Engineering electronic and optical properties of semiconductors by tuning the population of dopant defects: first principles simulations of Chalcogen hyperdoped Si

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Since Mott's work the insulator-to-metal transition (IMT) in doped semiconductors has been studied both for its interest in fundamental physics and for its relevance in technological applications. In this framework, hyperdoping (i.e., doping beyond the solubility limit of the impurity) creates a new materials playground to investigate impurity mediated IMTs in semiconductors and provides a key material in forthcoming devices based on Si and Ge technology.

Hyperdoping is currently being used to engineer new materials with unique and exotic properties: rectifying junction and photodiodes with S and Se hyperdoped Si. Furthermore, Si and Ge hyperdoped with chalcogens (Ch=S, Se, and Te,) are considered promising candidates as building blocks for infrared absorbers and intermediate band photovoltaics. Hyperdoping is also a promising technique to reach density of the order of one carrier per cubic nanometer, which may be necessary to develop nanometer-sized ballistic devices. Unfortunately, at hyperdoped concentration, the elements usually employed to dope silicon -like P, As, or Sb- form complexes that acts as electrical deactivation centers, producing the phenomena of carrier saturation, thus preventing to reach the carrier density needed for nano-devices.

Among dopants, chalcogens provide superior electronic properties (high carrier concentration, and no saturation) than traditional column V dopants [1] (see Fig.1). Within the framework of density functional theory, by plane-waves pseudopotentials techniques and the supercell method, we systematically investigated chalcogen hyperdoped Si by computing, for different types of Ch complexes, the formation energy as a function of Ch concentration.

We enlightened the microscopic mechanisms responsible for the disappearance of electrical deactivation defects as the chalcogen density approaches the critical concentration, x_c, at which the IMT occurs. Our study showed that, as the Ch concentration approaches x_c, the electrical deactivation defects are energetically unfavored due to their formation energy significantly higher (1 eV or more, depending on the type of defects) than the ones of donor complexes, identified as the Ch monomer (a single substitutional dopant), Ch-Ch dimer (two nearest neighbor substitutional dopants), and the VCh3 (VCh4) complexes formed by a Si vacancy having 3 (4) nearest neighbor substitutional Ch (Fig.2). We discuss the electrical properties of Ch complexes in Si, finding the best doping range in which the Ch density can be tuned to engineer both x_c and the optical properties of the material.

By combining our first-principles data with a random distribution model for estimating the relative percentage of distinct types of S complexes in S-hyperdoped silicon, we predict an unprecedented tunability of the IMT transition at the critical dopant concentration, with a key role played by the relative abundance of the different complexes. By assuming the possibility to tune the latter during the sample synthesis, we predict that optical absorption spectra of S-hyperdoped Si can be engineered from the short wavelength infrared to far infrared region.

References

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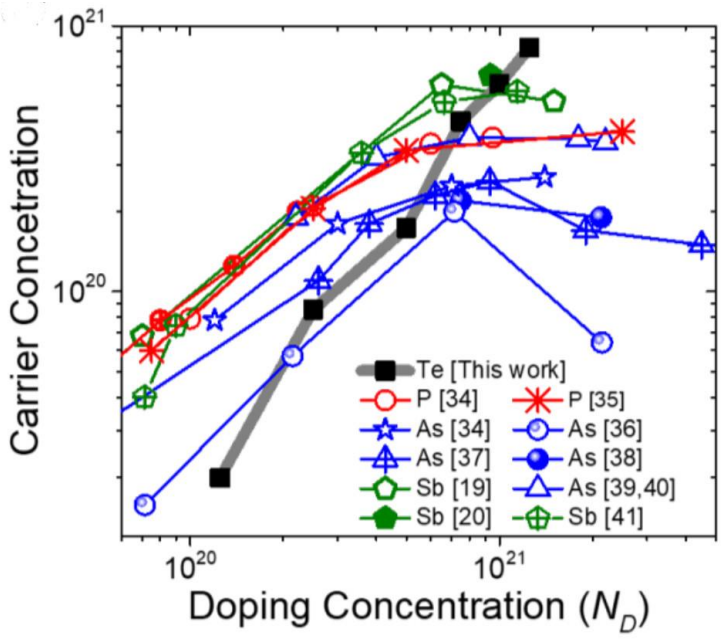

Figure 1. Electron concentrations as a function of dopant concentration in hyperdoped silicon for different types of dopants [adapted from Wang et al. Phys.Rev.Appl. 11, 054039 (2019) (Ref. [1])]

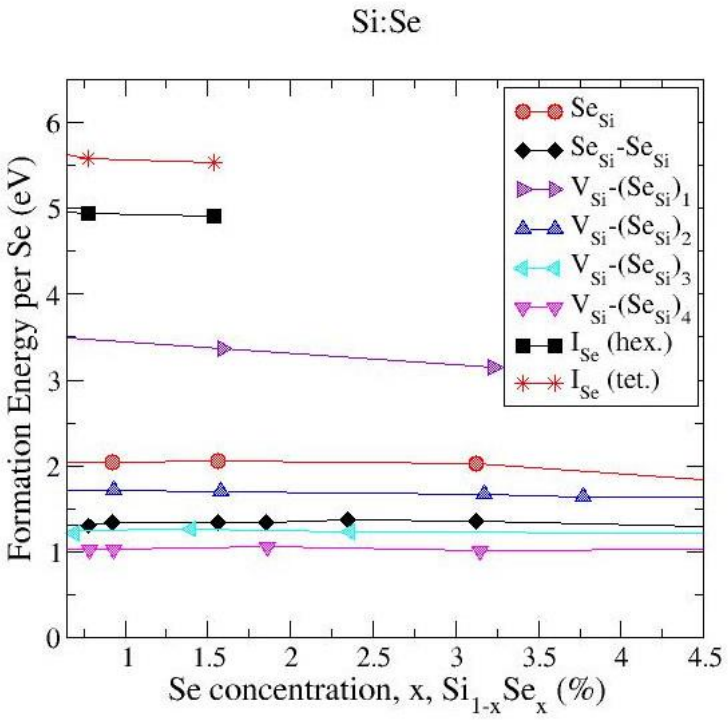

Figure 2. Symbols: first principles formation energy as a function of dopant concentrations for different types of complexes in Se hyperdoped Si (Ref.s [2,3]). Solid lines are a guide for eyes.