

Invited

New Doping Method in Semiconductors Proposed by  
ab initio Electronic Structure Calculation

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1. Introduction

We propose a new valence control method, the "codoping method (using both *n*- and *p*-type dopants at the same time)", for the fabrication of low-resistivity *p*-type CuInS<sub>2</sub>, ZnSe, and GaN crystals based on the *ab initio* electronic structure calculations. We find that *p*-type doping lead to destabilization of ionic charge distribution due to a shift of anion levels towards higher energy region. We clarified the stabilization of ionic charge distributions for *p*-type CuInS<sub>2</sub>: VCu + InCu + 2PS, ZnSe: InZn + 2NSE or ClSe + 2NSE, and GaN: SiGa + 2Mg(Be)Ga or ON + 2Mg(Be)Ga.

2. Results and Discussion

We proposed materials design using donor dopants, InCu with poly valence, to fabricate low-resistivity *p*-type CuInS<sub>2</sub> having almost a band gap of 1.5 eV with chalcopyrite structure for solar cell applications[1-3]. Very recently, we have applied the codoping method using donor dopants (Si and O) and acceptor ones (Be and Mg) to GaN crystals [4].

GaN with a wide band gap, 3.39 eV, has recently gained attention because of its possible use in blue small-emitting diodes and UV-emitting laser diodes. Valence controls to realize low-resistivity *p*-type wide-band-gap semiconductor GaN crystals are one of very important problems to develop large-scale application of GaN and its related semiconductor technology. Several authors reported low-resistivity *p*-type GaN films [5-8]. Very recently, Brandt *et al.* produced high-conductivity *p*-type GaN using acceptor dopants, Be, and donor dopants, O [9]. While the properties of the GaN crystals are known, little is known about the relation between the cause of difficulty in fabricating *p*-type GaN and a change in the electronic band structure or in the nature of chemical bonds of *p*-type doped GaN crystals. In this work, first, we discuss in more detail the difference in effects of between *p*-type Be or Mg doping and *n*-type Si or O doping on the electronic structures employing the *ab initio* electronic band structure calculations. Then we investigate crystal structures and electronic structures of GaN codoped with *n*-type dopants (Si, O) and *p*-type dopants Be in order to clarify the advantage of the codoping method.

We show the total density of states (DOS) for undoped and codoped CuInS<sub>2</sub>, ZnSe, and GaN in Fig. 1a, 1b, 1c, which shows that the conduction type of the codoped crystals is *p*-type. As well as the two *n*-type doped materials above, we find that electronic structures of the doped crystals with higher doping levels,  $2.3 \times 10^{21} \text{ cm}^{-3}$ , have the same band shape as that of undoped crystals, that

