Retardation of O diffusion through polycrystalline Pt by Be doping

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A serious problem preventing the use of high dielectric oxide materials (e.g., barium-strontium-titanate) for capacitors as part of future dynamic random access memory is the oxidation of or the O diffusion through the electrodes. Platinum electrodes do not oxidize, but they allow for rapid O diffusion through the Pt film while the dielectric is deposited and annealed. This causes unwanted oxidation below the Pt film. Using first-principles electronic structure calculations, we first determine the O diffusion mechanism in polycrystalline Pt. We find that O diffuses as interstitial O along the grain boundary (GB) that we study. The calculated barrier is compatible with the experimental estimate. We screen nine elements for their potential to retard O diffusion if added to the Pt in small amounts. Beryllium is the most promising candidate. Be segregates to Pt GB's at interstitial and substitutional sites. As GB interstitial Be diffuses at a rate comparable to that of O and it repels O. This leads to a stuffing of the GB. As substitutionally absorbed Be, Be has a high diffusion barrier, and it forms strong bonds to O. Thus O is trapped in the GB. Preliminary experimental results confirm our theoretical predictions. [S0163-1829(99)01923-2]

I. INTRODUCTION

A large number of materials issues are related to interdiffusion in polycrystalline materials. Examples are corrosion, dopant diffusion through poly-Si, and Cu diffusion through barrier layers or along grain boundaries and interfaces during electromigration. In most cases interdiffusion has detrimental consequences, and therefore measures are developed to control interdiffusion.[1]

Here we are concerned with the diffusion of O from high-*k* dielectrics through Pt electrodes.[2–4] High-*k* dielectrics like barium-strontium-titanate are investigated as materials that increase the capacitance of integrated capacitors, e.g., in dynamic random access memories (DRAM's), at constant leakage current between the electrodes. These dielectrics are deposited and annealed at temperatures of around 600 °C at high O partial pressure. Under these conditions, almost every electrode material oxidizes thus increasing the oxide thickness and reducing the capacitance. Platinum is used in electrodes because it does not oxidize. The problem with Pt is that O diffuses through the Pt film during oxide deposition and subsequent anneal, which causes oxidation of the material below the Pt film.

II. THEORY

All the theoretical results reported in this study were obtained using the efficient first-principles total-energy code VASP (Vienna *Ab initio* Simulation Package).[5] We use the generalized gradient approximation (GGA) for exchange and correlation.[6] Electronic wave functions are expanded in a plane-wave basis. The atomic cores are represented by ultrasoft pseudopotentials[7] that allow for a reduced plane-wave basis set. For example, we find that energy differences for systems containing O atoms are practically converged with a 270-eV cutoff as tests with a 396-eV cutoff show. The calculated Pt lattice constant is 3.992 Å, 1.0% above the experimental value, which is typical for a well-converged GGA calculation. Earlier calculations of O/Pt surface systems using a very similar theoretical approach to that taken here gave results in good agreement with experiment.[8]

To model grain boundaries (GB) in polycrystalline Pt, we chose the $\Sigma 5(310)[001]$ symmetric tilt GB. The tilt axis is in the [001] direction, and the GB plane is of (310) orientation. The $\Sigma 5$ GB has been chosen because a number of studies exist using it as a model and because it contains a fair number of different voids and differently coordinated atoms representative of grain boundaries in general.[9–12] Obviously, experimental polycrystalline Pt films contain a large number of other grain boundaries, also areas where different GB's meet, and additionally there will be nonuniform stresses that affect diffusion along grain boundaries. It is to be expected that O diffusion or dopant segregation in a Pt film is affected by the film's microstructure, which is largely unknown. The segregation and diffusion energies calculated here only sample the huge variety found in a real Pt film. Comparison with experiment will show if our choice is representative.

