Stability and pinning points in substrate-confined liquids

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Confinement of liquid by concavities in a substrate surface is treated with reference to contemporary interest in growing semiconductor crystal on inert substrates. Instabilities that occur during or after filling of simple concavity shapes are considered, with particular attention to the influence of discontinuities of slope in the substrate.

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Thin films deposited on a suitable substrate are receiving serious consideration as a crystal-growth medium. Perhaps the best-known example is silicon on sapphire (SOS), presently being utilized in integrated circuits.¹ In SOS, as in graphoepitaxy² and other more recent cases,³ the substrate plays an important role in crystal nucleation. In yet other instances,^{4,5} however, the substrate mainly provides mechanical support for a thin liquid film, from which crystal growth occurs. Recently, we discussed⁶ the latter instances and demonstrated how liquid may be confined in contours produced in the substrate surface. The liquid film is so confined, i.e., does not ball up as it would on an open flat surface, due to an interplay between geometry and surface tensions. The efficacy of variously shaped depressions in confining liquid stably, however, varies widely, and the purpose of the present paper is to consider the factors that enter into this situation.

The problem of obtaining liquid confinement in a substrate surface is twofold: first, the liquid must be put into some desired configuration and, secondly, this configuration must be stable, at least against small perturbations. The latter problem is the more susceptible to analysis. We shall deal primarily with it in what follows, with more qualitative comments on the former problem.

The crystals of primary interest for growth by the present methods are the semiconductors. Applications where *in situ* crystal growth of these materials would be useful are manifold, most notably in integrated circuits, solar cells, and arrays of devices like detectors. The characteristic dimension in most of these devices is a few microns, and an extensive lithographic art is now available to fashion structures to such dimensions. In what follows, we usually have in mind structures of such size. However, the applicable physical laws⁷ would permit a wide range of sizes, which can be contemplated equally well in the following discussion.

Given that one is ultimately interested in growing semiconductor thin-film crystals, what substrate materials are most appropriate? Many materials have been considered in the solar cell art: Mo, W, kovar, various glasses, to name a few. In the present case, we think materials that interact the least with the liquid are to be preferred. Amorphous SiO₂ is such a material, though Si₃N₄ may interact negligibly in some cases. The implication for the present paper is that useful contact angles θ between liquid and substrate are likely to be large, most probably in the range $90^\circ < \theta \leq 150^\circ$,

which is approaching what is often called "nonwetting." To accustom the reader to this regime, all the schematics in this paper illustrate the case $\theta = 135^\circ$.

The simplest shapes to deal with in the confinement of liquids are spherical due to the high symmetry and lack of singularities. We have chosen as a prototype structure for the following discussion a hemispherical depression. This is easily produced in the contemporary art by opening a small hole in an overlayer of photoresist or oxide, followed by an isotropic etch which does not attack the overlayer.

I. BOUNDARY CONDITIONS

Each droplet of liquid at rest on a substrate surface must meet the usual boundary conditions^{8,9} on its meniscus. Curvature of the meniscus implies that the liquid is at a pressure p with respect to the adjoining vapor phase. For the spherical shapes primarily discussed here

$$p = (2/r)\sigma, \quad (1)$$

where r is the radius of curvature of the sphere, σ the surface tension at the liquid-vapor interface, and a convex liquid surface is assigned a positive value of r . For the troughs discussed in the latter part of the paper, p is half the value given by Eq. (1). In any case, since the pressure must be everywhere the same in a contiguous body of fluid at rest, the meniscus must everywhere have a constant curvature.

Furthermore, the meniscus must approach the substrate surface at a given contact angle θ , where θ depends on the materials involved. In cases discussed later where the surface has a discontinuity of slope, a range of θ values is permissible. A non-negligible practical problem is the great sensitivity of θ to certain contaminants. However, this problem is surmountable for many semiconductor materials, such as GaAs and InP, as has been demonstrated in the liquid-phase-epitaxy (LPE) art. It should be noted at this point that Si is not one of these materials, and additional considerations^{5,10} will be necessary if Si is to be grown from liquids as discussed here.

II. DEPOSITION METHODS

In principle, any of a large number of techniques for depositing thin films, from electroplating to molecular beams, could be used. In practice, one prefers methods yielding high purity films, or at least films containing only contaminants that are easily cleaned up. For example, chemical-

FIG. 1. Schematic for *simultaneous* deposition and liquefaction of material M in a hemispherical depression. Evolution of the liquid configurations during the course of deposition is depicted in (a)–(d). Final state in (d) is a single contiguous body of fluid, whether partly (1.41) or completely (0.71) filling the depression. Relative pressure p is imposed on the fluid by meniscus curvature. $\theta = 135^\circ$.

vapor-deposition (CVD) and vacuum evaporation have proven most useful in our experiments.

