

# Doping in semiconductors with variable activation energy

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A concept of doping that permits for the first time the freedom to design the desired activation energy of a dopant in a semiconductor is introduced and demonstrated. This doping engineering (DE) may also offer the possibility of achieving dopings in semiconductors in which a normally employed doping process is not successful, such as in wide band-gap II-VI semiconductors. Experimentally, we demonstrated that the normal activation energy,  $\sim 19\text{--}25$  meV of beryllium (Be) in GaAs was reduced to 4 meV in DE GaAs/ $\delta$ -Al<sub>0.3</sub>Ga<sub>0.7</sub>As(Be) sample.

When a semiconductor is doped with donor or acceptor impurities, impurity energy levels are introduced in the forbidden band. For each specific impurity in a semiconductor, there is one (and in some cases, more than one) characteristic ionization energy (also referred to as activation energy). This activation energy is fixed and cannot be changed under normal operation conditions. For hydrogenlike shallow impurities, the ionization energy is given by the Rydberg constant corrected for the carrier effective mass and the dielectric constant of the semiconductor

$$E_i = \frac{1}{2} (4\pi\epsilon)^{-2} \frac{e^4 m^*}{\hbar^2}, \quad (1)$$

where  $\epsilon$  is the permittivity of the semiconductor and  $m^*$  is the electron or hole effective mass. As a result, there is very limited choice of dopants for each semiconductor. In some semiconductors such as the wide-gap II-VIs there can be a complete lack of one type of effective dopant. Very often for each semiconductor there is actually only one or two dopants that are found to be suitable for use when other constraints such as, its solid solubility in the semiconductor, its easiness and compatibility with the doping process and device processings, and its solid-state diffusion are considered.

It has been shown previously<sup>1,2</sup> that Eq. (1) cannot be applied to impurities located in a quantum well. Upon placing impurities in a quantum well, the quantum well potential must be considered in addition to the  $1/r$  Coulomb potential. As a result, the impurity activation energy increases if the impurities are located in the well. The magnitude of the increase can be four times the effective Rydberg energy for the limiting case of an impurity atom confined to two dimensions.<sup>3</sup> In this letter, we demonstrate for the first time the effective Rydberg of an impurity atom cannot only be increased but also be *decreased* by introducing impurities into the thin barriers. We further show that impurity ionization energies can be *eliminated*, i.e., can approach values of zero. Thus, impurity activation energy can be *designed* with a high degree of freedom. We refer to this technique as doping engineering (DE).

Figure 1 schematically shows the basic idea.  $n$ -type doping is chosen as an example. Figure 1(a) shows the

normal  $n$ -type doping with the dopant having a fixed  $E_A$  in a uniform semiconductor host A. In Fig. 1(b), the donor atoms instead are confined to a lattice plane inside a different semiconductor host B, which is only a few monolayers thick (e.g.,  $\lesssim 4$  monolayers). The ionization energy in a quantum well is also modified by the confinement of the impurity wave function by the quantum well. This effect has been considered in the literature.<sup>1,2</sup> Calculations show that the binding energy increases with decreasing well width but, rather than reaching a maximum at zero well width, reaches a maximum at a non-zero well width. For clarity in this schematic diagram this slight energy modification of  $E_B$  due to quantum effect of donor atoms located inside a narrow energy well, and energy potential well modification due to  $\delta$  charge is not included. The donor atoms confined to semiconductor host B will have an activation energy  $E_B$  relative to the conduction band edge of semiconductor B. Relative to semiconductor host A, the effective activation energy,  $E_{A\text{eff}} \approx \Delta E_C + E_B$ , where  $\Delta E_C$  is the conduction band discontinuity between semiconductors A and B. Since semiconductor B is made very thin, the structure behaves as if having a donor doping with an effective activation energy  $E_{A\text{eff}}$  in the uniform semiconductor host A. By varying  $\Delta E_C$ , i.e., having a different semiconductor B, one can have different  $E_{A\text{eff}}$ . As an example, semiconductor A can be InP and semiconductor B can be InGaAsP. Since semiconductor B layers are kept to a thickness of not more than a few monolayers, strained layers can also be used without incurring misfit dislocations. This further opens up the range of  $E_{A\text{eff}}$  that can be achieved. The equivalent 3-dimensional (3D) doping concentration is then determined by the 2-dimensional (2D) doping density and the periodicity of the semiconductor B layers. In the above case,  $E_{A\text{eff}}$  is usually larger than  $E_A$ .

