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Possible *p*-type doping with group-I elements in ZnO

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Based on first-principles calculations, we suggest a method for fabricating *p*-type ZnO with group-I elements such as Li and Na. With group-I dopants alone, substitutional acceptors are mostly self-compensated by interstitial donors. In ZnO codoped with H impurities, the formation of compensating interstitials is severely suppressed, and the acceptor solubility is greatly enhanced by forming H-acceptor complexes. The H atoms can be easily dissociated from these defect complexes at relatively low annealing temperatures, and thus low-resistivity *p*-type ZnO is achievable with dopants different from group-V elements.

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Zinc oxide (ZnO) has attracted much attention because of possible applications for wide-band gap optoelectronic devices.[1–3] Because of the large exciton binding energy of 60 meV, ZnO is known to be the brightest emitter of available wide-gap semiconductors. Alloying this material with Mg extends device applications to the uv range. Despite other advantages such as the availability of large-area substrates, high radiation resistance, and low material costs, one major problem remains to be solved; it is difficult to obtain low-resistivity *p*-type ZnO, while this material exhibits intrinsically *n*-type conductivity. Among group-V elements, N is used as a popular *p*-type dopant,[4–11] while *p*-type samples have also been successfully obtained with other dopants such as P and As.[12,13] However, other findings were also reported of unrealistically high hole mobilities and hole concentrations, with low reproducibilities. Theoretical studies indicated that the acceptor level of N is so deep that it is difficult to explain the activity of N acceptors at room temperature,[14] although a compensation mechanism was introduced.[15] For P and As dopants with deeper acceptor levels than for N, it is even more difficult to explain observed high hole densities. Substitutional group-I elements behave as a shallow acceptor; however, these dopants tend to occupy the interstitial site, leading to the self-compensation.

In this paper, we search for other *p*-type dopants rather than group-V elements, and propose a method for fabricating low-resistivity *p*-type ZnO with group-I elements such as Li and Na, based on first-principles density-functional calculations. Although substitutional Li and Na acceptors are mostly self-compensated by coexisting Li and Na interstitials, we find that an intentional codoping with H impurities suppresses the formation of compensating interstitials, and enhances greatly the solubilities of Li and Na acceptors by forming H-acceptor complexes. These H atoms can be easily evolved out of ZnO by postannealing at relatively lower temperatures, as compared to GaN. Thus, we expect that H-passivated acceptors are electrically reactivated, resulting in low-resistivity *p*-type ZnO.

Our calculations are performed within the local-density-functional approximation (LDA).[16] Norm-conserving pseudopotentials are generated by the scheme of Troullier and Martins[17] and then transformed into a separable form of Kleinman and Bylander.[18] Nonlinear partial core corrections[19] are included for the exchange-correlation potential to express the overlap between the Zn 3*d* core and valence electron densities. A real-space multigrid method[20] is used to deal with the localized orbitals in the valence shell, with the Laplacians in Poisson and Kohn-Sham equations expressed up to the twelfth order, based on a finite-difference method.[21] For a supercell containing 64 host atoms in the wurtzite structure, the real-space grids are generated by the $76\times44\times72$ mesh, with the spacings (h) of 0.280, 0.279, and 0.273 a.u., respectively, which correspond to the effective kinetic energy cutoff $[E_{\text{cutoff}}=(\pi/h)^2]$ of about 130 Ry. Testing various sets of fine grids up to $E_{\text{cutoff}}=200$ Ry, we find the grid spacing of about 0.280 a.u. to be sufficient to ensure the total energy precision better than 0.02 eV per unit molecule. The summation of the charge densities over the Brillouin zone is carried out using the zone center point. The calculated lattice parameters and bulk modulus for ZnO are $a=3.23$ Å, $c/a=1.6$, and $B_o=1.48$ Mbar, in good agreement with the measured values of $a=3.25$ Å, $c/a=1.6$, and $B_o=1.43$ Mbar.[22] The heat of formation (ΔH) of ZnO is calculated to be 3.44 eV, as compared to the experimental value of 3.61 eV.[23]

