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The Structure Properties of $Mg_x Zn_{1-x} O$

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Abstract: A first principles calculation is used to simulate the changes of the lattice constant, band gap, total energy and structure of $MgZnO$ semiconductor alloys with the different MgO mole fractions. The calculated results show that the lattice constant diminishes and the crystal structure departs gradually from the wurtzite type as the MgO mole fraction increases. By comparison with the different positions of the Mg atom, it is suggested that the structure of $Mg_x Zn_{1-x} O$ alloy will change and the possibility of the phase transition will be higher than that of the phase separation as the MgO mole fraction increases. On the other hand, when the MgO mole fraction is increased, the band gap enlarges, which is mainly attributable to the shift of the top of the valence band away from the Fermi level. By constructing the influence of all kinds of electronic states in Mg atom on the valence band, it shows that the contribution of Mg to the energy band near the top of the valence band takes turn from its p , d , s states. The density of the p states near the top of the valence band enhances prominently when the MgO mole fraction is increased. It indicates that the sp hybridization not only affects the structure of the crystal but also plays an important role for its electronic structures.

Key words: $MgZnO$ semiconductor; lattice structure; the first principle calculation

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1 Introduction

Recently, considerable attention has been paid to ZnO material for realizing a room-temperature ultraviolet laser, which was enabled by the wide direct band gap ($E_g = 3.4$ eV) and large exciton binding energy (60 meV) at room temperature. To obtain high-quality optoelectronic devices, the key problem is to find a way to adjust the band gap while keeping the lattice constants similar to the materials for constructing the heterojunction. Magnesium oxide (MgO) has a band gap of 7.9 eV. The ionic radius of Mg^{2+} (0.057 nm) is similar to that of Zn^{2+} (0.06 nm), so replacement of Zn by Mg should not cause a significant change in lattice constants. By mixing suitable MgO into ZnO , it may be possible to obtain the $Mg_x Zn_{1-x} O$ alloy with a wider band gap than that of pure ZnO , yet still having a lattice constant

similar to that of pure ZnO ^[1,2]. But MgO has a cubic crystal structure differing from wurtzite type of ZnO , the phase separation and transition are likely to occur as the MgO mole fraction increases^[3-5]. Therefore, it is significant to understand the structure characteristics of $Mg_x Zn_{1-x} O$ varying with different MgO mole fractions.

In this work, a first principles calculation is used to simulate the changes of some main parameters of $MgZnO$ alloys with the MgO mole fractions, including the lattice constant, band gap, total energy, and so on.

2 Calculations and Models

The Vienna *ab-initio* Simulation Package (VASP) is used to calculate in this work. VASP is a complex package for performing *ab-initio* quantum-mechanical molecular dynamic (MD) simulations.

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using pseudopotentials and plane wave basis set. The approach implemented in VASP is based on the local-density approximation with the free energy as a variable and an exact evaluation of the instantaneous electronic ground states at each MD-step using efficient matrix diagonalisation schemes and an efficient Pulay/Broyden charge density mixing. These techniques avoid all problems possibly occurring in the original Car-Parrinello method.

The supercells of wurtzite type $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys with the different MgO mole fractions and different Mg distributions are constructed. The supercells of ZnO with 64 and 32 atoms are firstly used to study the change of the basic characteristics under the different sizes. In addition, the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys with $x = 0.000, 0.0625, 0.1250, 0.1875,$ and 0.2500 are constructed to understand the influence of the different MgO mole fractions on the structure characteristics. Finally, the structures with different Mg distributions at the same MgO mole fraction are investigated in order to know the possible changes of structure of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

3 Results and Discussion

Comparing the calculated data of the supercells of ZnO with 64 and 32 atoms, no change of their basic parameters, such as lattice constant, band gap

and so on, have been observed within the computing error. Thus, the supercell with 32 atoms is mainly calculated and discussed as follows.