In Fig. 1(c), semiconductor B has a wider band gap than the host semiconductor A. The  $E_{A\text{eff}}$  can then be smaller than  $E_A$ . Actually, in Fig. 1(d),  $E_{A\text{eff}}$  becomes negative implying no energy is needed to ionize the donor atoms. In fact, this can be considered as the limiting case of modulation doping in which the thicknesses of both the impurity doping is confined to a lattice plane and the wide band-gap semiconductor layers (a few monolayers) are pushed to the very thinnest limit. An example of cases (c)

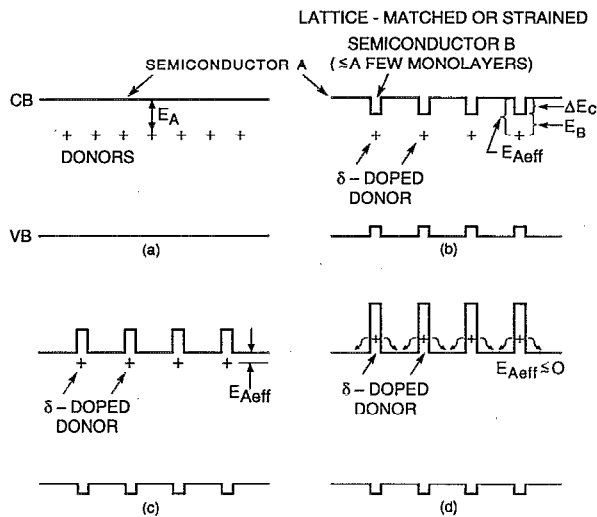


FIG. 1. (a) The normal  $n$ -type doping with the dopant having a fixed  $E_A$  in a uniform semiconductor host A. (b), (c), and (d) illustrate the new concept of doping engineering under three different conditions.

and (d) can be realized in  $\text{GaAs}/\delta\text{-Al}_x\text{Ga}_{1-x}\text{As}$  or  $\text{InP}/\delta\text{-Ga}_x\text{In}_{1-x}\text{P}$  for lattice-matched and strained-layer systems, respectively. In addition, our DE differs from modulation doping (MD) as we illustrate in Fig. 2. In MD the carriers are spatially removed from the parent acceptors and are no longer bound by Coulomb attraction to its parent. In many MD structures the dopant is found displaced from the heterointerfaces by distances that are larger than an impurity Bohr radius. Instead, the free carriers occupy energy eigenstates at the bulk heterointerfaces as our example illustrates in Fig. 2(a). However, in DE, we chemically change only the dopant location for distances smaller than the impurity Bohr radius. The quasi-free-carriers still remain partly bound to its parent accep-

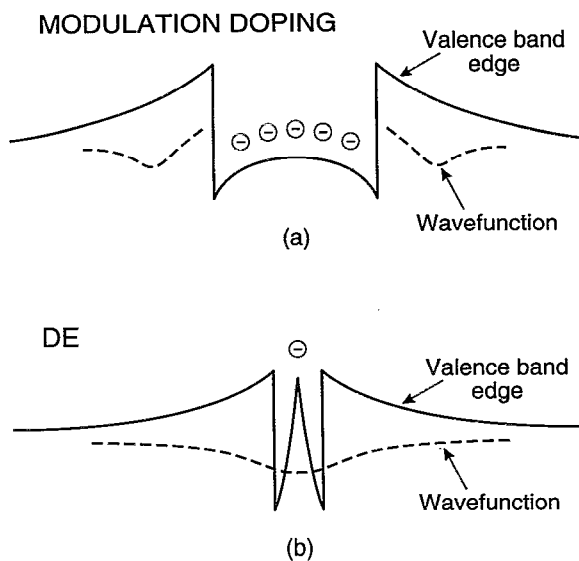


FIG. 2. (a) A  $p$ -type modulation doped (MD) structure, (b) a  $p$ -type doping engineered (DE) structure. It illustrates the difference between MD and DE.

