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Stranski–Krastanov mechanism of growth and the effect of misfit sign on quantum dots nucleation

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ABSTRACT

The thermodynamics of the Stranski–Krastanov mode of epitaxial growth and the effect of the sign of the lattice misfit are discussed. The Stranski–Krastanov mode of growth represents a sequence of layer-by-layer or Frank-van der Merwe growth followed by the formation of three-dimensional (3D) islands or Volmer–Weber growth. The occurrence of both growth modes mentioned above is in compliance with the wettability criterion of Bauer. The positive wetting function required for the occurrence of the Volmer–Weber growth is originated by the vertical displacements of the atoms close to the edges of the two-dimensional (2D) islands as a result of the relaxation of the lattice misfit. The monolayer high islands become unstable against bilayer islands, bilayer islands in turn become unstable against trilayer islands, etc. beyond some critical islands sizes. Monolayer islands appear as necessary precursors of three-dimensional (3D) islands. The critical island size for mono-bilayer transformation increases steeply with decreasing lattice misfit and diverges at a critical value of the misfit. This value divides the regions of Frank-van der Merwe and Stranski–Krastanov modes in a phase diagram of coordinates wetting-misfit. The transformation of monolayer to multilayer islands takes place either by consecutive nucleation and growth of 2D islands (layer-by-layer transformation), or by nucleation and lateral (2D) growth of multilayer islands (multilayer 2D transformation). The former occurs in the case of “stiff” overlayer materials and mostly in compressed overlayers. The latter takes place in the case of “soft” materials like Pb and In, mostly in tensile overlayers. Tensile films show non-nucleation transformation compared with the nucleation-like behavior of compressed films.

1. Introduction

In 1958 Ernst Bauer published his famous thermodynamic criterion for the classification of the mechanisms of epitaxial growth [1,2]. He derived an expression for the equilibrium shape, given by the ratio h/l (height/width), of a cubic crystal on a foreign substrate in terms of the interrelation of the specific surface energies of the substrate σ_s, epilayer, σ, and the substrate-epilayer interface, σ_i. The change of the surface energy, $\Delta\sigma = \sigma + \sigma_i - \sigma_s$ associated with the formation of the epilayer, represents in fact a measure of the wetting of the substrate by the film material. In the case of incomplete wetting, $\Delta\sigma > 0$, the growth proceeds by the formation and growth of separate three-dimensional (3D) islands, a mechanism for which Bauer coined the term Volmer–Weber (VW) growth[3]. When $\Delta\sigma \leq 0$ and the lattice misfit is negligible, the height of the 3D island is equal to zero and two-dimensional (2D) islands form instead giving rise to layer-by-layer or Frank-van der Merwe (FM) growth [4,5]. And finally, when $\Delta\sigma < 0$ and the lattice misfit is non-zero the growth begins by the formation of a *wetting layer* consisting of a few monolayers-thick film followed by the growth of 3D islands on top. This is the well-known Stranski–Krastanov mode of growth[6].

The equilibrium shape of a crystal on an unlike substrate had been earlier derived by Kaischew in 1950 in terms of the binding energies between two atoms of the deposit (cohesion energy, ψ) and between an atom of the substrate and an atom of the film (adhesion energy, ψ') [7,8]. Both expressions, due to Bauer and Kaischew, respectively, for the equilibrium shape are in fact identical[9]. The condition $\psi' < \psi$ is equivalent to $\Delta\sigma > 0$, $\psi' = \psi$ corresponds to $\Delta\sigma = 0$ and $\psi' > \psi$ corresponds to $\Delta\sigma < 0$. It follows that the mechanism of growth depends on the interrelation of the cohesion and adhesion energies. As will be shown below, the lattice misfit plays a crucial role only when $\psi' \geq \psi$ ($\Delta\sigma \leq 0$). Note that the above conclusions about the mechanism of growth are based on the concept of the equilibrium crystal shape.

