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Effect of donor and acceptor dopants on Schottky barrier heights and vacancy concentrations in barium strontium titanate

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Abstract

This paper discusses the effect of donors and acceptors on the electronic band structure and defect properties of $Ba_{0.7}Sr_{0.3}TiO_3$ film (BST). Based on X-Ray Photoelectron Spectroscopy (XPS) data and an extension of previous work by Robertson and Chen (Robertson, J. and Chen, C. W., Schottky barrier heights of tantalum oxide, barium strontium titanate, lead titanate, and strontium bismuth tantalate. *Appl. Phys. Lett.,* 1999, **74**, 1168–1170), Schottky barrier heights are calculated for BST films in which La and Mn dopants have been added (0.7%). The barrier height expression of Cowley and Sze (Cowley, A. M. and Sze, S. M., *Journal of Applied Physics,* 1965, **36,** 3212) is discussed with attention to the term neglected in their original paper. The effect of dopants on the oxygen vacancy concentration is also discussed.

Keywords: $BaTiO_3$ and titanates; Electrical conductivity; Electrical properties

1. Introduction

Doping of ferroelectric thin films is one way in which the important electrical properties of the film may be modified. Relatively few quantitative studies have been reported on donors and acceptors in barium strontium titanate (BST), lead zirconate titanate (PZT), and other ferroelectrics of interest for random-access memories. Readers are referred to earlier work on Nb in PZT by Klissurska et al.[1–4], on La, Mn and Fe in $SrTiO_3$ by Hofman et al.,[5,6] on Sc and Nb in PZT by Yoo and Desu,[7] on Nb and Na in PZT by Wouters et al.,[8] on Ni doped strontium titanate by Waser et al.[9] and on Mn and Ce doped barium titanate by Waser and Klee.[10]

2. Film fabrication

The undoped and doped $Ba_{0.7}Sr_{0.3}TiO_3$ thin films were grown on 4 inch platinum coated silicon wafers by means of a chemical solution deposition (CSD) method using an propionate based solution.[11,12] The dopants were added as compensational dopants, i.e. Mn was added on Ti-site and La was added on Ba/Sr-site taking into account the charge compensation by cation-vacancies. The single phase BST thin films of approx. 300 nm thickness exhibit a polycrystalline structure with a columnar morphology.

3. Effect of dopants on Fermi level

In bulk intrinsic ferroelectric materials the Fermi level is known to lie in the middle of the band-gap. However, an *n*-type inversion layer exists near the electrode-ferroelectric interface in many titanate thin-film samples, this is thought to be due to large concentrations of oxygen vacancies in this region of the film (as evidenced, e.g. by the presence of Ti^{3+}) that act as donors, raising the Fermi level considerably. This point is not agreed to by all authors; see for example Tagantsev and Stolichnov.[13] The *n*-type nature of the surface of BST is clearly demonstrated here by X-ray photoelectron spectroscopy (XPS) measurements of the valence band (Fig. 1). The oxygen vacancies, in the absence of an electric field, act as fixed positive charges (if they lie above the Fermi

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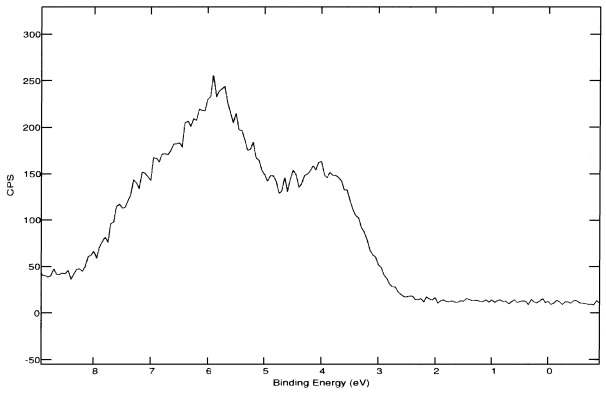

Fig. 1. XPS valence band measurement for undoped BST sample. Valence band edge is approximately 2.9 eV below the Fermi level.

