around the center: the spiral "noses" at small radii rotate at an angular velocity $v_n/r$ which is submultiple $m$ of the natural chemical frequency $\omega$. Moreover, the entire spiral pattern appears to turn as a solid at angular velocity $(\partial\theta/\partial t)_{r,c} = \omega/m$, as is evident from Eq. 4. Here too is indication that the more highly curved a chemical wave, the lower its normal velocity.

This case of only two reactive species, one immobilized, which obey linear reaction kinetics and diffusion laws is no doubt too simple to describe accurately the Belousov-Zhabotinskii reaction in membranes or in shallow dishes [we performed experiments resembling those of Winfree (*6*) in shallow dishes]. Nevertheless, the oversimplified model indicates what is possible with only diffusion and chemical reaction in more complicated, multicomponent systems that lack oscillating chemical sources or "pacemakers." What waves appear in a system hovering on instability depends on chance nonuniformities and transitory perturbations. The model shows that the wave speed decreases when the wave-front curvature increases. The experimental observations suggest that this is responsible for the shape instability leading to spontaneous growth of spiral waves from an isolated perturbation or fluctuation in a homogeneous system. The model shows that the involute of a circle is not the only wave shape in which rotation and time translation are interchangeable (*13*) and makes plain that the pitch and velocity of a spiral chemical wave, like the wavelength and speed of plane, harmonic chemical waves, are completely dependent on chemical kinetics and diffusivities.

Membranes can be washed and reused. New wave patterns appear randomly; there is no evidence of "pacemaker centers" (*6*). The interaction of wave dynamics and membrane structure can be studied (*14*). Figure 2 shows propagation across slits; the propagation is from top to bottom. When the wave velocity and slit length coincide in direction (as at the slit shown in the upper right in each photograph), waves propagate in phase along the slit. When a wave impinges on a slit obliquely the front divides and propagates out of phase along the edges. At the horizontal slit in Fig. 2, the branch propagating along the lower edge is also moving away from the slit, creating an arc of high curvature that advances more slowly than the upper branch. Figure 2c shows a wave reappearing on the lower edge, as though the wave on the upper side has bridged the ferroin-free gap. The most probable mechanism is diffusion of mobile species; the estimated diffusion time for a slit 0.006 cm wide and for $D = 10^{-6}$ to $10^{-5}$ cm$^2$/sec is 3 to 30 seconds, in agreement with the observations.

The dynamic state of a developing pattern can be halted and recorded permanently by using a membrane precoated with silver bromide. As dynamic patterns develop, the areas occupied by oxidized ferroin blacken with precipitate. In water the darkened regions remain and record the state of the pattern at the time of washing; see Fig. 3. Fixation yields examples of static patterns whose origins lie in the interaction of several dynamic processes. Pattern generation by interfering diffusion and chemical reaction underlies the theory of biological morphogenesis first suggested by Turing (*15*).

