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Q1 Thermal effects in nano-sized adsorbate islands growth processes at vapor deposition

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HIGHLIGHTS

- Local changes in surface temperature govern transient dynamics of thin film growth when adsorbate islands start to organize.
- A temperature of adsorbate clusters becomes larger comparing to the substrate at initial stages of adsorbate clusters formation.
- An increase in the reheat coefficient of the surface leads to transformation of distribution of adsorbate islands over sizes.
- The mean linear size of adsorbate islands is of nano-meter range.

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ABSTRACT

We study a model of pattern formation in adsorptive systems with a local change in the surface temperature due to adsorption/desorption processes. It is found that thermal effects shrink the domain of main system parameters, when pattern formation is possible. It is shown that an increase in a surface reheat efficiency delays ordering processes. We have found that a distribution of adsorbate islands over sizes depends on relaxation and reheat processes. We have shown that the mean linear size of stationary adsorbate islands is of nano-meter range.

1. Introduction

It is well known that nano-sized objects (nanodots/nanoholes, stripes) are widely used in modern opto-electronics to manufacture new electronic devices, fabricate integrated circus, etc. Industrial applications of nano-sized patterns have become more and more complicated. Therefore, it is of great scientific and technological interest to understand a role of main mechanisms governing and controlling a nano-structuring of thin films. It was shown previously, that nano-structured thin films of different materials are characterized by exceptional functionality, namely, giant magnetoresistance [1], tunable optical emission [2], high efficiency photovoltaic conversion [3], ultralow thermal conductivity [4]. These unique properties give a possibility to use such materials in magnetoresistive sensors, memory devices, quantum dot lasers and detectors which can be exploited at quantum communications.

There are several methods for nano-structured thin films fabrication. Among them are: chemical vapor deposition (atmospheric pressure, low pressure or high vacuum deposition); physical vapor deposition (electron beam, pulsed laser or sputter deposition); homo-, hetero- and pendeo-epitaxy. By exploiting different techniques for deposition one can use

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effectively mechanisms for nano-sized islands growth (adsorption/desorption, diffusion, interaction of adatoms) leading to formation of different types of patterns: periodic array of vacancy islands [5], elongated islands of adsorbed semiconductors Ge/Si and Si/Si [6,7] and metals Cu/Pd, Ag/Cu [8,9]. During last few decades equiaxed and elongated nano-sized structures of different materials on different substrates were observed in real experiments and by numerical modeling at vapor or ion-beam deposition [10–13], ion-beam sputtering [14–19], pulsed laser irradiation [20–22], molecular beam epitaxy [23–29].

From the theoretical viewpoint to describe a deposition from a gaseous phase (vapor deposition) one deals with a model of reaction–diffusion systems. These systems play an important role in the study the generic spatiotemporal behavior of nonequilibrium systems. Usually, such models contain main contributions related to both local dynamics (chemical reactions of a birth-and-death type) and mass transport. Novel experimental methods such as field ion microscopy and scanning tunneling microscopy are able to monitor chemical reactions on the metal surfaces on the atomic level. It is known that adsorption and substratum mediated desorption are equilibrium reactions, related to exchange of particles between substrate and a large gas reservoir. Such reactions promote a formation of transient patterns [30]. In order to get stationary structures the adsorption–desorption model should be generalized by taking into account non-equilibrium chemical reactions [31–36]. Such reactions are related to associative desorption or formation of stable complexes, as usual. It was shown that adsorbate clusters are governed by a formation of surface complexes and their rearrangement at nucleation [37,38] representing nonequilibrium chemical reactions.

Previously in Ref. [39] authors used reaction–diffusion system to describe adsorbate islands formation at deposition from gaseous phase by taking into account nonequilibrium chemical reactions, corresponding to dimers formation. By using a condition of small but finite relaxation time for the adsorbate flux it was found oscillatory behavior of both statistical moments and linear size of adsorbate islands. Stochastic overdamped adsorption–desorption system with internal multiplicative noise was discussed in Ref. [40], where it was shown that fluctuations, satisfying fluctuation–dissipation relation, can change a topology of adsorbate clusters and govern their linear size.

By studying processes of nano-sized pattern formation at deposition from gaseous phase one usually assumes that a temperature of the surface remains a constant during adsorption/desorption processes. This approach seems to be an idealization meaning that temperature of the surface relaxes very quickly to equilibrium value and no local temperature change is possible during the system evolution. From a physical viewpoint when an atom from gaseous phase attaches the substrate and becomes adatom the surface temperature locally increases. From the other hand, if adatom desorbs from the substrate then the temperature locally decreases. Hence, during exposing time a competition of such processes even on mesoscopic level leads to local change in temperature of the surface [27]. It should be noted that in problems of soft-matter aggregation and in biomedicine small changes in temperature may have an important influence onto dynamics of crystal or aggregates formation. It was found previously that the averaged growth rate of protein crystal depends on the local variations of the temperature along the radius of the crystal [41].

In this work we are aimed to study an influence of local temperature changes onto nano-sized pattern formation at condensation from gaseous phase by taking into account nonequilibrium chemical reactions responsible for stable dimers formation. We will show, that this system manifests first-order phase transitions. In the framework of linear stability analysis it will be shown that local temperature change leads to a shrink of the domain of main system parameters, when pattern formation is possible. By using numerical simulations we will discuss an influence of temperature change onto transient dynamics of adsorbate islands growth and stationary distributions of adsorbate islands over sizes.

The work is organized in the following manner. In the next section we present a model of adsorptive system by taking into account nonequilibrium chemical reactions and local change in the surface temperature. In Section 3 we perform linear stability analysis and find conditions for pattern formation. Section 4 contains results of numerical simulations. We conclude in Section 5.

2. Model

To study the problem of adsorbate islands formation at deposition from gaseous phase we will deal with the one-layer model and monitor the local coverage $c(\mathbf{r}, t) \in [0, 1]$, where t is the time variable, $\mathbf{r} = \{x, y\}$ is the space coordinate. Following previous studies [32–36,42–44] we assume that particles (atoms/molecules of one sort) can be adsorbed by the substrate (become adatoms), can desorb back into gaseous phase from a substrate, interact among themselves and diffuse along a substrate. Hence, we deal with the reaction–diffusion system whose dynamics is described by evolution equation for adsorbate concentration (coverage) in the standard form:

$$\partial_t c = R(c) - \nabla \cdot \mathbf{J}. \tag{1}$$

Here the term $R(c)$ defines quasi-chemical reactions type of "birth-and-death" or adsorption/desorption processes, and the last term relates to the adsorbate flux $\mathbf{J}$ representing mass transport.

Following Ref. [33] the adsorption rate, i.e. the probability of the arrival of an atom/molecule from the gas phase at a given vacant site of the lattice $(1 - c)$ is $\varpi_a = k_a P$, where k_a is the sticking coefficient and P is the partial pressure of the gaseous phase. Hence, adsorption processes are defined as: $k_a P(1 - c)$. The desorption rate, i.e. the probability per unit time that an atom/molecule leaves its site $\mathbf{r}$ and goes into the gas phase, is $k_d = k_d^0 \exp(U(\mathbf{r})/T)$, where k_d^0 is the desorption rate for noninteracting particles (atoms/moleciles) which relates to the life time scale of adatoms $\tau_d = [k_d^0]^{-1}$ [33]. We admit that only substratum mediated interactions are possible, where $U(\mathbf{r})$ is the interaction potential. Therefore, the desorption

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