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NEW OUTLOOK ON CONTROL OF CRYSTALLINE AND CHEMICAL PERFECTION DURING GROWTH OF SILICON

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Significant progress has been made in our understanding of the Czochralski crystal growth process with the realization that the incorporation of oxygen into silicon is directly related to the internal gettering capability of wafers during device fabrication. Stringent oxygen concentration requirements in silicon brought about intensive studies of crucible (SiO_2) dissolution, oxygen accumulation in the melt, its transport to the growth interface, and its incorporation into the growing solid. In context, it was also recognized that the electronic properties exhibited by silicon during various stages of device fabrication were significantly affected by the thermal history of the silicon during the post-growth cool-down period. These studies led to a comprehensive analysis of the heat and mass transport behavior in conventional Czochralski growth systems, and resulted in the evolution of new concepts for their control.

Turbulent melt convection, induced by unavoidable destabilizing thermal gradients, was found to interfere with homogeneous dopant (and oxygen) incorporation and to influence markedly the dynamics of non-equilibrium point defects in the solidified silicon matrix during the cool-down period.

Moreover, both segregation and point defect dynamics appear adversely affected by asymmetry in heat transfer to and from the melt.

Growth control, with the crystal diameter as the primary control objective (ADC), while responsive to optimized silicon throughput requirements, is now considered inadequate (if not inappropriate) in view of stringent bulk property requirements.

In view of the unavoidability of destabilizing thermal gradients in conventional crystal growth configurations, melt stabilization through the application of magnetic fields is generally considered as a viable approach. Large melts do experience pronounced damping of temperature oscillations and a corresponding decrease in non-rotational segregation effects under applied vertical and horizontal magnetic fields . The accompanying reduction of the rate of heat transfer in the melt, however, generates complications through changes in the prevailing temperature gradients and in the time constant of the hot-zone which still have be overcome. An additional side effect of magnetic field stabilization is the spatial reorganization of convective melt flow patterns which may alter the radial temperature distribution and thus lead to changes in segregation behavior.

Control of heat input to the melt through heat pipe systems, as used during growth of germanium, cannot be applied to industrial growth of silicon. Required heat pipe systems with operating temperatures of about 1400°C are as yet not available; moreover, the effectiveness of peripheral heat pipes in generating radially symmetric thermal fields in the melt is found to decrease with increasing cavity diameter. Recent studies have shown that heat exchange systems located coaxially about a growing crystal can be used to stabilize and control not only heat transfer in the grown crystal, but also in the melt adjacent to the solidification interface. This approach is expected to provide for controllable, quantifiable, and reproducible thermal boundary conditions at critical parts of growth systems and shows promise as a parameter for growth with bulk crystal perfection as the control objective.

FIGURE CAPTIONS

Fig. 1 Heat transfer system associated with Czochralski growth of semiconductor systems. The defect structure of material obtained by this technique reflects the non-uniformity and uncontrolled nature of heat input and heat loss; related thermal gradients in the melt are destabilizing and give rise to turbulent convection; thermal field distribution is asymmetric, leading to non-axisymmetric convective flow patterns and to related deficiencies in segregation.

Fig. 2 Microsegregation behavior exhibited by silicon doped with antimony. Compositional variations on a microscale revealed by differential etching reflect growth perturbations at frequencies ranging from 10-0.1 Hz caused by temporal and spatial variations in convective melt flows.

Fig. 3 Schematic presentation of convective interference with equilibrium segregation during liquid-solid phase transformation of binary system in Czochralski configuration.

Fig. 4 Origin of rotational (semi-macro) and non-rotational (micro) segregation during Czochralski growth.

Fig. 5 Achievement of radially symmetric heat input to a semiconductor melt through the use of a heat pipe located coaxially between the graphite heater and the melt confining crucible. This approach is as yet limited to operation at less than 1100°C because of the unavailability of high temperature heat pipe materials. It should also be noted that the effectiveness of this approach is limited to heat pipe cavities with I.D.'s of less than about 4"; at larger cavity diameters, unavoidably asymmetric heat losses lead to asymmetric thermal field distributions and to related segregation effects.