To construct the $\Sigma 5$ GB, we use two (310)-oriented slabs in an orthorhombic supercell without vacuum (see Fig. 1). The cell dimension in the [310] direction is optimized with all the Pt atoms allowed to relax. The [001] and $[\bar{1}30]$ dimensions of the cell are determined by the calculated Pt lattice constant. In the [001] direction the cell consists of two layers. Four-layer calculations give qualitatively the same results in the cases tested. The whole GB model contains 36 Pt atoms. We sample the Brillouin zone of our supercell using a special *k*-point mesh[13] with two ticks in the [001] direction and one in the two other directions. Electronic states are occupied according to a Methfessel-Paxton distribution with a smearing width of 0.2 eV.[14]

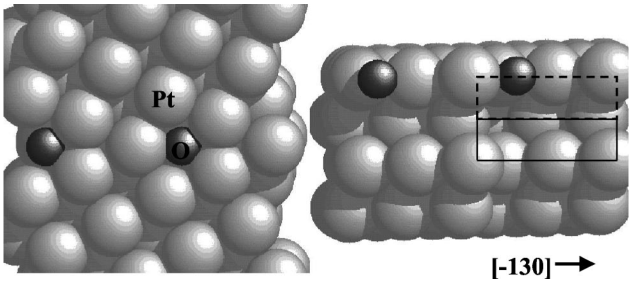

FIG. 1. Structure of the (310) GB plane. Left: view along the tilt [001] axis; right: the in-plane unit cell with its two symmetrical halves is indicated.

The binding energy of dopants in bulk Pt, substitutional or interstitial, is calculated using a rhombohedral 4^3 Pt cell and a 2^3 k-point mesh.[13] The Pt_3X alloy phase is modeled by replacing a Pt atom in a four atom conventional Pt-fcc cell (6^3 k points). The lattice constant for each alloy phase is optimized. All binding energies quoted in this paper are with respect to the spin averaged free atom within GGA; thus only quoted binding energies for the same species can be compared directly. The overall error margin in the calculated numbers is difficult to quantify. From our own convergence tests and from published theory-experiment comparison,[8] we expect that binding energy differences are typically off by less than 0.1 eV.

Nudged elastic band method to determine diffusion paths

Important for our study is the use of the nudged elastic band (NEB) method[15] to determine accurately minimum barrier diffusion paths. The NEB method begins with the choice of the initial and the final geometry, typically local minima. Then a chain of geometries interpolating linearly between the initial and final geometry in the 3N-dimensional hyperspace is defined. This initial chain is iteratively optimized such that upon convergence the chain of geometries tracks the minimum-energy path connecting the initial and final configuration (see Fig. 2). In each iteration first the ionic forces for each geometry are calculated. Then the tangential component of these forces, i.e., the component that points along the chain in 3N dimensions, is removed. The resulting forces are used to update the atomic positions. The optimization of the diffusion path ends when all components of the modified forces are below a preset limit. The NEB procedure ensures that the chain tracks the minimum-energy path without cutting corners and without the individual geometries bunching around energy minima along the path.

An advantage of the NEB algorithm is that it is intrinsically parallel making optimal use of modern computers. As a refinement of the basic NEB method, we interpolate the energy along the path between the individual geometries using splines and the tangential projection of the 3N force on each geometry (see Fig. 2). The spline construction allows us to reduce the density of geometries along the path about threefold at constant accuracy, and it indicates more reliably if a refinement of the chain is necessary.

The NEB is a very robust tool to determine diffusion paths. It can be conveniently used for all diffusion problems where traditional ''atom dragging'' and ''*ad hoc* reaction coordinate'' approaches work. However, it even works when these methods fail like in atomic exchange processes or for dopant diffusion in semiconductors.[16]

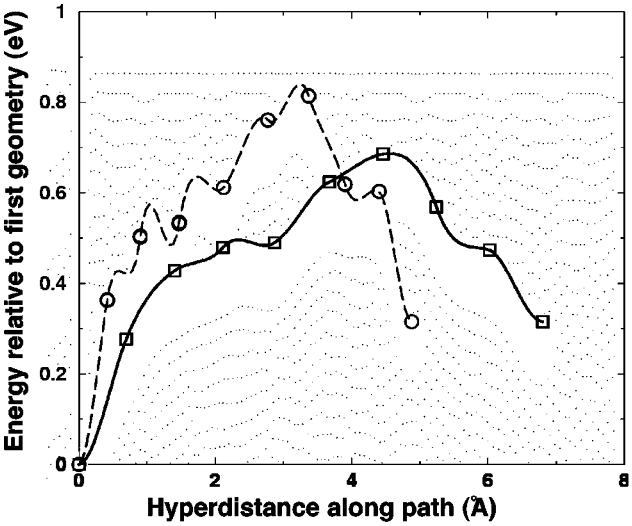

FIG. 2. Spline interpolation of the total energy along the diffusion path of O diffusion in the $[\bar{1}30]$ direction of the GB (solid line). The dashed line indicates the path at an early stage of the optimization. The length in 3N dimension of the diffusion path increases as the path deviates from the initial linear interpolation.

