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"Crystal Growth in Substrate-Confined Liquids"

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SUMMARY

The objectives of this task is to develop crystal growth techniques utilizing substrate-confined-liquids (S.C.L.). In particular, the crystals will mostly be grown as arrays of single crystals and will include semiconductor crystals useful as detectors.

The primary technical problem is to learn how to produce stable arrays of pools of liquid in the substrate surface (S.C.L.) and to grow a single crystal from each liquid pool.

The approach to the problem is primarily experimental. A classical theoretical framework already exists to guide the experiments, which now must test a number of parameters to optimize stability and crystal growth.

Some results have been obtained with germanium and are treated in the next section of this report. An important finding at this time is that, at least under some conditions, germanium appears to nucleate within the fluid phases rather than at the substrate/liquid interface. The implication of this for further research is that there is a possibility to align crystals grown from S.C.L.

Most hardware development at this time has to do with pattern design for the substrates and the subsequent processing of the substrates.

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DETAILED REPORT

Crystallization of a semiconductor thin film on the substrate where it is to be ultimately used is being widely investigated. Most such studies of *in situ* growth utilize laser or other dynamic heating means for zone melting and growth of Si sheet crystal⁽¹⁾; an appropriate substrate is an oxidized Si wafer, which in some cases determines an orientation for the growing Si sheet via openings in the oxide.

A rather different scheme adopted in the present work^(2,3) is the isothermal heating of a substrate with surface concavities which stably contain liquid; crystal growth from the contained liquid may proceed by any of various conventional methods, e.g. Bridgman technique. Indeed the proposed scheme may be viewed as an extension of traditional growth techniques to smaller dimensions in which liquid stability is maintained by the combined effects of surface tension and geometry. Previous papers have treated various aspects of liquid stability in an individual concavity. In the present paper, we study various experimental techniques to stably fill an *array* of concavities with liquid and make some qualitative observations suggesting that a single crystal may grow from each liquid pool. If such crystals were to be of sufficient quality, arrays of this sort should be useful as detectors or for photovoltaic energy conversion.

I. General Experimental Considerations

Experiments were undertaken to test several possible variables implicit in our earlier proposal^(2,3). Briefly, we proposed that liquid held captive in concave depressions in a substrate surface be used as a crystal growth medium. One variable, for example, is the concavity size used to contain liquid, which by being of the order of the capillary height or less, extends the size

range for crystal growth to much smaller dimensions than are commonly used. In the present experiments, some concavities were prepared by machining to millimeter dimensions, and thus are comparable in size to capillary heights of the liquids studied, whereas in other cases lithographic methods were used and micrometer-sized structures were obtained. The machining was done on high-density, high-purity graphite without lubricant and under a canopy to avoid pick-up of dust. Lithographic preparation was conventional, utilizing oxidized (100) Si wafers and a single mask with a hexagonal array of circular openings with a repeat distance of 20 μm . The circular openings in the mask, and hence the openings cut in the SiO_2 surface, were $\sim 8 \mu\text{m}$ in diameter. On chemically etching the Si, however, the concavities enlarged in a horizontal as well as a vertical sense and became similar to the "hemispherical concavity modified by insertion of a central flat region" discussed earlier⁽³⁾. After enlargement of the pits, SiO_2 was removed by etching and then the whole wafer covered uniformly with thermal oxide $\sim 0.2 \mu\text{m}$ thick. An array of such concavities appears in several figures in this paper and is labeled the "honeycomb structure". Typical concavity depth is $\sim 6 \mu\text{m}$.

An important variable in containing liquids in the surface of a substrate is the contact angle, θ . For liquid Ge against either graphite or SiO_2 , we observed $\theta \gtrsim 150^\circ$, which makes containment rather precarious, though a corresponding gain is that chemical interaction across this interface appeared to be minimal. Heavy elements nearby to Ge such as In and Sn provided intermediate contact angles against SiO_2 surfaces of $\theta \sim 110^\circ$, favorable for containment. To explore behavior at low contact angles, $\theta < 90^\circ$, we chose the Au-Ge eutectic against SiO_2 . The small θ provided by this choice may be associated with some interaction between substrate and liquid⁽⁴⁾, however. In addition, eutectic nucleation and growth is more complex than is crystal growth with single elements.

