Nitrogen- and fluorine-doped ZrO$_2$: a promising p–n junction for an ultraviolet light-emitting diode

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Received 21 March 2012, in final form 29 May 2012
Published 18 July 2012
Online at stacks.iop.org/JPhysCM/24/335801

Abstract
In this work we study the effect of nitrogen (N) and fluorine (F) doping on the electronic properties of ZrO$_2$ by using ab initio electronic structure calculations. Our calculations show the importance of on-site Coulomb correlation in estimating the correct band gap of ZrO$_2$. The N and F doping provide hole- and electron-type impurity states in the band gap closer to the top of the valence band and the bottom of the conduction band, respectively. The formation of such impurity states may be exploited in fabricating a p–n junction expected to be useful in making an ultraviolet light-emitting diode.

1. Introduction
The doping of N in place of oxygen (O) in the technologically important oxide semiconductors has attracted a great deal of attention in the last couple of years [1–8]. Most of these activities are directed towards the creation of magnetism by non-magnetic doping in the conventional dilute magnetic semiconducting materials like TiO$_2$, ZnO, MgO, etc [5–8]. It has been shown that the doping of N at O sites is equivalent to creating holes in these systems. Recently, we have shown that F doping in TiO$_2$ is equivalent to electron doping in it [5]. Thus one expects that N- and F-doped oxide semiconductors may be useful in fabricating many technologically important materials where p- and n-type conductions are to be exploited.

Here we explore such a possibility for a technologically important wide band gap semiconductor, namely ZrO$_2$ [9–11]. At room temperature it shows monoclinic structure and it converts into tetragonal and cubic structures with increasing temperature. The compound is a direct band gap semiconductor and its band gap is reported to vary from 5 to 7 eV depending upon the structural phases and experimental methods used in extracting it [12–14]. It is a crucial refractory material used in insulation, abrasives, enamel, etc. It is also an important high k dielectric compound predicted to be useful as a gate dielectric material [15, 16].

In this work we study the modification of the electronic structure of monoclinic ZrO$_2$ when N and F are doped at O sites by using the supercell method of ab initio electronic structure calculation. The on-site Coulomb interaction is found to be important in getting the correct band of the compound. N- and F-doped TiO$_2$ are found to be p- and n-type semiconductors, respectively. It is proposed that these semiconductors may be useful in fabricating a p–n junction which can be used as an efficient ultraviolet (UV) light-emitting diode (LED).

2. Computational details
The spin unpolarized electronic structure calculations for ZrO$_2$–$_x$N$_x$ and ZrO$_2$–$_x$F$_x$ ($x = 0, 1/32, 1/16$ and $1/8$) compounds have been carried out by using the state-of-the-art full-potential linearized augmented plane wave (FP-LAPW) method [17]. The lattice parameters used in the calculations are taken from the literature [18, 19] and correspond to monoclinic and tetragonal structure. Here one should keep in mind that on general grounds lattice parameters are expected...
Figure 1. The total density of states (TDOS) and the partial density of states (PDOS) of ZrO$_2$ are shown in (a) and (b). The inset of (a) shows the evolution of the band gap of ZrO$_2$ with increasing strength of the on-site Coulomb interaction ($U$).

3. Results and discussion

As mentioned above, the ground state structure of ZrO$_2$ is experimentally found to be monoclinic (space group $P2_1/c$) and it shows a structural transition from monoclinic to tetragonal (space group $P4_2/nmc$) above room temperature. The total energy calculations for ZrO$_2$ in monoclinic and tetragonal phases also suggest that the monoclinic structure is a true ground state, as its energy is found to be $\sim 170$ meV less than that of the tetragonal structure. In the monoclinic phase each unit cell contains one kind of Zr atoms and two...
The total densities of states (TDOS) of ZrO$_{2-x}$N$_x$ for $x = 1/32$, 1/16, and 1/8 are shown in (a), (b), and (c), respectively.

