Achievement of Well Conducting Wide-Band-Gap Semiconductors: Role of Solubility and Nonequilibrium Impurity Incorporation

G. F. Neumark

Division of Metallurgy and Materials Science, Columbia University, New York, New York 10027

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The long-standing problem for wide-band-gap semiconductors is that of achieving good bipolar conductivity. Here it is shown that this difficulty can be understood via solubility considerations of dopant incorporation. Reports of good conductivity in such materials are likely due to nonequilibrium impurity incorporation, and prior literature is reinterpreted to provide examples of this view.

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The achievement of good bipolar conductivity in wide-band-gap semiconductors has been an elusive aim of research for many years (see, for example, Refs. 1–4). I show in the present Letter that this difficulty is caused, *fundamentally,* by solubility limits rather than, as previously thought,[2,4–8] merely by strong tendencies toward compensation. The net result is that good conductivity in such cases in general requires *nonequilibrium* impurity incorporation. In the past, such incorporation was mostly accidental, so that its significance has not been previously realized. A basic problem with past attempts at understanding this conductivity problem is that the focus was on the *difficulties* of obtaining good conductivity; based on the present results, it should have been on the *opposite* problem, i.e., why in some cases such good conductivity *has* been achieved.

It is well known that in order to obtain conductivity in semiconductors the usual procedure is to incorporate impurities of a valence $Z_i = Z_s \pm 1$, where Z_s is the valence of the semiconductor host. For Z_i one charge higher than Z_s, the resultant donor provides an electron which can be excited into the conduction band where it will provide *n*-type conductivity (and *mutatis mutandis* for one charge lower, which gives acceptors and *p*-type conductivity). In order to obtain any one level of conductivity, one requires a corresponding number of electrons in the band. It is reasonably obvious that this requires first, a sufficient solubility of the donors, and second, a sufficiently small energy separation between the donors and the band so that the donors are readily ionized (i.e., the donors must be shallow). However, there is also a *third* requirement, which is that there be relatively low compensation. Compensation consists of the presence of opposing impurities (or defects) in a doped material (e.g., of $Z_s - 1$ in material doped with $Z_s + 1$ so as to give *n*-type material), or can take place with amphoteric impurities, i.e., impurities which act differently on different lattice sites; it is equivalent to the removal of dopants [e.g., $(Z_s+1)+(Z_s-1)=2Z_s$]. In cases where one desires good conductivity such compensation is detrimental. However, it is difficult to avoid since wide band gaps give a strong energy incentive for compensation,[5–8] resulting in a strong tendency for the introduction of contaminants or native defects.[2,4–8] In the past, the lack of good conductivity was blamed on such compensation.[2,4–8]

In the present Letter I show that, instead, fundamental limits are established by the lack of adequate dopant solubility in wide-band-gap materials. The free energy (μ_d) of incorporating N_d dopants in a host with N_s lattice sites can be expressed as[6,9]

$$\mu_d = B(T) + kT\ln[N_d/N_s] + E_F - E_D + kT\ln 2 - kT\ln\{1 + 2\exp[(E_F - E_D)/kT]\}, \quad (1)$$

where E_F is the Fermi energy, E_D is the donor energy (referred to the valence band), T is the temperature, k is the Boltzmann's constant, $B(T)$ does not depend on the donor properties, and it is assumed that $N_s \gg N_d$. Assume now that this material is in equilibrium with the same melt as an intrinsic[10] host (Fermi level E_I) with a donor concentration N_i. The chemical potentials will then be the same, and can be equated, with the result[11]

$$kT\ln(N_d/N_i) = E_I - E_F - kT\ln\{1 + 2\exp[(E_F - E_D)/kT]\} + kT\ln\{1 + 2\exp[(E_I - E_D)/kT]\}. \quad \text{(2a)}$$