In any case, a crucial consideration is whether one liquefies the film during deposition or subsequently, as this can substantially affect agglomeration of the liquid. The former case is the easier to analyze and is illustrated in Fig. 1. A flux of material M arrives at the surface and agglomerates into droplets which initially may be quite small. As deposition continues, the droplets grow until they touch, whereupon coalescence occurs, reducing the pressure per Eq. (1). In this way larger droplets evolve as indicated in Fig. 1(b). The pressure exerted on the fluid by its curved meniscus, per Eq. (1), is indicated on a scale where $p = 1$ for $r =$ radius of the hemispherical depression. The magnitude of p for depressions a few μm wide, and with σ a few hundred $\text{ergs}/\text{cm}^2 = \text{mJ}/\text{m}^2$ as is the case for elements near Ge in the periodic chart,¹¹ is roughly 1 atm. Thus, one may think of the values of p in the figures in an approximate way as representing atmospheres. For convenience, a single size droplet is shown at each stage of deposition in the figures, though actually a distribution of sizes occurs.

To this point agglomeration in the hemisphere is similar to what it would be on a flat surface. Upon further deposi-

tion, however, only two droplets, and eventually only one, will fit into the depression. When the entire surface of the hemisphere is wetted, the structure may be said to be filled ($p = 0.71$ in Fig. 1). For $\theta \geq 135^\circ$ droplets on the flat surface between depressions, i.e., on the *field*, could touch the confined droplet, thereby possibly emptying the structure. Various steps can be taken to prevent such occurrences, some of which are mentioned later.

One notes that until a concavity is filled, the continuing deposition reduces p monotonically, i.e., $dp/dv < 0$, where v is the volume of M in the concavity. This produces no instability for an isolated concavity, which eventually fills when the proper amount of M is deposited regardless of the detailed history of the filling process. However, if two concavities were connected, e.g., via a subterranean conduit, one would rob the other of fluid, a well-known instability.¹² Furthermore, if Fig. 1 were the cross section of a long trough, a lengthwise instability would occur, since $dp/dv < 0$, encouraging liquid to bunch up along the length of the trough.

We now consider melting M subsequent to its deposition, shown schematically in Fig. 2. The deposition itself will in general produce a continuous thin film, bridging concavities and field, a situation labeled "step coverage" in integrat-

FIG. 2. Schematic to illustrate *sequential* deposition and liquefaction. Surface of deposited film in (a) reproduces substrate contours, but following suitable melting procedures the surface becomes flat (b). Subsequently, the film may be delimited to desired locations only, by conventional lithographic procedures, as indicated by dashed lines.

FIG. 3. Overfilling and the role of pinning points, denoted P in the schematic. The two recesses differ only in the presence or absence of an overhang at P . Effective contact angle α may exceed true contact angle θ by as much as 90° in this example.

ed circuit technology. If the films were completely melted at this time, many concavities, in fact most, would lose fluid to the field. One may, however, first level the surface of the thin film, illustrated in Fig. 2(b). Melting of only the surface portions of the film, as is done in contemporary laser technology, should smooth the film, or pressure against a flat plate can accomplish the same purpose. Furthermore, material M can be removed from the field, e.g., by lithographic techniques, so that M remains only in or adjacent to concavities. Upon melting then the material tends to remain in the concavity.

III. OVERFILLING AND PINNING POINTS

Deposition can proceed to fill structures beyond the level illustrated in Fig. 1(d). We label this situation overfill and illustrate it in Fig. 3. Here the fluid may exhibit an apparent contact angle α , with respect to the hemispherical surface, that exceeds θ , due to the discontinuity of slope at point P . As long as α does not become so large that liquid can move laterally across the field, exhibiting the proper contact angle θ there, the pinning point P becomes a boundary for the liquid. With this boundary in effect, continued addition of

FIG. 4. Detachment of liquid from substrate to produce a void. Two possible positions of a hypothetical lower meniscus are shown, both implying a nonpositive pressure in adjacent fluid. In this example, upper meniscus, with $p > 0$, prevails and void is squeezed out.

FIG. 5. Void formation in a conical depression. Depending on η and the amount of filling, void may or may not be stable.

fluid pushes the meniscus upward and increases the pressure, i.e., $dp/dv > 0$, until α reaches 180° . This adds considerably to the stability, and the examples cited earlier, interconnected concavities and long troughs, now become stable.

The effect of the pinning point may be somewhat enhanced by the addition of an overhang, shown to the right in Fig. 3. The overhang is easily fabricated on composite substrates, e.g., SiO_2 on Si. It permits larger percentage changes in v in the favorable stability range $dp/dv > 0$, and also allows, in principle, a negative pressure meniscus, which might be useful in some circumstances. Also, an overhang can prevent the step coverage mentioned earlier and separate thin film on the field from that in the concavities.⁶

Filling beyond the level $\alpha = 180^\circ$, so that fluid protrudes over the field, can still offer some stability. However, in such a case, $dp/dv < 0$, and there comes to be more liquid above the concavity than in it, so that one will usually prefer a lesser filling.

