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Percolation-Controlled Semiconductor Doping

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The effect of percolation, both of the static and dynamic type, on diffusion is well-known from the field of polymer physics[1,2] and has been found to describe well processes in polymer-based solid-state ionics. Powders and macroscopically porous systems often show a percolation threshold, below which no diffusion occurs.[3] At very high concentrations of defects, correlation effects of diffusion can be described in terms of percolation,[4] and atomic scale (static) percolation has been suggested to play a role in metallurgy, for both vacancy and interstitial diffusion in alloys. However, until recently, clear experimental evidence was lacking.[5] The recently observed inhibition of dezincification of α-brass by minute (0.05 atom %) concentrations of impurities[6] is explained well by frustration of atomic scale percolation (of Zn, via divacancies).[6,7] Another recent inorganic solid-state chemical example of percolation-controlled behavior is the metal−insulator transition in lithiated $ZrSe_2$.[8]

Here we note that the remarkable behavior of Ag in $Hg_xCd_{1-x}Te$[9,10] can be understood by invoking atomic scale percolation. The novel aspect is that this behavior is expressed not only by sharp changes in diffusion of Ag in this semiconductor solid solution, but also by its *doping* action.

Experimentally Ag is found to dope $Hg_xCd_{1-x}Te$ p-type.[9−16] However, below $x \approx 0.2$, n-type material results, as is the case for pure CdTe below 200 °C. Doping is at concentrations of $10^{-4}-10^{-2}$ atom % Ag. This same composition separates fast ($x > 0.2$) from slow ($x < 0.2$) Ag diffusion in p-$Hg_xCd_{1-x}Te$.[10] As long as the Hg content is below about 20% of the total metal content, the room-temperature diffusion coefficient of silver is $<10^{-15}$ cm^2/s, which is very small for this type of system.[17] For Hg contents of 20% or more, the diffusion coefficient jumps to such high values (estimated as $>10^{-8}$ cm^2/s) that evaporated silver contacts on clean surfaces can vanish ("dissolve") in a few hours, and, under small positive bias, even in a few minutes.[10,12]

Hitherto this behavior has been explained as an example of substitutional-interstitial diffusion.[10] For $x \geq 0.2$, Ag is thought to act in this material predominantly as an acceptor,[18] as part of some $\{Ag-Hg\}_{Hg}$ complexes.[19−21] The acceptor-type complex, which is a p-type dopant, is in equilibrium, via a two-electron transfer, with small amounts of a fast-diffusing complex with opposite effective charge, i.e., a donor.[9,12] At room temperature the equilibrium between the two forms is established within a few seconds:[10]

	$\{Ag{-}{-}{-}{-}Hg\}_{Hg}^{-}$ $\longleftrightarrow$	$\{Ag{-}{-}{-}{-}Hg\}_{Hg}^{+} + 2e^{-}$	
DIFFUSION	slow	fast	(1)
DOPING action[18]	*acceptor*	*donor*	

The above-mentioned experimental data show clearly that there is a minimal Hg requirement ($x > 0.2$) for fast diffusion and p-type doping, something that is not accounted for by this diffusion mechanism. To explain this we consider first the need for Hg, to enable p-type doping by Ag.

Even though both Cd−Ag and Hg−Ag complexes are known (because of Ag 5s − Hg 6s orbital overlap),[22] Hg and Cd differ in their ability to form the lower valent (formally monovalent) species that is formally needed

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(18) A defect in a semiconductor is classified as an acceptor (donor) if it can accept (donate) an electron, from the valence band (to the conduction band), thus adding a hole (electron) to the valence (conduction) band. If holes (electrons) dominate, the material will be p-type (n-type). The charges that are assigned to the defects are with respect to the neutral lattice. Thus $\{Ag-Hg\}_{Hg}^{-}$ refers to a species with formal charge of 1+, rather than 2+, expected for the Hg site in the neutral lattice.

