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Wetting droplet instability and quantum ring formation

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InAs islands on GaAs substrates undergo a morphological change into ring-shaped configurations upon deposition of a GaAs layer after island growth. By invoking an analogy of the InAs islands to wetting droplets on solid substrates, we suggest that this transition might be brought about by a change of the surface free-energy balance at the three-phase contact-line between GaAs, InAs, and vacuum (or As atmosphere). Our scenario can also be tested in conventional liquid systems (e.g., polymers).

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Recent experiments on self-assembled InAs/GaAs quantum dots revealed a morphological change upon covering the dot by additional GaAs layers and annealing at growth temperature [1] (see also [2,3]). The shape of the quantum dots changes from a lens or droplet of diameter $D \approx 20$ nm and height $F \approx 7$ nm [see Fig. 1(a)] to a volcanolike shape with a hole in the interior with diameter $D_H \approx 20$ nm, a rim height $F_R \approx 2$ nm, and an increased diameter of 60–140 nm [see Fig. 1(b)]. An explanation for the mechanism behind this shape change has so far not been given, although a relation to dewetting phenomena was noticed [4].

In this paper, we point out an analogy of the morphological change of the InAs quantum dots to an instability of wetting droplets which might catch an essential element of the former process, and could also be tested experimentally in more conventional (liquid) wetting systems. We first explain the morphological instability for a wetting droplet whose shape is governed by interfacial free energies, and subsequently discuss the modifications for the quantum dot system with its crystalline structure of the InAs/GaAs/vacuum interfaces. Note that our reasoning is entirely based on equilibrium arguments; the role of kinetic effects on the morphological transition is not investigated here, but some (necessary) remarks are made.

Figure 2(a) shows a droplet on a solid substrate. We focus on the base of the drop and therefore represent it as a wedge. We assume that this configuration applies equally well to a liquid droplet on a solid substrate and a pyramidlike quantum dot (which is not an uncommon assumption for an InAs island, see, e.g., [5,6]). Our assumption that the latter can indeed be considered as a solid/liquid/vapor system is supported by two facts: (i) there is no experimental evidence that InAs dots deform the GaAs and hence have the shape of a biconvex lens and (ii) a quantitative estimate of the deformation due to the out-of-plane surfaces force component shows that it is ≈0.01 nm, thus negligible [7]. Out-of-plane contributions in the surface force balance can therefore be ignored in our discussion.

The three interfacial tensions (or surface-free energies) acting at the droplet border are denoted by $\gamma_{ab}, \gamma_{bc}, \gamma_{ac}$ where, for a wetting droplet on a solid substrate, a equals the solid phase, b is the liquid, and c is the vapor phase, respectively. For the InAs/GaAs system, a equals the GaAs phase (plus the additional InAs wetting layer, see below), b is the InAs phase, and c is vacuum (or As vapor).

In an equilibrium configuration, the surface forces balance as described by Young's equation