Though the experimental techniques will be discussed in detail for each particular system studied, one further problem is common to all systems and needs comment here. No matter how densely one packs concavities on a substrate surface, there must remain some surface between concavities, albeit small. This is the region called the *field* in integrated circuit technology. When one deposits material onto the substrate, as solid or as liquid, some deposit accumulates on the field and usually needs to be removed. The method we have found most generally useful for clearing the field of unwanted deposition takes advantage of the disparity in size of deposits on the field and in concavities. The deposits on the field are usually much the smaller and thus are consumed in processes like etching or evaporation long before the material in the concavities. Also, much used in the present experiments are multi-step depositions, alternating between liquid deposits and solid deposits. The rationale for this is that a previously melted film may be further coalesced by a freshly deposited thin intermediate connecting layer.

II. Ge on SiO₂ and C

One of the simplest systems to study would be an elemental semiconductor melting against an inert substrate, e.g. Ge against SiO₂ or graphite. This particular example, which is known from the early days of zone melting to give a large contact angle, provides a feasibility test for substrate-confined liquids at large θ . Graphite substrates were machined, using the precautions mentioned earlier, to produce hemispherically-bottomed pits typically with radius of 0.84mm. Liquid Ge in such a pit was found to be more stable if the hemispherical pit reached the surface through a short section of cylindrical hole of the same radius as the hemisphere. The length of this cylindrical section of the pit was typically only one-third the radius of the hemispherical bottom. After machining, the graphite

substrates were heated at $\sim 1200^{\circ}\text{C}$ in flowing purified H_2 for several minutes.

Chunks of semiconductor-purity Ge of millimeter size or somewhat less were etched in (5:5:1, $\text{HNO}_3:\text{CH}_3\text{COOH}:\text{HF}$) and loaded by tweezer into each pit. The Ge was then melted under pure H_2 . Usually, more chunks were added to fill the pits, followed by remelting. After the final filling and melting, a moderately slow cooling, estimated to be $\sim 1^{\circ}\text{C}/\text{sec}$, was employed near the melting point. Appearance of the Ge after solidification is illustrated in Fig. 1. Notable are the crystallographic features suggesting that the boule is composed of at most a few crystals, and the large effective contact angle, approaching 180° , between Ge and graphite.

Behavior of Ge on SiO_2 surfaces was studied using the "honeycomb structure" mentioned earlier. The substrate was heated $\sim 120^{\circ}\text{C}$ above the melting point of Ge in a vertical cold wall CVD reactor containing a pure H_2 ambient. The Ge deposition was initiated by the introduction of GeH_4 into the H_2 stream. Germanium was deposited at a rate of $\sim 2\text{--}3\ \mu\text{m}/\text{min}$. This is an example of the process labeled *simultaneous* deposition and liquefaction in an earlier discussion⁽³⁾.

Figure 2 illustrates agglomeration of Ge after various deposition times. In the early stages of deposition many globules of Ge can occupy a single pit. As deposition continues, however, globules coalesce until eventually only one globule can occupy a pit. Also, illustrated in the figure is the formation of globules on the field. Where the area of the field is relatively small, as in Fig. 2a and 2b, such globules tend to be relatively small, whereas the larger field area in Fig. 2c permits relatively larger globules on the field. Also, evident in Fig. 2 is the large contact angle between Ge and SiO_2 .