Figure 2. The total densities of states (TDOS) of ZrO$_2$–N, for $x = 1/32$, 1/16, and 1/8 are shown in (a), (b), and (c), respectively.

kinds of O atoms (O1 and O2) occupying the 4e Wyckoff positions. Therefore, each unit cell contains four Zr atoms and eight O atoms and every Zr atom is surrounded by seven O atoms. The atomic positions of Zr, O1 and O2 atoms after geometry optimization are found to be (0.2743, 0.0433, 0.2091), (0.0648, 0.3248, 0.3512) and (0.4493, 0.7558, 0.4676), respectively, which are slightly different from the experimentally obtained values of (0.2758, 0.0404, 0.2089), (0.069, 0.342, 0.345) and (0.451, 0.758, 0.479) for the Zr, O1 and O2 atoms, respectively [18].

The total density of states (TDOS) and partial density of states (PDOS) of the ZrO$_2$ compound are plotted in figure 1. The insulating ground state for the ZrO$_2$ compound is clearly evident from figure 1(a), where one can see a large band gap of 4 eV. The valence band (VB) and conduction band (CB) predominantly consist of O 2p and Zr 4d states, respectively, as seen from figure 1(b). One can also observe small contributions of the Zr 4d and O 2p PDOS in the VB and CB, respectively. Under a pure ionic model for the compound one would not have expected the presence of Zr 4d and O 2p states in the VB and CB. This behaviour may be considered a signature for the breakdown of pure ionic character of Zr–O bonds. Although our calculated band gap of 4 eV is ~1 eV less than the experimental one [13], it provides a somewhat better estimate of the band gap in comparison to the earlier calculated LDA based gaps of 3.35 eV [26] and 3.58 eV [14].

Here one should keep in mind that the GGA is a better approximation than the LDA, and use of the GGA is expected to improve the gap. Moreover, the FP-LAPW method used in the present work was found to provide a better estimate of the gap in comparison to other methods [27]. Thus the use of the GGA within the FP-LAPW method could be the reason for the better estimate of the band gap in the present work.

The correct band gaps of ZrO$_2$ are obtained by carrying out GGA + $U$ calculations where we consider different values of $U$ for Zr 4d and O 2p electrons. The use of $U$ for these two orbitals can be justified by looking at the PDOS shown in figure 1(b) where we have seen the presence of O 2p and Zr 4d states in the valence band as well as in the conduction band. The $U$ dependent band gap of the compound is shown in the inset of figure 1(a). It is evident from the inset that the band gap monotonically increases with increasing $U$, and $U \approx 3.5$ eV provides a correct band gap of 5 eV. This value of $U$ is a reasonable estimate for 4d and 2p electrons and closer to those values of $U$ which are found to provide fairly good electronic and magnetic properties of MgO and Sr$_3$NiRhO$_6$ (3d and 4d electron system) compounds [6, 28].
Figure 3. The total densities of states (TDOS) of ZrO$_2$-$xF_x$ for $x = 1/32$, 1/16, and 1/8 are shown in (a), (b), and (c), respectively.

The energy of monoclinic Zr$_4$O$_7$N is found to be $\sim 448$ meV less than that of tetragonal Zr$_4$O$_7$N. On comparing this energy difference with that of ZrO$_2$, one can say that the N doping gives more stability to the monoclinic structure. This suggests that the monoclinic structure is a true ground state structure for the N-doped compounds studied here. N doping at the O site changes the electronic structure of the compound drastically and N-doped ZrO$_2$ becomes metallic, as is evident from figures 2(a) to 1(c). The N 2p states mainly contribute around the Fermi level ($\epsilon_F$) and one can see three peak structures corresponding to three crystal-field-split p orbitals. The energy distribution of O 2p and Zr 4d states remains very similar to that of pure ZrO$_2$. There is a large density of unoccupied N 2p states just above the $\epsilon_F$. This indicates that N doping is equivalent to creating holes in the system and unoccupied N 2p states form an unoccupied impurity band. The width of the unoccupied impurity band increases with increase in N content and is found to be about 0.11, 0.18 and 0.19 eV for $x = 1/32$, 1/16 and 1/8 compounds, respectively.

