

Nonlinear Diffusion in Multilayered Semiconductor Systems

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Using quantitative chemical mapping, we study the low-temperature interdiffusion of HgCdTe/CdTe multilayers, sampling volumes 14 orders of magnitude smaller than previously needed for such measurements. Our results shown interdiffusion to be strongly depth dependent and nonlinear, and allow the direct determination of thermodynamic parameters of interest at individual interfaces. The high spatial resolution of our technique establishes that the stability of a layer can depend sensitively on its depth from the surface.

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The advent of highly perfect epitaxial interfaces, across which only the composition changes precipitously, allows the investigation of two questions of fundamental and technological interest. The first concerns the chemical relaxation of inhomogeneous solids which are far from equilibrium, for example by nonlinear diffusion and mixing. The second regards the room-temperature stability of modern multilayered systems, which may well be governed by processes not observable at high temperatures. To study such effects, it is necessary to investigate extremely small interdiffusions on an atomic scale. Twenty years ago, Cook and Hilliard¹ introduced a method capable of measuring small interdiffusivities ($\sim 10^{-20}$ cm²/s), thus verifying the predicted importance of nonlinearity in the intermixing of the metallic Au/Ag system.² This method monitors the intensity of the x-ray satellites produced by the presence of a stack of alternating layers of different composition, and thus averages over a number of interfaces, sampling a volume typically $\sim 5 \times 10^{-6}$ cm³.

In this Letter, we apply the recently developed chemical mapping technique³ to study *local* diffusion in the Hg/CdTe system. Our method samples a volume about 14 orders of magnitude smaller than that sampled by x-ray techniques, but is still capable of measuring interdiffusivities of $\sim 10^{-20}$ cm²/s. We thus study, quantitatively and with atomic-layer resolution, the initial stages of interdiffusion across individual HgCdTe/CdTe interfaces. Our results can be summarized as follows: (i) Interdiffusion is a sensitive function of the distance from the sample surface, varying by up to 2 orders of magnitude as the interface depth is changed from 100 to 7000 Å. This establishes the vital importance of investigating interdiffusion at high spatial resolutions, and questions the general validity of techniques that average over a number of interfaces at different depths. (ii) Linear analysis of interdiffusion in terms of a concentration-independent diffusion coefficient yields a depth-dependent activation energy. (iii) Explicit consideration of the concentration dependence of the diffusion coefficient yields depth-independent free ener-

gies, with a depth-dependent preexponential factor. (iv) At least in the Hg/CdTe system, low-temperature interdiffusion is strongly concentration dependent, and thus highly nonlinear.

A stack of fifty alternating, 50-Å-thick Hg_{0.73}Cd_{0.27}Te and 100-Å-thick Hg_{0.15}Cd_{0.85}Te layers were deposited on a 2-μm CdTe buffer layer grown on a 0.3-μm ZnTe layer on GaAs at 180°C.⁴ (We loosely refer to these layers as HgCdTe/CdTe hereafter.) Bulk samples were sandwiched between CdTe wafers and annealed in Ar for $\frac{1}{2}$ hour in the temperature range 200–265°C. Cross-sectional samples were subsequently chemically prepared, and chemical lattice images obtained^{5,6} and analyzed by a digital vector pattern-recognition algorithm as described previously.³ This procedure compares a given 3.2×3.2 -Å² unit cell of the lattice image with corresponding templates for HgCdTe and CdTe, quantitatively determines the Hg content of each image unit cell rel-

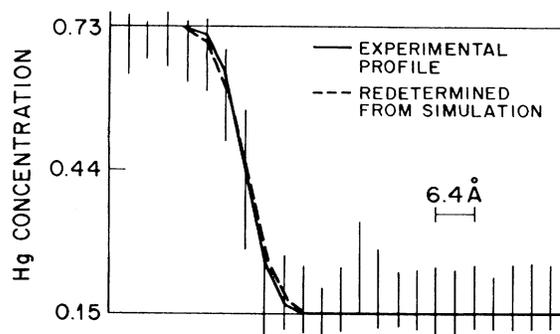


FIG. 1. Hg concentration profile across a single interface, as grown. The successive composition measurements refer to individual molecular monolayers. The solid line is the experimental profile; the dashed line the profile deduced from the simulated image of a sample with a profile given by the solid line. Note that the close agreement between the two profiles shows that nonlinear and nonlocal effects are unimportant under our experimental conditions, and that the experimental profiles accurately reveal the actual composition of each atomic plane in the sample.

ative to the templates, and yields a confidence level for this determination. Composition profiles were obtained for individual interfaces before and after anneals, by averaging the Hg content along 100-Å segments of individual atomic planes parallel to the interface. Since the cross-sectional sample thickness is ~ 200 Å, the determined composition at each atomic plane refers to a volume of $\sim 5 \times 10^{-20}$ cm³.