Even with the considerable field areas exhibited by the present specimens, however, it is possible to clear the field of Ge, so that Ge remains only in the array of pits. Figure 3 demonstrates this result, obtained with a multi-step

processing. With the substrate at 620°C, and the deposition rates mentioned above, Ge was deposited for 45 sec, i.e. to a thickness of $\sim 2 \mu\text{m}$. Substrate was then heated to $\sim 1050^\circ\text{C}$ to agglomerate the Ge and, while at this temperature, another $\sim 2 \mu\text{m}$ of Ge was deposited. Temperature was then lowered to 620°C and the above sequence repeated. After the last deposition at 1050°C, specimen was cooled, going moderately slowly ($\sim 1^\circ\text{C}/\text{sec}$) through the melting point of Ge. Specimen was then etched in (5:5:1, $\text{HNO}_3:\text{CH}_3\text{COOH}:\text{HF}$) to clear the field and, further, to exhibit facets on the surviving Ge in each pit.

Several features of Fig. 3 deserve comment. The field has been cleared completely, but the fairly extended etching needed to do so tends to enhance any inequalities in the filling of the pits. Indeed with only modest additional etching some pits would be cleared along with the field. Also, noteworthy is the faceting on the remaining Ge, which indicates that the globule remaining in each pit gave rise to at most a very few crystals.

III. In and Sn on SiO_2

Much of the difficulty in growing Ge directly from substrate-confined liquid arises from the large contact angle just noted. Further experiments were done with In and Sn liquids on the honeycomb structure to study behavior at intermediate values of θ near 110° . These liquids, which turn out to be rather well behaved, may be useful later for solution growth of Ge and perhaps other semiconductors as well.

Indium was deposited by vacuum evaporation onto honeycomb structure at room temperature. Substrate was heated to melt the In, then cooled to room temperature. This procedure was repeated several times. Specimen was then etched in dilute HCl to clear the field, followed by heat treatment at 700°C for two hours in forming gas (13% H_2 in He) to deoxidize the In and allow it to form equilibrium shapes on the substrate. Figure 4 illustrates the results obtained after four

deposition cycles as just described. Again, the field has been cleared completely. Compared to the Ge examples in Fig. 3, a more uniform filling of the pits was obtained. An incidental result of the processing described above is that some In evaporated during the 700°C treatment, thus somewhat exaggerating non-uniformities in filling of the pits.

Similar experiments were performed using Sn. Since Sn is more brittle than In, it was possible to prepare cleaved sections to exhibit clearly the occupation of a concavity or pit by a globule. Figure 5 illustrates this situation for partial filling of the concavities and without clearing the field. This specimen was prepared by evaporating 2.23 μm of Sn onto a substrate heated above the melting point of Sn. After cooling the substrate, an additional 0.65 μm of Sn was evaporated onto the cold substrate, followed by heating above the melting point, then cooling. Cleaving was done at liquid nitrogen temperatures.

Incidentally, Fig. 5 exhibits clearly the concavity shape obtained by chemical etching in the honeycomb structure. The inclined sidewalls of the concavity are less favorable for liquid containment than would be vertical sidewalls as produced, for example, by plasma etching.

IV. Au-Ge Alloy on SiO_2

Germanium-rich hypereutectic alloys in this system were studied as an example of solution growth. The rather substantial Ge growths produced from solution were accompanied by fairly extensive eutectic structures, adding complexity to the results. The eutectic composition in this system, at least, does provide a contact angle less than 90° against SiO_2 , a matter of interest for liquid stability.

Figure 6 provides an overall view, without clearing the field of the sort of growths that were produced. In this instance, a 21.7 wt/o Ge alloy with Au was evaporated in a vacuum system with a baseline pressure of $\sim 3(10)^{-9}$ Torr onto

a honeycomb substrate heated sufficiently to insure that the alloy would be completely liquid on the substrate. The charge evaporated was enough to yield an average thickness of $2.9\text{ }\mu\text{m}$ of deposited material. After five minutes at temperature, an additional charge of Ge corresponding to a deposition thickness on the substrate of $0.32\text{ }\mu\text{m}$ was evaporated. Thus, the final composition was 25.3 wt/o Ge, i.e. about twice as rich in Ge as the eutectic. Specimen was cooled somewhat faster than the $1^\circ\text{C}/\text{sec}$ mentioned earlier. One notes from Fig. 6 that fairly uniform filling was obtained with indications of some diversity of structure from pit to pit. After etching the Au with $\text{I}_2:\text{KI}:\text{H}_2\text{O}$, much of the structure in the pits was clarified. For example, Fig. 7 shows Ge growths remaining in position after partial removal of Au. Further application of Au etch cleared such pits entirely, i.e. cleared of Ge crystal as well as Au. Thus, Ge crystal appears not to have been in direct contact with the substrate and, consequently, must have nucleated within the liquid or at the liquid-vapor interface. Faceting observable on the Ge growths again suggests that rather large crystals relative to the pit size are being grown.