(19) The existence of defect complexes is deduced from indirect evidence, in this case the dependence of the Ag doping efficiency on Hg content (cf. refs 10−12, and references therein). The occurrence of complexes or associates of defects is thought to be energetically less costly than single, isolated point defects, except in the extreme dilute limit. Besides the well-known EL2 complex in GaAs, defect complexes are invoked also in the more ionic semiconductors, such as (Hg,Cd)-Te[20] and $CuInSe_2$.[21]

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to get the acceptor complex. From inorganic chemistry we know that the Hg_2^{2+} species (known best from calomel, Hg_2Cl_2) is much more stable than the Cd one. The reason is the poorer shielding of the 6s electrons of the Hg by its 4f shell than the shielding of the Cd 5s ones by their d shell. We note that the transition from Hg(I) to Hg(II) is always a two-electron one.[23]

However, this does not explain why things change so drastically around $x \approx 0.2$. The clue is that at this concentration the Hg atoms can form a continuous, *percolating* network through the material. This can be understood by realizing that the zinc blende structure, adopted by (Hg,Cd)Te and CdTe can be viewed as containing interpenetrating Te and metal sublattices. These sublattices are face-centered cubic (fcc) ones, i.e., the same as α-brass. The metal sublattice can, furthermore, be viewed as a random alloy of Cd and Hg.[16] The percolation limit in an ideal fcc lattice is 19%.[7] This is, within the accuracy of our stoichiometry determinations (by energy dispersive, electron-induced X-ray fluorescence, EDS), indistinguishable from 20%. Thus, $x \approx 0.2$ is the percolation limit for Hg in (Hg,Cd)Te. How can this explain the observed behavior?

The acceptor complex can be viewed as Ag in or near an interstitial position, bridging two Hg atoms. Such a configuration is found in, for example, imiterite, Ag_2HgS_2 (with a 133° Hg−Ag−Hg angle and 3.35, 3.14 Å Hg−Ag distances).[24] An even closer parallel, based on Ag/Hg ratio and formal valence state, is found in $AgHg_2PO_4$,[25] with Hg−Ag−Hg angles of 97° and 122°. For the 97° case, the Hg−Ag and Hg−Hg distances are 3.09 and 4.63 Å, respectively. In MCT ($x = 0.3$) Hg−Hg = 4.57 Å. As long as the mercury content is sufficiently high that migrating Ag atoms can find two Hg neighbors (Hg^A and Hg^B, in eq 2), the diffusion process occurs by flipping the Ag−Hg bond around one of the Hg atoms (Hg^B, in eq 2) until a new bridging position with another Hg (Hg^C in eq 2) is reached (Figure 1). Equation 2 includes also valence-state book keeping, something that should be viewed only as a formalism here, because of the extended bonding nature of the material.

$$\begin{array}{lcc} & {}_{Hg}\{\mathbf{Hg^A}\text{---}\mathbf{Ag}\text{--}\mathbf{Hg^B}\}_{Hg}^{-} \longleftrightarrow & \\ \text{STATE of Hg} & \text{"}Hg_2^{2+}\text{"} & \\ \textit{DOPING action}^{18} & \textit{acceptor} & \\ \{\mathbf{Hg^B}\text{---}\mathbf{Ag}\}_{Hg}^{+} + 2e^{-} & \longleftrightarrow & {}_{Hg}\{\mathbf{Hg^B}\text{---}\mathbf{Ag}\text{--}\mathbf{Hg^C}\}_{Hg}^{-} \\ \text{"}Hg^{2+}\text{"} & & \text{"}Hg_2^{2+}\text{"} \\ \textit{donor} & & \textit{acceptor} \end{array} \qquad (2)$$

This process requires a continuous “chain” of Hg atoms, something that is possible only above the percolation limit. If there are enough Hg neighbors, the acceptor forms dominates. Decrease of Hg content decreases possible ways for complex formation. At $x < 0.2$, most Ag atoms find themselves without pairs of Hg atoms to bridge between. The fast diffusion stops. The Ag atoms will now behave as normal interstitials, i.e., donors, although possibly still as a complex involving also Hg.