$$\gamma_{ac} = \gamma_{ab} + \gamma_{bc} \cos\theta, \tag{1}$$

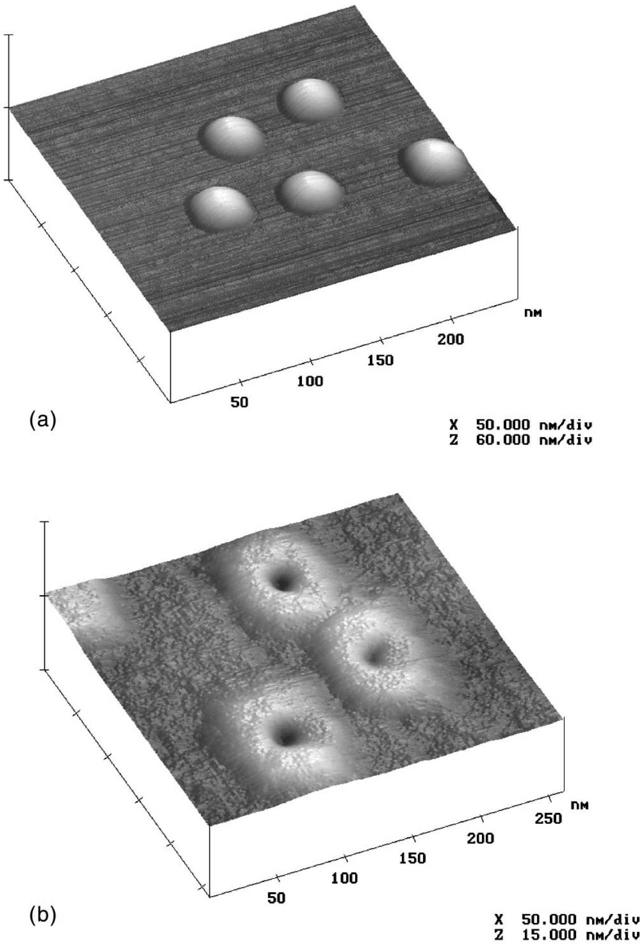

FIG. 1. Atomic force micrograph of (a) InAs/GaAs quantum dots and (b) InAs/GaAs quantum rings.

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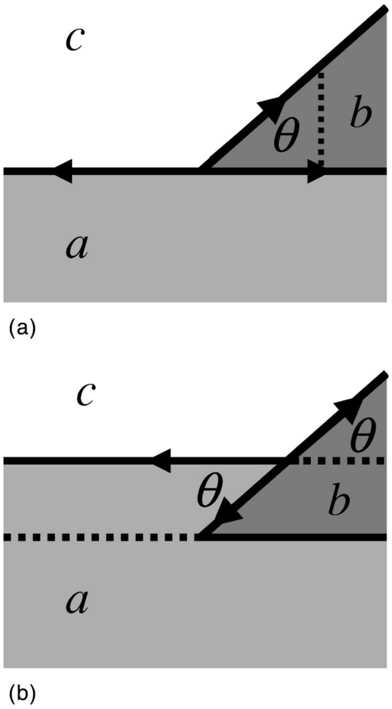

FIG. 2. (a) Wetting droplet or InAs island with surface tensions acting at the contact line. The phases are indicated as solid/GaAs (a, light gray), liquid/InAs (b, dark gray), and vapor (c). The arrows represent the interfacial tensions. The dotted line is the projection of the liquid-vapor surface tension to the solid-liquid interface. (b) Wetting droplet/InAs island with surface tensions acting at the contact line introduced after GaAs covering. Dotted lines: former location of the ac interface and projection of the interfacial tension between InAs and vapor.

where θ is the contact angle between the forces per unit length pulling along the *ab* (solid-liquid) and *bc* (liquid-vapor) interfaces.

The addition of a new layer of the solid phase *a* on top of the substrate shifts the *ac* interface away from the bottom of the droplet; likewise, the three-phase contact line is lifted up [see Fig. 2(b)]. Here, in equilibrium, a surface force balance must be sought, however, in the configuration shown it would read

$$\gamma_{ac}+\gamma_{ab}\cos\theta=\gamma_{bc}\cos\theta, \tag{2}$$

assuming a thin coverage layer and neglect of curvature at the *bc* interface. Obviously, Eq. (2) can in general not be reconciled with Young's Eq. (1). The resulting imbalance of the configuration can be expressed in terms of an uncompensated Young force [8] simply as

$$\Delta F\equiv\gamma_{ab}(1+\cos\theta), \tag{3}$$

where Young's relation has been used. Thus, the system has to seek a new equilibrium to relax from this unstable situation, which is determined by the surface forces now pulling *radially outward* from the contact line with a force of magnitude ΔF. A possible equilibrium configuration which is consistent with our basic assumption that the droplet/dot shape fulfills a balance of in-plane interfacial forces, and is also in accord with experiment, is shown in Fig. 3.