Table 1 shows the calculated total energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys with the different MgO mole fractions. It is obvious that the total energy of the system becomes more and more small with the increase of x , i.e. the system becomes more and more stable. According to Ref [6], the measured results of X-ray diffraction have showed that there exists an obvious MgO diffraction peak when the MgO mole fraction is higher than 0.22, which means that the phase separation occurs. Generally, the phase separation is possible to happen if the total energies of ZnO and MgO are minima. However, the data in Table 1 reveal that the total energy of ZnO is maximum and the total energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ does not increase with the MgO mole fraction even $x = 0.25$. It illuminates that the bonding energy of Mg—O is larger than that of Zn—O. The more Zn atoms are replaced by Mg atoms, the more the number of Mg—O bonds increases, so that the total energy of the system decreases and the system becomes more stable. Therefore, it excludes theoretically the possibility of the phase separation at low MgO mole fraction. The experiment result deviated from the calculation seems reflecting unusual characteristics of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$.

Table 1 Partial calculated parameters of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$.

x		0	0.0625	0.1250	0.1875	0.2500
Total energy (eV)	Before relaxation	-145.3143	-148.2150	-151.1158	-154.0024	-156.8927
	After relaxation	-145.3167	-148.2462	-151.1756	-154.0929	-157.0085
Lattice constant a (nm)		0.32682	0.32656	0.32630	0.32589	0.32569

In addition, the lattice constant of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ becomes smaller with the increase of the MgO mole fraction x . These results are compared with the experimental values, as showed in Fig 1. The calculated lattice constant is a bit larger than the experimental value, but the difference between them is within the experimental error range. It further proves the rationality and reliability of the calculation method, model structure and simulation results mentioned above.

Generally, the variation of the lattice constant

is attributable to the bond flex of anion and cation, radius difference of substitutional ion, and change of the crystal structure. In order to clarify the physical origin that the lattice constant varies with the MgO mole fraction, we further calculate the above models with ion relaxation. It is known that there are the different distributions of Mg atoms at a certain MgO mole fraction. The total energies of all kinds of the distribution models are calculated. Their average value is obtained by the weight which is determined by the possibility that each distribution occurs. The

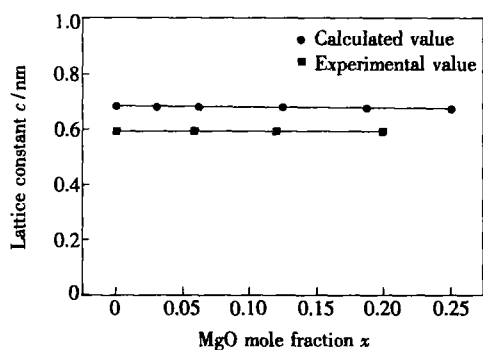


Fig 1 Dependence of lattice constant in c -axis on the MgO mole fraction

calculated results listed in Table 1 exhibit that the total energy minishes after relaxation and the minished magnitude increases obviously as the MgO mole fraction increase. It indicates that the locate stress in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ around the substitutional Zn in Mg site due to the length difference between the Mg—O and Zn—O bonds, caused by the electro-negativity difference between Mg and Zn and the ion radius difference of Mg (0.057 nm) and Zn (0.06 nm), will be released after relaxation. Therefore, the total energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ after relaxation is lower and the structure becomes more stable.

By comparing the atom positions before-and-after relaxation, it can be seen that the atoms surrounding substitutional Mg atom relax outward. The relaxation magnitude increases with increasing of the MgO mole fraction and reach up to 1.5% ~ 1.7% and 1.2% ~ 1.4% along a and c axes, respectively. This relaxation anisotropy indicates that the stress in a axis is larger than that in c axis after Mg substituting into Zn site. As the result of the relaxation anisotropy, the angle between the bonds changes up to 5° and forces $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ deviating from wurtzite structure gradually. At the same time, it is interesting that Mg—O bond is longer than Zn—O bond although the radius of Mg ion is larger than that of Zn ion. It further shows that the lattice constant decrease with the increase of the MgO mole fraction, and it is mainly caused by the variation of crystal structure. This implies that phase transition from wurtzite to cubic structure will occur when the MgO mole fraction exceeds a certain value.