V. Discussion and Conclusions

The present experiments explored several systems for *in situ* growth of semiconductor crystals from substrate-confined liquid. The systems encompassed a substantial range of contact angle, size of substrate concavity, and techniques for stable filling of concavity as well as for clearing the field of deposits. In most instances, an *array* of concavities was used since such an arrangement would be directly useful in applications.

Observations in the various systems indicated that several goals are attainable. Large crystals of Ge, i.e. of size comparable to the concavity used, appear to grow fairly readily, suggesting that the same may be true of other semiconductors with little reactivity toward the substrate. Fairly uniform filling of the

concavities making up an array was also demonstrated, particularly when the contact angle is not very large. Clearing of the field area between concavities of material deposited incidental to the filling of the concavities was also demonstrated. These goals are not necessarily independent of one another, however, and trade-offs between them may be needed.

Of more immediate interest, however, are improvements suggested by the present work. Oxidized Si substrates could present appreciably smaller field area by utilizing oxide openings that pack more densely than the present circular openings, e.g. hexagonal or square openings. Vertical sidewalls in the concavities would offer improved stability. Also, where chemical etching is employed, the Si wafer should have appropriate symmetry for the shape of oxide opening, e.g. (100) wafers for square openings, since even nominally isotropic etches are in fact slightly anisotropic as one notes in Fig. 2. Improved substrates as suggested above are planned for future experiments. The new substrates should not only facilitate the goals mentioned above, but also allow us to explore possibilities to orient the growing crystals. Since the crystals appear to be unattached *within* fluid phases, at least in the AuGe case, they may be alignable by various forces, e.g. magnetic or from bounding surfaces via surface tension⁽⁵⁾.

References

1. For accounts of recent work see, for example,
H. W. Lam, R. F. Pinizzotto, and A. F. Tasch, Jr., J. Electrochem. Soc., 128, 1981 (1981);
E. W. Maby, M. W. Geis, Y. L. Le Coz, D. J. Silversmith, R. W. Mountain, and D. A. Antoniadis, IEEE Electron Device Letters, EDL-2, 241 (1981);
B. Y. Tsaur, John C. C. Fan, M. W. Geis, D. J. Silversmith, and R. W. Mountain, Appl. Phys. Lett. 39, 561 (1981);
T. J. Stultz and J. F. Gibbons, Appl. Phys. Lett. 39, 498 (1981);
R. A. Lemons and M. A. Bösch, Appl. Phys. Lett. 39, 343 (1981).
2. T. F. Kuech and J. O. McCaldin, Appl. Phys. Lett. 37, 44 (1980).
3. J. O. McCaldin and T. F. Kuech, J. Appl. Phys. 52, 803 (1981).
4. K. N. Tu and S. H. Libertini, J. Appl. Phys. 48, 420 (1977) describe interactions at the Au/SiO₂ interface.
5. E. Hartmann, N. N. Sheftal, and V. I. Klykov, Acta Physica Academiae Scientiarum Hungaricae, 47, 185 (1979).