J. A. DeSimone
D. L. Beil
L. E. Scriven

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis 55455*

### References and Notes

1. C. W. Carr and K. Sollner, *J. Gen. Physiol.* **28**, 119 (1944).
2. H. P. Gregor and K. Sollner, *J. Phys. Chem.* **50**, 53 (1946).
3. B. P. Belousov, in *Sb. Ref. Radiat. Med.* (Collection of abstracts on radiation medicine) (Medgiz, Moscow, 1959), p. 145; A. M. Zhabotinskii, *Dokl. Akad. Nauk SSSR* **157**, 392 (1964); V. A. Vavilin and A. M. Zhabotinskii, *Kinet. Katal.* **10**, 83 (1969).
4. A. M. Zhabotinskii, in *Oscillatory Processes in Chemical and Biological Systems* (Science Publishers, Moscow, 1967), p. 149.
5. H. G. Busse, *J. Phys. Chem.* **73**, 759 (1969); M. Herschkowitz-Kaufman, *C. R. Acad. Sci. Ser. C* **270**, 1049 (1970); A. N. Zaikin and A. M. Zhabotinskii, *Nature* **225**, 535 (1970); R. J. Field and R. M. Noyes, *ibid.* **237**, 390 (1972).
6. A. T. Winfree, *Science* **175**, 634 (1972).
7. The parameters $a_{i0}$ and $a_{jk}$ can be managed to account for interchange between reservoir and membrane, which can be described by $H_i(c_i' - c_i)$; see Gmitro and Scriven (*8*).
8. J. I. Gmitro and L. E. Scriven, in *Intracellular Transport*, K. B. Warren, Ed. (Academic Press, New York, 1966), p. 221.
9. In the case of systems described by linear equations of the form of Eq. 1, the behavior depends on the independent invariants of a matrix of reaction rate constants, a matrix of diffusion coefficients, and the products of those two matrices (*8*).
10. The constants $c_1{}^0$ and $c_2{}^0$ are chosen to eliminate the terms $a_{10}$ and $a_{20}$ from the reaction-diffusion equations, that is,
$$c_1{}^0 = \frac{a_{20}a_{12} - a_{10}a_{22}}{a_{11}a_{22} - a_{12}a_{21}},\quad c_2{}^0 = \frac{a_{10}a_{21} - a_{20}a_{11}}{a_{11}a_{22} - a_{12}a_{21}}$$
We restrict $c_1{}^0$ and $c_2{}^0$ to positive values; $A_1$ and $A_2$ are amplitudes and are arbitrary except that they may not be greater than $c_1{}^0$ and $c_2{}^0$, respectively; $\phi$ is the phase angle by which the concentration wave of species 2 lags that of species 1.
11. J. Higgins, *Ind. Eng. Chem.* **59** (No. 5), 18 (1967).
12. H. M. Cundy and A. P. Rollett, *Mathematical Models* (Oxford, London, ed. 2, 1961), p. 73.
13. Winfree (*6*) assumed that the magnitude of the phase velocity is independent of position on the wave. This leads to involutes of circles as solutions. The spiral solutions admitted by a reaction-diffusion analysis indicate that $v_n$ varies and in general decreases as the curvature increases.
14. Ferroin-collodion membranes appear to offer a means by which the Belousov-Zhabotinskii reaction may be coupled to transmembrane electric current in diffusion cell studies. Transport and conductance measurements across membranes with variable charge density may be useful models for active transport in biomembranes.
15. A. M. Turing, *Phil. Trans. Roy. Soc. London Ser. B* **237**, 37 (1952).
16. The authors thank C. W. Carr and E. Grim for aid in preparing membranes and R. Aris for criticism and a timely reminder. J.A.D. held an NIH postdoctoral fellowship.

11 January 1973

■

## Crystal Growth of Silicon and Germanium in Metal Films

Abstract. *Amorphous silicon in contact with silver films and amorphous germanium in contact with aluminum films form crystalline precipitates when heated to temperatures well below those at which any liquid phase is present. Crystallization occurs by an initial dissolution of the semiconductor into the metal film solvent followed by the growth of crystals out of the solvent.*

Crystal growth can occur from any nutrient medium: vapor, liquid, gel, or even solid (*1*). As an example of crystal growth in a solid, we find that solid metal films can provide a medium for the growth of semiconductors such as Si and Ge at temperatures well below those at which any liquid phase is present (that is, eutectic temperatures). For example, we have observed the crystal growth of Ge in Al films at temperatures as low as 100°C. In this case, the metal dissolves the semiconductor at one interface, transports it, and permits it to grow into crystals at another location, with all processes occurring some 300°C below the eutectic temperature.