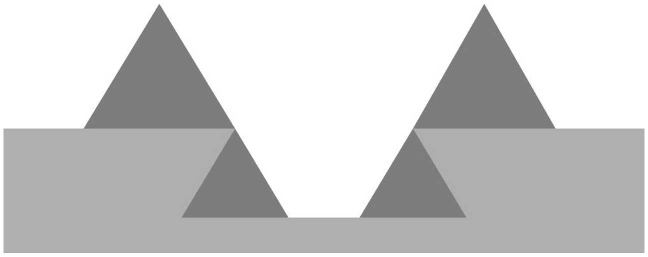

FIG. 3. Profile of the InAs-quantum ring after equilibration.

We now discuss the modifications of this basic scenario for the InAs/GaAs quantum dots. Several additional factors enter in the discussion: (i) the quantum dot is probably faceted with surface free energies depending on facet orientation; (ii) the InAs quantum dot does not rest on the GaAs substrate but on a thin wetting layer of InAs; (iii) elastic effects (strain) have to be taken into account; (iv) line tension contributions or edge effects might occur; and (v) kinetic effects, e.g., alloying and diffusion of the constituents will be present.

None of these effects alters the morphological instability in a principle way. The presence of facets (i) modifies the force balance quantitatively, and might do so differently for the different facets the quantum dot presents to the additional GaAs layer. This might, similarly to the presence of strain (iii) (which otherwise is included in the surface free energy balance) and anisotropic diffusion (iv), lead to an asymmetry of the quantum rings. A slightly oval shape is in fact observed in the quantum rings [see Fig. 1(b)]. A line tension or edge effect (v) is likewise not relevant for the surface force balance. First, the contact line of the droplet is transformed into the interior contact line of the hole with the same radius: the additional contribution $\sim\tau/R$ with line tension τ to Eq. (1) is thus unchanged before and after the morphological change. As the outer radius of the ring is much larger than the droplet radius, the contribution of the contact line at the outer boundary of the ring is negligible for the surface force balance.

Point (ii), however, might be potentially very important, as it modifies the surface force balance, Eq. (1), to

$$\gamma_{ab}+\overline{\gamma}_{bc}=\gamma_{ab}+\gamma_{bc}\cos\theta, \tag{4}$$

where $\overline{\gamma}_{bc}$ is the surface tension of the InAs(film)-vacuum interface which differs from γ_{bc} due to facetting effects, as shown by density functional calculations [10–13]. Since, for a given chemical potential of As and comparable facet orientation, the surface free energy of the GaAs/vapor interface is larger than that of the InAs/vapor interface, while the GaAs/InAs-interfacial free energy is presumably small [9], our analysis is thus qualitatively unaffected by inclusion of the InAs film.

Finally, kinetic effects (v) may be relevant as well since lateral segregation effects can occur leading to a diffusion of InAs from the initial layer to the GaAs/vapor interface [14–16].

In conclusion, we are led to expect that due to the small differences in surface tensions, a large change in contact angle as indicated in Fig. 2(b) can be sufficient to destroy the surface force balance between the GaAs/InAs/vapor interfaces, resulting in the formation of a pronounced ringlike rim of InAs, which is difficult to explain assuming species diffusion as the main driving force for quantum ring formation. It can be expected that the proposed instability mechanism by capillary forces ceases to be efficient enough for thick GaAs covering layers. If the InAs islands are almost completely buried in the GaAs layer, the magnitude of the surface forces is not sufficient to rupture the dot. An analysis of this situation must therefore involve the full free energy balance, not surface forces alone. In experiments for GaAs coverings >5 nm indeed only quantum dotlike electronic spectra are observed, indicating that the morphological change from dots to rings has been suppressed [4].

We close by noting that it would be interesting to test the proposed droplet instability experimentally in conventional liquids, e.g., with polymers. Here, an excellent control of droplet shapes down to nanometric sizes has recently been achieved [17]. A possible experiment could thus consist in the covering of a substrate partially or pseudopartially wetted by droplets by a liquid which is preferentially wetted by the droplet material or phase. In the liquid systems, for sufficiently large droplets, the morphological instability of the wetting droplet might be a means to trigger rim instabilities of the resulting liquid rings, which are absent in the InAs/GaAs system due to its solidlike character and its small size.

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