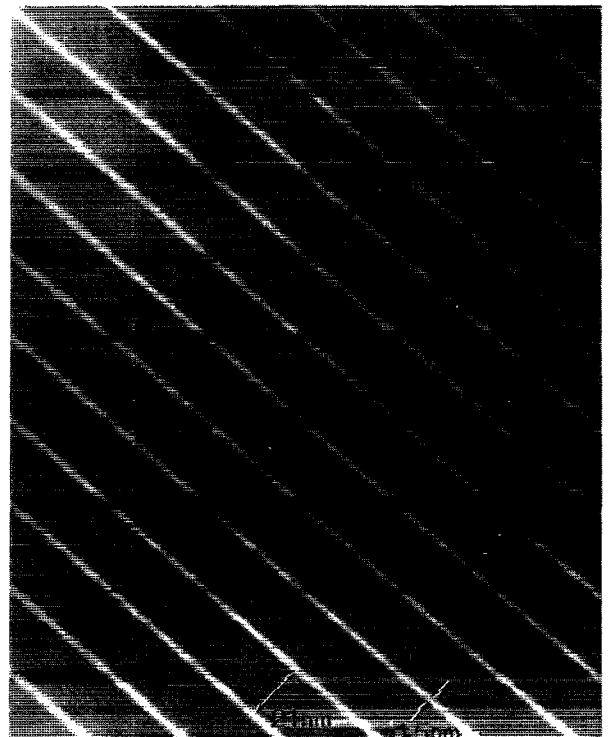


FIG. 3. A TEM photograph of a  $\text{GaAs}/\delta\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(\text{Be})$  DE sample.

tor but with reduced energy activation as illustrated in Fig. 2(b).

In essence, doping engineering permits the freedom to design the  $E_A$  of a dopant in a semiconductor. In fact, it may prove to be particularly useful for achieving dopings in semiconductors in which a normally employed doping process is not successful. An example is  $p$ -type doping in  $\text{ZnCdSe}$ , which has not been very successful so far. By interleaving  $\text{ZnCdSe}$  with  $p$ -type (e.g., Be)  $\delta$ -doped  $\text{Al}_x\text{In}_{1-x}\text{P}$   $p$ -doped wider band-gap II-VI layers,  $p$ -type doping of  $\text{ZnCdSe}$  may be possible.

To demonstrate the concept of doping engineering, we have grown a  $\text{GaAs}/\delta\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(\text{Be})$  structure shown by the transmission electron microscopy (TEM) photograph in Fig. 3. For the DE sample, the  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$  thickness is  $\sim 15 \text{ \AA}$  and contains a  $\delta$ -doped Be (2D concentration  $2 \times 10^{10} \text{ cm}^{-2}$ ) layer at the center. The GaAs thickness is  $210 \text{ \AA}$ . The total thickness of the sample is  $1.5 \text{ \mu m}$ . This combination should result in an equivalent bulk hole concentration of  $10^{16} \text{ cm}^{-3}$  in GaAs. For comparison, the same periodically modulated structure was grown but it was uniformly doped with Be at the  $10^{16} \text{ cm}^{-3}$  level.

Experimentally, Be  $\delta$ -doping is achieved by growth interruptions during epitaxial growth by gas-source molecular beam epitaxy described previously.<sup>4,5</sup> A relatively low growth temperature of  $\sim 500 \text{ }^\circ\text{C}$  is employed to avoid undesired diffusion and segregation effects. The absence of such redistribution effects under appropriate growth conditions was previously demonstrated.<sup>5</sup> Schottky contacts (diameter =  $250 \text{ \mu m}$ ) are used for the capacitance-voltage ( $C$ - $V$ ) evaluation. A HP 4194 impedance analyzer is used

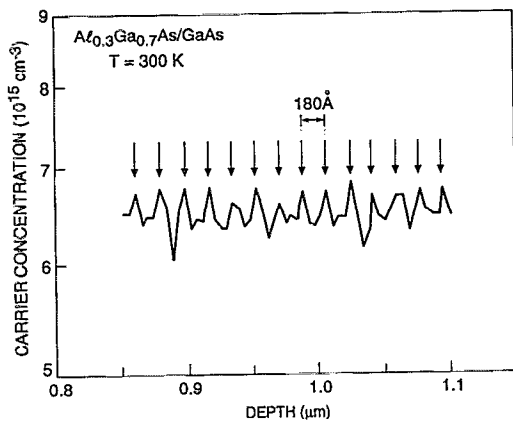


FIG. 4. Shows the  $C$ - $V$  hole concentration profile as a function of depth for the sample shown in Fig. 3.

for the measurements. Care is taken to verify a phase angle close to  $90^\circ$  for all voltages applied to the samples. Figure 4 shows the  $C$ - $V$  hole concentration profile as a function depth. The spikes are periodic with a period of  $\sim 190 \text{ \AA}$ , which agrees quite closely with that measured from TEM. The averaged hole concentration measured by  $C$ - $V$  technique is  $\sim 10^{16} \text{ cm}^{-3}$ , again agrees quite well with the intended doping and the Hall measurements shown in Fig. 5.

