Reduced O diffusion through Be doped Pt electrodes

R. Stump,* C.-L. Liu, and C. Tracy
Motorola, Embedded Systems Technology Laboratories, Los Alamos, NM 87545-1663
(June 15, 2021)

Using first principles electronic structure calculations we screen nine elements for their potential to retard oxygen diffusion through poly-crystalline Pt (p-Pt) films. We determine that O diffuses preferentially as interstitial along Pt grain boundaries (GBs). The calculated barriers are compatible with experimental estimates. We find that Be controls O diffusion through p-Pt. Beryllium segregates to Pt GBs at interstitial (i) and substitutional (s) sites. i-Be is slightly less mobile than O and it repels O, thus stuffing the GB. s-Be has a high diffusion barrier and it forms strong bonds to O, trapping O in the GB. Experiments confirm our theoretical predictions.

A serious problem preventing the use of high dielectric oxide materials (e.g. BaSrTiO$_3$) for capacitors as part of dynamic random access memory devices is the O diffusion through the electrodes and subsequent oxidation under the electrodes. Pt electrodes do not oxidize but they allow O to diffuse through the p-Pt film during deposition and anneal of the dielectric. This causes unwanted oxidation below the Pt film. It has been proposed (but not yet demonstrated) that O diffusion can be reduced by doping of the Pt film. The addition of barrier layers or the use of different electrode materials are other attempts to cope with the oxidation issue.

All the theoretical results reported in this study are obtained using the first principles total-energy code VASP (Vienna *Ab-initio* Simulation Package) within the generalized gradient approximation (GGA). Electronic wavefunctions are expanded in a plane wave basis. The atomic cores are represented by ultrasoft pseudopotentials which allow for a reduced plane wave basis set (cut-off 270 eV).

It has long been assumed that O diffuses along grain boundaries in the p-Pt films used as electrodes. The model GB we choose for our diffusion study is the Σ5(310)[001] symmetric tilt GB (See Fig. 1). To determine the O diffusion mechanism from theory we first have to find the preferential site for O in Pt (see Table 1). The calculated binding energy for the O$_2$ molecule is 4.91 eV per O atom. The most stable site for O in bulk fcc-Pt is the tetrahedral interstitial with a binding energy of 3.45 eV. Interstitial sites at the Σ5 GB have binding energies up to 4.60 eV. Thus O in Pt strongly segregates to GBs. In agreement with experiment our results indicate that Pt does not oxidize and even the O in GBs is unstable with respect to the formation of gaseous O$_2$.

Any diffusion of O involving sites in bulk Pt has a high activation energy of at least 2.64 eV. To diffuse through bulk-Pt, O first has to move from the GB to a bulk site which costs 1.15 eV as bulk-interstitial or 2.17 eV as bulk-substitutional. For O interstitial migration one has to add the tetrahedral-octahedral energy difference of 1.49 eV. Substitutional O likely migrates with the help of a Pt vacancy which has a calculated formation energy of 0.73 eV. Thus crystalline Pt films act as O diffusion barriers. If such films could be deposited reliably, at low stress, and with good adhesion the O inter-diffusion problem would be solved.

To calculate the diffusion barriers for interstitial O in the GB we use two different techniques. In the traditional approach we determine the potential energy surface (PES) for an O atom moving within the GB. This is done by calculating the total energy of the GB system with an O interstitial fixed at the points of a rectangular 10×6 grid spanning the irreducible (310) interface cell. The O’s coordinate perpendicular to the GB plane and the position of most of the Pt atoms are relaxed at each mesh point. Four Pt atoms distant to the O are fixed to prevent a rigid translation of the Pt film. The resulting potential energy surface (PES), Fig. 2, indicates one main minimum at coordinate (5.5, 4.5), at least one secondary minimum at (9, 4), and a clear diffusion path in the [001], i.e. the short, direction with a barrier (at 5.5,1) of about 0.7 eV. In the [130] direction the O has to cross at least two saddle points. The highest saddle is at (8,4,5) and appears to have a barrier of about 0.9 eV.