To calculate the formation energies and concentrations of defects in the supercell, we use Li_2O and Na_2O_2 as the Li and Na sources,[24] respectively, during crystal growth. The maximum chemical potentials of Li and Na satisfy the relations, $2\mu_{\text{Li}}^{\text{max}}=\mu_{\text{Li}_2\text{O}}-\mu_{\text{O}}$ and $2\mu_{\text{Na}}^{\text{max}}=\mu_{\text{Na}_2\text{O}_2}-2\mu_{\text{O}}$, where μ_{O} is the oxygen chemical potential. Here we use the measured values for the heat of formation of Li_2O (6.21 eV) and Na_2O_2 (5.32 eV) to calculate $\mu_{\text{Li}_2\text{O}}$ and $\mu_{\text{Na}_2\text{O}_2}$ from the relations, $\mu_{\text{Li}_2\text{O}}=2\mu_{\text{Li metal}}+\mu_{\text{O}_2}/2-\Delta\text{H}(\text{Li}_2\text{O})$ and $\mu_{\text{Na}_2\text{O}_2}=2\mu_{\text{Na metal}}+\mu_{\text{O}_2}-\Delta\text{H}(\text{Na}_2\text{O}_2)$. The stoichiometry of ZnO is described by the parameter λ, which lies between 0 and 1 under extreme Zn- and O-rich conditions, respectively.

Nitrogen is considered as a good *p*-type dopant among group-V elements, because of the smallest atomic size and lowest *p*-orbital energy.[14,25] However, it is a difficult task to obtain highly reproducible, low-resistivity *p*-type samples with N impurities because of the deep acceptor level of 0.4–0.5 eV relative to the valence-band maximum (VBM).[14,26] Although recent experiments demonstrated that it is possible to fabricate *p*-type ZnO with P and As dopants,[12,13] substitutional *p*-type doping was suggested to be even worse as going from N to P to As, because the increase of the *p*-orbital

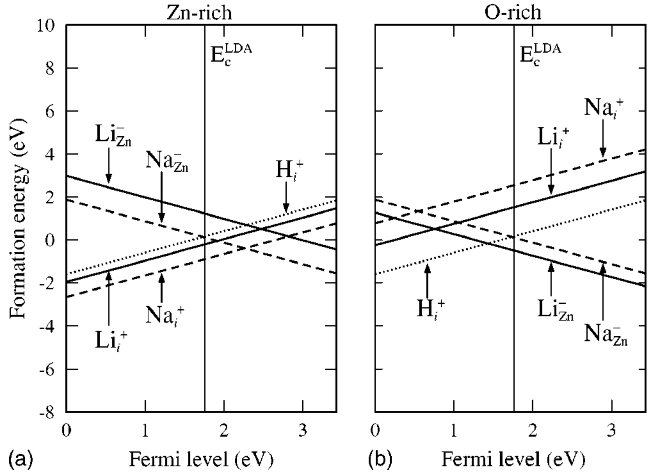

FIG. 1. Defect formation energies as a function of the Fermi level for Na-, Li-, and H-related defects in ZnO under extreme (a) Zn- and (b) O-rich conditions.

levels lead to deeper acceptor levels inside the gap.[14] On the other hand, group-I elements such as Li and Na occupying the Zn lattice site (henceforth denoted by Li_{Zn} and Na_{Zn}, respectively) were shown to behave as a shallow acceptor. From the formation energies, the $(-1/0)$ transition levels of Li and Na acceptors are found to lie at 0.04 and 0.11 eV, respectively. Compared with other group-I and -V dopants, the shallowness of the acceptor levels of Li_{Zn} and Na_{Zn} are attributed to the reduction of strains around the dopant atoms and couplings between the anion and cation orbitals, which perturbs very weakly the valence band edge state. For Li_{Zn}, almost no lattice relaxations occurs around the impurity atom, while Na_{Zn} induces small outward lattice relaxations of about 0.2 Å for the surrounding O atoms.