To further confirm the relative stabilization of

the structure variation, we compare the differences of the total energies with different Mg atom distributions for the same composition. The total energies vary from -151.1664 to -151.1810 eV, -154.0418 to -154.1147 eV, and -156.9753 to -157.0351 eV for the MgO mole fractions of 0.1250, 0.1875, and 0.2500, respectively. Detailed analysis shows that the stabilities are different for Mg atoms aligned in between a and c axes. For example, for $x = 0.1250$ as shown in Fig 2 (a) and (b), the calculated total energies are -151.1145 and -157.0351 eV, respectively, which indicates that the distributions with Mg atoms aligned in c axis are more stable than that in a axis. This also agrees with the above analysis that the stress around Mg along a axis is larger than that in c axis. Secondly, the difference between the Mg congregated together to form MgO cluster and distributed uniformly is analyzed, as models of $x = 0.1875$ shown in Fig 2 (c) and (d). The total energy of the former is -153.9853 eV and evidently higher than that of the later of -154.0929 eV. This further confirms the result mentioned above that the phase separation is hard to happen in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys, which seems attributable to the total energy enhancement due to the interaction between the second nearest neighbor Mg atoms. Furthermore, we compare the difference between the two Mg atoms at the second nearest neighbor in the same horizontal and vertical planes, as models of $x = 0.2500$ shown in Fig 2 (e) and (f), respectively. The total energy of the former is -156.9753 eV larger than -157.0085 eV of the later one, which indicates that the structure with the two Mg atoms at the second nearest neighbor in the same vertical plane is more stable than that in the same horizontal plane. On the basis of above results, it is believed that the phase transition from wurtzite to cubic structure may occur rather than the phase separation if the structure of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys will change as the MgO mole fraction increases.

The calculated density of states (DOS) of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys with different MgO mole fractions shows that the energy band changes only in the valence

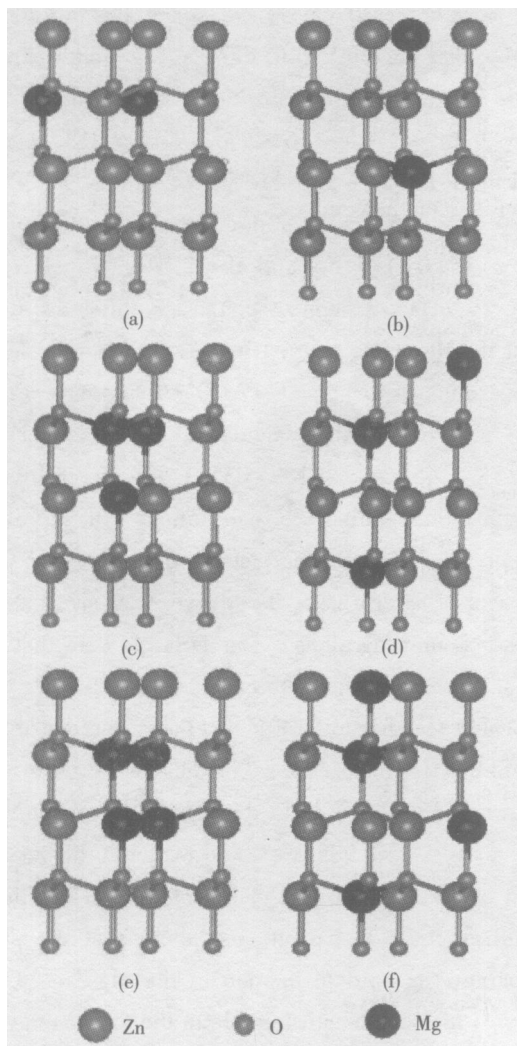


Fig 2 The models of different distributions for MgO mole fractions

and conduction bands when Zn is substituted by Mg and no Mg-related states appear in band gap. Furthermore, the band gap enlarges with increasing the MgO mole fraction, as Fig 3 shown, which agrees with the experimental results. In view of this, MgO and ZnO are suitable to form the semiconductor alloy with adjustable band gap. The band gap enlargement as the MgO mole fraction increase is mainly contributed to the shifts of the valence and conduction bands away from the Fermi level where the former is more visible. If the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys are used to fabricate a heterojunction, the band offset of the valence band will be larger than that of the conduction band. These theoretical data appear more important at present without adequate experimental results.

