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Theory of surfactant-mediated growth on semiconductor surfaces

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Abstract

The surfactant effect, first demonstrated by Copel et al. [Phys. Rev. Lett. 63 (1989) 632] by using As to promote epitaxial growth of Ge on Si(100), has now been studied in a wide variety of systems, thus making systematic studies possible. We present theoretical models that account for the observed behavior of various surfactants on semiconductor surfaces, including homo-epitaxial and hetero-epitaxial growth. The theoretical models include first-principles calculations of the relative energy of different structures associated with surfactant layers and the activation energies for diffusion and exchange mechanisms, as well as solid-on-solid Monte Carlo simulations.

Growth of high quality semiconductor films on different substrates at low temperature is a difficult and challenging problem. Homoepitaxy at low temperature produces a large number of defects, which degrade the film quality. Heteroepitaxy is also difficult, since the lattice mismatch between substrate and deposited layers leads usually to three dimensional island growth with poor film quality. Copel et al. [1] first demonstrated that the use of surfactants can be beneficial in extending the heteroepitaxial growth of Ge on Si(100); in that experiment, the surfactant was a layer of As. Following that work, a number of experimental papers reported similar results for both homo-epitaxy and hetero-epitaxy, on Si and III–V substrates, using a variety of adsorbates as surfactants [2–12].

While the surfactant effect has been demonstrated convincingly experimentally, the mechanisms by which this effect takes place are not well understood. Several attempts at modeling this effect theoretically have been made recently [13–17]. We describe here some of these attempts, which we believe capture the basic physics of the surfactant effect as manifested on semiconductor surfaces.

The most important consideration for an adsorbate that can potentially act as a surfactant, is its ability to float during growth on top of the newly deposited atoms. This will involve breaking of bonds between the surfactant and the substrate and exchange of positions between the surfactant and the new deposits. Kaxiras has argued that understanding the structure of the adsorbate layer on top of the substrate is a crucial step in determining the ability of an element to act as a surfactant [13]. For example, it was determined through first-principles calculations that among group-V elements, As and P form a substitutional structure on Si(111), while Sb forms

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trimer or chain structures [13]; these results are in agreement with experimental observations on the structure of group-V monolayers on Si(111) [18–20]. The trimer and the chain structure are weakly bonded to the substrate with one covalent bond per adsorbate atom, while the substitutional structure is strongly bonded to the substrate with three covalent bonds per adsorbate atom. Based on these observations it was predicted that Sb would act as a good surfactant on Si(111) whereas As would be ineffective [13]. This prediction was subsequently verified by experiment [21].

An equally important consideration is the competition between diffusion on top of the surfactant layer and exchange between surfactant atoms and newly deposited atoms. Certain experiments find that in the presence of a surfactant, there is a dramatic increase of the density of islands [2,5] while other experiments find that no islands are nucleated on top of terraces and growth proceeds in step-flow mode [11,8]. The latter case can be interpreted in a straight-forward manner as implying enhanced diffusion on top of the surfactant and incorporation of the new deposits at steps, where chemical reactivity is enhanced.

The interpretation of the former case is somewhat more problematic: It is customary to associate the average distance between islands with a diffusion length. Thus, the high density of islands might be taken to indicate a short diffusion length [2,5]. This explanation, however, is surprising and counterintuitive, since the surfactant typically produces a passivated non-reactive surface on top of which the activation barrier for diffusion should be low. The activation barrier for exchange between surfactant and newly deposited atoms on the other hand, should be significantly larger than for diffusion, since exchange involves more bond-breaking than diffusion. An exception to this general rule may be exchange at unpassivated steps where chemical reactivity is increased.

Kandel and Kaxiras [17] have reported first-principles calculations for exchange and diffusion mechanisms on Sb covered Si(111), with newly deposited Ge layers. They find that indeed the activation energy for exchange is significantly larger than the activation energy for diffusion on top of the surfactant. Using the results of the first-principles calculations, they performed solid-on-solid Monte Carlo (SOS–MC) simulations to show that for surfactants which passivate the surface steps, an increased density of small islands is observed without having to invoke a reduced diffusion length. In contrast, for surfactants that do not passivate surface steps, a layer-by-layer growth by step flow is obtained [16]. These results are in excellent agreement with experimental results: the group-V elements As and Sb are known to passivate steps on the Si(100) and Si(111) surfaces, and lead to increased density of small islands during growth [2,5]. The elements Sn or Au on the other hand do not passivate surface steps on the Si(111) surface, due to their chemical nature, and lead to step-flow growth [8,11]. In all cases, the diffusion length of newly deposited atoms on top of the surfactant layer is enhanced, contrary to previous suggestions [2,5]. For surfactants that passivate surface steps, the possibility that single atoms buried under the surfactant can de-exchange, allows for smooth growth despite the presence of many small islands [17].

Finally, Kandel and Kaxiras have addressed the issue of strain in surfactant mediated heteroepitaxial growth [17]. They employed the results of Tersoff et al. [22] for the elastic energy per unit volume of a strained island, to take into account the strength of lateral bonds in islands of new deposits that are buried under the surfactant. This argument makes the strength of lateral bonds depend on the size of the island on top of which the new deposits are incorporated. This dependence will affect the probability of de-exchange of buried deposits on islands of different size. Using SOS–MC simulations with the island-size dependent strength of lateral bonds, these authors showed that growth at low temperature should proceed in a layer-by-layer mode, while at higher temperature three dimensional islands are formed. Thus, the surfactant in the hetero-epitaxial case prohibits the system from reaching its preferred mode of growth (which is 3D islands) by requiring the newly deposited atoms to exchange with the surfactant layer before they become incorporated in the film. This effect cannot be sustained at higher temperatures, where the preferred mode of growth is recovered and the surfactant is no longer effective. Again, these results are in excellent agreement with the observed behavior [5].

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