

Solitons and Their Role in the Degradation of Doped Silicon Germanium Alloys *

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Abstract

The long-term performance of Si-Ge alloy thermocouples in Hectowatt radioisotope thermoelectric generators (RTG's) is known to be significantly reduced by degradation effects which are, in part, due to the precipitation of dopants in the thermo couple legs. The time-dependent behavior of both polarity types of Si-Ge alloys obeys the kinetics of a diffusion-limited precipitation model. We show how the growth of precipitate zones is controlled by the low energy instabilities of solitons in the continuum Ising model of binary phase systems. The soliton description provides a simple intuitive picture of the kinetics of precipitate growth and reproduces the correct rate law usual by extracted with greater difficulty from the conventional diffusion-based models.

I dont know what it means, that nature chooses these curious forms, but maybe that is a way of defining simplicity. Perhaps a thing is simple if you can describe it fully in several different ways without immediately knowing that you are describing the same thing.

—R. P. Feynman

Introduction

The rate of precipitation of the dopants Phosphorus and Boron from solid solution in SiliconGermanium alloys is well-known [1, 2] not to conform to the conventional empirical rate law [3, 4] usually applied to the precipitation of dopants in semiconducting materials. Moreover, since the rate of precipitation is a significant factor in determining the long-term reliability of devices such as Hectowatt RTG's based on doped Si-Ge alloy thermocouples, considerable effort has been devoted to determining the appropriate rate law and also to improving our theoretical understand-

ing of why the conventional law is not applicable to Si-Ge systems.

I would like to take the opportunity presented by this conference on thermoelectric energy conversion to tell you about some of the most current thinking regarding the kinetics of precipitation in two-component systems. In our case the two components are identified with the Si-Ge alloy on the one hand and the dopant on the other.

Ekstrom and Dismukes [1] were able to show early on that the rate of precipitation of Phosphorus in Si-Ge under isothermal annealing conditions obeyed a kinetic model developed by Wagner [5] and Lifshitz and Slyozov [6] for the spinodal decomposition of binary systems. In this (postnucleation) model the conventional diffusion theory is modified to incorporate the interfacial surface tension, σ , between the precipitate zone and the solvent. The rate of zone coalescence is parametrized by a critical zone radius, r_0 , below which precipitate zones redissolve, while zones with radii greater than r_0 are amplified at the expense of the smaller zones. This consumption mechanism is the essential feature of the model which determines its unique rate law. The growth of the precipitate volume is given explicitly by

$$\overline{r(t)}^3 = \left(\frac{8m\sigma D}{9kT\delta} \right) t \quad (1)$$

where $\overline{r(t)}$ is the average zone radius at time t , m is the molecular mass of the alloy, D is the diffusion coefficient for the dopant in Si-Ge, δ is the alloy density, k is Boltzmanns constant and T is the Kelvin temperature. Lifshitz and Slyozov derived equation (1) using asymptotic scaling conditions but, unfortunately, the mathematical machinery of their analysis obscures the physics behind this remarkable result. Raag [2] confirmed the applicability of this model for both *n*type and *p*type alloys over much longer annealing times, and extrapolated the reliability data for the Si-Ge alloy thermocouples up to 12 years. Langer [7] in his

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pioneering study of first-order phase transitions [7–9] showed that equation (1) could be derived by considering the stability of stationary solutions to a generalized FokkerPlanck equation. More recently [10], it has been shown that a consistent treatment of these kinds of firstorder phase transitions can be developed on the basis of a continuum Ising model [11–14]. In this latter treatment it is found that both the approach to the firstorder phase transition (nucleation) and the kinetics of precipitation (coalescence) are controlled by the low energy fluctuations of a certain kind of wavelike solution to the Ising model; the *kink-soliton*. Before proceeding with the main purpose of this paper, I want to say a brief word about solitons since they seem to be creeping into all areas of science and there is no reason why scientists involved in thermoelectric energy conversion should be allowed to avoid them!

