appearance of Weibull-type time-to-failure distributions in electromigration, thermomigration, and stress-induced degradation processes.

The cumulative probability of failure is commonly represented as

$$F(t) = 1 - e^{-(t/\tau)^m}, \tag{12}$$

where m is the Weibull exponent and τ is the characteristic lifetime.

Remarkably, this mathematical form is identical to the classical Kolmogorov–Avrami expression describing phase transformation kinetics:

$$X(t) = 1 - e^{-Kt^n}, \tag{13}$$

where $X(t)$ is the transformed fraction.

This similarity may be more than purely formal [52–55].

In classical Avrami kinetics, transformation proceeds through:

(1) nucleation of new regions,

(2) growth of transformed domains,

(3) and overlap (impingement) between them.

A closely analogous picture emerges naturally in degradation phenomena:

(1) local defects or voids nucleate,

(2) damage regions grow under sustained fluxes,

(3) and eventually coalesce into a critical failure path.

Thus, failure probability may be interpreted as the transformed fraction of a progressively damaged structure.

6.3. Failure as Collective Evolution of Damage

Within this interpretation, degradation becomes a collective transformation process driven by externally sustained fluxes of atoms, vacancies, stresses, or electric momentum transfer. The analogy between transformation kinetics and reliability can be summarised schematically in Table 3. In this picture, a microelectronic structure does not fail instantaneously at a single critical event. Instead, it gradually evolves toward failure through progressive accumulation and spatial organisation of defects. The Weibull exponent therefore acquires a possible physical meaning beyond empirical fitting. Similar to the Avrami exponent, it may reflect:

Table 3. **Comparison of Kolmogorov–Avrami transformation and failure evolution**

Transformation kinetics	Reliability evolution
nucleus	defect cluster/void
phase growth	damage accumulation
impingement	coalescence of defects
transformed fraction	failed fraction

(1) dimensionality of damage spreading,
(2) kinetics of defect generation,
(3) interaction between growing damage regions,
(4) and coupling between transport and stress evolution.

6.4. Entropy Production and Critical Degradation

From the viewpoint of non-equilibrium thermodynamics, sustained diffusion and electromigration fluxes continuously produce entropy through irreversible dissipation processes.

The local entropy production rate $\dot{S}$ (non-divergent part of the entropy time derivative $\partial S/\partial t$) may be written schematically as

$$T \cdot \dot{S} \propto J \cdot \nabla\mu\,, \tag{14}$$

where J denotes the relevant atomic or defect flux and $\nabla\mu$ the corresponding chemical-potential gradient.

Accumulation of structural damage may therefore be associated with cumulative irreversible evolution of the system [56–61]. In this interpretation, failure occurs when the evolving defect structure reaches a critical state characterised by:
(1) critical void connectivity,
(2) critical crack length,
(3) critical defect density,
(4) or critical accumulated dissipation.

This viewpoint is consistent with thermodynamic approaches, in which mean time to failure is related to entropy production during electromigration, thermomigration, or stress migration. Importantly, the concept of 'critical entropy' should not be interpreted as an abstract universal scalar quantity, but rather as a shorthand description of irreversible structural evolution driven by sustained fluxes.

6.5. Joining and Failure as Complementary Open-System Processes

The examples discussed throughout the present review suggest that many seemingly different phenomena in microelectronic joining systems may be interpreted within a unified open-system framework.

Reactive diffusion, silicide formation, soldering, porosity evolution, direct bonding, and reliability degradation all involve:
(1) externally sustained fluxes,
(2) moving interfaces,
(3) evolving free-volume topology,
(4) and competition between transport, reaction, and structural relaxation.

Within this perspective:
(1) soldering creates interconnected transport pathways,

(2) porosity evolution reorganises free volume,
(3) direct bonding progressively eliminates free volume,
(4) and failure corresponds to the emergence of critical damage connectivity.

Thus, joining and degradation appear not as unrelated technological stages, but as complementary manifestations of flux-driven structural evolution in open systems. In closed systems, thermodynamic equilibrium tends to suppress further evolution. In contrast, microelectronic interconnect systems often remain permanently open under thermal, electrical, mechanical, or chemical driving forces. Their structures therefore continue evolving long after fabrication itself is completed. Understanding joining, therefore, ultimately requires understanding failure as well.

7. Conclusions

Microelectronic joining technologies involve a broad spectrum of physical phenomena, including reactive diffusion, phase formation, soldering, porosity evolution, direct bonding, and long-term reliability degradation. Although these processes are often studied separately, the examples discussed in this review suggest that many of them can be interpreted within a unified framework of flux-driven evolution in open systems.