As a practical demonstration of the DE concept, we perform variable temperature Hall effect on the two structures specified above. Figure 5 shows the carrier concentration versus reciprocal temperature as circles for the DE sample and triangles for the homogeneously doped specimen. In these investigations we have chosen the Be concentration to be an order of magnitude lower than the critical concentration corresponding to a Mott transition of

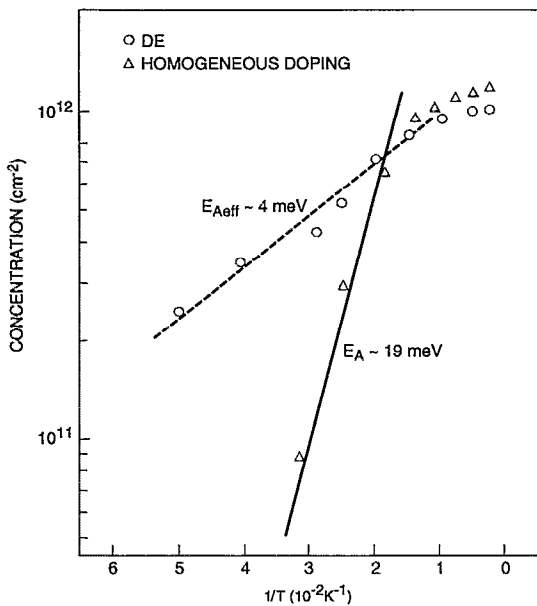


FIG. 5. A plot of the hole concentration measured by Hall technique for both the uniformly doped and DE samples as a function of inverse temperature.

holes in GaAs. By doing so, our variable temperature results should reflect the true ionization energy of the dopant instead of reduced energy activation caused by impurity banding effects. Indeed, the thermal behavior of the homogeneously doped sample shows this to be the case. Figure 5 illustrates that hole freeze-out commences at temperatures just below 100 K. By 30 K the hole concentration has fallen to one-tenth of its room temperature. Clearly, this behavior is the expected thermal characteristics of lightly Be doped GaAs. By contrast, the thermal dependence of the carrier concentration is observed to be much weaker for the DE sample. For instance at 30 K the DE concentration has only fallen by a factor of two of its room-temperature value. One further feature of the low-temperature carrier concentration dependence is that both structures exhibit Arrhenius behavior at very low temperature. We may analyze their dependencies to quantify more precisely the change in impurity ionization induced by the DE concept. However, to simplify the analysis we assume the thermal dependence of the carrier concentration is associated with only carrier freeze out whereas other thermal dependencies from interface/surface depletion and band transport factors are negligible in comparison. As Fig. 5 shows both the DE and homogeneous doping may be fit by an Arrhenius expression at very low temperature as evidenced by the solid and dashed lines. From their slopes we estimate the impurity ionization is 19.0 meV for homogeneous doping and 4 meV for DE. The 19 meV energy is in reasonable accord for the known binding energy of Be (25 meV) in GaAs.

The reduction in Be ionization energy induced by the DE concept is remarkable since we have reduced the impurity binding energy by a factor of five its value in conventional doping. For comparison, changes in acceptor binding energy in GaAs brought about by different chemical dopants are only about 30% of the acceptor binding energy. The fact that carriers in the DE sample are weakly bound  $\sim 4 \text{ meV}$  instead of zero binding energy, i.e.,  $E_{Aeff} = 0$  as argued in Fig. 1, is because the quasi-free-carriers still remain partly bound to its parent acceptor as illustrated in Fig. 2(b). The measured hole mobilities of the uniformly doped and DE samples are  $380 \text{ cm}^2/\text{V s}$  and  $300 \text{ cm}^2/\text{V s}$  at room temperature and  $3800 \text{ cm}^2/\text{V s}$  and  $4300 \text{ cm}^2/\text{V s}$  at 77 K, respectively. No significant difference was observed. Hence, our DE structure retains bulk-like transport characteristics and not the enhanced mobility typical of MD structures. The DE contains, of course, the flexibility in design of the ionization energy.

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