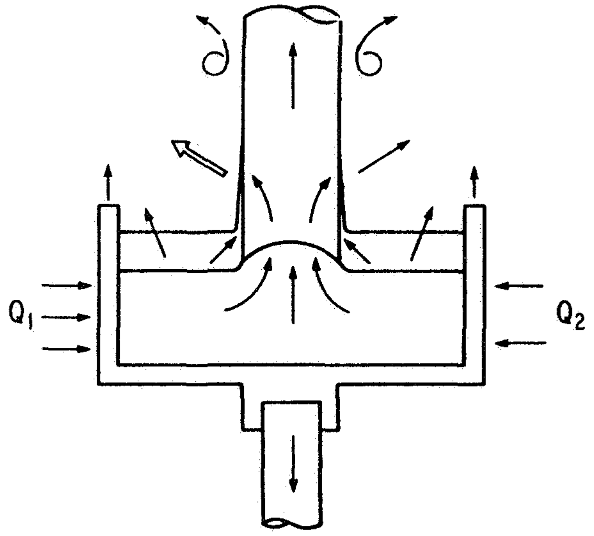
Fig. 6 Heat pipe based heat exchange system to control thermal gradients in growing semiconductors. The heat pipe located coaxially about the growing crystal provides for constnat, controllable ambient temperature which significantly affects thermal stress generation and the dynamics of supersaturated point defects. Using Peltier heating or cooling respectively, it is possible to maintain ambient temperatures ranging from about 500-1100°C.

Fig. 7 Radial thermal stress distribution in GaAs during LEC growth with and without controlled heat exchange. It should be noted that the resolved shear stress at all axial locations exceeds critical resolved shear stress by up to one order of magnitude.

Fig. 8 Heat exchange system providing for controllable axial thermal gradient in crystal grown by the Czochralski technique.

Figure 1. Conventional Cz and LEC Growth Without Heat Transfer Control

- Asymmetric heat input and loss
- Interface Morphology to a limited extent controllable by speed rotation
- Encapsulation film thickness uncontrolled
- Vertical thermal gradient about interface not easily controllable
- Radial thermal gradient in crystal uncontrolled
- *History of temperature field, T($\hat{x}$, t), in* growing crystal unknown and uncontrollable