As shown by Rudolf Peierls, the mechanism of growth is closely connected with the sign of the derivative of the chemical potential with respect to the number of atoms in the overlayer, $d\mu/dN$[10]. As seen in Fig. 1, the VW growth is associated with $d\mu/dN < 0$ and the FM growth requires the condition $d\mu/dN > 0$. This means that the VW growth is connected with a negative curvature, $d^2G/dN^2 < 0$, of the N-dependence of the Gibbs free energy of the thickening film, whereas the FM growth is connected with the opposite behavior, $d^2G/dN^2 > 0$. This implies that in the case of SK growth, the dependence of the Gibbs free energy on film thickness must possess an inflection point, N_i, at which the curvature of G, d^2G/dN^2, changes sign from positive to negative with increasing film thickness. The analysis of the problem shows that the planar film is stable up to some critical thickness, N_{cr}, which is slightly smaller than

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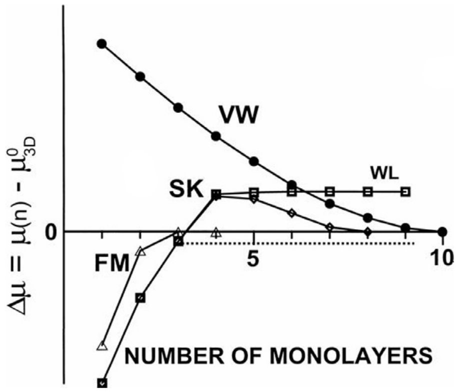

Fig. 1. Illustration of the dependence of the chemical potential of the overlayer on the film thickness in number of monolayers for the three modes of growth: Volmer–Weber (VW), Frank-van der Merwe (FM) and Stranski–Krastanov (SK). The upper straight line denoted by WL gives the chemical potential of the unstable wetting layer (a monolayer in excess which will be transformed into 3D islands), whereas the lower dotted line gives the chemical potential of the uppermost monolayer belonging to the stable wetting layer. (J. E. Prieto, I. Markov, Phys. Rev. B 66, 073408 (2002)). By permission of the American Physical Society.

N_i. At $N = N_\mathrm{cr}$ $\mu = \mu_\infty$ and $P = P_\infty$ where μ_∞ and P_∞ are the chemical potential and the equilibrium vapor pressure of the infinitely large bulk deposit crystal, respectively. Thus N_cr and N_i determine the thicknesses of the stable and unstable wetting layers, which are given in Fig. 1 by the lower dotted and the upper straight lines, respectively. Note that in the analysis of Peierls the dependences of the film Gibbs free energies on film thickness are smooth and differentiable, which results in $\Delta\mu(N_\mathrm{cr}) = 0$. The analysis of Peierls leads to the same criterion as the one derived by Bauer $\Delta\sigma = \sigma + \sigma_i - \sigma_s \gtrless 0$. For more details the reader is referred to Section 4.3.4 of Ref. [9].

It is obvious that the SK growth represents an instability of the planar growth against clustering owing to the accumulation of strain energy in the wetting layer. This led to the concept of nucleation of islands due to the trade-off between the cost of the additional surface energy of the 3D islands and the gain of energy due to the elastic relaxation of the 3D islands relative to the wetting layer [11–13]. Although this approach gives a valuable insight into the problem, it does not allow the determination of the mechanism of formation of the 3D islands on top of the wetting layer. The essence of the problem is that the coherent (dislocationless) SK mode consists of the formation of 3D islands of a material A on the same (strained) material A[14].

On the other hand, Mo et al.[15] observed with the help of scanning tunneling microscopy (STM) Ge islands representing elongated pyramids ("hut" clusters) bounded by (105) facets. The authors suggested that the hut clusters are a step in the pathway to the formation of larger islands with steeper side walls [16–18]. The ways of relaxation of lattice misfit in the transition from hut clusters to larger islands with steeper side facets has been reviewed by Teichert[19]. Tersoff et al. have shown that the growth of SiGe superlattices up to 2000 layers resulted in a very narrow size distribution of the quantum dots[20]. Chen et al.[21] and Vailionis et al. [22] studied the initial stages of formation of the hut clusters and found three- to four monolayers-high prepyramids with rounded bases in a narrow interval of Ge coverages. Sutter and Lagally [23] suggested another scenario for the formation of SiGe alloy clusters at low misfit. They observed by low-energy electron microscopy (LEEM) the formation of an array of stepped mounds (ripples) as precursors of the hut clusters. These ripples are inherent to strained films to relax the misfit strain as suggested by many authors [24–27]. Based on these observations, Sutter and Lagally suggested the concept of barrierless (nucleationless) formation of the 3D islands[23]. Similar views on the idea of barrierless transformation of the ripples into faceted islands were suggested by Tromp et al.[28] and by Tersoff et al.[29] The contradiction of the above-mentioned concepts of nucleation and nucleationless formation of 3D islands, as well as many other aspects of the growth modes gave rise to intensive theoretical studies of the Stranski–Krastanov morphology by making use of both analytical approaches [31–33], and computer Monte Carlo [34–37] and molecular dynamics [38–41] simulations, and were debated in numerous review papers and monographs [42–45]. However, among the most important questions remains the following: Is the nucleation concept of 3D clustering consistent with the wettability concept of Bauer?