Despite the fact that Li and Na are good shallow acceptors, *p*-type doping difficulty remains due to self-compensation by donors generated by occupying the interstitial site. For two high symmetry positions in the wurtzite structure, i.e., octahedral and tetrahedral sites, the octahedral site is found to be more stable by 0.54 and 1.62 eV for positively charged Li and Na interstitials (Li_i^+ and Na_i^+), respectively. The existence of both substitutional acceptors and interstitial donors was in fact identified in ZnO doped with Li dopants.[27] The stability of the positively charged interstitial donor relative to the negatively charged substitutional acceptor increases as the Fermi level decreases. Under the extreme Zn-rich condition, the formation energies of these two defects are crossed at 2.47 and 2.26 eV for Li and Na dopants, respectively, as shown in Fig. 1.[28] At the crossing point which can be regarded as the equilibrium Fermi-level position,[29] the charge neutrality condition is satisfied and thus leads to a complete self-compensation, with equal concentrations for acceptors and donors. In going to the extreme O-rich condition, the equilibrium Fermi level positions are shifted to 0.76 and 0.54 eV for Li and Na, respectively. Although this result indicates that O-rich conditions are better for *p*-type doping than Zn-rich conditions, the equilibrium Fermi-level position is still far above the VBM, where *p*-type doping is usually achieved.

To overcome the *p*-type doping difficulty with group-I elements, we examine the effect of simultaneous hydrogen incorporation on the self-compensation and doping efficiency. In recent theoretical studies, the most stable form of H in ZnO is an interstitial, which acts as a shallow donor,[30] while interstitial H is an amphoteric defect in GaN.[31] In our calculations, H_i^+ is found to be more stable by 0.08 eV at a bond-centered site on the *c* axis than that off the *c* axis, while previous calculations[30] showed that the bond-centered site off the *c* axis is energetically more favorable by 0.02 eV. This discrepancy results from the use of different parameters in calculations such as supercell size, *k*-point sampling, and zero-point energy correction. Nevertheless, we point out that our results for the hydrogenation effect on the Li or Na doping are not affected by the stable position of H_i^+, because the energy difference between the two bond-centered sites is very small. In Fig. 1(b), the formation energy of interstitial H_i^+ is compared with those for Li_i^+ and Na_i^+ under the extreme O-rich condition. We use the maximum values for the Li and Na chemical potentials with the H chemical potential set to be $\mu_{H_2}/2$. We find that H_i^+ is a more stable donor, compensating dominantly for the substitutional acceptors. The equilibrium Fermi level positions between the H donor and substitutional acceptor are found to increase by 0.67 and 1.19 eV for Li and Na dopants, respectively, as compared to the doping without H. Since the Fermi level increases, the formation energies of negatively charged Li and Na acceptors are lowered, whereas those for Li and Na interstitials are enhanced [see Fig. 1(b)]. Thus, the solubility of substitutional acceptors relative to interstitial donors is greatly enhanced. However, the hole carrier concentration is still expected to be low, because the increased concentration of acceptors is fully compensated by H interstitials.

We also investigate the stability of H–group-I-acceptor complexes, which are electrically neutral. The calculated binding energies of Li_{Zn}-H_i and Na_{Zn}-H_i complexes are listed for various interstitial positions including the bond-centered and antibonding sites in Table I. In the wurtzite structure, each acceptor has two types of acceptor-dopant-O bonds due to the hexagonal symmetry: one bond aligned on the *c* axis, the other three bonds off the *c* axis. For the Li_{Zn} acceptor, the total energy is lowest when H_i is positioned at the bond-centered site of the Li-O bond on the *c* axis, as shown in Fig. 2(a). In the Na_{Zn}-H_i complex, the antibonding site of the O atom, which forms three Na_{Zn}-O bonds off the *c* axis, is the most stable position [see Fig. 2(b)], similar to the Mg_{Ga}-H_i complex in GaN.[31] For the interstitial positions considered, we find positive binding energies of 0.64–1.22 eV, indicating that H atoms are more likely to form neutral defect complexes with acceptors.