On the other hand, the obvious shift of the

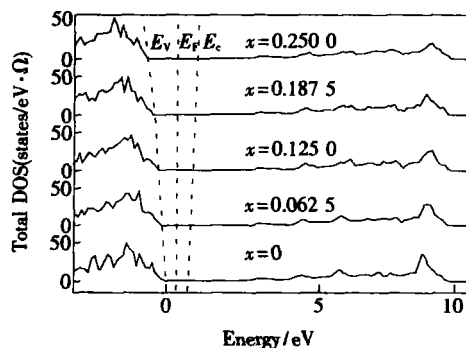


Fig 3 The density of states with the different MgO mole fractions

valence band as the MgO mole fraction increase implies that the influence of Mg atom on the electronic structure mainly concentrates on the valence band. In the light of this, we investigate the effects of the various electronic states of Mg atom on the valence band by comparing the total and partial DOSs of the Mg atom. It is seen from Fig 4 (a) that the contributions to the top of the valence band takes turn from the p, d, and s states of Mg. This contribution is prominently enhanced when the MgO mole fraction is increased, as partial DOSs of the p states with different MgO mole fraction shown in Fig 4 (b). It shows that the sp hybridization not only affects the

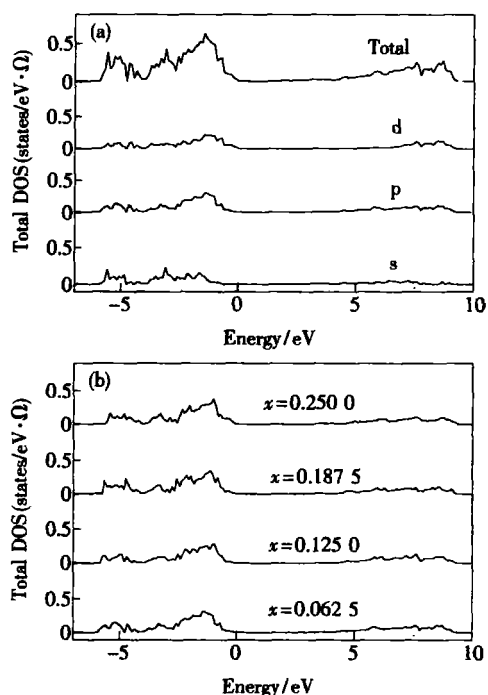


Fig 4 The density of states of a Mg atom (a), and of p states for different MgO mole fractions (b).

geometrical structure of the crystal but also plays an important role in its electronic structures

4 Conclusion

VASP has been used to calculate the geometrical and electronic structures of $Mg_xZn_{1-x}O$ alloys with different MgO mole fractions. The calculated results show that the lattice constant diminishes and the crystal will depart gradually from the wurtzite

structure as the MgO mole fraction increases. On the other hand, when the MgO mole fraction is increased, the band gap enlarges which is mainly attributable to the shift of the valence band away from the Fermi level. It is important to point out that the variations of the lattice constants is small while that of the band gap is large as MgO mole fraction change, which is an advantage for fabrication quantum structures with heterointerfaces.

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$Mg_xZn_{1-x}O$ 结构性质

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摘要: 采用第一性原理计算模拟了不同组分的 $Mg_xZn_{1-x}O$ 半导体混晶的晶格常数、总能、结构, 以及禁带宽度的变化。计算结果显示, 随着 Mg 组分的增加, 晶格常数逐渐减小, 晶体逐渐偏离纤锌矿结构。对各种不同的 Mg 原子排列情况进行比较认为, $Mg_xZn_{1-x}O$ 的结构随组分 x 的增大, 发生从纤锌矿到岩盐矿的结构相变的可能性高于发生相分离。另一方面, 禁带宽度随组分增大主要由价带顶的移动所致。进一步分析 Mg 原子各种电子态对价带的影响表明, Mg 对价带顶附近能带的贡献依次来自 p、d、s 态电子。随着组分 x 的增加, p 态电子在价带顶附近的密度明显提高, 说明 sp 轨道杂化不但对晶体的几何结构产生影响, 而且对其电子结构也起重要作用。

关键词: MgZnO 半导体; 晶格结构; 第一性原理计算

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