In addition, the mechanism of growth of quantum dots in the SK mode depends strongly on the sign of the lattice misfit. In compressed overlayers the film atoms interact through the steeper repulsive branch of the interatomic potential, whereas in tensile overlayers the interaction through the weaker attractive branch prevails. The anharmonicity of the chemical bonding influences the adhesion of the 3D islands to the wetting layer or, in other words, the wettability as defined by Bauer, through the relaxation of strain both laterally (in-plane) and vertically (out-of-plane) at the steps forming the boundaries of the islands. This strain relaxation leads to two different mechanisms of 2D-3D transformation, the consecutive transformations of islands with gradually increasing height by nucleation of single monolayers, and a mechanism in which multilayer islands nucleate and then laterally (two-dimensionally) grow. Note that the two-dimensional multilayer islands grow only laterally keeping their height constant in contrast to three-dimensional islands which grow both in length and height.

The paper is organized as follows. In consecutive sections we consider the equilibrium vapor pressure of the 2D and 3D phases, the effect of lattice misfit on the film-substrate adhesion, the thickness of the stable wetting layer, the stability of mono- and multilayer islands, the layer-by-layer growth of 3D islands, and the multilayer growth of 3D islands. We then compare our findings with experimental data and discuss the results.

2. Equilibrium vapor pressure of the 2D and 3D phases

In 1929 Stranski [46,47] studied the stability of separate monolayers of a monovalent ionic crystal K^+A^- on the surface of the isomorphous divalent crystal $K^{2+}A^{2-}$ by making use of the newly discovered concept of the half-crystal or kink position [48–50]. He found that the equilibrium vapor pressure of the first momolayer, P_1, is much lower than the equilibrium vapor pressure, P_0, of the bulk monovalent crystal. The reason is that the monovalent ions are attracted by the underlying divalent ions more strongly than by the corresponding monovalent ions of the same crystal. As the ions of the second monolayer are repulsed more strongly by the underlying divalent ions of the substrate crystal, its equilibrium vapor pressure will be higher than the equilibrium pressure P_0. The equilibrium vapor pressure of the third monolayer will be smaller than P_0, and that of the fourth monolayer will be already nearly equal to P_0, i.e. the energetic influence of the divalent substrate disappears beyond four monolayers. Thus they concluded that the chemical potential of a thin film of K^+A^- on $K^{2+}A^{2-}$ varies with its thickness.

Ten years later Stranski and Krastanov extended the considerations of the same model by calculating the Gibbs free energies of formation of 2D nuclei of the first, second, third, etc., monolayers, as well as of two and four monolayers-thick 2D nuclei[6]. It turned out that 2D nuclei of the first monolayer can be formed at a vapor pressure P which is larger than P_1, but smaller than P_0. This means that the first monolayer can be deposited at *undersaturation* with respect to the bulk crystal for the reasons given above. The work of formation of 2D nuclei of the second monolayer is very large but that of 2D nuclei consisting of two monolayers belonging to the second and third level, (or in fact three-dimensional), is much smaller. The reason is that the chemical potential of a bilayer deposited on the first monolayer is lower than that of a single monolayer but still higher than P_0. It was found that the chemical potential of the bilayer is equal to the arithmetic average of the chemical potentials of the second monolayer (larger than the bulk chemical potential) and the third monolayer (slightly smaller than the bulk chem-