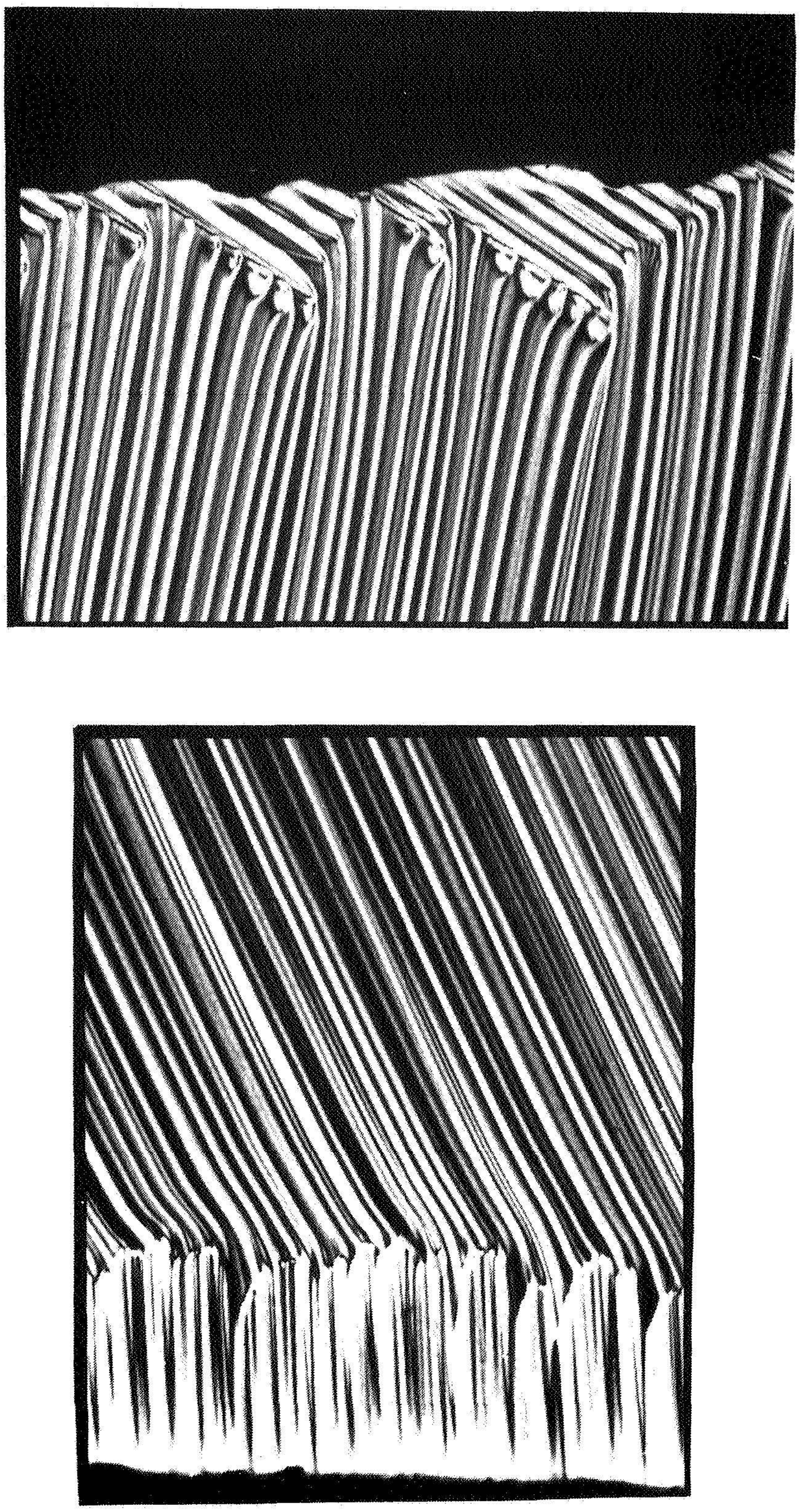
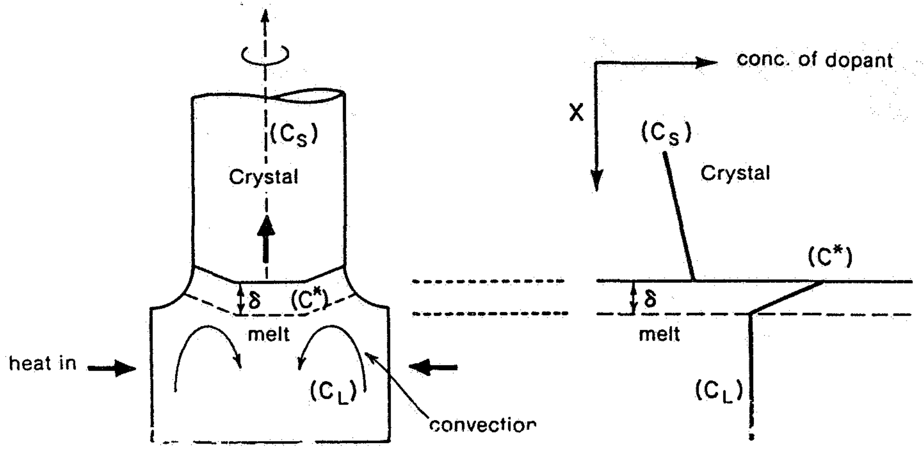


Figure 2

Figure 3. Melt Growth Configuration and Associated Composition Profile



C = concentration of minority constituent: (C_S) in solid
(C_L) in melt
(C^*) at melt-crystal interface

δ = diffusion boundary layer thickness (controlled by convection and/or crystal rotation)

Convection: leads to longitudinal *macrosegregation:*

$$C_S\ (X) = k_{eff}\, C_L(0)(1-g)^{k_{eff}-1}$$

$k_{eff} = \frac{C_S}{C_L}$
g = fraction melt solidified
C_L (0) = starting melt composition