The expressions for E_I and E_F are well known[12]:

$$E_I = \tfrac{1}{2}E_G + \tfrac{3}{4}kT\ln(m_h^*/m_e^*), \quad \text{(3a)}$$

where E_G is the band gap, and m_h^* and m_e^* are the density-of-states mass ratios for holes and electrons, respectively. The Fermi level at relatively high temperatures (as generally used for growth or diffusion) is well approximated up to low degeneracy [up to $(E_F - E_G)/kT < 1$, see, e.g., appendix C3 of Blakemore[12]] by

$$E_F \approx E_G - kT\ln[(N_c/N_d) - 0.27], \quad \text{(3b)}$$

for $E_F > E_I$, with $E_F \approx E_I$ subsequently. Here, N_c is the conduction-band (effective) density of states. A useful simplification can be obtained under conditions sufficiently nondegenerate so that $E_F \ll E_D$ and $E_I \ll E_D$, so that Eq. (2a) reduces to

$$kT\ln(N_d/N_i) \approx E_I - E_F\,. \tag{2b}$$

Since the 0.27 term in Eq. (3b) is now negligible, substitution of Eq. (3) into Eq. (2b) gives

$$2\ln(N_d) \approx \tfrac{3}{4}\ln(m_h^*/m_e^*) + \ln(N_i N_c) - E_G/2kT\,. \tag{4}$$

Given a solubility in intrinsic[10] material, a band gap, a donor energy, the effective masses, and the temperature, Eqs. (2) and (3) can be solved self-consistently [with alternate use of Eq. (4) when it is applicable] to give a corresponding donor solubility. Of interest here are the maximum (i.e., equilibrium) solubilities, N_i^e and N_d^e, respectively. One problem with this calculation is that intrinsic equilibrium solubilities are not known for wide-gap materials[13]; however, results obtained with use of reasonable estimates are instructive. For specificity, I shall compare the isocoric compounds ZnSe ($E_G=2.8$ eV at 0 K), GaAs ($E_G=1.5$ eV at 0 K), and Ge ($E_G=0.74$ eV at 0 K), and assume that these have comparable equilibrium intrinsic solubilities. Solubilities in Ge have been reported[14] up to $\approx 4\times10^{20}/\text{cm}^3$ (from $\approx$700–1100 K), and the band gap of Ge is sufficiently low that these should correspond, approximately, to the intrinsic value.[13] Reasonable typical values for the effective masses are $m_e^* \approx 0.1$ and $m_h^* \approx 0.5$, which are intermediate to those of ZnSe and GaAs. Since for good conductivity one desires shallow dopants, it is reasonable to use $E_D \approx E_G$. The remaining parameter is the temperature; this would be either the treatment temperature (assuming that this is applied long enough for equilibrium) *or* the temperature at which atomic mobility effectively ceases,[15] whichever is lower. The results for $T=800$, 1000, and 1200 K, are given in Table I; the band-gap variation with temperature was taken here as

$$E_G(T) = 2.822 - 8.59\times10^{-4}T^2/(T+405) \tag{5a}$$

for ZnSe (Ref. 16) and

$$E_G(T) = 1.519 - 5.405\times10^{-4}T^2/(T+204) \tag{5b}$$

for GaAs (Ref. 17).

It is apparent from Table I that, for example, at 800 K, the solubility in ZnSe is a factor of 4×10^4 lower than the selected intrinsic solubility. The actual value of $10^{16}/\text{cm}^3$ is relatively quite low, particularly considering that we have used the highest solubility value in Ge (that of Ga and Al), where other values can be appreciably lower (down to $10^{15}/\text{cm}^3$ for Ag and Fe, with even that for In being only $7\times10^{18}/\text{cm}^3$—see Ref. 14); moreover, in wide-gap materials the "standard" dopants ($Z\pm1$) often introduce deep levels (for a summary for ZnSe see, for example, Ref. 3), so that there is a somewhat limited availability of appropriate shallow dopants, and thus less choice in finding ones with high intrinsic solubility (as well as having a relatively low atomic mobility, see below). As regards GaAs, it can be seen that the corresponding solubility is close to 2 orders of magnitude higher than that in ZnSe. The decrease in solubility is thus pronounced for wide gaps, and moreover is a strong function of band gap.

TABLE I. Dopant solubilities (cm^{-3}) for an intrinsic solubility of 4×10^{20} cm^{-3}.