The word *soliton* has been around for over a decade [15–17] but its origins are much older. The concept stems from the carefully documented observations of a *solitary wave of translation* by the engineer John Scott-Russell early last century [18]. Solitons are not just traveling waves in the usual sense, they are the stable result of a NONLINEAR disturbance in a DISPERSIVE medium. Generally speaking, these two conditions mean that things should fall apart very quickly. Dispersion implies that different Fourier components propagate with different velocities, so that an initial solitary wave pulse should disintegrate. But, solitons owe their remarkable stability precisely to the nonlinearity which couples these different Fourier modes in such a way that it exactly compensates the tendency to disperse. Only a few types of nonlinear models are known to support solitons and the Ising model is one of these.

The physical soliton that Russell witnessed is more commonly referred to as a *hydraulic bore* nowadays, and they are indeed very stable wavefronts, having been seen miles upriver from their point of origin. (It seems Russell was required to make his study on horseback!). Another physical example of a soliton, more closely related to our discussion, is the stable wavefront or *wall* between two magnetic domains of opposite spin alignment in a ferromagnet. The interface between the two domains is very similar to the precipitate interface mentioned earlier. I could say much more about solitons but this is not the place to do it. Until recently we had these apparently independent strands of theory, some of which concerned diffusion models and others relating to solitonbearing models. Now we have found that the Ising model unifies some of these strands into a single fabric. This unification

process is very much a current trend in physics and other sciences. Maybe, as Feynman suggests in the rubric, this is a measure of simplicity in science. Let us concentrate now on the role of solitons in precipitation kinetics.

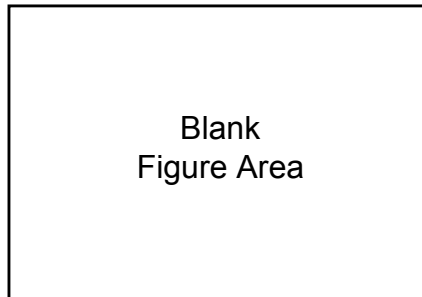


Figure 1: Parabolic potential well above the transition temperature T_c .

The TwoPhase Model

The starting point for our treatment is a version of the so called Ising model first developed as a twostate model of a magnetism. You can think of the two states as being the up and down orientations of a classical spin system representing a ferro magnet. In our case they refer to the two components in the binary (alloy and dopant) system.

The energy of such a system can be represented in the following way. Imagine we are above the transition temperature, T_c , where there exists a single stable homogeneous phase. We can represent this phase by the parabolic well shown in Fig. 1. The stability of this phase is represented mechanically by the unique minimum energy value at the origin. As we descend below the transition point at T_c , the single phase separates rapidly into two well-defined phases. (Incidentally, the mechanism for such a sharp transition is only now just being understood by physicists.) In our mechanical analogy, the single well has now developed two minima and represents a bifurcated anharmonic oscillator (Fig. 2). The two minima correspond to the two stable phases below T_c . This mechanical analog is valid only for a single point particle (or atom if you prefer).

In an alloy or fluid we see the cooperative effects of many-particle interactions—so many that we have to deal with statistical averages: statistical mechanics. One way of going about this is to think of the alloy as a continuum rather than a lattice structure, then position coordinates, x , are replaced by density functions which I’ll call $\phi(x)$ —it is the spin-density or

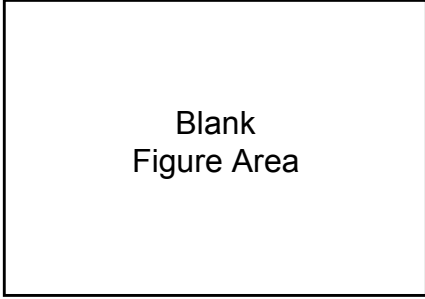


Figure 2: The double-well below T_c .