III. OXYGEN DIFFUSION

It has long been assumed but never firmly established that O diffuses along grain boundaries.[17] To determine the O diffusion mechanism from theory we first have to find the preferential site for O in Pt. The calculated binding energy for the O_2 molecule is 4.91 eV per O atom.[18] The most stable site for O in fcc Pt is the tetrahedral interstitial with a binding energy of 3.45 eV. In polycrystalline Pt interstitial sites at GB's are the most stable. At the $\Sigma 5$ GB we find binding energies up to 4.60 eV. Thus O in Pt strongly segregates to GB's. In agreement with experiment our results indicate that Pt does not oxidize and even the O in GB's is unstable with respect to the formation of gaseous O_2.[18]

Diffusion of O involving sites in bulk Pt has a high activation energy of at least 2.64 eV for the two mechanisms we consider.[20] To diffuse through bulk Pt, O first has to move from the GB to a bulk site that 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[21] that has a calculated formation energy of 0.73 eV.

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 PES, Fig. 3, indicates one main minimum at

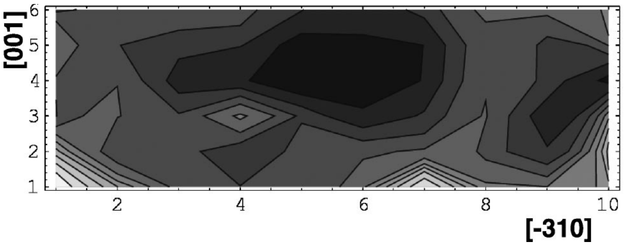

FIG. 3. Potential-energy surface (PES) for O in the $\Sigma 5$ GB corresponding to the lower rectangle in Fig. 1. The contour spacing is 0.2 eV. The PES is calculated on a 10×6 mesh corresponding to a 6.312 Å × 1.996 Å cell.

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 $[\bar{1}30]$ 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 NEB method leads to a more accurate determination of the O diffusion barriers in the $\Sigma 5$ GB. In the [001] direction the barrier is 0.68 eV and the saddle point at the mirror plane at coordinate (5.5,1). In the $[\bar{1}30]$ 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. 3. Also, the full variability of the energy along the diffusion path in the $[\bar{1}30]$ direction is not reflected in the calculated PES. The NEB is more reliable in predicting diffusion path and barriers.

It is surprising that the diffusion barriers are practically the same in the two main directions in the GB. Diffusion along the tilt axis is expected to be faster than perpendicular diffusion because of its channels for interstitial diffusion.[10,11] Our results show that this is not generally the case. Also, the fact that we find three saddle points with practically the same energy indicates that O diffusion in GB's, which always involves breaking and forming of Pt-O bonds and ''squeezing'' through narrow openings, might be characterized by a small variation of energy barriers. This would justify our restriction to study one type of GB only.

Analysis of the experimental O diffusion rate determination

It is not clear if diffusion along the $\Sigma 5$ GB is representative of O diffusion in poly-crystalline Pt. Thus we compare our results to experimental findings. In the most careful study of O diffusion through nanocrystalline Pt films, Schmiedl *et al.* determined the diffusion rate of O at room temperature.[17] The measured value is about $D = 10^{-19}$ cm^2/s, depending on the microstructure of the Pt film, especially the density of GB's. 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 experimental diffusion rate

$$D = D_0 e^{-E_D/k_B T}. \tag{1}$$

The grain size of the Pt films grown by Schmiedl *et al.* is about 100 Å. This means that only about 1/100 of the area of the film allows O diffusion. Thus the diffusion rate in the GB is 10^{-17} cm^2/s. We assume a typical diffusion prefactor $D_0 = 10^{-3}$ cm^2/s and $k_B T = 0.025$ eV. Solving Eq. (1) for E_D results in $E_D = 0.8$ eV. The error margin for this estimate is at least 0.2 eV. We conclude that the calculated diffusion barrier of 0.68 eV is compatible with experiment.