Application of the nudged elastic band (NEB) method leads to a more accurate determination of the O diffusion barriers in the Σ5 GB. In the [001] direction the barrier is 0.68 eV and in the [130] direction we identify two saddle points with almost the same barriers: 0.68 eV at (1,3) and 0.67 eV at (8,2). Note that the low barrier at (8,2) is not obvious from Fig. 2. Also, the full variability of the energy along the diffusion path in the [130] direction is not reflected in the calculated PES. The NEB is more reliable in predicting diffusion paths and barriers.

It is not clear if diffusion along the chosen Σ5 GB is representative of O diffusion in p-Pt. Thus we compare our results to experimental findings. In the most careful study of O diffusion through nanocrystalline Pt films Schmiedl et al. have determined the diffusion rate of O at room temperature. The measured value is about $D = 10^{-19}$cm$^2$/s, depending on the microstructure of the Pt film, especially the density of GBs. This dependence indicates that GB diffusion is the dominant diffusion mechanism. To compare with the calculated value we estimate an O diffusion barrier $E_d$ from the experi-
The main goal of this study is to identify dopants that reduce the O diffusion through p-Pt films and thus keep the oxidation of material below the p-Pt at tolerable levels. Potential dopants have to meet certain conditions. For example, the dopant element should have a high melting point so that sputter targets can be produced easily. In addition, the dopant should not form a volatile oxide. From the elements that pass those pre-conditions we choose Be, B, Mg, Ti, V, Cu, Rh, Ta, and Ir for initial investigation.

Only if a dopant segregates to the GB can it affect O GB-diffusion effectively. To check which elements segregate to Pt GBs we calculate the dopant’s binding energy in the stable elemental phase, in a fictitious Pt$_3$-dopant alloy, at substitutional and interstitial sites in a Pt bulk matrix, and at different substitutional and interstitial sites at the Pt GB (see Table 1). Only the binding energies for the most stable sites out of five substitutional and three interstitial sites at the GB are listed. We find that only the two smallest elements, Be and B segregate strongly to the grain boundaries and we determine their effect on O diffusion.

A dopant at the GB can reduce O diffusion as interstitial (i) or substitutional (s) species. If the dopant prefers i-sites and if the dopant or a stable dopant-O complex diffuses more slowly than the O alone the dopant blocks the O diffusion by “stuffing” of the GB. Boron goes interstitial and it repels O in the GB. The calculated binding energies for the most stable sites out of five substitutional and three interstitial sites at the GB are listed. We find that only the two smallest elements, Be and B segregate strongly to the grain boundaries and we determine their effect on O diffusion.

If the dopants prefer s-sites at the GB then a slow diffusion of O is expected. To confirm this we test two possible saddle configurations for O diffusion with i-Be near by. We find that i-Be increases the barrier for O diffusion by about 0.1 eV.

The interaction between s-Be and O is strongly attractive which leads to high O diffusion barriers. We calculate the O binding energy at seven different sites close to a s-Be at the GB. At the new global minimum the O is 0.90 eV lower in energy than at the most stable site at the GB without Be. This interaction reduces the barrier for O to leave the bridge site is above 2.5 eV. We note here that in the presence of O in the GB it is energetically favorable for i-Be to convert to s-Be that is bound to O, thus trapping the O.

We conclude that Be reduces O diffusion along Pt GBs in various ways. The actual O diffusion rate in the presence of Be depends on the Pt microstructure and the Be concentration and absorption site. We test our theoretical prediction experimentally by measuring the WO$_3$ formation beneath a clean and a Be doped p-Pt film under O anneal. The Pt is sputter deposited at 400°C to a nominal thickness of 100 nm on a substrate consisting of 450 nm of CVD W on a TiN adhesion layer on SiO$_2$/Si. The 1.5 at.\% Be implant is performed at 40 keV and 7° tilt with a dose of $10^{16}$ cm$^{-2}$. For comparison we prepare an identical wafer without the Be implantation. Each of the two wafers are pre-annealed at 600°C in a carefully controlled Ar ambient for 30 minutes prior to the 5 minutes oxidation heat treatment at 500°C in open air. XRD analysis revealed WO$_3$ peaks in both samples. The WO$_3$ (110) peak counts of the Be-implanted sample are 3.1 times smaller than those of the Be free sample. This result indicates that Be implantation indeed delays the diffusion of O$_2$ through Pt. We expect that the Be effect would be even bigger if the Be was co-deposited with the Pt such that more of the Be has a chance to segregate to the Pt GBs.