concentration of the continuum at the point x . Solid-state physicists also call $\phi(x)$ a scalar order parameter. The Ising model, then, is the continuum analog of the quartic potential in Fig. 2 written in terms of $\phi(x)$ instead of x , and it looks like this:

$$V[\phi] = -\frac{1}{2}\mu^2\phi^2(x) + \frac{1}{4}g\phi^4(x) \quad (2)$$

where μ has the dimensions of mass and g is the coupling strength. This form of the energy is directly related to the free-energy curves for binary alloys with which material scientists are very familiar. It is the potential energy expression for the Ising model and differentiating the energy with respect to ϕ gives us the corresponding field equation of motion.

$$\nabla^2\phi(x) - \mu^2\phi(x) + g\phi^3(x) = 0 \quad (3)$$

But what is it that is in motion?

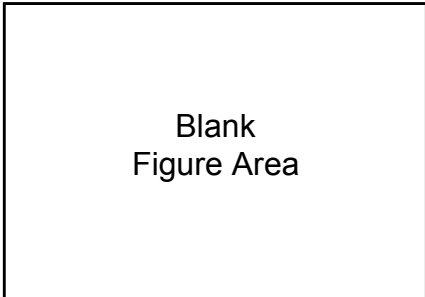


Figure 3: The soliton solutions at the phase boundary and the corresponding energy density of the interfacial profile.

Well, as it stands this is a classical field-theoretic equation, so you might anticipate that all kinds of so-

lutions are possible, depending on the boundary conditions, but that most of these solutions would be intractable analytically—just as one finds in Maxwell's equations for electromagnetic radiation. It turns out however, that if we impose the boundary condition that ϕ begin in one potential well, say at $x \rightarrow -\infty$ and end in the other well at $x \rightarrow +\infty$ then the lowest energy solution to equation (3) (in one dimension) is a stable solitary wave—the *soliton* (Fig. 3). It is described analytically by a hyperbolic tangent function,

$$\phi_c(x) = \frac{\mu}{\sqrt{g}} \tanh \frac{\mu}{\sqrt{2}} (x - x_0) \quad (4)$$

(By the way, there are no solitons in Maxwell's theory because the equations are *linear* in the fields.) Our soliton is the wavefront or interface between the two phases characterized by different densities—it is the density profile between the SiGe and the dopant. As shown in Fig. 4, you can envisage the soliton as a piece of string which straddles the double well potential. Since the well extends in infinity along the x -axis, it would take an infinite amount of energy to unravel the string so that it lay in one well only. There is yet another way of visualizing the stability of the soliton, and Ill refer to this point later in the discussion.

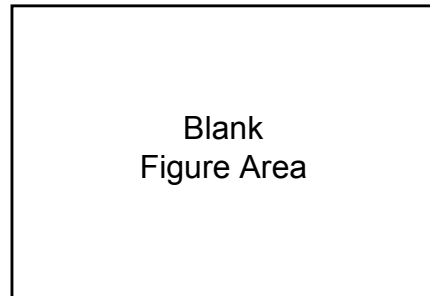


Figure 4: The soliton interpolates between the minima of the double-well potential function.

Although it is not apparent from what we have said so far, there is a conservation law in operation. This law says that the binary composition of the alloy must be maintained always. In Fig. 3 you can see that the corresponding energy density of the soliton is confined to a width $\sim \mu^{-1}$ about the origin at x_0 . Since the amplitude of ϕ_c is set by the barrier height between the two wells, this energy cannot diffuse away without the soliton moving to $x = \pm\infty$ would be tantamount to having a single phase and that situation disobeys the conservation rule. The rate of precipitation is controlled in a very special way by small, thermally driven

fluctuations of the soliton, and this is what I want to address more carefully, while at the same time avoiding most of the impediments that arise from the mathematical details. To develop a better feel for the connection between the soliton and precipitates I want to use what we have learnt so far to illuminate the earlier comment concerning the critical radius, r_0 . For simplicity (without loss of generality), we will assume the precipitate zone to be spherical, then the soliton represents the interfacial profile at the spherical zone boundary—in fact, the sphere is enclosed by two solitons on its diameter; one the reflection of the other. The free energy (\mathfrak{F}) of this spherical zone of radius r can be represented by the difference of two terms: A surface energy S which is area-dependent, and a volume-dependent bulk contribution B , such that,