Assuming the charge neutrality condition,[26] we estimate defect concentrations $[N^{(q)}(\alpha)]$ in the presence of H interstitials by solving the following equations:

$$N^{(q)}(\alpha) = N_s(\alpha)\exp[-E_f^{(q)}(\alpha)/k_BT] \tag{1}$$

$$n_e(\mu_e) - p_h(\mu_e) = \sum_{\alpha} q(\alpha)N^{(q)}(\alpha), \tag{2}$$

where $E_f^{(q)}(\alpha)$ is the formation energy of a defect α in charge state $q, N_s(\alpha)$ is the number of sites where the defect α can

TABLE I. The formation energies (E_f) are compared for Li and Na acceptors. For each complex, the H atom is positioned at the bond-centered (BC) site of the Li-O (or Na-O) bond or the antibonding (AB) site of one of the O atoms bonded to the acceptor. Here *on* and *off* denote the Li-O (or Na-O) bonds aligned on and off the *c* axis, respectively, and ΔH is the heat of formation of ZnO. The binding energies (E_b) are given relative to the isolated configuration of negatively charged acceptor and positively charged H interstitial.

Complex	H position	E_f (eV)	E_b (eV)
Li_{Zn}-H_i	BC_{on}	$0.97-\Delta H/2$	1.22
Li_{Zn}-H_i	AB_{on}	$1.48-\Delta H/2$	0.71
Li_{Zn}-H_i	BC_{off}	$1.08-\Delta H/2$	1.11
Li_{Zn}-H_i	AB_{off}	$1.27-\Delta H/2$	0.92
Na_{Zn}-H_i	BC_{on}	0.38	0.70
Na_{Zn}-H_i	AB_{on}	0.44	0.64
Na_{Zn}-H_i	BC_{off}	0.43	0.65
Na_{Zn}-H_i	AB_{off}	0.13	0.95

be formed per unit volume, and $n_e(p_h)$ is the electron (hole) concentration at the electron chemical potential μ_e. Besides extrinsic defects generated by external sources, we include O and Zn vacancies, which behave as donors and acceptors, respectively, among dominant native defects in ZnO.[15] To simulate experimental conditions, we control the total concentration of dopants by varying the dopant chemical potentials, μ_{Li} and μ_{Na}, with keeping the O-rich condition of $\lambda=0.7$. Here Zn-rich conditions are not suitable for the *p*-type doping, because the formation energies of compensating donors such as dopant interstitials and O vacancies are relatively low. For a pure Li source, the calculated defect concentrations at 673 K are plotted as a function of the total Li concentration in Fig. 3(a), with use of $\mu_H=\mu_{H_2}/2-0.8$ eV. The solubility limit of Li_{Zn}^- is estimated to be about 10^{19} cm^{-3}, and Li interstitials almost compensate for substitutional acceptors, as discussed earlier. Similar results are also found for a pure Na source, while the solubility limit of Na_{Zn}^- is reduced to about 10^{17} cm^{-3}. When H is codoped with Li, the solubility limit of Li is greatly enhanced, with the maximum Li concentration of about 10^{20} cm^{-3}. We find that Li can exist as an isolated Li_{Zn} acceptor or a Li_{Zn}-H_i complex, as shown in Fig. 3(b), while the Li_i^+ concentrations are below 10^{12} cm^{-3}, which is much lower than for Li_{Zn}^-. If the value of μ_H increases to $\mu_{H_2}/2$, the concentrations of Li_{Zn}-H_i and H_i^+ are greatly enhanced, while the formation of Li_i^+ is severely suppressed by increased H interstitials. For Li concentrations above 10^{14} cm^{-3}, the Li_{Zn}-H_i complex becomes the most abundant Li-related defect. Similarly, H incorporation increases the maximum Na concentration up to 10^{20} cm^{-3}, severely suppressing the formation of Na interstitials.