Figure 1 shows the composition profile for a quantum well, as grown, while Fig. 2 shows the composition profile of the same interface after a 265 °C, $\frac{1}{2}$ -hour anneal. Such composition profiles are obtained by pattern recognition from chemical lattice images, which are produced by electron scattering and imaging. Since such processes are in general nonlinear, and may be nonlocal, it is important to establish the accuracy with which the deduced profiles reflect the actual composition in the sample. To this end, we use a large unit cell and standard multislice procedures⁷ to simulate the chemical image of an interface, which actually has the composition profile deduced from our data (Fig. 1). Then, using the pattern-recognition algorithm, we redetermine the profile from the simulated image of such an interface. Shown dotted in Fig. 1, the redetermined profile traces the input profile almost perfectly. (This close agreement is not sensitive to the details of the simulation procedure). Even when the sample thickness and lens defocus are allowed to deviate from optimum by up to 20% (when significant image changes indicate deviation from appropriate conditions), the resultant profiles lie well within the experimental error bars. From these results, we conclude that our approach yields a composition for each atomic plane, which correctly and accurately reflects the actual composition of the corresponding plane in the sample. We are thus confident that the profiles we obtain accurately represent the actual composition profiles in the sample. Our method essentially measures the composition of individual group-III atom columns each ~ 30 atoms high. Be-

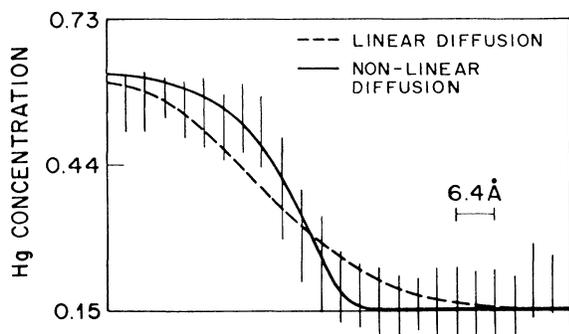


FIG. 2. Hg concentration across interface of Fig. 1 after a $\frac{1}{2}$ -hour anneal at 265 °C. Solid line is the results of a fit from nonlinear diffusion theory, and the dashed line from linear diffusion theory.

cause of random alloy statistics, the Hg content of a 30-atom column of Hg_{0.73}Cd_{0.17} can deviate from 0.73 by up to $\sim \pm 0.1$, which is comparable with the error bars of $\sim \pm 0.14$ in Fig. 1. The accuracy of our measurements is thus close to being limited only by the effect of random alloy statistics in the volume we sample.

Our analysis of the profiles in terms of linear diffusion theory proceeds as follows. The solution of the linear diffusion equation for a periodic set of layers,⁸

$$C(x,t) = C_0 + \sum A_k \cos(kx) \exp(-k^2Dt)$$

[$A_k = (2/T) \int C(x,0) \cos(kx) dx$, $k = 2n\pi/T$, n integral, and T the layer period], is fitted to the comparison profile for each quantum well before annealing. With each of the resultant fits as the initial profile $C(x,0)$ for a given quantum well, and using the diffusion coefficient as free parameter, we fit the annealed profiles for the same quantum well to deduce D as a function of temperature and quantum-well position in the multilayer stack. To determine the uncertainty in the deduced values of the diffusion coefficient D , we calculate the total probability of the fit as D is varied, deducing the most probable values, and lower and upper bounds for D (defined as points at which the fit probability drops to 60% of its maximum value). These probability distributions are later used to deduce similarly defined upper and lower bounds for other parameters such as activation energies.