In reactive diffusion systems, phase selection is controlled not only by equilibrium thermodynamics but also by transport constraints, nucleation conditions, and flux-balance requirements at moving interfaces. Sequential silicide formation, suppression of competing phases, and nucleation under sharp concentration gradients represent different manifestations of the same non-equilibrium kinetic competition.

During soldering, the presence of liquid transport channels transforms the reacting interface into a dynamically evolving transport network. Under these conditions, morphology evolution, scallop coarsening, and flux-driven ripening become strongly coupled processes. The same sustained diffusion fluxes that initially facilitate rapid joining may later generate vacancy supersaturation, Kirkendall voiding, and porous intermetallic structures.

Direct metal bonding represents, in many respects, the inverse problem. Instead of generating free-volume connectivity, the system progressively eliminates interfacial free volume through stress-assisted diffusion and surface creep. From this viewpoint, reactive soldering and direct bonding may be regarded as two complementary directions of non-equilibrium topological evolution.

The analysis further suggests that reliability degradation should not be viewed as a phenomenon fundamentally separate from joining itself. Electromigration, thermomigration, void coalescence, and damage accumulation continue the same flux-driven structural evolution at later stag-

es of the system lifetime. In this sense, joining and failure represent complementary manifestations of persistent non-equilibrium dynamics in constrained open systems.

The open-system perspective discussed here does not replace detailed kinetic or atomistic models developed for particular technologies. Rather, it provides a broader conceptual framework linking transport, reaction, morphology evolution, and mechanics across different classes of interconnect systems. Such a unified viewpoint may become increasingly important as modern microelectronics continues toward smaller dimensions, higher current densities, and more complex three-dimensional architectures.

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Authors' Contributions. A.M. Gusak: conceptualisation, methodology, writing original draft. S.O. Abakumov: software, numerical simulations, visualisation. Ch. Chen: experimental background, methodology, writing final draft, funding acquisition.

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С.О. Абакумов[1], *Ч. Чен*[2], *А.М. Гусак*[1,3]
[1] Черкаський національний університет імені Богдана Хмельницького,
бульв. Шевченка 81, 18031 Черкаси, Україна
[2] Національний університет Ян Мін Чяо Тун,
No. 1001, Daxue Rd., East Dist., Hsinchu City 300093, Тайвань
[3] Центр досконалості ENSEMBLE3,
Wolczyńska 133, 01-919 Варшава, Польща

З'ЄДНАННЯ В МІКРОЕЛЕКТРОНІЦІ ЯК ПРОБЛЕМА ВІДКРИТИХ СИСТЕМ: ВІД СИЛІЦИДІВ ДО ПРЯМОГО ЗВ'ЯЗКУ

Процеси з'єднання в мікроелектроніці традиційно аналізуються в межах окремих технологічних підходів, що охоплюють утворення силіцидів, лютування, ріст інтерметалевих фаз, пряме прикріплення та деградацію надійності. В огляді показано, що ці, на перший погляд, різнорідні явища можуть бути описані в межах єдиного фізичного підходу як керовані потоком перетворення у відкритих системах за наявності геометричних і механічних обмежень. Розглянуто ключові результати теорії реакційної дифузії, важливі для мікроелектроніки, зокрема послідовне фазоутворення в силіцидах, зародження та ріст у різких концентраційних градієнтах, потоково-кероване укрупнення зерен під час лютування, еволюцію пористості та пряме металеве прикріплення. Особливу увагу приділено ролі топології шляхів масоперенесення, конкуренції між характерними кінетичними процесами та взаємозв'язку між дифузією, реакцією й еволюцією дефектів. Реакційне лютування та пряме прикріплення інтерпретовано як два протилежні типи нерівноважної топологічної еволюції. У системах лютування зовнішні потоки речовини можуть спричинити формування зв'язаних пористих структур і потоково-керованих нестійкостей, тоді як у разі прямого прикріплення ті самі дифузійні механізми поступово усувають вільний міжфазний об'єм і формують неперервний перехід між металами. В огляді підкреслено, що процеси з'єднання в мікроелектроніці визначаються не лише рівноважною термодинамікою, а й кінетичними обмеженнями, пов'язаними із зовнішніми потоками, нестаціонарними мережами масоперенесення та механічними полями. Ця перспектива забезпечує спільну концептуальну мову для розуміння фазової вибірковості, еволюції морфології, сполучення та відмов у сучасних технологіях мікроелектронних з'єднань.

Ключові слова: дифузія, з'єднання, реакції, лютування, змочування, пряме прикріплення, вибірковість фаз, зародження, комірковий розпад, потоково-керована коалесценція, пороутворення, надійність.