IV. OXYGEN DIFFUSION BLOCKING SCENARIOS

In this study we try to identify dopants that, when added to a Pt film, reduce the diffusion of O through the Pt film enough that the oxidation of material below the Pt is 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. Also, the dopant should not form a volatile oxide. From the elements that pass these preconditions we choose Be, B, Mg, Ti, V, Cu, Rh, Ta, and Ir for further investigation.

We now discuss scenarios in which the O diffusion is reduced by dopants. Based on the fact that the major diffusion path for O is along Pt GB's, it is an obvious condition for the dopant that it segregates to the GB instead of staying in bulk Pt, alloying with Pt or precipitating. Only if the dopant is at the GB can it affect O diffusion along GB's.[19] A further condition is that the dopant level can be adjusted such that all GB's in the polycrystalline Pt film are filled with just under a ''monolayer'' of dopants. Monolayer here is loosely defined as a continuous layer of the dopant dense enough such that a diffusing O atom in the GB is usually within a bond length of at least one dopant atom. Only if a uniform layer like this is stable can all the O diffusion channels in the GB be blocked. A clustering of the dopant in the GB is not desirable.

A dopant at the GB can reduce O diffusion as interstitial or substitutional species. If the dopant prefers interstitial sites and if it diffuses more slowly than the O, it will block the O diffusion by ''stuffing'' of the GB. If instead the dopant and the O form strong bonds, O diffusion can also be suppressed. The additional condition is that the O-dopant complex is less mobile than O alone.

If the dopants prefer substitutional sites at the GB, then a slow diffusion of the dopant is almost guaranteed. Diffusion of substitutional species in close-packed materials typically involves vacancies.[21] Calculated vacancy formation energies at the Pt $\Sigma 5$ GB range from 0.72 eV to 1.08 eV. Adding the vacancy migration barrier of about 1 eV, results in a diffusion activation energy of at least 1.5 eV. The immobile dopant will, if its interaction with interstitial O is sufficiently different from the Pt-O interaction in the GB, reduce the O diffusion. If the dopant is more attractive for the O, the diffusing O gets trapped at each dopant site, and it costs extra energy for the O to diffuse away from the dopant. If instead the dopant-O interaction is effectively repulsive, diffusing O atoms get trapped at sites with no dopant neighbors.

V. DOPANT SEGREGATION

To reduce O diffusion at GB's, dopants should segregate to Pt GB's rather than stay in the Pt bulk matrix, form a Pt-dopant alloy, or form a pure elemental phase. If the dopant preferred sites in bulk Pt, the necessary dopant concentration to affect O diffusion at the GB would be too large. The formation of the Pt-dopant alloy phase or of the pure

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. The elemental phase is O_2 for oxygen (Ref. 18) and the pure bulk phase for the other elements. For substitutional absorption, we assume that the removed Pt atom gains the Pt-bulk cohesive energy. Atomic radii, i.e., half the interatomic distance in the element, should be compared to 1.37 Å for Pt.

	O	Be	B	Mg	Ti	V	Cu	Rh	Ta	Ir
Pure element	4.91	3.74	5.76	1.52	7.74	8.9	3.77	7.17	11.77	8.71
Pt_3X	1.92	4.72	4.79	3.93	10.85	10.39	4.25	7.18	13.89	8.40
Substitutional	2.43	4.91	4.58	4.04	11.67	11.31	4.23	7.15	15.45	8.47
Oct. interstitial	1.96	3.98	7.14	1.00	6.86	7.33	0.37	2.37	9.54	3.45
Tet. interstitial	3.45	2.43	6.04	−2.48	5.90	6.52	−1.10	0.74	8.16	1.70
GB substitutional	3.97	5.33	7.10	3.98	11.63	11.26	4.07	7.15	15.37	8.56
GB interstitial	4.60	5.69	7.83	2.96	10.44	10.48	3.24	6.08	13.72	7.40
Atomic radius	(0.60)	1.11	0.80	1.60	1.45	1.31	1.28	1.35	1.43	1.36

dopant phase would consume the dopants at the Pt GB's, and it would lead to changes in the Pt film microstructure.

To check which elements segregate to Pt GB's, we calculate the binding energy in the stable elemental phase, in a fictitious Pt_3-dopant alloy, substitutional and interstitial in a Pt bulk matrix, and at different substitutional and interstitial sites at the Pt GB (see Table I). All geometries are fully relaxed. The alloy phase consists of a repeated four atom conventional fcc unit cell containing three Pt and one dopant atom. Its lattice constant is optimized. Only the binding energies for the most stable out of five substitutional and three interstitial sites at the GB are listed in Table I. For O, B, and Be a more complete search for stable interstitial sites has been done.

