



Step bunching during the epitaxial growth of a generic binary-compound thin film

Paolo Cermelli^a, Michel E. Jabbour^{b,*}

^a Dipartimento di Matematica, Università di Torino, Via Carlo Alberto 10, 10123 Torino, Italy

^b Department of Mathematics, University of Kentucky, Lexington, KY 40506, USA

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ABSTRACT

A discrete-continuum theory for the step-flow growth by chemical beam or metalorganic vapor-phase epitaxy of a generic binary-compound thin film is developed from basic considerations of continuum physics in accordance with the second law of thermodynamics. Our theory accounts for dissipation, chemical and otherwise; allows for departures from equilibrium; and generalizes the classical, variationally derived Gibbs–Thomson relation along the steps. In contrast to existing models, the diffusing species are coupled through a chemical reaction whereby bulk molecules are crystallized from adatoms attaching to the step edges. The linear stability analysis of the resulting free-boundary problem for a periodic train of rectilinear steps yields pairing in the presence of the normal Ehrlich–Schwoebel barrier for both species, counter to the predictions of standard Burton–Cabrera–Frank models for single-species growth. In particular, we show that the onset of step bunching occurs as long as the adatom equilibrium coverage of either species is sufficiently high, a condition met, e.g., during the epitaxy of gallium arsenide. The physical origin of this instability is to be found in the dependence of the step chemical potential on the jump in the adatom grand canonical potential, a term that couples adjacent terraces and—counter to elastic, entropic, or electrostatic interactions between steps—is attractive.

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1. Introduction

At sufficiently high temperatures, but below the roughening temperature, crystal growth on a vicinal surface proceeds by step flow, i.e., the lateral migration of pre-existing steps upon attachment–detachment of highly mobile diffusing adatoms. Interestingly, step flow is typically accompanied by one- or two-dimensional instabilities, with recent experiments confirming their coexistence, cf. Néel *et al.* (2003) as well as the discussion below. The former (step bunching) refers to the segregation of a train of initially equidistant rectilinear steps into regions of high step density separated by wide terraces, whereas the latter (step meandering) denotes the formation and evolution of in-phase wavy steps.¹

Attachment kinetics along step edges is asymmetric in the sense that an adatom attaching to a descending step has to overcome an energy barrier higher than that which characterizes ordinary diffusion; this is the so-called Ehrlich–Schwoebel (ES) effect, cf. Schwoebel and Shipsey (1966a) and Ehrlich and Hudda (1966). The validity of the ES barrier is

* Corresponding author.

E-mail addresses: paolo.cermelli@unito.it (P. Cermelli), jabbour@ms.uky.edu (M.E. Jabbour).

¹ For an overview of crystal growth in general and step dynamics on vicinal surfaces in particular, see Saito (1996), Pimpinelli and Villain (1998), Jeōng and Williams (1999), Michely and Krug (2004), and Krug (2005).

well accepted for metallic vicinal surfaces, cf. Krug (2005) and the references therein. By contrast, recent experiments indicate that an inverse Ehrlich–Schwoebel (iES) barrier—favoring adatom attachment to descending steps—is operative on semiconductor vicinal surfaces such as Si(111), at least above the transition temperature from (7×7) to (1×1) reconstruction, cf. Chung and Altman (2002). Importantly, it is generally accepted that the ES effect is *stabilizing against step bunching during growth* (with a reversal of stability upon switching to evaporation), cf., e.g., Pimpinelli and Villain (1998) and Krug (2005).² However, the ES barrier has also been shown to destabilize against meandering, cf. Bales and Zangwill (1990). It would therefore seem that step bunching and meandering are a priori mutually exclusive.

To account for step bunching, one needs to postulate the aforementioned iES barrier—still a matter of controversy among practitioners of crystal growth, see the discussion of Krug (2005)—or otherwise have recourse to extraneous mechanisms such as the presence of impurities, cf. Kandel and Weeks (1994); electromigration induced by a heating current, cf. Stoyanov (1991); elastic interactions between steps due to the presence of misfit strain during heteroepitaxy, cf. Tersoff et al. (1995); or chemical interactions between terrace adatoms of distinct species, cf. Pimpinelli and Videcoq (2000) and Chua et al. (2008).