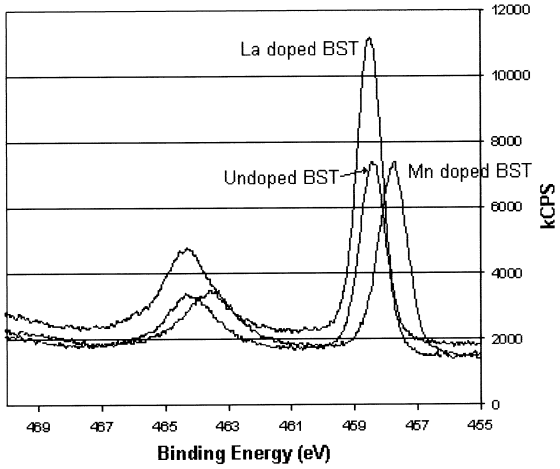

Fig. 2. Ti 2p XPS peak for doped and undoped BST.

level), i.e. they do not thermally relax away. This result is also important in the explanation of fatigue effects in PZT thin films.[14–17]

From the following valence band measurement the Fermi level is found to lie about 0.4 eV below the conduction band edge in an intrinsic sample. This is determined from the known band-gap of BST (3.3 eV) and the observation that the valence band lies 2.9 eV below the Fermi level. Neilson[18] found the same value for a different BST film.

To measure the effect of the dopants on the Fermi level high-resolution measurements of the titanium 2p peak were taken using XPS. The shift in the peak gives the relative shift of the Fermi level. Three samples were used, intrinsic BST, 0.7% lanthanum (donor) doped BST, and 0.7% manganese (acceptor) doped BST. The Fermi level of the La-doped BST was shifted up by 0.1 eV, while the Fermi level of the Mn-doped BST was shifted down by 0.7 eV, as shown in Fig. 2.

4. Schottky barrier height

When a metal electrode such as platinum is attached to the film a Schottky barrier is formed if the metal work-function is greater than that of the material to which it is attached. The barrier heights for platinum on a number of ferroelectric materials have been considered by Robertson and Chen.[19] They use the formula of Sze and Cowley[20,21] (1), which takes into account surface states on the metal semiconductor interface.

$$\phi_{Bn} = S(\phi_m - \chi) + (1 - S)\big(E_g - \phi_0\big) - \Delta\phi \tag{1}$$

In the limiting ionic case of $S=1$, the simple band-bending picture holds and the barrier height is simply the difference between the metal work function (ϕ_m) and the semiconductor electron affinity(χ). In the other (covalent or trap-dominated) limiting case where $S=0$ the barrier height is simply the difference between the conduction band edge and ϕ_0. ϕ_0 is the charge neutrality level, it is the level below which all surface states must be filled for charge neutrality at the surface, before the application of the metal it coincides with the Fermi level. If the surface states are equally distributed in energy then one might expect that the change in the charge neutrality level when dopants are present would be the same as the change in the Fermi level before the application of contacts. If this is not the case the change would be in the same direction, but of different magnitude. We have determined the charge neutrality level by adding the measured difference in the Fermi level of Mn and La doped BST compared to undoped BST to the charge neutrality level of the undoped BST. Table 1 contains the relevant barrier parameters and barrier heights.

The equation of Cowley and Sze above (1) is based on an approximation, that as has been pointed out by Rhoderick and Williams,[22] is equivalent to ignoring the space charge in the depletion width.

The full expression for the barrier height that Cowley and Sze derive is

$$\begin{aligned}\phi_{Bn} = {} & \big[S(\phi_m - \chi) + (1 - S)\big(E_g - \phi_0\big) - \Delta\phi\big] \\ & + \left\{\frac{S^2 C}{2} - S^{\frac{3}{2}}\left[C(\phi_m - \chi) + (1 - S)\big(E_g - \phi_0\big)\frac{C}{S}\right.\right. \\ & \left.\left. - \frac{C}{S}\big(E_g - E_F + kT\big) + \frac{C^2 S}{4}\right]^{\frac{1}{2}}\right\}\end{aligned} \tag{2}$$

In the above $C = \frac{2q\varepsilon_s N_D \delta^2}{\varepsilon_i^2}$. When $\varepsilon_s \approx 10\varepsilon_0$ and $N_D < 10^{18}$ cm^{-3} C is of the order of 0.01 eV and it is reasonable to discard the $\{.\}$ term as Cowley and Sze did. However, here both ε_s and N_D are probably considerably larger than this and so the $\{.\}$ term may be significant. In Table 2 the size of the correction is evaluated over a range of values for C for doped and undoped samples.