Figure 3 is an Arrhenius plot of the diffusion coefficients at three different distances from the surface (i.e., from the top of the uppermost CdTe layer). These diffusion coefficients are deduced from a linear analysis, and are shown together with a representative selection of published data from the literature. Remarkably, the activation energy varies strongly with the depth of the

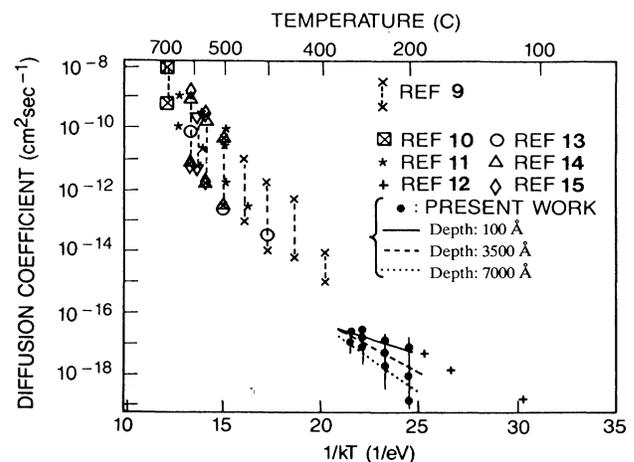


FIG. 3. Arrhenius plot of interdiffusion coefficients deduced from linear diffusion theory. A selection of data from the literature is also shown. Dashed vertical lines show variation of diffusivity with Hg content or ambient conditions.

quantum well beneath the surface, decreasing by nearly a factor of 2 from 0.83 to 0.47 eV, as the depth changes from 7000 to 100 Å. Figure 3 also demonstrates the paucity of low-temperature measurements; up to now x-ray techniques have been the only means of studying low-temperature interdiffusion. However, since such techniques average over many quantum wells at different depths, and interdiffusion is a sensitive function of depth, the interpretation of the x-ray data remains unclear.⁹

Analysis in terms of linear diffusion is unsatisfactory for two reasons. First, the depth dependence of the activation energy for interdiffusion is most surprising, and difficult to understand in terms of a microscopic model for diffusion. Secondly, at high temperatures, the quality of the fits to the composition data is far from satisfactory (Fig. 2). There is strong evidence from measurements at higher temperatures that the interdiffusion coefficient in Hg/CdTe is concentration dependent [see, e.g., Refs. 9–15]. It is possible to carry out a Boltzmann-Matano analysis, but to gain physical insight we use instead an explicit form of the diffusion coefficient, which assumes a linear variation of the defect formation energy with composition:⁸

$$D(C, T) = \tilde{D}(T) \exp(-\Delta H_{\text{CdTe}}/kT) \\ \times \exp[-C_{\text{Hg}}(\Delta H - T\Delta S)/kT] \\ = D_0(T) e^{\alpha(T)C_{\text{Hg}}},$$

where $\Delta H_{\text{material}}$ is the activation enthalpy of the diffusing species in the specified material,

$$\Delta(H, S) = [\Delta(H, S)_{\text{HgTe}} - \Delta(H, S)_{\text{CdTe}}],$$

and C_{Hg} is the Hg concentration. We have numerically solved the nonlinear diffusion equation

$$\frac{\partial C}{\partial t} = D_0 e^{\alpha C} \left[\frac{\partial^2 C}{\partial x^2} + \alpha \left(\frac{\partial C}{\partial x} \right)^2 \right].$$

The solutions were fitted to the experimentally determined profiles, using D_0 and α as free parameters. It is clear from Fig. 2 that the fits are significantly improved. Figure 4 shows plots of $\ln D_0$ and α vs $1/kT$. The form of the exponent α is consistent with $(\Delta H - T\Delta S)/kT$. Remarkably, diffusion throughout the sample can now be described in terms of the same activation energies.¹⁶ The concentration-independent exponent ΔH_{CdTe} is 0.3 ± 0.1 eV. The values for the concentration-dependent exponents are $\Delta H = 1.5$ eV (upper and lower bounds 1.9 and 0.8 eV); $\Delta S = 37.5k$ (upper and lower bounds $21.5k$ and $47k$). The depth dependence of interdiffusion is not entirely contained in the preexponential factor. Collating these results, interdiffusion at low (\sim room) temperature can be described by

$$D \approx D_z \exp[(-0.3 \text{ eV})/kT_{\text{RT}}] \\ \times \exp[(-0.5 \text{ eV})C_{\text{Hg}}/kT_{\text{RT}}],$$

where $T_{\text{RT}} \sim$ room temperature, and D_z is $9 \times 10^{-16} \text{ cm}^2/\text{s}$ at $z = 3500$ Å, and $1.8 \times 10^{-16} \text{ cm}^2/\text{s}$ at $z = 7000$ Å. The reason for the depth dependence of the activation energy deduced from a linear analysis is now clear. A large preexponential factor causes fast interdiffusion and thus a rapid drop in C_{Hg} . Since in nonlinear diffusion C_{Hg} occurs in the exponent, there is a strong coupling between the preexponential factor and the exponent. In a linear analysis, the depth dependence of the preexponential factor inevitably leads to an erroneously depth-dependent activation energy.