The total energy calculations of Zr$_4$O$_7$F in monoclinic and tetragonal structures also suggest that the monoclinic phase is a true ground state as its energy is found to be $\sim 1634$ meV less than that of the tetragonal structure. On comparing this energy difference with that of ZrO$_2$ and Zr$_4$O$_7$N one can say that the F doping is providing better stability to the monoclinic structure, which is a true ground state structure for all the concentrations studied here. The TDOS of F-doped compounds are shown in figure 3. In contrast to the case for N-doped compounds, the $\epsilon_F$ of the F-doped compounds is pinned at the CB, consisting of Zr 4d states. In contrast to the case for the N 2p crystal-field-split state, three F 2p bands contribute deep inside the VB and 10 eV below $\epsilon_F$. One may be surprised by this result, as the simple picture of impurity doping in a semiconductor does not appear to hold here. In this picture, replacing some of the O by F is equivalent to doping electrons in the system and one would have expected that an extra F 2p electron should contribute near the bottom of the CB as an occupied impurity band. However, Zr 4d electrons are found to contribute in the occupied impurity band. Here it is important to note that the simple picture of impurity doping in the semiconductor is historically based on studies of covalent semiconductors [29]. The present system under study is an ionic semiconductor. In the case of ZrO$_2$, the charge neutrality condition requires that two Zr 4d electrons should be transferred to the O atoms. However, replacing O by F requires only one Zr 4d electron to be transferred to F and the remaining Zr 4d electron is expected to contribute in the CB in accordance with the...
calculated result. The width of the occupied impurity band increases with increase in the F content and is found to be about 0.12, 0.14 and 0.24 eV for the $x = 1/32$, 1/16 and 1/8 compounds, respectively.

The present work clearly shows the p- and n-type doping when O is replaced by N and F, respectively, and the bandwidth of the hole- and electron-like impurity bands can be tuned by varying the doping concentration. Thus N- and F-doped ZrO$_2$ may be used to fabricate a p-n junction. Since ZrO$_2$ is a direct band gap semiconductor and its band gap lies in the UV range, such a p–n junction is expected to be useful in manufacturing UV LEDs. It is important to note that the light extraction in LEDs is a major research area where people are trying to obtain more light, so that the device may be useful for various purposes. Reducing the heating effect of LEDs is another important area of research. Both issues are related to the higher refractive indices of the materials conventionally used in manufacturing the LEDs. The higher the refractive index of the material separating the device from the air, the lower the critical angle of total internal reflection and hence the greater the amount of light that gets back to the material (less will pass through the air), this itself resulting in more heating of the material. The refractive indices of most of the materials used in manufacturing LEDs are above 3 [30]. However, the refractive index of ZrO$_2$ is ~2.6 at 5 eV and expected to provide better light extraction capability in the UV range. Recently, it has been shown that ~265 nm (i.e. ~4.7 eV) UV radiation acts as an effective disinfectant [31]. The bandwidths of the unoccupied and occupied impurity bands are found to be about 0.12 eV each for $x = 1/32$ N- and F-doped compounds. Furthermore, these band gaps can be further increased by increasing the doping concentrations. Thus, one expects radiation emitted from LEDs manufactured from p–n junctions made of N- and F-doped ZrO$_2$ to be useful as an effective sterilizing agent. At this juncture it is important to note that N-doped ZrO$_2$ has already been synthesized [32], and comparison of the ionic radii of N and F with respect to O also suggests that the synthesis of F-doped ZrO$_2$ may not be a problem. In the light of these observations it is tempting to suggest that the N- and F-doped ZrO$_2$ are important p- and n-type semiconductors, respectively, that are expected to be useful in making many semiconducting devices.

4. Conclusions

The effect of N and F doping on the electronic properties of ZrO$_2$ has been investigated by using ab initio electronic structure calculations. In order to find the correct band gap one needs to consider the on-site Coulomb interactions among the Zr 3d and O 2p electrons. Replacing O by N and F is found to create hole- and electron-like impurity states in the band gap closer to the top of the valence band and the bottom of the conduction band, respectively. It is proposed that such electron- and hole-doped semiconductors may be useful in fabricating p–n junctions. Such p–n junctions are expected to work as efficient UV LEDs, which may be used as disinfectants.