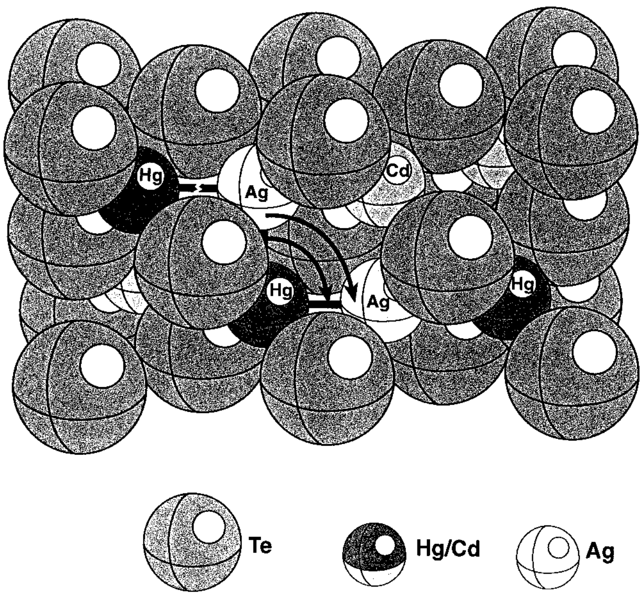

Figure 1. Schematic illustration of Ag diffusion in $Hg_xCd_{1-x}Te$ with $x \geq 0.2$. Ag hops from one to another position where it bridges between two Hg atoms. Even though Hg and Cd are randomly distributed on the metal sub-lattice, in the figure Cd and Hg are shown with different colors, to illustrate the argument made in the text. A color version of the figure can be found on the World Wide Web (www.weizmann.ac.il/material/subjects/percolat.htm).

Is there any additional indication for percolation in (Hg,Cd)Te? Elsewhere we have shown that the observed separation of a Ag-rich phase at ultralow Ag concentrations is explained very well by Ag-induced elastic distortion of the (Hg,Cd)Te lattice and that the {Hg−Ag} complex has an elastic dipole of ≤50 eV associated with it.[15,26] “Direct” diffraction evidence for such behavior is hard to get because of the random nature of the alloy and the similarity of Ag and Cd in X-ray diffraction; possibly EXAFS measurements can give more direct evidence for this. Accepting the lattice distortion due to Ag, we looked for composition-dependent data on the elastic behavior of (Hg,Cd)Te. Such data are embedded in the composition dependence of the microhardness of the (Ag-free) material.[27] The data show that the derivative of the microhardness with respect to Hg content has extrema at $x \approx 0.2$ and $x \approx 0.8$ (percolation limit for Cd). (The same is found for the hardness of α-brass at 20% Zn.[28]) This means that a small change in Hg (or Cd) concentration results in a drastic change in the microhardness. Secondary Ion Mass Spectroscopy (SIMS) analyses of Ag-doped films of (Hg,Cd)Te, grown by molecular beam epitaxy, provide experimental indications for unusual behavior around $x \approx 0.8$. It was observed that Ag moves to the surface during SIMS analysis. This effect is strong for $x \geq 0.8$ and relatively weak for $x < 0.7$.

The remarkable difference between this process and what is observed in α-brass[6] or percolation processes

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in polymers[29] is that no vacancies (open volume) or extended defects are involved.[30] This has a significant effect on the "elementary step" of the percolation process. Instead of random opening or closing of possible diffusion paths, the usual case, the probability for the next step of Ag−Hg complex movement is defined by the probability to find another Hg atom as nearest neighbor. Because of the random distribution of Hg and Cd atoms on the cation sublattice, the total behavior is a percolation type of diffusion (cf. Figure 1). We can thus understand how percolation in a crystalline body can manifest itself as a change of many orders of magnitude in the diffusion coefficient of a minor impurity (similar to alkali metals in some polymer electrolyte mixtures[29]). Furthermore, we see that open volume defects are not necessary for the percolation process.

The fact that percolation can influence processes in semiconductors at room temperature and can lead to extremely fast diffusion of impurity atoms, as well as change their mode of doping, may be of interest for device technology (especially, preparation, efficiency, and stability of detectors and light-emitting devices) based on semiconductors, such as CdTe and its alloys.[16]

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(30) Such a statement can be made because we used Hg-annealed samples, to minimize Hg vacancies, to assure that Ag will not diffuse via a vacancy mechanism (cf. refs 10 and 15).