T (K)	800	1000	1200
GaAs	8×10^{17}	2×10^{18}	5×10^{18}
ZnSe	1×10^{16}	1×10^{17}	6×10^{17}

It is also apparent from Table I that the solubility depends strongly on the temperature; this is partly due to the decrease of the Fermi level (for a given dopant concentration) with increasing temperature, and partly due to the decrease in band gap. An immediate consequence of this observation is that not only should good dopants have a high solubility, but they should also have a relatively low atomic mobility (i.e., a low diffusion). In this connection it is of interest that there seem to be, empirically, more problems with poor conductivity in II-VI semiconductors than in the III-V's (even for comparable band-gap values). Another difference between these materials is that diffusion coefficients appear to be higher[18] in the II-VI's; this of course leads to a lower temperature for cessation of atomic mobility, and thus explains the differences in problems of achieving good conductivity. Assuming cessation of atomic mobility in GaAs to be at $\approx$1200 K and for ZnSe to be at $\approx$800 K, the resultant difference in dopant incorporation (for the given intrinsic solubility of $4\times10^{20}/\text{cm}^3$) is 5×10^2; definitely a nontrivial difference. It must also be realized that for dopant concentration of $\gtrsim 10^{17}/\text{cm}^3$, a band-gap shrinkage is predicted,[19] leading to higher concentrations than predicted by Table I (which does not include this effect[19]).

A somewhat different perspective can be given for the above argument, in order to further clarify the background physics. The ease of dissolving one material in another is given, neglecting entropy aspects, by the appropriate enthalpies of solution. An important point here is that given a (hypothetical[10]) value for intrinsic material, one would then have to *add the energy required to bring the electron of the dopant atom from the intrinsic level up to the Fermi level.* In order to obtain an estimate for values in intrinsic material, a recent theory by Harrison and Kraut[20] appears useful. Specifically, their[20] Table VII gives the enthalpies of solution $H_{CD}(AB)$ per atom pair, where $H_{CD}(AB)$ represents the energy required to dissolve compound AB in compound CD (and where AB and CD represent the elemental, the group III-V, or the group II-VI semiconductors; i.e., the sum of the absolute values of the ionic charges of $A+B$ and of $C+D$ are each equal to 8). Thus when compound AB is dissolved in CD it leaves CD neutral, i.e., compensated. These energy values are thus averages of those for donors (say A) and for acceptors (say B) in CD. The values for half a pair (i.e., incorporation of a single atom) are 0.4 eV for GaAs in Ge and 0.7 eV for GaAs in ZnSe (the values for Ge and ZnSe in GaAs are intermediate to the above two). Assuming the values for the donors and acceptors to be comparable, one obtains an energy (hypothetical[10]) of ≈ 0.5 eV for incorporating dopants into intrinsic material. For comparison, consider that for ZnSe the energy required to bring an electron from E_I to E_F for, say $N_d = 10^{18}/\mathrm{cm}^3$ at 800 K, is 1.0 eV; thus the energy required to produce n-type material from intrinsic material is about *twice* that which would be required to produce intrinsic material. In view of this it hardly seems surprising that the intrinsic solubility is severely degraded (Table I) by the requirement that the electron be incorporated at the Fermi level.

Given the above constraints on dopant solubility, a remaining question—already mentioned—is why good conductivity *has* been achieved in some instances (for example, in n-type ZnSe). This aspect can, however, be understood if there is *nonequilibrium* impurity incorporation, where a dopant is introduced in excess of its equilibrium solubility at a particular temperature *and* concentration of compensating species. In favor of this argument, I now reinterpret a number of typical literature results to show that the past achievement of good conductivity has often (perhaps always, although this is difficult to prove) resulted from such nonequilibrium incorporation.