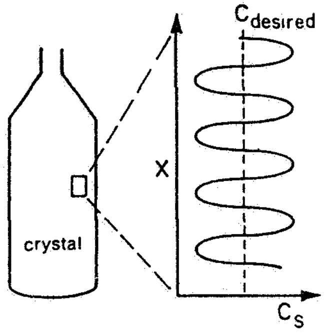
Temporary perturbations: lead to *microsegregation:*

$$C_S = \frac{k C_L}{k+(1-k)e^{-\frac{\delta R}{D}}}$$

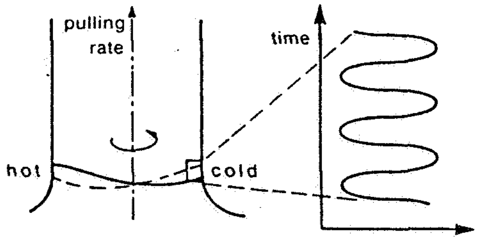
$k = \frac{C_S}{C^*}$
D = diffusion constant
R = rate of growth

Figure 4. Origin of Microscopic Compositional Inhomogeneities in Melt-Growth Matrices

(a) rotational striations:

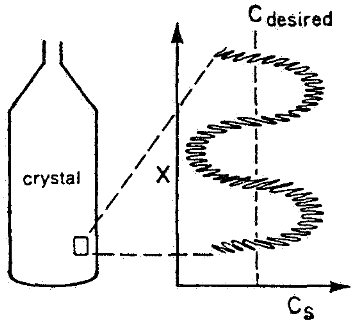


REASON:
crystal rotation in non-asisymmetric thermal environment:

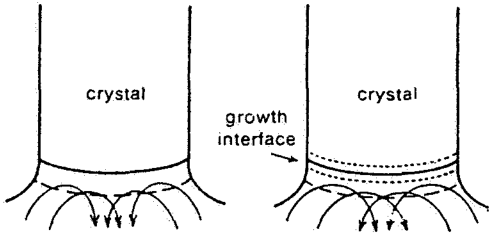


$$C_S = \frac{kC_L}{k + (1-k)e^{-\frac{\delta R}{D}}} \leftarrow \text{R varies periodically}$$

(b) non-rotational striations:



due to turbulant convection δ and R vary randomly in high temperature systems:



δ variations in melt

R variations due to T fluctuations because of temporal relocations of growth interface

$$C_S = \frac{kC_L}{k + (1-k)e^{-\frac{\delta R}{D}}} \quad \text{δ and R vary randomly}$$

Figure 5. Cz Grown With Heat Pipe for Radially Symmetric Thermal Field Distribution in Melt

- Effectiveness Limited by Crucible Diameter

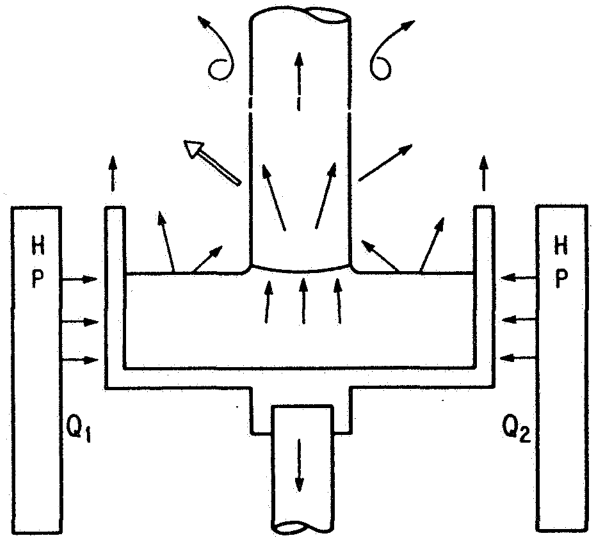
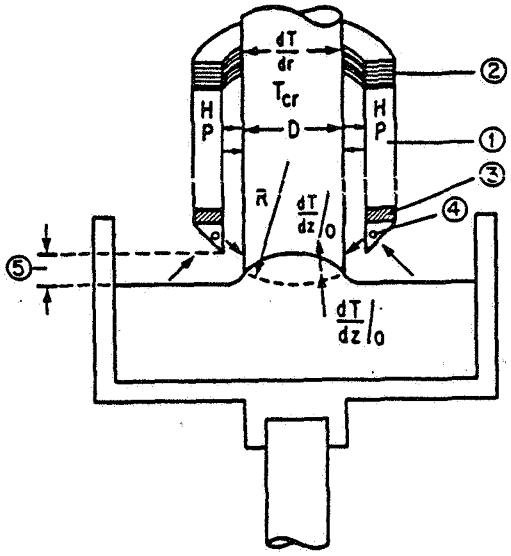