IV. VOID FORMATION

A difficulty that can arise, particularly when concavities other than hemispherical are contemplated, is detachment of fluid from the substrate, i.e., formation of a void, as illustrated in Fig. 4. In this way a lower meniscus is created,

FIG. 6. Hemispherical cavity modified by insertion of a central flat region. Meniscus labeled "max flat" circumscribes the largest droplet that fits onto the flat region. For the relative dimensions in this example, this droplet protrudes less than the one that fills the cavity.

FIG. 7. Depression produced by plasma etching, and which roughly resembles the modified hemispherical cavity of Fig. 6. Depth is $\sim 4 \mu\text{m}$.

which must be in equilibrium with the upper meniscus. For the small voids shown in Fig. 4, the lower meniscus will clearly be unstable against the upper one and the void will collapse. In fact, it is easily shown that any size void in a hemispherical cavity is unstable when $\theta \geq 90^\circ$.

Other cavity shapes are more prone to void formation, however. The conical cavity of Fig. 5 would have a planar, i.e., $p = 0$, lower meniscus for values of $\theta = 90^\circ + \frac{1}{2}\eta$, where η is the vertex angle. Larger values of θ can stabilize a void at the vertex, though we note that the pinning point again helps by increasing pressure in the overfill regime.

The above considerations may be helpful when one considers that cracks in a substrate, with small values of η , are unlikely to fill and induce spurious nucleation during crystal growth. On the other hand, when one deliberately introduces interior right angle corners, as in the overhang structure of Fig. 3 or for controlled nucleation in graphoepitaxy,² there may be problems in cases where $\theta \gtrsim 135^\circ$.

V. OTHER CAVITY SHAPES

Though hemispherical depressions afford stability during deposition and are not subject to voids, they do not necessarily afford an optimum shape for crystal growing. For example, a large flat area, or sheet, will often be a preferred

FIG. 8. Indium filling the depression of Fig. 7, with a comparison globule of In on planar surface (*field*). Viewed 75° from surface normal. The substrate surface is thermally grown SiO_2 (on Si).

FIG. 9. Indium filling a trough $\sim 15 \mu\text{m}$ wide with cross section similar to that in Fig. 7. Comparison droplets are attached to various contours. Viewed $\sim 82^\circ$ from surface normal. SiO_2 surface.

shape. Some modification of the hemispherical depression toward this end does not change meniscus shapes too much as suggested in Fig. 6. While droplets can form on the flat region in this figure, they cannot grow very much, or protrude very much, before becoming bounded by curved surfaces which shape the meniscus much as in Fig. 1. The concavity of Fig. 6 can be produced by isotropic etching with the original lithographic opening an appreciable fraction of the ultimate diameter of the structure. Alternatively, one may produce roughly similar shapes by plasma etching, an example of which appears in Fig. 7. When the contact angle is in the lower end of the range of interest, $\theta \lesssim 120^\circ$, sensitivity to the details of the shape seems to be not too great in various experiments we have performed. An example appears in Fig. 8, where In fills such a structure to the pinning point. This result was obtained by sequential deposition and liquefaction.

If the central flat region of Fig. 6 becomes sufficiently enlarged, however, many droplets, including large ones, can now form on the flat region and protrude well above the substrate surface. Indeed, even in Fig. 6, if θ approaches 180° , a droplet can protrude substantially. Thus, one may obtain, instead of the flat sheet of liquid desired, one or more large protruding droplets.

Another shape of interest for crystal growth would be long troughs. The presence of one long dimension would enable one to use temperature gradients and perhaps other features of macroscopic crystal-growth technology. The stability of troughs can be considered with the aid of Figs. 1–3, now imagining the figures to represent midsections through a trough. Simultaneous deposition/liquefaction as in Fig. 1 no longer yields stable agglomerations due to the $dp/dv < 0$ consideration discussed earlier. Thus, one must resort to sequential deposition/liquefaction, sketched in Fig. 2. If there is sufficient deposition to engage the pinning point, dp/dv becomes positive and the liquid is stable. However, overfilling sufficient to make $\alpha \gtrsim 180^\circ$ in Fig. 3 causes $dp/dv < 0$ and lengthwise instability sets in. An example of a filled trough appears in Fig. 9, where clearly the pinning point is engaged.

One notes troughs to either side of the filled one where lengthwise collapse has occurred, though portions of the resulting globules still lie within the troughs.

VI. SUMMARY

A first consideration in growing crystal from liquid captive on an inert substrate is that the liquid configuration be mechanically stable. Equilibrium considerations were used to analyze stability for various substrate geometries. Greatest stability occurs when protruding regions of substrate, labeled pinning points, cause the internal pressure p in the liquid to increase upon addition of more liquid, i.e., $dp/dv > 0$. The lesser stability afforded in $dp/dv < 0$ regimes may still be useful, however, particularly for certain substrate geometries. Also important is the manner of depositing and melting desired material on the substrate, a topic discussed more qualitatively.

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