My examples of nonequilibrium incorporation will focus on n-type ZnSe as a typical wide-gap semiconductor for which well conducting material has been achieved (i.e., material with a conductivity greater than $\approx 0.1/\Omega\,\mathrm{cm}$). The standard method here[1,3] (for bulk material) has been the extraction of impurities by use of excess Zn (either during growth or via an annealing step), as first suggested by Aven and Woodbury.[21] It has been shown that in this method, accidental impurities such as Cu (an acceptor on the Zn site) are removed.[21] Thus, effectively (and accidentally), the desired (donor) dopant has here been introduced *together* with a *compensating*—and *relatively mobile*—species (Cu), with the *subsequent* removal of the compensating species. The compensation aspect of course increases the solubility, and the fact that the species is mobile means that it can subsequently be removed. [Note that the presence of the *mobile* compensating species also would prevent (or reduce) the incorporation of other, less mobile, compensating species.] However, (to my knowledge) it was *not* realized previously (1) that the solubility of the donor dopant was increased by the original presence of such acceptor impurities, and (2) this method essentially gave nonequilibrium incorporation. More recent work[22] on epitaxial n-type ZnSe has used low-temperature growth methods, namely, metal-organic chemical-vapor deposition (MOCVD) and molecular-beam epitaxy (MBE). This presumably also gives nonequilibrium incorporation, where the dopant now remains "locked in" at such low temperatures. It can be added that well conducting p-type ZnSe has been difficult to obtain, with only a few, poorly reproducible reports. Various considerations show that nonequilibrium incorporation appears to be involved in these cases, but this is being discussed separately.[23]

It must also be emphasized that ZnSe is hardly unique among wide-band-gap semiconductors in terms of the difficulties in obtaining good conductivity of one or the other carrier type. The situation for ZnTe, where it is difficult to obtain good n-type material, has been extensively reviewed by Marfaing.[2] Moreover, difficulties with p-type ZnS, CdS, and CdSe are also well known.[1] Similarly, there are also problems with n-type diamond.[24] The present considerations thus shed light on problems in a large class of materials.

Overall, solubility aspects plus the hypothesis that good conductivity has generally been accompanied via nonequilibrium means can explain past observations both in regard to the difficulties of achieving good conductivity, as well as to why it sometimes *has* been accomplished. The prior[2,4-8] view that these phenomena were due to compensation does not address the *fundamental* problem of poor solubility.

The present analysis has thus clarified the physical understanding of conductivity in wide-band-gap materials. The results also show that in terms of device aspects, i.e., of actually obtaining good bipolar conductivity, future work should focus on good methods of nonequilibrium impurity incorporation. It is apparent that one aspect here will involve finding dopant impurities with *low* atomic mobilities, to increase the solubility (Table I), and so that the conductivity remains "locked-in" over reasonable time scales (at usual operating temperatures); also, it seems fruitful to search for compensating impurities—with *high* atomic mobilities—which ultimately could be eliminated (or reduced) once they have increased the solubility of the desired dopant. With such an approach, chances of obtaining useful devices from wide-band-gap materials should be vastly improved.

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[10] It should be noted that the intrinsic case with only donor doping is hypothetical, since such donor doping would lead to *n*-type material. However, this intrinsic case would correspond to fully compensated material.

[11] A similar analysis was used in Ref. 6, but the resultant Eq. (6.4b) was incorrect.

[12] See, for example, J. S. Blakemore, *Semiconductor Statistics* (Dover, New York, 1987).

[13] Such solubilities would be the measured solubilities for narrower-gap materials provided the measurement temperature is high enough so that $E_F \approx E_I$.

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[15] In general, the equilibrium solubility decreases with temperature, so that as long as impurities are mobile those in excess could coalesce and form a second phase; however, once the system reaches a temperature such that there is minimal ion motion, the equilibrium at that temperature will be "frozen in."

[16] Obtained from the 0-K band gap as given by P. J. Dean, D. C. Herbert, C. J. Werkhoven, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **23**, 4888 (1981), with the temperature dependence given by Y. Shirakawa and H. Kukimoto, J. Appl. Phys. **51**, 2014 (1980).

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[18] A comparison of literature data, given in Ref. 2, shows that self-diffusion coefficients tend to be appreciably higher in the II-VI compounds than in the III-V compounds. It seems reasonable to assume that the same would also hold for impurity diffusion.

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