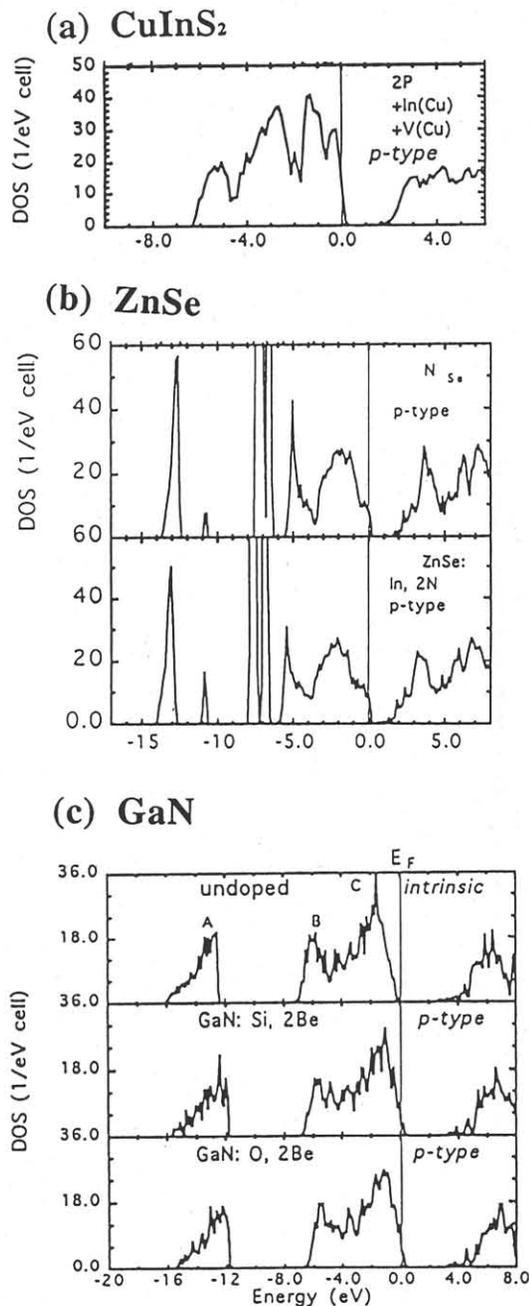
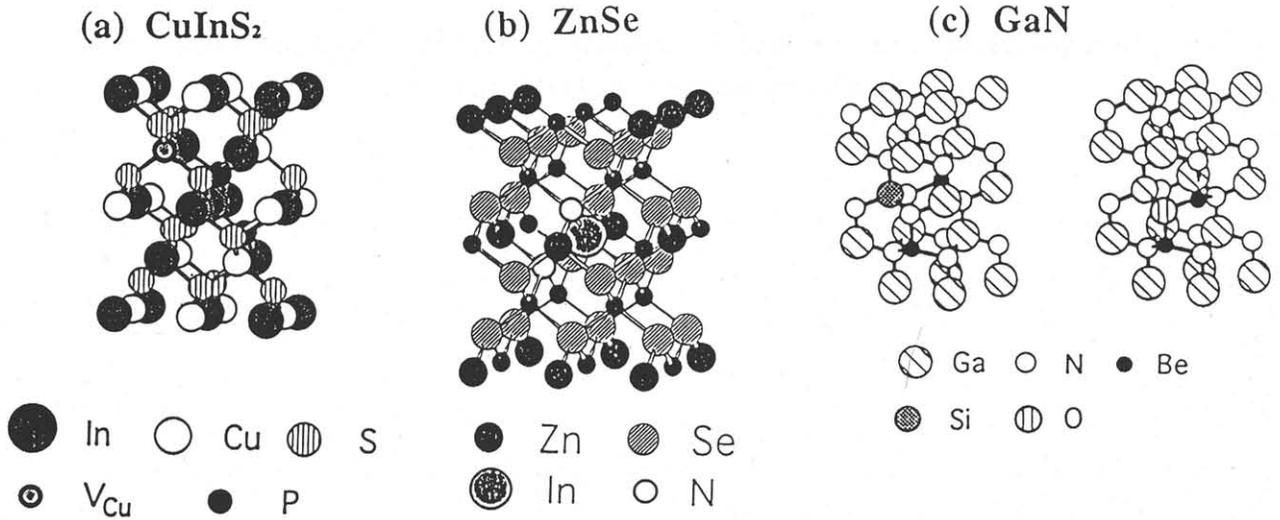


Figure 1. Total density of states of (a) undoped and codoped CuInS<sub>2</sub>, (b) undoped and codoped ZnSe, and (c) undoped and codoped GaN.



**Figure 2.** Crystal structure of (a) codoped  $\text{CuInS}_2$ , (b) codoped  $\text{ZnSe}$ , and (c) codoped  $\text{GaN}$ .

is, there is little change in electronic structures except for the energy regions near the band edge.

For  $p$ -type  $\text{GaN}$ : Si, 2Be, from site-decomposed DOS and population analysis, we find a large delocalized impurity states near the Fermi level, which results in small effective mass of positive holes introduced. In addition, Table II shows that the codoping leads to the condensation of acceptor dopants (see distances between the two Be atoms in Fig. 2) with a decrease in  $E_M$ , which gives rise to an increase in the net carrier densities, to fabricate low-resistivity  $p$ -type  $\text{GaN}$  crystals.

### 3. Conclusion

We have studied the electronic structures of undoped,  $p$ - $n$ -type doped and codoped  $\text{CuInS}_2$ ,  $\text{ZnSe}$ , and  $\text{GaN}$  crystals using *ab-initio* electronic band structure calculations. The main results obtained are shown below: (a)  $p$ -type doping leads to destabilization of ionic charge distributions due to an increase in the Madelung energy; (b)  $n$ -type doping gives rise to stabilization of ionic charge distributions due to a decrease in the Madelung energy; (c) Codoping of  $n$ -type dopants and  $p$ -type dopants, being in the ratio of 1 to 2 will cause a decrease in the Madelung energy, resulting in prevention of self-compensation. From these results and delocalized holes in wide impurity bands of the codoped crystals, we propose a valence control method, the "codoping method" for the fabrication of high-conductivity  $p$ -type  $\text{CuInS}_2$ ,  $\text{ZnSe}$  [10], and  $\text{GaN}$  crystals.

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