All binding energies correspond to $T=0$. Entropy effects at finite temperatures should be considered. However, this is computationally demanding, and we do not expect that inclusion of entropy changes our results drastically.[9,12]

Both Be and B strongly segregate to the grain boundaries and are therefore candidates for O diffusion retardation. The most stable site for both is a GB interstitial site like for O. For Be the most stable GB substitutional site is a close second being only 0.36 eV higher in energy. For Mg, Ti, V, Cu, Rh, Ta, and Ir substitutional sites are at least 0.8 eV more stable than interstitial site at GB's. In bulk Pt the difference is at least 1.6 eV.

The preference for interstitial or substitutional absorption can be rationalized as a consequence of the size of the dopant atoms (see Table I). Boron is the smallest element studied. The oxygen is partially ionic in Pt; thus its radius is in between the atomic radius 0.60 Å and the ionic radius 1.38 Å. Beryllium is the largest member of the ''small'' group. The rest of the dopants have atomic volumes at least 50% larger than that of Be. The interstitial sites in bulk Pt are too small for all but the smallest elements, O and B. GB's have more spacious interstitial sites so that larger atoms like Be are still stable. Note that O, B, and Be prefer quite different interstitial sites at the GB based on their size and their preferred coordination. The O minimum is at (5.5,4.5), the one for B is at (4,2), and the one for Be at (7,6). This shows that a careful search for the minimum-energy interstitial site at the GB has to be done for each dopant.

At substitutional sites the situation is reversed. The smaller elements O, Be, and B cannot fill in the void a removed Pt atom (atomic radius 1.37 Å) leaves behind, and only the seven larger elements are stable at substitutional sites. The size model even helps to predict which of the different substitutional sites at the GB is more stable. Some of the Pt atoms at the GB are under compressive, others under tensile stress that can be inferred from the different average bond length and coordination of Pt atoms at the GB. Consequently, larger atoms prefer to replace Pt atoms under tensile stress and smaller atoms those under compressive stress. The smaller atoms, O, B, and Be, are up to 2.3 eV more stable substituting Pt atoms under compression at the GB than at substitutional sites in Pt bulk. For the elements that are more similar in size to Pt, the availability of compressive and tensile substitutional sites is much less important. In our sample the variation in binding energies at different substitutional sites at the $\Sigma 5$ GB ranges from about 0.5 eV for Mg, Ti, and Ta to 0.1 eV for Rh. This is a much smaller variation than found for O, B, and Be.

The stress of Pt atoms at the GB also influences the vacancy formation energies at GB. They vary from 0.72 eV to 1.08 eV. Removing a Pt atom under compressive stress generally costs less energy than removal of an atom under tensile stress. Surprisingly, the smallest vacancy formation energy at the $\Sigma 5$ GB is only slightly below the bulk Pt value (0.73 eV). If vacancy formation at the GB would cost significantly less energy than in the bulk, we would expect that some of the substitutional dopants Mg, Ti, V, Cu, Rh, Ta, and Ir clearly segregate to Pt GB's.

Our results on segregation agree with the general observation that low concentrations of dopant atoms that are similar in size to host atoms prefer solid solution to segregation.[9,12] We note that our prediction that Ti does not segregate to Pt GB's provides an explanation for a recent experimental result. Grill and Brady attempted to reduce O diffusion through Pt films by alloying the Pt films with up to 3% of Ti.[2] However, the Ti had no measurable effect on the O diffusion. Our study indicates that the Ti concentration at the Pt GB's was too small.

VI. BORON EFFECT ON OXYGEN DIFFUSION IN PLATINUM GB

Our results show that B segregates strongly to interstitial sites at Pt GB's. B interstitials at the $\Sigma 5$ GB are 0.65 eV more stable than B interstitials in bulk Pt that results in a segregation coefficient of about 10 000 at 600 °C, a typical annealing temperature.

According to the scenarios discussed in Sec. IV, B could reduce O diffusion in Pt GB's if it or a stable B-O complex diffuses more slowly. We performed a number of NEB runs to determine the B diffusion barrier in the GB. B migration is fastest in the [001] direction at a barrier of 0.54 eV. The B diffusion barrier is thus 0.14 eV lower than the O diffusion barrier.