Figure 6. Heat Exchange System for Optimized Control of the Following Interdependent Parameters:

- Crystal temperature (range 500 °C - 1100 °C)
- Growth interface morphology
- Temperature gradients about the growth interface
- Radial thermal symmetry in the vicinity of the growth interface
- Radial thermal gradient in growing crystal



① Inconel Heat Pipe with Operating Range from 500 °C - 1100 °C.
② Peltier Heating / Cooling System.
③ Thermal Insulation.
④ Auxiliary Heating Element.
⑤ Axial Position of Heat Exchange System (adjustable)

Figure 7. Effect of Heat Exchange System on Reduction of Stresses at Periphery of a GaAs Crystal

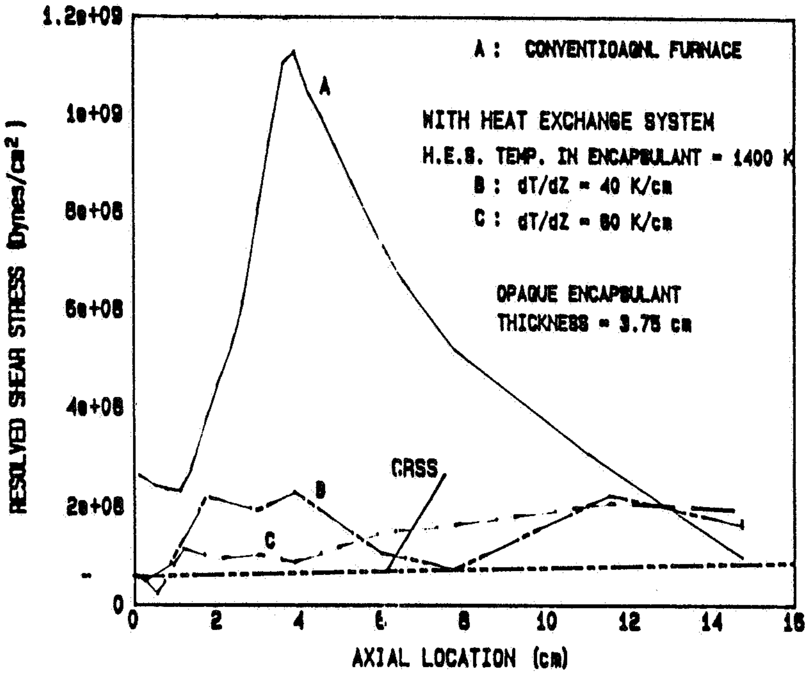
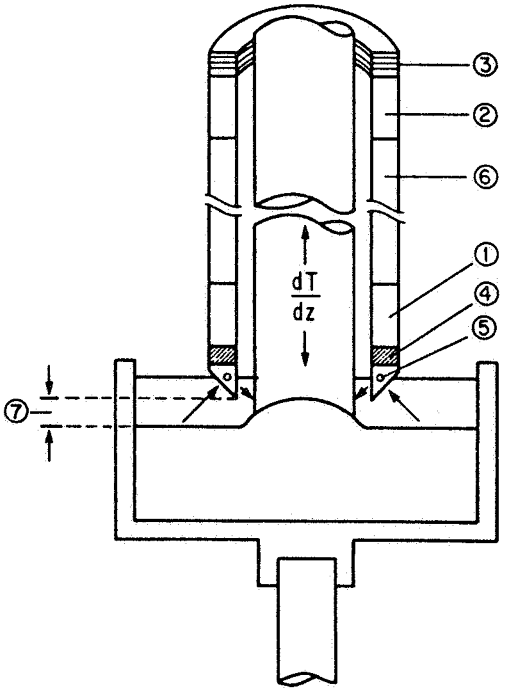


Figure 8. Heat Exchange System for Optimized Control of Axial Temperature Gradient in Growing Crystal



①② Inconel Heat Pipes with Operating Range from 500 °C - 1100 °C.
③ Peltier Heating / Cooling System.
④ Thermal Insulation
⑤ Auxiliary Heating Element
⑥ Controlled Gradient Region
⑦ Axial Position of Heat Exchange System (adjustable)

DISCUSSION

WITT: My colleague, Dr. Schwuttke, is convinced that he can get the degree of contamination in Czochralski growth to the level of float-zoning. I am pessimistic about this. If I look at all of the evidence that has been compiled so far, I don't see it.

