Topic 2: How do point defects change electronic properties?

Overview

Point defects, specifically solutes, are intentionally introduced into semiconductors for the changes they induce in electronic properties. This can be to "donate" conduction electrons ("n"-type doping) or the "accept" valence electrons that introduces holes ("p"-type doping). This is described via defect reactions, where a dopant changes its charge state by interacting with electrons or holes, causing "ionization," and resulting in different concentrations of the charge states of the dopant in a semiconductor, depending on the ionization energy, Fermi energy and temperature. Some donors / acceptors are shallow, where they are nearly fully ionized and contribute electrons / holes that increase mobility; while other donors / acceptors are deep centers that act as traps or recombination sites that limit electron / hole lifetimes or reduce carrier concentrations. In addition, dopants can have multiple states in the bandgap, allowing it to donate or accept multiple electrons!

Dopants are useful not just for the changes in electronic properties they induce in a semiconductor, but also the ease with which they can be introduced in a controllable manner.

Reading

For this topic, you will want to read some of review articles about dopants in semiconductors.

- "The electronic structure of impurities and other point defects in semiconductors." Sokrates T. Pantelides, *Rev. Mod. Phys.* **50**, 797-858 (1978): doi:10.1103/RevModPhys.50.797, Sections I-VI
- "Point defects and dopant diffusion in silicon." P. M. Fahey, P. B. Griffin, and J. D. Plummer. *Rev. Mod. Phys.* **61**, 289-384 (1989): doi:10.1103/RevModPhys.61.289, Sections I-VI

Team assignment

The European Union, fresh off eliminating lead from solder, has now decided that phosphorus can no longer be used in electronic devices.[1] Putting aside questions about the wisdom of a widespread ban on phosphorus, your team is immediately concerned about the best possible replacement to manufacture n-doped Si, if P would no longer be available.

1. What dopant(s) would you suggest for production of n-doped Si in devices?
2. What would you consider to be the biggest challenge in processing with your suggested replacement?

[1] This is, no doubt, to protect the European steel industry, where P is well-known to cause embrittlement of grain boundaries in steels.

Prelecture questions

1. In a crystal the concentration of electrically neutral vacancies is described by a law of mass action $[\mathrm{V}^{\times}] = A\ \exp(-\Delta G_{\mathrm{v}}/k_{\mathrm{B}}T)$. These vacancies can act as acceptors, and the concentration of ionized vacancies is given by

$$[\mathrm{V}'] = \frac{[\mathrm{V}_{\mathrm{t}}]}{1 + g^{-1}\exp([E_{\mathrm{A}} - E_{\mathrm{F}}]/k_{\mathrm{B}}T)}$$

   where E_{A} is the acceptor energy level, E_{F} is the Fermi energy, the total concentration $[\mathrm{V}_{\mathrm{t}}] = [\mathrm{V}^{\times}] + [\mathrm{V}']$, and the degeneracy $g = 2$. When the Fermi energy E_{F} is moved by the addition of substitutional dopants, how does the total vacancy concentration change? Assume no interaction between dopants and vacancies, so E_{F} is shifted independently of everything else.
2. Estimate the ionization energy and the "size" of the electron wavefunction for a shallow donor using a hydrogen-like model in a semiconductor with an effective mass $m^* = 0.3m_{\mathrm{e}}$ and a dielectric constant of $\epsilon = 10\epsilon_0$ compared with the vacuum dielectric constant ϵ_0.

Suggested background

These may help you think about the papers and questions raised; you may want to look beyond these, too.

- Ibach, H. and Lueth, H. *Solid-State Physics*. (Springer Berlin Heidelberg: Berlin, Heidelberg, 2010). doi:10.1007/978-3-540-93804-0. Chapter 12 covers semiconductors, doping, and much more.
- Chapter 4, "Deep Centers in Semiconductors" by H. Feichtinger, from Handbook of Semiconductor Technology (2000). (you may also find some of the other chapters helpful)
- "Charged point defects in semiconductors." Edmund G. Seebauer and Meredith C. Kratzer. *Mater. Sci. Eng. R* **55**, 57-149 (2006): doi:10.1016/j.mser.2006.01.002
- Course webnotes:
  - 2.3.1 General remarks about point defects in semiconductors
- Slides (on Google Drive):
  - 07.semiconductors
  - 10.electronic-structure

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