The B-O interaction in the GB is strongly repulsive at short distances and levels off at larger distances. Thus there is no stable B-O complex in the GB. Consequentially B will not affect the O diffusion much. Most likely O exposure of B-doped Pt films will cause out diffusion of the B from the GB to form B_2O_3 at the Pt film surface. After most of the B is consumed, O will diffuse along the almost B-free GB's of the Pt film. This analysis is compatible with the findings of Grill and Brady:[2] alloying of Pt films with up to 3% of B does not change the O diffusion through the Pt significantly.

VII. BERYLLIUM-INDUCED RETARDATION OF OXYGEN DIFFUSION IN GB

Be segregates to Pt GB's and is therefore a candidate to retard O diffusion. To investigate if Be actually works we have to determine the energetics of Be diffusion and of the Be-Be and Be-O interaction for interstitial and substitutional Be. We will first focus on the GB interstitial Be since it is 0.36 eV more stable than the substitutional Be at low Be concentration.

Interstitial Be at the $\Sigma 5$ GB experiences a migration barrier of 0.70 eV in the [001] direction as determined by a set of NEB calculations. The barrier for motion in the $[\bar{1}30]$ direction is 0.70 eV for the part of the path we investigated. With an additional interstitial or substitutional Be per GB cell the barrier increases. A substitutional Be increases the barrier for interstitial Be to about 0.8 eV caused by a small repulsive interaction. An extra interstitial Be leads to a larger increase because of a stronger short-range repulsion between the two interstitial Be atoms. To quantify the barrier increase requires the study of a large number of paths that has not been done here. Our analysis shows that at low-concentration Be GB diffusion barriers are only slightly higher than those for O. At higher concentrations, i.e., when Be-Be interactions become important, Be diffusion barriers increase.

The interaction between interstitial Be and O is repulsive. The repulsion energy is about 0.5 eV at neighboring local minima and about 0.1 eV at second nearest-neighbor sites depending on the detailed configuration. The O-Be repulsion hinders O diffusion. The vicinity of a Be atom increases the O diffusion barrier between 0.03 eV and 0.23 eV for the O diffusion paths studied.

The interaction between substitutional Be and O is strongly attractive. With one Be at the most stable substitutional site in the 1×1 GB cell, we calculate the O binding energy at seven different sites in the vicinity. 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. The diffusion barrier of O in the [001] direction is increased from 0.68 eV to 0.81 eV. In the $[\bar{1}30]$ direction the diffusion barrier is above 2 eV.

To get a more complete picture of the Be effect on O diffusion at Pt GB's, we also consider clusters of nearest-neighbor substitutional Be atoms at GB's and their interaction with O. GB substitutional Be atoms attract or repel depending on the configuration. A limited search indicates that Be atoms like to have at most one Be nearest neighbor. At higher concentrations the Be atoms rather dissolve into bulk Pt. Oxygen stabilizes pairs of substitutional Be at the GB by occupying the bond center site between the two Be atoms. The most stable such configuration consists of two Be atoms replacing two Pt atoms under compressive strain that directly face each other across the GB plane. The O atom bridges between the two Be atoms. This configuration is 1.28 eV more stable than having the two Be and the O at the most stable isolated interstitial sites. The breaking of the bonds of the O with its two Be neighbors, which is necessary for O diffusion, costs at least 2.53 eV. Thus interstitial O and substitutional Be can form very stable and immobile complexes. The complexes can be viewed as the initial stages of the formation of the even more stable Be-O with its calculated binding energy of 14.44 eV per Be-O pair. The formation of Be-O complexes is activated and it is most likely at high temperatures and high Be concentration. Be-O complexes have the potential of quadrupling the O diffusion barriers in Pt GB's if they are formed at a large enough concentration.

VIII. Be IMPLANTATION INTO Pt AS AN OXYGEN BARRIER AT 500 °C

To test the effectiveness of Be as an O diffusion barrier in Pt films we implant between 1–2 at. % Be into a Pt film that has been sputter deposited on a W-covered SiO_2/Si wafer. Oxidation of the W layer in subsequent air anneals can be detected using x-ray diffraction and is used to indicate O diffusion through the Pt film.