$$\mathfrak{F} = S(r^2) - B(r^3) \quad (5)$$

If r is less than a certain value, r then the surface term dominates and the zone shrinks ($\mathfrak{F} > 0$), while if $r > r_0$ the volume term wins and the zone grows ($\mathfrak{F} < 0$). The precise value of r can be determined by minimizing the energy of Ising model due to the soliton contribution. The mathematical details are given in Ref. [10]. So when $r > r_0$ it corresponds to the soliton-pair moving apart and when $r < r_0$ they approach each other. This part is easy to understand, but what is not so *obvious* (as Lifshitz and Slyozov would have us believe!) is the essential feature of their model whereby the larger zones consume the smaller zones. The soliton picture provides a beautifully simple representation of this effect, but to appreciate its virtue we need to understand the nature of the fluctuations mentioned previously. As a precursor I'm just going to tell you, without a full explanation, that the fluctuations in the soliton are precisely of the same type as those that arise in the droplet-model of large atomic nuclei. Since the energy is bounded at the surface of the zone or droplet, the allowed energy states are *quantized*! These discrete levels are generated by an eigenvalue equation of the form,

$$M \chi_\ell = E_\ell \chi_\ell \quad (6)$$

and are given approximately by the formula,

$$E_\ell \simeq \frac{(\ell - 1)(\ell + d - 1)}{r_0^2} \quad (7)$$

where $\ell = 0, 1, 2, \dots$ is the (orbital) angular momentum quantum number and d is the number of spatial dimensions. What is unusual about this expression for the fluctuation energy is that when $\ell = 0$, E_0 does not

vanish but is negative! E_1 vanishes and E_ℓ for $\ell > 2$ is positive. What do these values mean physically? Well, the positive energy solutions simply correspond to stable distortions of the droplet (p modes, etc.). The zero energy solution belongs to translations of the droplet since the origin is unspecified. The negative energy solution is to be identified with radial dilatations of the droplet or zone. It is this dilatation mode which controls both the nucleation process [10] and the precipitation rate, via equation (6) which is the analog of the diffusion equation.

Growth Mechanics

Lets drop back to one dimension to see in detail how the dilatations are related to the consumption mechanism. The secret to understanding the connection is that we can no longer confine our attention to just one soliton-pair or zone, rather we must consider a linear array of n -zones or $2n$ -solitons. For ease of calculation we assume the configuration is already coarse so that we have a “sawtooth” train of zones (Fig. 5), each of separation λ . This linear superposition of solitons corresponds to a new eigenvalue problem with χ in equation (6) replaced by the Bloch wave

$$\chi_k(x) = \sum_{j=0}^{n-1} \exp(ik\lambda j) \operatorname{Sech}^2(x - \lambda j) \quad (8)$$

where $k = (\text{integer}) \frac{2\pi}{n}$ is the wave vector. The fluctuations are then determined by the explicit form of the eigenvalues, $E(k)$, in equation (6) with the appropriately redefined operator M . You'll find the complete calculation of $E(k)$ in Langer [7] but I want to emphasize the physical nature of $E(k)$ here.

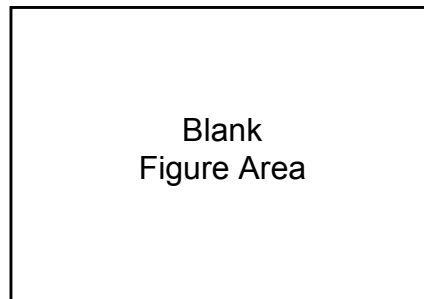


Figure 5: Superposition of soliton anti-solitons forming a Bloch wave the tight binding approximation.