References

[1] Nakano Y, Morikawa T, Ohwaki T and Taga Y 2005 Appl. Phys. Lett. 86 132104
[2] Batzill M, Morales E H and Diebold U 2006 Phys. Rev. Lett. 96 026103
[3] Cao Y, Miao L, Tanemura S, Tanemura M, Kuno Y and Hayashi Y 2006 Appl. Phys. Lett. 88 251116
[4] Wu H, Stroppa A, Sakong S, Picozzi S, Scheffler M and Kranzer P 2010 Phys. Rev. Lett. 105 267203
[5] Pandey S K and Choudhary R J 2011 J. Phys.: Condens. Matter 23 276005
[6] Slipukhina I, Mavropoulos Ph, Blugel S and Lezaic M 2011 Phys. Rev. Lett. 107 137203
[7] Ellimov I S, Rusydi A, Ciszar S I, Hu Z, Hsieh H H, Lin H-J, Chen C T, Liang R and Sawatzky G A 2007 Phys. Rev. Lett. 98 137202
[8] Drera G, Mozzati M C, Galinneto P, Diaz-Fernandez Y, Malavasi L, Bondino F, Malvestuto M and Sangaletti L 2010 Appl. Phys. Lett. 97 012506
[9] Gutowksi M, Jaffe J E, Liu C-L, Stoker M, Hegde R I, Rai R S and Tobin P J 2002 Appl. Phys. Lett. 80 1897
[10] Eichler A and Kresse G 2004 Phys. Rev. B 69 045402
[11] Zheng J X, Ceder G, Maxisch T, Chim W K and Choi W K 2007 Phys. Rev. B 75 104112
[12] French R H, Glass S J, Ohuchi F S, Xu Y-N and Chang W Y 1994 Phys. Rev. B 49 5133
[13] Ikarashia N and Manabe K 2003 J. Appl. Phys. 94 480
[14] Jiang H, Gomez-Abal R I, Kinke P and Scheffler M 2010 Phys. Rev. B 81 085119
[15] Puthenkovilakam R, Carter R E and Chang J P 2004 Phys. Rev. B 69 155329
[16] Zhao X, Ceresoli D and Vanderbilt D 2005 Phys. Rev. B 71 085107
[17] http://elk.sourceforge.net
[18] McCullough J D and Trueblood K N 1959 Acta Crystallogr. 12 507
[19] Teuffer G 1962 Acta Crystallogr. 15 1187
[20] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[21] Zunger A, Lany S and Raebiger H 2010 Physics 3 53
[22] Stroppa A and Kresse G 2009 Phys. Rev. B 79 201201(R) Stroppa A, Kresse G and Continenza A 2011 Phys. Rev. B 83 085201
[23] Siculo S, Palma G, Di Valentin C and Pacchioni G 2007 Phys. Rev. B 76 075121
[24] Virojt F, Hayn R and Boukortt A 2011 J. Phys.: Condens. Matter 23 025503
[25] Bullmark F, Cricchio F, Gränis O and Nordström L 2009 Phys. Rev. B 80 035312
[26] Dutta G, Hembram K P S S, Rao G M and Waghmare U V 2006 Appl. Phys. Lett. 89 202904
[27] Ong K P, Blaha P and Wu P 2008 Phys. Rev. B 77 073102
[28] Pandey S K and Maiti K 2008 Phys. Rev. B 77 045120
[29] Ashcroft N W and Mermin N 1976 Solid State Physics (New Delhi: Brooks/Cole Cengage Learning) chapter 28
[30] http://refractiveindex.info
[31] Mori M, Hamamoto A, Takahashi A, Nakano M, Wakikawa N, Tachibana S, Ikehara T, Nakaya Y, Akutagawa M and Kinouchi Y 2007 Med. Biol. Eng. Comput. 45 1237
[32] Liu Y, Li J, Qiu X and Burda C 2007 J. Photochem. Photobiol. A, 190 94