The Pt is sputter deposited at about 400 °C to a nominal thickness of 100 nm on a substrate consisting of 450 nm of chemical vapor deposition W on a TiN adhesion layer on SiO_2/Si. The Be implant is performed at 40 keV and 7 deg 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 preannealed at 600 °C in a carefully controlled Ar ambient for 30 min prior to the 5 min oxidation heat treatment at 500 °C in open air. X-ray diffraction 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.

The implant experiment is not an ideal test of the Be effect since it is not clear how much Be is able to segregate to the GB's. Substitutional Be in bulk Pt diffuses very slowly with a diffusion activation energy of above 2 eV in a vacancy assisted mechanism. This estimate is based on our calculations and experimental numbers.[21] Even bulk interstitial Be, which is produced by implanting, has a calculated diffusion barrier of 1.55 eV. Thus only a small amount of the implanted Be can diffuse from bulk sites to the Pt GB at the annealing temperature of 600 °C. As discussed before, the O diffusion retardation effect should increase with the Be concentration and hit a maximum close to a ‘‘monolayer’’ of Be in the GB plane.

IX. CONCLUSIONS

This study proposes a first-principles based model that predicts that Be doping of polycrystalline Pt films reduces the O interdiffusion. Our experimental results support the model. First principles based modeling not only helps to understand fairly complicated processes like interdiffusion in polycrystalline materials but also shows the way to engineer measures to reduce the detrimental interdiffusion by adding a dopant to the Pt film. This significant step forward for modeling is made possible by advancements in first principles codes (e.g., VASP),[5] which now allow us to calculate large systems containing ''hard'' elements like O and Pt efficiently and accurately. Parallel computers facilitate the study of the hundreds of configurations necessary to model real world problems. The ''nudged elastic band'' method[15] allows us to calculate diffusion paths in complicated cases.

We discuss scenarios in which dopants retard interdiffusion along GB's of close-packed metals. The first requirement is that the dopant has to segregate to the GB. The relative atomic size of the dopant and host is important in determining the segregation energy and absorption site. The smaller elements segregate strongly to the GB interstitial sites. If they are not too small, which leads to fast diffusion, they will ''stuff'' the GB and reduce interdiffusion. If the dopants are more size matched to the host, they prefer interstitial sites at the GB which leads to slow dopant diffusion. If these dopants then interact differently with the interdiffusing species than the host, the interdiffusion is hindered by site blocking or by trapping. In all cases there is an optimum concentration of the dopant at the GB. To optimize the manufacturing of the doped film with respect to microstructure and dopant concentration is mostly an experimental challenge.

There are still a number of issues on which modeling and simulation of interdiffusion could improve on. In order to get real segregation coefficients or diffusion rates, we will have to perform free-energy calculations, i.e., include the vibrational and configurational entropy. We also need to know more about the microstructure of the film and how it evolves with temperature and under the influence of the dopants. This knowledge would tell us, for example, which GB's are the important ones. The $\Sigma 5$ GB is certainly not the only GB present in polycrystalline Pt. Other GB's (or dislocations)[20] have different segregation coefficients[9] and diffusion rates.[10,11] All these issues are very complex, and it will take a long time before thin-film microstructure, temperature-dependent segregation coefficients, or interdiffusion rates will be predicted completely from first principles.

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[18] The energy of the O dimer is calculated with the spin polarization turned on in VASP, which leads to the correct magnetic moment of two. The free O atom reference is arbitrarily chosen to be the valence energy of the spin-averaged free O atom within GGA. With the spin-polarized free O atom taken as reference, the calculated binding energy of the O_2 dimer reduces from 4.91 eV to 3.35 eV per O atom. This value is larger than the experimental value of 2.59 eV. Binding energies are generally overestimated in the GGA (Ref. 6), however, differences in binding energy are more reliable. We note here that the O_2 calculations require the harder version of the O pseudopotential (Ref. 7) and a plane-wave cutoff of 396 eV.

[19] In principle, it would be enough if the dopant stays dispersed in the bulk Pt matrix and only segregates to the GB's once the O is there. This requires that the dopant diffuses faster in bulk Pt than O in the GB. For the dopants discussed here that is not the case.

[20] Preexisting dislocations in the Pt film could lower the activation energy for through-bulk diffusion. See, e.g., R. G. Hoagland, A. F. Voter, and S.M. Foiles, Scr. Mater. **39**, 589 (1998). This is not considered here.

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