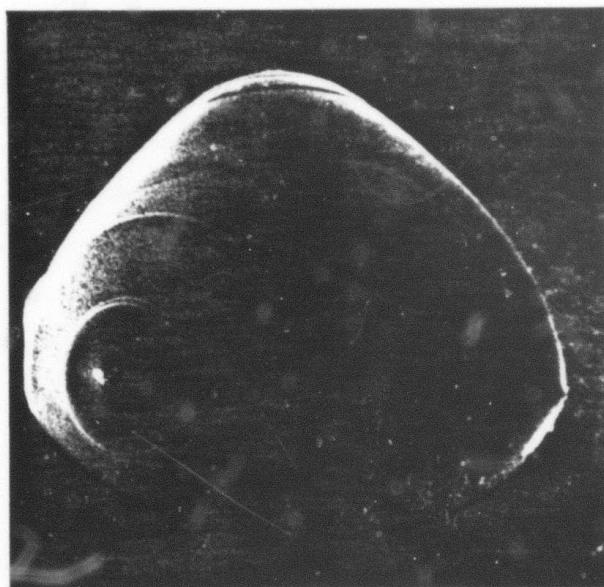


Figure 1 Germanium crystallized in pit in a high-density graphite substrate. The pit, 1.68 mm across, was machined into the substrate and was loaded with Ge by hand before heating.

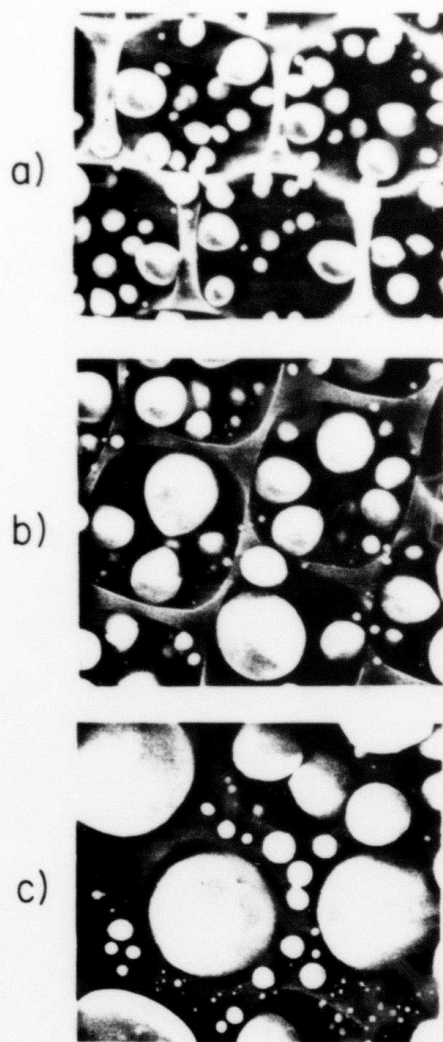


Figure 2

Germanium accumulation on substrate heated above the melting point of Ge. Substrate is the "honeycomb structure" described in the text, with 20 μm repeat distance and a maximum concavity depth of $\sim 6 \mu\text{m}$. Duration of the CVD deposition is a) 30 sec, b) 60 sec, and c) 120 sec.

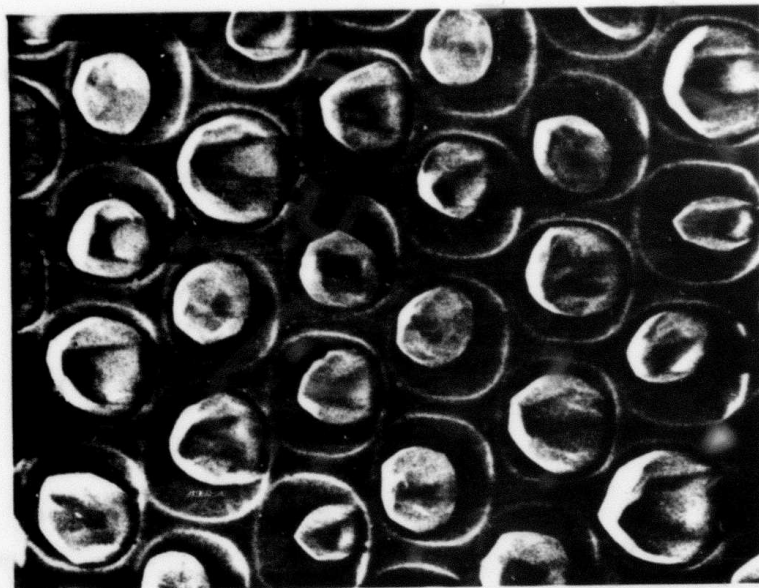


Figure 3 Isolation of Ge in pits and clearing of Ge from the field. Processing is described in the text. Horizontal streaking in the picture is an artifact due to charging of the specimen.