Although Li and Na acceptors are electrically deactivated by the formation of defect complexes with H, hole carrier densities can be enhanced if a proper postannealing process is used. A similar method was successfully employed for activating H-passivated Mg acceptors in GaN, resulting in low resistivity *p*-type samples.[32] Using the nudged elastic band method, we find that the activation energies for dissociating the H atoms from the Li_{Zn}-H_i and Na_{Zn}-H_i complexes are 1.88 and 1.02 eV, respectively. These energies are comparable to or even lower than the H dissociation energy of 1.5 eV for the Mg_{Ga}-H_i complex in GaN.[31] Deuterium diffusivity measurements[33] showed that most deuteriums are evolved out of ZnO by annealing to 500°C, while much higher temperatures above 800°C are needed for GaN.[34,35] Thus, it is likely that H impurities incorporated in ZnO doped with group-I elements are removed at relatively lower annealing temperatures, increasing the electrical activity of H-passivated acceptors. In ZnO codoped with H and N, a hole concentration of about 10^{16} cm^{-3} was obtained; however, this value is too low for device applications.[10] For Li

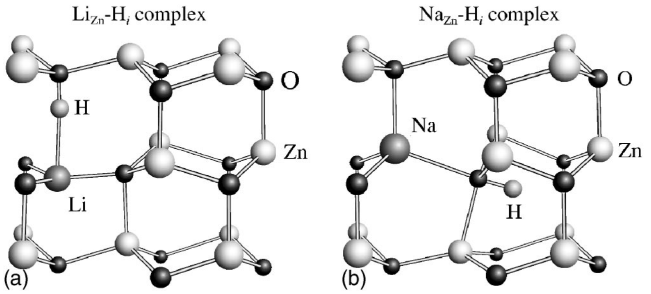

FIG. 2. Atomic structures of the (a) Li_{Zn}-H_i and (b) Na_{Zn}-H_i complexes, with the H atoms positioned at the BC and AB sites, respectively.

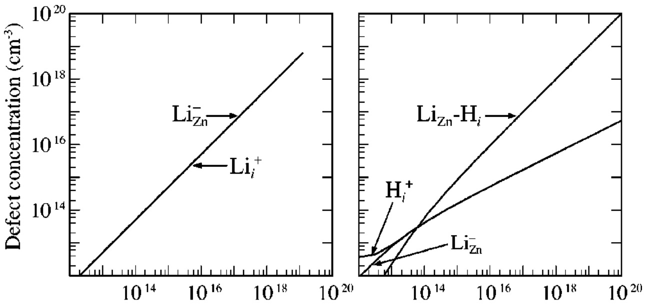

FIG. 3. Defect concentrations as a function of the total Li concentration for the cases (a) with and (b) without H incorporation.

and Na acceptors, since the H dissociation energies are lower and the acceptor levels are shallower than for N, the *p*-type doping is expected to be highly enhanced by the codoping technique with H. Since the growth of ZnO is simulated at relatively low temperatures, i.e., 673 K, where the conversion of H_2 into H_2O is suppressed by kinetics, the upper limit of μ_H is set to be $\mu_{H_2}/2$. We note that even if the upper limit of μ_H satisfies the relation of $\mu_H^{max}=(\mu_{H_2O}-\mu_O)/2$, the Li_{Zn}-H_i or Na_{Zn}-H_i complex is still the most abundant species for the Li or Na codoping with H, indicating that our results are applicable for growth using the H_2O source.

In conclusion, we suggest a method for fabricating low-resistivity *p*-type ZnO with group-I impurities such as Li and Na through first-principles density-functional calculations. We find that Li and Na are better acceptors with shallower acceptor levels than for N, while they are mostly self-compensated by Li and Na interstitials, respectively. However, we find that a codoping of H impurities and a subsequent annealing process greatly enhance the electrical activity of group-I dopants, similar to Mg-doped GaN. We hope that our proposed method may shed a light on researches of finding other good dopants rather than group-V elements such as N.

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