Oscillations in the linear array shown in Fig. 5 suggest there is going to be some overlap of the wavefunctions defined in equation (8). We want to pick out

those overlap terms which are unstable, i.e., those contributions which give negative values of $E(k)$. Looking at equation (8) you can see that the k -dependence of $E(k)$ will come entirely from the Fourier factor in the sum since the hyperbolic function is independent of k . You can think of the eigenvalues as arising in the following way. The dominant contribution comes from first-order overlap terms, i.e., the sum up to $j = \ell$, so that $E(k)$ has the form,

$$E(k) \simeq (e^{ik\lambda} - e^{-ik\lambda})^2 f(\lambda) \quad (9)$$

where the minus sign means we are seeking the least stable solutions and $f(\lambda)$ is determined by integrating the hyperbolic products over x . We can keep things simple by recognizing that equation (9) can be rewritten as

$$E(k) = -4 \sin^2(k\lambda) f(\lambda). \quad (10)$$

This is the dispersion law for the unstable dilatations of the linear array of precipitate zones in Fig. 5. The explicit k -dependence is shown in Fig. 6. As you can see, maximal instability (the most negative value) occurs at $k = \pm\pi/2\lambda$ while minimal instability sets in as k approaches 0 or $\pm\pi/\lambda$. (Actually the value $k = 0$ is unphysical since it corresponds to only one phase existing in contravention of the conservation law mentioned earlier.)

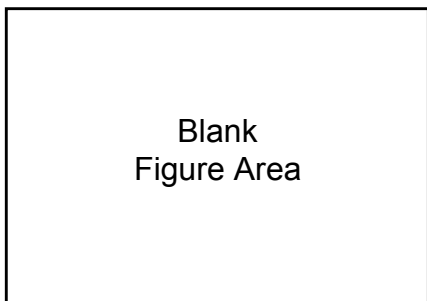


Figure 6: Dispersion relation for the dilatation modes.

Now, the value $k = \pm\pi/2\lambda$ when inserted into the exponent in equation (8) generates coefficients in the sum over of the type $(\pm i)^j$. This degenerate pair of modes corresponds physically to the inward and outward translation of alternate pairs of solitons as shown in Fig. 7. β -rich zones grow and diminish in size alternately, while the α -rich zones retain their size as they move toward each other—the end result of the dilatations being a doubling in the coarseness parameter λ . The other mode simply corresponds to permuting α and β .

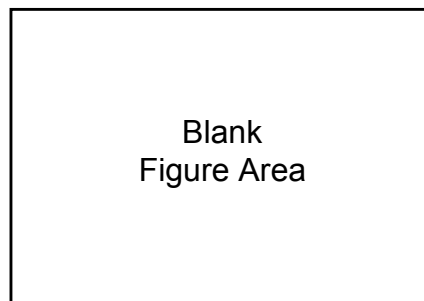


Figure 7: Coalescence of the α and β phases as a consequence of the long-wavelength fluctuations.

Another more stable (slower) mode of consumption occurs near $k = \pm\pi/\lambda$ where $E(\pm\pi/\lambda) = 0$ corresponds to a translation mode as described before. Near $k = 0$ on the other hand, the modes correspond to the coalescence of large groups e.g., α -zones growing throughout half the alloy and shrinking throughout the other half. This is a very slow deformation process which would result in complete separation of the two phases.

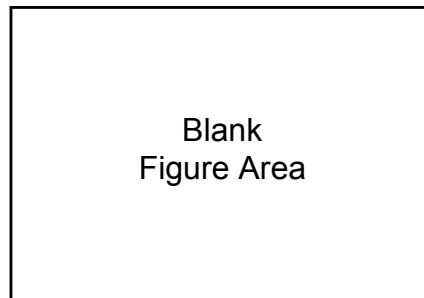


Figure 8: Computer generated plot of soliton anti-soliton annihilation.