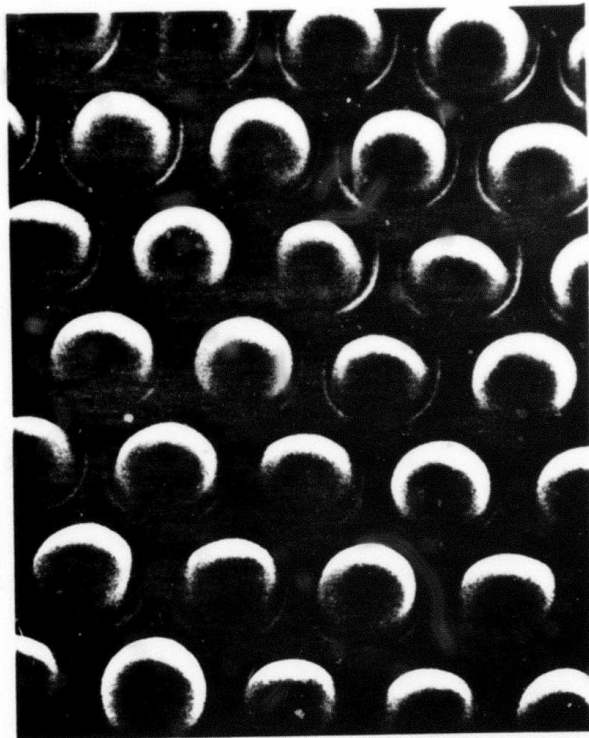


Figure 4

A more uniform filling of the pits. Indium liquid used in this example produces contact angle near 110° against the SiO_2 substrate surface.

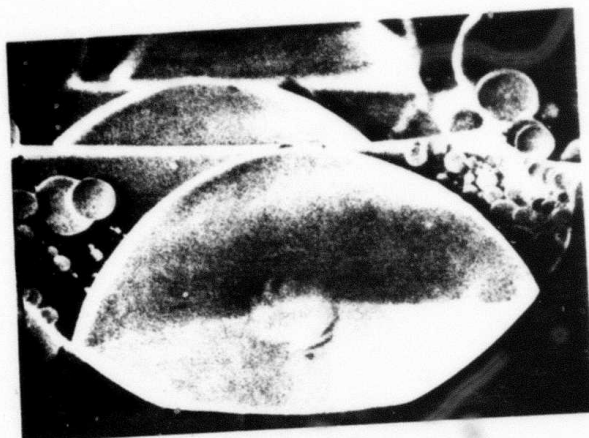


Figure 5

Cleaved section of "honeycomb" substrate with pits partially filled with Sn. The cleaved surface of the substrate lies in the plane of the paper; the nearest large globule of Sn did not cleave and protrudes from the substrate toward the reader. Contact angle, Sn on SiO_2 , is somewhat greater than 90° .



Figure 6

Au-Ge hypereutectic (i.e. Ge-rich) mixture on a "honeycomb" substrate. Fairly uniform filling was obtained in two-step vacuum evaporation onto hot substrate as described in text.

a)



b)

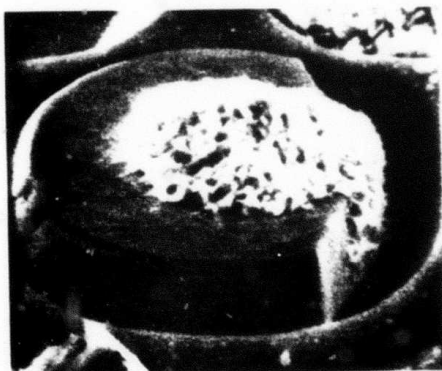


Figure 7

Germanium growths remaining in pit after partial removal of Au by etching of structures in the previous figure. White material is residue from the incomplete etching of Au.