Recently, Néel et al. (2003) have recorded the concomitant occurrence of step bunching and meandering—the latter acting as a precursor of the former—during the homoepitaxial step-flow growth of copper vicinal surfaces. These experiments have important repercussions on theories of crystal growth. Indeed, as discussed by these authors, the observed step bunching cannot be attributed to the presence of an iSE barrier, since the latter precludes step meandering. Moreover, its origin does not trace back to the presence of impurities, for these would have induced bunching in the low-temperature regime where only meandering was detected. Further, in the absence of lattice mismatch (as is the case during homoepitaxy), it cannot follow from elastic step interactions, insofar as these are known to be repulsive. Finally, chemical interactions in binary systems of the type that results in an effective iES barrier are ruled out, inasmuch as dimers—viewed as a species distinct from adatoms—tend to dissociate at high temperatures for which bunching was identified. Néel et al. conclude that a one-dimensional treatment of bunching instabilities is insufficient, in agreement with the two-dimensional theory of Politi and Krug (2000) whereby diffusion along the edges of meandered steps can trigger bunching at high temperatures.

This is certainly a plausible conclusion. Another, which underlies the present study, is that BCF-type models are in need of careful reconsideration.³ Specifically, we aim at providing evidence that neither the iES nor the other physical mechanisms alluded to above are necessary for step bunching. Indeed, we will show that bunching occurs during the step-flow growth of binary-compound films in the presence of the normal ES barriers for both species as long as the equilibrium adatom coverage of either species is not negligible. Interestingly, this condition is satisfied during, e.g., step-flow growth by molecular beam epitaxy of gallium arsenide, see Tersoff et al. (1997). Importantly, the physical basis of this instability can be found in the dependence of the step chemical potential on the jump in the adatom grand canonical potential, whereby adjacent terraces are coupled through the boundary conditions along the edges of the steps that separate them.

The bulk of the theoretical literature on step-flow epitaxy concerns single-species systems, despite the predominance of alloy and, more importantly for the purposes of the present article, compound films in technological applications, e.g., semiconductor GaAs and SiC for micro- and opto-electronic devices to mention only two of the most experimentally studied compounds. Of the few existing theoretical investigations of binary growth, only Pimpinelli and Videcoq (2000) and Chua et al. (2008) are based on BCF-type models. Both assume that vapor metalorganic precursors decompose upon adsorption releasing adatoms of the growth species, therefore confining the coupling of species to the terraces. Both predict step bunching as a result of a net downhill adatom current, interpreted as resulting from an effective iES barrier, for the growth species. Ours differs from the above studies in that, rather than assume that the growing crystal consists of one type of atoms or molecules, we postulate that incorporation into the bulk phase occurs only when adatoms released upon chemisorption of two different kinds of vapor-phase precursors react chemically *along the step edges* to produce molecules of the binary compound.⁴ Hence the coupling is to be found in the boundary conditions along steps instead of in the terrace reaction–diffusion equations. Moreover, we do not merely extend existing BCF-type models for single-species growth to

² This “established wisdom” (to use the words of Néel et al.) is the fruit of linear stability analyses of infinite trains of straight steps with various initial configurations (e.g., initially equidistant steps), cf. Schwoebel and Shipsey (1966b) and Krug (2005), with the underlying theory an extension of the original work of Burton et al. (1951) to account for finite attachment kinetics along step edges. By contrast, Cermelli and Jabbour (2007) have derived a thermodynamically compatible generalization of the BCF theory, one that leads to step bunching under the assumption of an ES effect.

³ In particular, compatibility with the second law allows for more general constitutive equations than those prevalent in the literature on crystal growth, with far-reaching implications on our physical understanding and mathematical characterization of bunching instabilities. Specifically, in Cermelli and Jabbour (2005), a general thermodynamically consistent theory for multispecies step-flow growth is proposed, with arbitrary numbers of chemical constituents and reactions. Its specialization in Cermelli and Jabbour (2007) to single-species epitaxy yields novel boundary conditions along step edges whereby adjacent terraces are coupled via the jump in the adatom grand canonical potential, and step bunching is shown to occur as long as the adatom equilibrium coverage is sufficiently high. An explicit characterization of the aforementioned bunching instability is given in Cermelli and Jabbour (2010) in the case of a two-periodic train of rectilinear steps. Finally, in Jabbour (2006) and Haußer et al. (2007), emphasis is placed on diffusion—both in the bulk and on terraces—and its interplay with elasticity—both in the bulk and along steps—during phase segregation in step-flow epitaxy of binary-alloy films. Herein, we consider instead the growth of binary compounds.

⁴ We therefore circumvent the criticism of “two-particle models” in Néel et al. (2003), namely that Cu dimers dissociate at high temperatures, making them an unlikely candidate for the second species. Indeed, the present theory does not involve dimer nucleation or decomposition.

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