It is always tempting, and usually dangerous, to use the results of an interdiffusion study to speculate on the microscopic diffusion mechanism. The following remarks are therefore suggestive rather than definitive in nature. The depth dependence of the preexponential factor may be due to an inhomogeneous distribution of defects, such as vacancies or interstitials involved in the interdiffusion process. Such a distribution may be "grown in," because quantum wells at different depths are held at the growth temperature for different lengths of time, or may be due to injection of defects from the surface during the anneals. The concentration-independent enthalpy of 0.3 eV is indicative of the dominance of a fast diffusor, most likely interstitial Hg, lending support to the notion that with decreasing temperature, there is a switch from vacancy to interstitial-dominated diffusion.¹⁰ However, in contrast to previous low-temperature data, our concentration-dependent activation energy of 0.5 eV is in good agreement with observations at high temperatures, allowing a more consistent description of the concentration dependence of diffusion. The migration enthalpy change of 1.5 eV between HgTe and CdTe is indicative of a strongly concentration-dependent, and hence nonlinear diffusion

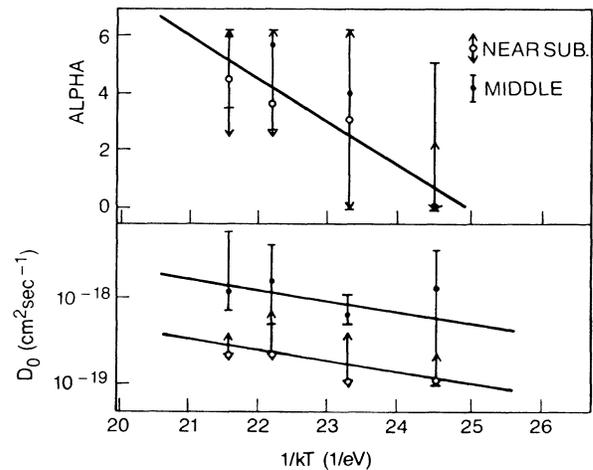


FIG. 4. Plots of the exponent α and $\ln D_0$ vs $1/kT$. Note that only the preexponential factor (given by the intercept of D_0 at large T) changes with depth.

coefficient, and highlights the danger of ignoring non-linearity in semiconductors, which has often been accorded the status of an afterthought.⁹ The relatively large entropy change of $\sim 40k$ may be understood in terms of a correlated response of the lattice to the diffusing species, which also changes strongly with composition. Theoretical estimates of this entropy term for the Hg interstitial are not at hand, but for the vacancy and interstitial in Si they are of the order of $20k$.^{17,18} Thus the value of $\sim 40k$ for Hg/CdTe, although large, may not be unreasonable.

We now speculate on the more general implications of our work. Although low-temperature interdiffusion is of primary interest in the Hg/CdTe system, there is recent evidence that the effects we observe also occur in other semiconductor systems.¹⁹ The depth dependence of interdiffusion stresses the need for the study of individual interfaces, and may have important consequences for the design of stable multilayered systems and devices.⁶ The combination of this depth dependence and the strongly concentration-dependent interdiffusion coefficient can lead to serious errors in activation energies for diffusion deduced from linear theory.

In conclusion, we have shown that it is possible to study, quantitatively and at near atomic resolution, the chemical relaxation of solids, sampling volumes many orders of magnitude smaller than previously needed for such investigations. It is this high spatial resolution that reveals interdiffusion in multilayered systems to be strongly depth dependent, thus questioning the general validity of techniques that average over a number of layers. Interdiffusion in semiconductor heterostructures can also be strongly nonlinear, and our approach has allowed the first direct measurements of the relevant thermodynamic parameters at very low temperatures. We believe the investigation of the relaxation of inhomogeneous solids far from equilibrium, quantitatively and at near-atomic resolution, is now an exciting practicality.

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