If $N_D = 10^{18}$ cm^{-3}, $\varepsilon_s = 400\varepsilon_0$, $\varepsilon_i = \varepsilon_0$ and $\delta = 5$ Å then $C = 3.6$ eV. N_D for the Mn doped sample is expected to be about 100 times bigger than this, and may be higher

Table 1
Important parameters in determining barrier heights, and barrier heights according to the approximate formula of Cowley and Sze,[20,21] the values of the parameters for undoped BST are obtained from Robertson and Chen[19]

	Undoped	Mn doped	La doped
Gap (eV)	3.3	3.3	3.3
S	0.28	0.28	0.28
ϕ_0	2.6	1.9	2.7
Electron affinity	3.9	3.9	3.9
Barrier height	0.89	1.40	0.82

Table 2
Size of term neglected by Cowley and Sze[20,21] for a wide range of values of C

	Correction to barrier height (eV)		
C (eV)	Undoped	Mn	La
0.01	−0.02	−0.01	−0.02
0.1	−0.06	−0.04	−0.06
1	−0.16	−0.11	−0.16
10	−0.33	−0.22	−0.35
100	−0.45	−0.27	−0.47
1000	−0.47	−0.27	−0.50
10000	−0.47	−0.27	−0.50
100000	−0.47	−0.27	−0.50
3.6	−0.25	−0.17	−0.26

for the undoped and La doped sample as well, depending on whether the appropriate value is the surface or bulk oxygen vacancy concentration. Oxygen vacancy concentrations are further discussed in Section 5. ε_i is probably larger but of the right order of magnitude. Based on a value of $C=3.6$ eV for the undoped and La doped sample and a significantly higher value of C (approx. 300 eV) for the Mn doped sample the expected barrier heights are given in Table 3.

From the above it is expected that BST films doped with Mn or other acceptors will have significantly lower leakage currents than intrinsic BST films, and those doped with La or other donors will have significantly higher leakage currents. This has indeed been observed experimentally by Hofman et al.[5] and by Kim and Park.[23] The Mn doped barrier height seems a little too high in comparison with the undoped barrier height. A very plausible explanation for this is that the distribution of surface states in energy is not uniform over the 0.7 V by which the Fermi level is shifted. Thus the change in the charge neutrality level is not as great as the change in the Fermi level for this sample.

Table 3
Expected barrier heights for platinum on BST according to the full expression of Cowley and Sze[20,21]

	Undoped	Mn doped	La doped
Barrier (eV)	0.64	1.13	0.56

The barrier height for undoped BST calculated here is in excellent agreement with the value measured experimentally by Zafar et al.[24] of 0.65 ± 0.06 eV and that calculated by Scott[25] of 0.6 eV.

5. Effect of dopants on vacancy concentration

What occurs on the addition of dopants depends greatly upon the site at which substitution occurs, which often is determined by ionic radius. Thus Mn^{3+} substitutes on the Ti^{4+} site of the perovskite unit cell and acts as an acceptor. On the other hand La substitutes on the Ba^{2+}/Sr^{2+} site of the unit cell and acts as a donor.

