STEP BUNCHING DUE TO IMPURITY ADSORPTION: A NEW THEORY

J. P. VAN DER EERDEN\(^1\) and H. MÜLLER-KRUMBHAAR\(^2\)

\(^1\)RIM Laboratory of Solid State Chemistry, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
\(^2\)Institut für Festkörperforschung der KFA, Postfach 1913, 5170 Jülich, B.R.D.

1. Introduction

Observation of a crystal surface, both in situ and ex situ, with optical microscopy usually reveals a large number of macrosteps. These macrosteps may arise from high Burgers vectors but also from piling up of monolayer steps. Indeed one often sees a structure like in Fig. 1, taken from ref. (1). The centre of a growth hillock contains many closely spaced steps of relatively low height, but further away from the centre step height and step spacing gradually increase. The subject of this paper is a model and its predictions for this phenomenon. The paper is meant as a summary of results given in ref. (2) and another paper treating the mathematical and numerical procedures in more detail is in preparation.\(^3\)

2. The Model

Two basically different approaches to the step bunching process are described in literature. Cabrera and Vermilyea\(^4\) describe the case that impurities adsorb on terraces between monolayer steps. These impurities will retard the motion of the steps. The longer a terrace has been in contact with the mother phase, the more impurities will it contain, hence the stronger will be the step retardation. Chernov,\(^5\) on the other hand, describes the case that the step velocity depends on the step heights, e.g. inversely proportionally. He does not specify the physical reason for this dependence but it could arise from a difference in atomic structure of high steps (more like a crystallographical face) and low steps, possibly in cooperation with some impurity effect.

In order to obtain observable phenomena from these models one has
Fig. 1. A well developed spiral hillock, ex situ observation on potassium hydrogen phthalate. In the centre of the growth hillock (top of photograph) steps are low and closely spaced, therefore hardly discernable. Far away from the centre they piled up to form widely spaced high macrosteps. Note that almost everywhere the steps are virtually straight and parallel.
used the kinematic wave theory presented originally by Frank. For the Chernov model this theory had to be generalized in order to incorporate a step density which depends not only on position and time but on step height as well. The result then is an average macrostep height and spacing which increase proportional to the square root of time. For the Cabrera and Levine model Frank suggested to take the age of a terrace proportional to its width. In that approximation any perturbation of an equidistant sequence of straight steps develops a shock wave, which could signify a macrostep. However, already Chernov\textsuperscript{5)} showed that the amplitude of this shock wave decreases with time and hence can not describe formation of macrosteps in the sense of Fig. 1.

In our model we again start from the Cabrera and Vermileya model, however we retain the age \( \tau \) of a terrace as the variable which determines the step velocity \( V = V(\tau) \). Two examples of the \( V(\tau) \) dependence are graphically depicted in Fig. 2. Essential is the increase of \( V \) with \( \tau \) at small \( \tau \) (physically related to the macrostep behaviour analogous to Chernovs model) and the exponential decrease of \( V \) to an asymptotic value \( \bar{V} \) at larger \( \tau \) (related to an exponential approach of the asymptotic impurity density at a step free surface).

The basic equation of our model directly follows from the definition of \( \tau \). Indeed if \( y_n(t) \) and \( \tau_n(t) \) are the position of the \( n \)-th step and the age of the terrace in front of it then by definition:

![Diagram](Image)

**Fig. 2.** Two examples of the function \( V(\tau) \), for different asymptotic step velocities. Small step velocities occur both for steps which follow rapidly after each other (macrostep physics) and for widely spaced steps (high impurity density on terraces).
\[ y_{n+1}(t - \tau_n(t)) = y_n(t) \] 

(1)

Upon differentiating this equation with respect to \( t \) and realizing that the velocity \( v_n(t) \) of the \( n \)-th step is determined by \( \tau_n \) one finds

\[ \frac{d\tau_n(t)}{dt} = 1 - \frac{V(\tau_n(t))}{V(\tau_{n+1}(t - \tau_n(t)))} \] 

(2)

which is our fundamental equation of motion.

