a-Si:H [48]. The $(+/0)$ level lies about 0.3 eV below the $(-/0)$ levels; the difference between the 2 levels is usually termed the *correlation energy* of the D-center [49].

The actual level positions apparently vary between doped and intrinsic a-Si:H [23], between intrinsic samples with varying densities of D-centers [48], and possibly between dark and illuminated states [50].

12.2.6 Doping

Doped layers are integral to *pin* solar cells. Doping itself, which is the intentional incorporation of atoms like phosphorus and boron in order to shift the Fermi energy of a material, works very differently in amorphous silicon than in crystals. For example, in crystalline silicon (c-Si), phosphorus (P) atoms substitute for silicon atoms in the crystal lattice. P has five valence electrons, so in the "fourfold coordinated" sites of the Si lattice, four electrons participate in bonding to neighboring silicon atoms. The fifth "free" electron occupies a state just below the bottom of the conduction band, and the dopants raise the Fermi energy to roughly this level.

In a-Si, most phosphorus atoms bond to only three silicon neighbors; they are in "threefold coordinated" sites. This configuration is actually advantageous chemically; phosphorus atoms normally form only three bonds (involving the three valence electrons in "p" atomic orbitals). The final two electrons are paired in "s" atomic orbitals, do not participate in bonding, and remain tightly attached to the P atom. The reason that this more favorable bonding occurs in a-Si, but not in c-Si, is the absence of a rigid lattice. As a thin film of a-Si grows, the network of bonds adjusts to incorporate impurity atoms in a nearly ideal chemical arrangement. In c-Si, it would be necessary to grossly rearrange several Si atoms in the lattice and to leave a number of dangling Si bonds, in order to accommodate the P atom in this configuration. The extra energy for this rearrangement is larger than what would be gained from more ideal bonding of P, and substitutional doping is favored.

Thus, phosphorus doping is a paradox in amorphous silicon. It is, at first, unclear why it occurs at all, since doping involves fourfold coordinated P, and P atoms are generally threefold coordinated in a-Si. This puzzle was first solved in 1982 by Street, who realized that independent formation of both a positively charged, fourfold coordinated P_4^+ and a negatively charged dangling bond D^- can occur occasionally instead of the more ideal threefold coordination [23]. This understanding leads to two important consequences. First, doping is inefficient in a-Si; most dopant atoms do not contribute a "free" electron and do not raise the Fermi energy. Second, for each dopant atom that does contribute an electron, there is a balancing, Si dangling bond to receive it. These defect levels lie well below the conduction band, so the fourfold coordinated phosphorus atoms are less effective in raising the Fermi energy than that in c-Si. Additionally, the negatively charged dangling bonds induced by doping are very effective traps for holes. Since bipolar transport of both electrons and holes is essential to photovoltaic (PV) energy conversion, photons absorbed in doped layers do not contribute to the power generated by solar cells.

12.2.7 Alloying and Optical Properties

The structural and optical properties we have described can be varied substantially by changes in deposition conditions. For example, changing the substrate temperature or the