In addition to the surprisingly rapid kinetics just noted, we find in evaporated films a naturally occurring and convenient driving force for the above reactions. In our earlier investigations (*2*) we have relied on a temperature cycle to obtain supersaturation of a solid metal solvent with Ge or Si and hence crystal growth; this is the familiar metallurgical process of saturating

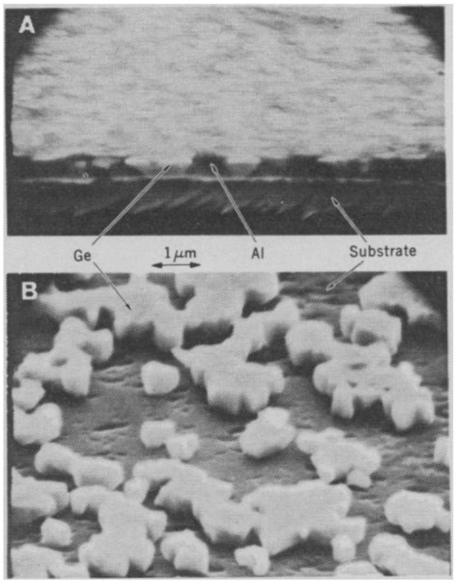

Fig. 1. View of a Ge/Al sample after heating to 300°C for 1 hour. (A) A cleaved surface shows Ge precipitates embedded in an Al matrix. (B) The Ge precipitates after the Al matrix has been etched away. The scanning electron micrographs were taken with 10-kev electrons incident at 80° to the surface normal. The sample was prepared by depositing 3600 Å of Al on 1800 Å of Ge evaporated on a Si substrate.

with solute at a fixed temperature followed by cooling to obtain supersaturation. In the work presented here, however, we have utilized the higher free energy of amorphous Ge (*3*) or Si as compared to their single-crystal counterparts to provide the driving force for supersaturation and crystallization.

Samples were prepared in an ion-pumped system by evaporating either Si or Ge at pressures of approximately $10^{-7}$ torr onto substrates held at room temperature. The evaporation conditions were such that amorphous films were produced (*4*). In the same pumping operation the amorphous films were overcoated with evaporated metal to form Ge/Al and Si/Ag composites. The thickness of the Ge films ranged between 50 and 2000 Å, and the Al films were held approximately constant in thickness at 4000 to 5000 Å. The Si films were 300 to 2000 Å thick, and the Ag films were about 2000 Å thick. After the evaporations had been completed, the samples were immediately heated and quenched in a dry $N_2$ atmosphere. For the samples described here, process temperatures were 300°C for Ge and 700°C for Si. However, the reactions were observed to occur, although more slowly, at temperatures as low as 100° and 400°C, respectively, for these two systems.

The properties of the semiconductor-metal films were analyzed by the backscattering of million-electron-volt $^4$He ions and by electron microprobe, scanning electron microscopy, and transmission electron diffraction techniques. The backscattering technique, used as a depth-sensitive microscope in material analysis (*5*), gives information on the distribution of mass in depth with a depth resolution of 100 to 200 Å. Our backscattering measurements showed the amorphous Ge and Si films in the process of dissolving into the metal film during heat treatment. With sufficient heat treatment the semiconductor films are completely dissolved by the metal film. Our electron microprobe investigations showed that the Ge and Si formed large precipitates within the metal with a lateral size of 2,000 to 40,000 Å. Because of the large size of the precipitates, it is unlikely that they are formed during the fast cool-down. Thus, both dissolution and precipitation take place simultaneously during the isothermal heat treatment.

The results of the electron microprobe analysis were confirmed by scanning electron microscopy, which showed in addition that the precipitates had nearly the same thickness as the composite film. Figure 1A shows a Ge/Al sample held at a temperature of 300°C for 1 hour that was cleaved in liquid $N_2$ to prevent smearing of the Al. The view of the cleaved surface shows the Ge embedded in an Al matrix. Figure 1A also clearly shows that the surface is flat. Figure 1B shows the same sample after the metal film had dissolved, leaving the precipitates exposed on the surface. This reveals again the "island" nature of the precipitates formed on the Si substrate.