SCHWUTTKE: We should strive to improve the Czochralski quality in terms of oxygen content to a point that is approaching what we have in float-zone after two passes, and that is around 10^{17}. We can produce Czochralski today with 2×10^{17}, and I think that is not even optimized.

MORRISON: One of the things that makes float-zone attractive, at least from a cost point of view, is the high thermal gradients giving high growth rates. In Czochralski growth all of the newly applied technologies to improve the process talk about adding heat. Adding heat has to slow the growth rate. Are there technologies where we can go the other way?

WITT: You bring out a very valid point. You want to optimize the growth rate. If you do that you have to operate under a very high thermal gradient but if you believe that that will lead to superior material along the lines of point-type defects you are wrong. I think you can stabilize your supersaturated point-type defect so that it does not coalesce or cluster and deteriorate. But on an absolute basis, you then have an inferior material, the more you remove yourself from the equilibrium phase transformation. Therefore, it is my contention that that in principle is the weak point of float-zoning. The complication that I see is the very strange and, in my opinion, non-quantifiable thermal boundary condition associated with the hour-glass type configuration of float-zone growth. I think an attempt at modelling and, therefore, optimizing float-zoning along these lines is not even on the horizon. In my opinion, if you want maximum throughput, you can get it and I think you can increase your throughput in Czochralski very, very significantly with no problem. I think the maximization of growth rates at what I heard today at two inches is far removed from what's theoretically possible. But the question is, do you want to? The material will have very negative side effects when you go to high-temperature processing.

LESK: When you rotate a crystal in a liquid you get a certain amount of pumping action. Is that anywhere near the significant thermal gradient effect?

WITT: Sure, you have two driving forces in that configuration. One of them is natural convection, due to the density gradient, which moves the system outward, up, and in towards the center. Counteracting that you have forced convection due to the crystal rotation, which has a centrifugal force that moves the fluid up and out. Unfortunately, the driving forces in much of the Czochralski system are so high for convection that in at least the bulk of the matrix I do not see the dominance of forced over natural convection. In addition to that, in many of these systems we are not dealing with an annular ring, as predicted by theory, but rather in one cell a typical consequence of the thermalized symmetry of the system. You are correct, in low-temperature systems. If you go to germanium or indium antimonide at 450° or at 940° then the driving forces are small, and if the volume in addition is small, then you get exactly what you want. You get, at low rotation rates, dominance of natural convection, and at high rotation rates, you get dominance of forced convection due to the seed rotation.

KIM: Your approach to achieve thermal symmetry is very logical, but I wonder if it is practical. Wouldn't it be an experimental nightmare to have six heaters controlled separately?

WITT: Fortunately, we are a university, so the nightmare isn't so great. At this stage we have two different approaches, as I indicated. The first approach is to test the effectiveness of the heat pipe coaxially. This is not a simple approach. If we see the responsiveness of the thermal field due to the location of the heat pipe then there is no longer a need for the radially asymmetric heat input. The second approach we are actively now engaged in is totally modifying the basic heater design. We are very concerned about the vertical gradient control and this is where we are designing our system with three independent ring-type heaters, which will allow us to get a handle on the heat losses on the bottom and on the gradient control, which are partially responsible for the convection.

KIM: Is it correct that you can measure the silicon melt temperature with plus or minus one degree resolution?

WITT: Yes, although absolute calibration is a problem. We are not interested in absolute temperatures in process control. We are interested in temperature changes. Therefore, the need for absolute calibration doesn't arise. If you do thermal imaging, the primary problem you must overcome is internal reflections.

ELWELL: Do you have any feeling or experimental evidence on whether surface tension forces are stronger than the buoyancy in a typical Czochralski growth?

WITT: I have none. I personally do not believe all the indicators, and the indicators that we do have suggest that we have indeed density driven convection. However, theoreticians, particularly in Europe, and several of them in this country, are not convinced that density-driven convections are the cause of our problem rather than surface-tension-driven convections.

SCHWUTTKE: Maybe they should do their experiment in space.

WITT: They have suggested that, but so far there were more failures than results.