If you have followed most of what I have said so far in this talk, you may be struck by something very odd in this soliton controlled growth picture. I started off by telling you about the remarkable stability of solitons and having convinced you of that feature I now seem to be saying that they are *not* stable but can mutually digest one another! Well, the point is that single, isolated solitons are stable, but pairs of solitons can interact or scatter in many different ways. In fact the soliton-pairs we have been discussing are really pairs consisting of a soliton and an antisoliton: like matter and anti-matter they annihilate one another.

other on contact. So everything really is consistent. A quick search of the technical literature [19] uncovered a computer-generated plot (Fig. 8) showing how the soliton-anti-soliton annihilate one another leaving a small oscillating remnant as the only evidence of their prior existence.

Finally, a remark about the form of $f(\lambda)$. As λ becomes larger, making k smaller, the consumption process slows down as the energy becomes less negative. These large groups do not interact as strongly as the original smaller zones—there is a kind of screening of the interaction which is separation-dependent. In fact, it turns out that this screening has the same form as Yukawas old model of the nuclear force, i.e., $f(\lambda) = \lambda^{-1}exp(-2\lambda)$. I don't know why there should be so much nuclear physics in Si-Ge alloys?

The Rate Law for 3-Dimensions

With the onedimensional representation of 3 in mind, it is now a relatively straightforward matter to go over to three dimensions and recover the rate law given by equation (1).

In three dimensions, the operator M of equation (6) now develops a *centrifugal barrier term* going like $\ell(\ell + 1)/2r^2$ and the eigenfunctions χ now involve spherical harmonics. These effects combined with the discrete levels given previously in equation (7) modify the explicit eigenvalues for a spherical zone of radius r . The frequency of the fluctuations is now given by

$$\omega_\ell = \frac{(\ell + 1)(\ell + 2)(\ell - 1)}{r^3} \quad (11)$$

If the number of spherical zones per unit volume is N and ω_0 is the inverse lifetime for the growth or decay of a single zone, then the appropriate rate law can be written as

$$\frac{dN(t)}{dt} = -|\omega_0|N(t). \quad (12)$$

But, N depends inversely on the zone volume r^3 . Substituting in this explicit r -dependence and integrating equation (12) furnishes the result

$$r(t) \sim const. (2\sigma t)^{1/3} \quad (13)$$

in agreement with equation (1) (as promised). The complete process of precipitate evolution is shown schematically in Fig. 9. The initial development consists of zone growth directly from the solution which continues until the degree of supersaturation has fallen to the point where the mean zone radius is of the same size as the critical radius whereupon coalescence supervenes at time t_c .

The initial stage obeys a parabolic rate law, $r^3(t) \sim t^{3/2}$, while the coalescence kinetics is given by

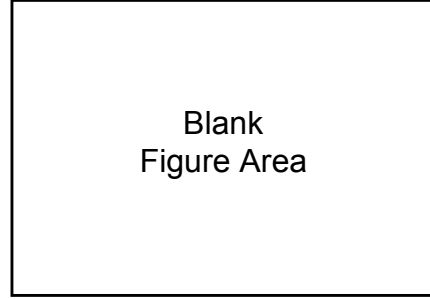


Figure 9: Early precipitate growth follows a parabolic rate law up to T_c and thereafter follows the Lifshitz-Slyozov law.

equation (13). In general we have shown that the most unstable fluctuations are those corresponding to evaporation from the smaller shrinking zones and complementary condensation into the larger growing zones. Whether this process is the dominant mechanism in all alloy coarsening is doubtful, in view of some more recent work [20] supported by compute which predict slower rate curves behaving like $t^{1/4}$ but a discussion of this point would take us too far afield.

In closing, I think it is worth reiterating that the current picture of precipitation kinetics, based on the exotic language of solitons, has provided us with the clearest picture yet of the real growth mechanism, and its intimate connection with the nucleation process. My hope is that this modern soliton picture can be developed further, or at least taken over into other areas of solid-solution kinetics and continue to improve our understanding of thermoelectric materials in general.

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