Innocent as the derivation looks this is an equation with many rather unusual features. From a classification point of view this is a set of non-linear coupled differential equations, with a memory effect whose time lag \( \tau_n \) contains the unknown function.

The system has many largely degenerate stationary solutions. Indeed, taking any speed \( V \) between the asymptotic value \( \tilde{V} \) and the maximum speed there are two possible \( \tau \) values, a small one \( \tau_- \) and a large one \( \tau_+ \) corresponding to this velocity. Any arbitrary division of steps in groups such that in a group (physically a macrostep) steps follow each other with a time \( \tau_- \) and that the groups follow each other with the time \( \tau_+ \) represents a stationary state.

A linear stability analysis shows that all of these stationary states are unstable, except for the state in which all steps have bunched into one single macrostep, moving with the velocity \( \tilde{V} \).

3. Some Results

Both the experimental observation, see e.g. Fig. 1, and numerical simulation indicate that the piling up of monolayer steps into higher and higher macrosteps represents a kind of self similar time evolution. Indeed at any moment of time almost all steps are distributed in groups which effectively behave similarly to the original monolayer steps. Only the average step spacing and step height increase gradually with time.

This behaviour suggests to use a scaling hypothesis to give an approximate theory. Indeed, we verified that a good hypothesis could be that the variance of the step ages does not vary in time. In ref. (2, 3) we show that this leads to a logarithmic increase of the macrostep spacing with time. This theoretical prediction is tested in Fig. 3 for the growth hillock of Fig. 1. The result is in good agreement with the theory and is even sufficiently good to show that (at least for this special experiment) a logarithmic time dependence is more satisfying than the square root behaviour which follows from Chernovs theory. \(^{3)}\)
Fig. 3. Test of the theory on the growth hillock of Fig. 1: step spacing ($\approx V_{\tau}$) against distance from centre ($\approx P_{\tau}$, logarithmic scale). Error bars: experimental points. Continuous straight line: logarithmic time dependence, following the theory. Dashed curve: square root time dependence, following ref. (5).

REFERENCES


DISCUSSION

Chernov

The physical origin of the decrease of step velocity at low $\tau$ and the influence of this part of $V(\tau)$ on further calculations?

A: For the most important results of the calculations, i.e. the asymptotic
behaviour, the precise dependence of $V$ on $\tau$ for small $\tau$ is irrelevant, only important is that $V(0)$ is small and $V(\tau)$ is increasing for small $\tau$. We took the behaviour which is found when adatom adsorption is rate determining.

Hallett
What is the magnitude of the time scales of the exponent? Could on experiment be derived to show the influence of an impurity by suddenly introducing an impurity to a growing isolated step?
A: The time scales depend on the type of system, but for pure solutions the typical time is of the order of 0.1 sec., meaning that step bunching becomes significant usually after a few seconds. The experiment you suggest could indeed be helpful to determine the $V(\tau)$ behaviour for large $\tau$ experimentally.

Bennema:
Can you explain what is the difference between the classical kinematic wave theory and this obviously more sophisticated theory?
A: In the classical kinematic wave theory (k.w.t.) the step density is treated as a continuous function of position and the step velocity is a single valued function of it. However our analysis shows that pairing of steps is the dominant instability (which can not be described in the k.w.t.) and the velocity is a multivalued function of the density, even in stationary situations. Moreover, k.w.t. excludes the possibility of the development of steeper slopes on a surface than the ones which were already present in the starting situation.

Nishinaga
What is the thickness of the macrostep in final stage?
A: The basic result of our model is that in principle the macrostep height increases until all monosteps are combined. However this process is very slow: the height varies linearly with $\ln(\tau)$. Therefore in experiments you may not see further coarsening any more.