Figure 2A shows an image of a Ge precipitate, and Fig. 2B shows the corresponding transmission electron diffraction pattern. These results clearly indicate the crystalline nature of the precipitate. Measurements of the channeling effect indicate that the majority of the crystallites have not grown epitaxially.

In summary, we find that the crystallization of an amorphous film in contact with a suitable, evaporated metal can proceed by way of the dissolution of the amorphous material into the metal solvent followed by the growth of crystals out of the solvent. The reaction proceeds at temperatures substantially below those at which any liquid phase is present.

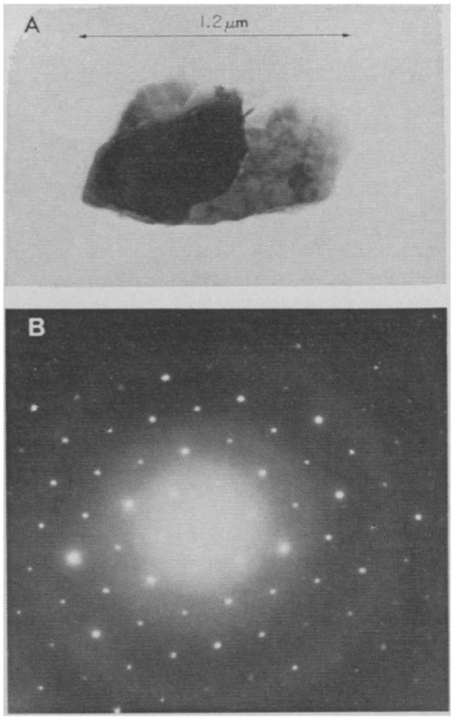

Fig. 2. (A) View of a Ge precipitate stripped from a Ge/Al sample after heat treatment at 300°C. (B) The transmission electron diffraction pattern from the same specimen.

*Note added in proof*: Transmission electron microscopy and diffraction studies of the evaporated Si and Ge films now clearly show these films to be amorphous.

G. OTTAVIANI,* D. SIGURD†
V. MARRELLO, J. O. MCCALDIN
J. W. MAYER
*California Institute of Technology,*
*Pasadena 91109*

### References and Notes

1. R. A. Laudisse, J. R. Carruthers, K. A. Jackson, *Annu. Rev. Mater. Sci.* **1**, 253 (1971); H. K. Henisch, *Crystal Growth in Gels* (Pennsylvania State Univ. Press, University Park, 1970); J. H. Brophy, R. M. Rose, J. Wulff, in *Structure and Properties of Materials*, J. Wulff, Ed. (Wiley, New York, 1964), vol. **2**, p. 112; M. Tannenbaum, in *Semiconductors*, N. B. Hannay, Ed. (Reinhold, New York, 1959), p. 87.
2. J. O. McCaldin and H. Sankur, *Appl. Phys. Lett.* **20**, 171 (1972); G. Ottaviani, V. Marrello, M-A. Nicolet, J. W. Mayer, J. M. Caywood, *ibid.*, p. 323; V. Marrello, J. M. Caywood, J. W. Mayer, M-A. Nicolet, *Phys. Status Solidi* (a) **13**, 531 (1972).
3. H. S. Chen and D. Turnbull, *J. Appl. Phys.* **40**, 4214 (1969).
4. T. M. Donovan, E. J. Ashley, W. E. Spicer, *Phys. Lett. A* **32**, 85 (1970); T. M. Donovan, thesis, Stanford University (1970).
5. M-A. Nicolet, J. W. Mayer, I. V. Mitchell, *Science* **177**, 841 (1972).

6. We thank J. Devaney of the Jet Propulsion Laboratory for carrying out the scanning electron microscopy and H. J. Arnel and R. Villagrana for carrying out the electron diffraction measurements. The work was supported in part by the Office of Naval Research.

* Permanent address: Physics Department, University of Modena, Modena, Italy.
† Permanent address: Research Institute for Physics, Stockholm, Sweden.

15 January 1973