In conclusion, we show that Be doping of p-Pt films...
reduces the O inter-diffusion. This conclusion is based on our first principles atomistic model and first experimental results. We expect that the optimization of the Be doping recipe will increase the Be effect significantly. Our study shows how first principles based modeling not only helps to understand fairly complicated processes like inter-diffusion in poly-crystalline materials; modeling even shows the way to modify the diffusion properties. Modeling also helps us determine rules that govern segregation and diffusion properties, e.g. the role of atomic size. This will be subject of a longer paper. This work was made possible by advancements in first principles codes (e.g. VASP) that allow to calculate large systems containing “hard” elements (e.g. O and Pt) efficiently and accurately. The NEB enables us to calculate diffusion paths in complicated cases. Finally, we need parallel computers to consider the hundreds of configurations necessary to solve “real world” materials science problems.

We acknowledge the use of Sandia National Laboratories computing resources.

* corresponding author; email: rrtump@sandia.gov

1 A. Grill and M.J. Brady, Integrated Ferroelectrics 9, 299 (1995).
2 D.E. Kotecki, Integrated Ferroelectrics 16, 1 (1997); D.S. Yoon, H.K. Baik, S.M. Lee, S.I. Lee, H. Ryu, and H.J. Lee, J. of Vac. Sci. and Techn. B 16, 1137 (1998).
3 G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); ibid. 49, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15-50 (1996); G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
4 J.P. Perdew et al., Phys. Rev. B 46, 6671 (1992).
5 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990); G. Kresse and J. Hafner, J. Phys.: Condens. Matter 6, 8245 (1994).
6 H. Jonsson, G. Mills, K. W. Jacobsen, in ‘Classical and Quantum Dynamics in Condensed Phase Simulations’, ed. B. J. Berne, et al. (World Scientific, 1998).
7 R. Schmiedl, V. Demuth, P. Lahnor, H. Godehardt, Y. bodschwinna, C. Harder, L. Hammer, H.P. Strunk, M. Schulz, and K. Heinz, Appl. Phys. A 62, 223 (1996).
8 The energy of the O dimer is the calculated spin polarized value. The free O atom reference is the valence energy of the spin averaged free O atom within GGA.
9 J.B. Adams, S.M. Foiles, and W.G. Wolfer, J. of Mat. Res. 4, 102 (1989) and references therein.
10 R. Stumpf, C.-L. Liu, and C. Tracy, to be published.

| Element | O | Be | B | Mg | Ti | V | Cu | Rh | Ta | Ir |
|---------|---|----|---|----|---|---|----|----|----|----|
| Pt_x    | 1.92 | 4.72 | 4.79 | 3.93 | 10.85 | 10.39 | 4.25 | 7.18 | 13.89 | 8.40 |
| s-bulk  | 2.43 | 4.91 | 4.58 | 4.04 | 11.67 | 11.31 | 4.23 | 7.15 | 15.45 | 8.47 |
| i-bulk  | 3.45 | 2.43 | 6.04 | -2.48 | 5.90 | 6.52 | -1.10 | 0.74 | 8.16 | 1.70 |
| s-GB    | 3.97 | 5.33 | 7.10 | 3.98 | 11.63 | 11.26 | 4.07 | 7.15 | 15.37 | 8.56 |
| i-GB    | 4.60 | 5.69 | 7.83 | 2.96 | 10.44 | 10.48 | 3.24 | 6.08 | 13.72 | 7.40 |

**TABLE I.** Binding energy of dopants as elements and at different sites in Pt. The energy reference is the spin averaged free atom in GGA. For substitutional absorption we assume that the removed Pt atom gains the Pt-bulk cohesive energy. The elemental phase of oxygen is O_2 and the pure bulk phase otherwise.

FIG. 1. Structure of the (310) GB plane. The in-plane unit cell with its two symmetrical halves is indicated.

FIG. 2. PES for O in the Σ5 GB corresponding to the lower rectangle in Figure 1. The contour spacing is 0.2 eV. The PES is calculated on a 10×6 mesh in a 6.312Å×1.996Å cell.
This figure "PtO_diff_img1.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9903082v1
This figure "PtO_diff_img3.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9903082v1