We have investigated the formation energies, ionization energies, and chemical natures of substitutional group-II, III, V, and VI impurity atoms in 4H-SiC. It is shown that the impurity atoms have lower formation energies on a carbon site than on a silicon site for nitrogen, oxygen, and sulfur regardless of the crystal growth conditions, whereas the favorable sites for boron and selenium depend on the composition. With the exception of the above elements, impurity atoms always substitute on a silicon site. The cluster calculations suggest that antimony introduces a much shallower donor level than those of conventional n-type dopants such as nitrogen and phosphorus. However, its high energy of formation will make it difficult to dope SiC with a high impurity concentration. These results suggest that antimony is a good candidate for an extremely shallow n-type dopant.