It is often thought on the basis of electroneutrality arguments that substitution of a donor ion such as La onto the A site will lead to a decrease in the number of oxygen vacancies. This is not necessarily the case, and in fact Y^{3+} and La^{3+} behave in quite different ways. Another possibility is that in fact more oxygen vacancies will be created by the lanthanum ions pulling electrons off the Ti^{4+} ions and forming bonds with them. If this occurs the oxygen will occupy an interstitial position and a vacancy will be formed within the lattice. However work has been done by Robey et al.[26] on $BaTiO_3$ which suggests that while this occurs when Y is substituted for the A cation, oxygen vacancies are not produced by the addition of La^{3+} ions. What appears to happen on substitution of a La^{3+} ion is that the surrounding oxygen ions are more closely attracted to the La^{3+} ion than they would have been to the A ion. There is a deformation of the lattice, resulting in an effective change in valency for the Ti ion from Ti^{4+} to Ti^{3+}, which is the cause of the modified Ti 3d states in the bandgap observed by Robey. These modified states are also observed in La doped $SrTiO_3$.[27,28]

High resolution XPS measurements that we carried out on 0.7, 1.5 and 3% La doped $SrTiO_3$ thin films did not show any evidence of modified Ti 3d states in the bandgap, which may suggest that in $SrTiO_3$ thin films as opposed to single crystals La does not in fact substitute for Sr and instead accumulates at grain boundaries.

Upon substitution of two Mn^{3+} ions onto adjacent Ti^{4+} sites an oxygen vacancy is produced. There are three oxygen ions per unit cell, and a unit cell has a volume of approximately 125 Å.^{3} This results in oxygen ion concentrations of about 2.4×10^{22} cm^{-3}. If 0.7% Mn is substituted then one can expect that 0.35% of these oxygen sites will become vacant. This results in an increase in oxygen vacancy concentration of 8.4×10^{19} cm^{-3}. Mihara[29] has found an oxygen vacancy concentration near to the surface of 5×10^{20} cm^{-3} and 10^{18} cm^{-3} in the interior of the film. This increase does not greatly add to the surface value of the oxygen vacancy concentration,

but does increase the bulk vacancy concentration by two orders of magnitude.

From the above discussion it seems to us that simple models of defect chemistry do not suffice to explain the effect of dopants in BST thin films and a more careful treatment is required.

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References

1. Klissurska, R. D., Tagantsev, A. K., Brooks, K. G. and Setter, N., Use of ferroelectric hysteresis parameters for evaluation of niobium effect in sol–gel derived PZT thin films. *J. Am. Ceram. Soc*., 1992, **80**, 336–342.
2. Klissurska, R. D., Tagantsev, A. K., Brooks, K. G. and Setter, N., Effect of Nb-doping on the hysteresis parameters of sol–gel PZT thin films. *Microelectronic Engineering*, 1995, **29**, 271–274.
3. Klissurska, R. D., Brooks, K. G. and Setter, N., Effect of dopants on the crystallisation mechanism of PZT thin films. *Ferroelectrics*, 1999, **225**, 327–334.
4. Klissurska, R. D., Brooks, K. G., Reaney, I. M., Pawlaczyk, C., Kosec, M. and Setter, N., Effect of Nb doping on the microstrucutre of sol–gel derived PZT thin films. *J. Am. Ceram. Soc*., 1995, **78**, 1513–1520.
5. Hofman, W., Hoffmann, S. and Waser, R., Dopant influence on dielectric losses, leakage behaviour, and resistance degradation of $SrTiO_3$ thin films. *Thin Solid Films*, 1997, **305**, 66–73.
6. Hoffmann, S., Klee, M. and Waser, R., Preparation of La doped $Sr(Ti(1–y)Zr_y)O_3$ dielectric ceramic thin films. In *Proc. Electroceram. IV*, Vol. 2, ed. R. Waser, S. Hoffmann, D. Bonnenberg and Ch. Hoffmann. Augustinus Buchhandlung, Aachen, 1994, pp. 1353–1360.
7. Yoo, I. K., Desu, S. B. and Xing, J., Correlations among degradations in lead zirconate titanate thin film capacitors. *Mater. Res. Soc. Symp. Proc*., 1993, **310**, 165–178.
8. Wouters, D. J., Wilems, G. J., Groeseneken, G., Maes, H., Brooks, K. and Klissurska, R, The influence of dopants on the leakage current in PZT thin-film ferroelectric capacitors. In *Science and Technology of Electroceramic Thin Films*, ed. O. Auciello and R. Waser. 1995, pp. 279–290.
9. Waser, R., Polarization, conduction and breakdown in non-ferroelectric perovskite thin films. In *Science and Technology of Electroceramic Thin Films,* ed. O. Auciello and R. Waser. 1995, pp. 223–248.
10. Waser, R. and Klee, M., Theory of conduction and breakdown in perovskite thin films. *ISIF-91. 3rd International Symposium on Integrated Ferroelectrics*. Univ. Colorado, 1991, pp. 288-305.
11. Hasenkox, U., Hoffmann, S. and Waser, R., Influence of precursor chemistry on the formation of MTiO/sub 3/ (M = Ba, Sr) ceramic thin films. *J. Sol-Gel Science and Technology*, 1998, **12**, 67–79.
12. Hoffmann, S. and Waser, R., Control of the morphology of CSD-prepared (Ba,Sr)TiO/sub 3/ thin films. *J. Eur. Ceram. Soc*., 1999, **19**, 1339–1343.
13. Stolichnov, I. and Tagantsev, A. K., Space-charge influenced-injection model for conduction in $Pb(Zr_xTi_{1-x})O_3$ thin films. *J. Appl. Phys*., 1998, **84**, 3216–3225.
14. Dawber, M. and Scott, J. F., A model for fatigue in ferroelectric perovskite thin films. *Appl. Phys. Lett*., 2000, **76**, 1060–1062.
15. Dawber, M. and Scott, J. F., *Appl. Phys. Lett*., 2000, **76**, 3655.
16. Scott, J. F. and Dawber, M., Oxygen-vacancy ordering as a fatigue mechanism in perovskite ferroelectrics. *Appl. Phys. Lett*., 2000, **76**, 3801–3803.
17. Scott, J. F., *Ferroelectric Memories*. Springer-Verlag, Berlin, 2000.
18. Neilson, M., BSc Honours thesis, University of New South Wales, Australia, 1999.
19. Robertson, J. and Chen, C. W., Schottky barrier heights of tantalum oxide, barium strontium titanate, lead titanate, and strontium bismuth tantalate. *Appl. Phys. Lett*., 1999, **74**, 1168–1170.
20. Cowley, A. M. and Sze, S. M., *Journal Appl. Phys*., 1965, **36**, 3212.
21. Sze, S. M., *Physics of Semiconductor Devices*. John Wiley & Sons, New York, 1981.
22. Rhoderick, E. H. and Williams, R. H., *Metal–Semiconductor Contacts*, 2nd edn., Oxford University Press, 1988.
23. Kim, S. S. and Park, C., Leakage current behaviours of acceptor- and donor-doped $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films. *Appl. Phys. Lett*., 1999, **75**, 2554–2556.
24. Zafar, S. et al., The electronic conduction mechanism in barium strontium titanate thin films. *Appl. Phys. Lett*., 1998, **73**, 3533–3535.
25. Scott, J. F., The physics of ferroelectric ceramic thin films for memory applications. *Ferroelectrics Rev*., 1998, **1**, 1–129.
26. Robey, S. W. et al., Substitution-induced midgap states in the mixed oxides $R_xBa_{1-x}TiO_{3-\delta}$ with R = Y, La, and Nd. *Phys. Rev. B*, 1993, **48**, 562–568.
27. Fujimori, A. et al., Doping-induced changes in the electronic structure of $La_xSr_{1-x}TiO_3$. *Phys. Rev. B*, 1992, **46**, 9841–9844.
28. Higuchi, T. et al., Electronic Structure in the band gap of lightly doped $SrTiO_3$ by high resolution X-ray absorption spectroscopy. *Phys. Rev .B*, 2000, **61**, 12860–12863.
29. Mihara, T. et al., Process dependent electrical characteristics and equivalent circuit model of sol–gel based PZT capacitors. *Integr. Ferroelectr*., 1992, **1**, 269–291.