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Molecular dynamics simulation of oxide thin film growth: Importance of the inter-atomic interaction potential

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ABSTRACT

A molecular dynamics (MD) study of $Mg_xAl_yO_z$ thin films grown by magnetron sputtering is presented using an ionic model and comparing two potential sets with formal and partial charges. The applicability of the model and the reliability of the potential sets for the simulation of thin film growth are discussed. The formal charge potential set was found to reproduce the thin film structure in close agreement with the structure of the experimentally grown thin films.

Materials science increasingly focuses on the design and understanding of materials at the atomic level. Atomistic simulations contribute essentially to a better understanding in this field. Atomistic simulation techniques use either a classical mechanical approach, i.e. classical molecular dynamics (MD) and Monte Carlo (MC) methods [1,2] based on using inter-atomic potentials; or a quantum mechanical approach, i.e. Hartree–Fock (HF) and density-functional-theory (DFT) methods [3] based on electron-structure methods. Both HF and DFT techniques are computationally very demanding and therefore limited to a rather small number of atoms, i.e. molecules or clusters. The classical mechanical approach can be divided into two classes, i.e. either stochastic (i.e. MC) or deterministic (i.e. MD) methods. The advantage of MD over MC is that it gives additional information about the dynamics of the system.

Classical MD methods are applied to a huge class of problems, e.g. properties of liquids, defects in solids, fracture, surface properties, friction, molecular clusters, polyelectrolytes and biomolecules [e.g. 4,5]. To calculate the dynamics of a classical many-body system, Newton's equations of motion are solved iteratively for each atom [1,2]. The method is based on using inter-atomic potentials to calculate the force acting on the atoms. Hence, the potential becomes the basic input for the simulation. Therefore, the application of the MD method is limited by the ability to obtain high-quality transferable inter-atomic potentials. Recently other techniques that combine the classical and quantum mechanical approaches have been developed, which apply the MD method to generate atom trajectories by using forces obtained directly from electronic structure calculations performed 'on the fly' as the simulation proceeds [6]. Such techniques, offer a very accurate representation of the interactions; but they are computationally very demanding and their applicability is restricted to very small sizes of systems.

Time-scale is another main limitation of the MD method. Even using currently available computer power, the MD simulations rarely reach a 'real time' greater than 10–100 ns. This means that events with low probability in such a time period cannot be simulated by the MD method. For example, if applying the method to solid-state diffusion, only systems with large diffusion coefficients (greater than 10^{-9} cm^2 s^{-1}) can be effectively modeled [4].

The quality of the potential and the time-scale limitations explain the limited application of the MD method to the simulation of metal oxide thin film growth [7–11]. However, the growth of thin films implies that the modeled system not only has a large number of atoms that increases during the simulation but also the region of deposition is not well defined in space. Both of these considerations present major obstacles for the application of the accurate electronic structure calculations during the MD treatment of the process.

We applied successfully a classical MD method to simulate the growth of complex metal oxide (Mg–Al–O, Mg–Cr–O and Mg–Y–O) thin films deposited by magnetron sputtering [11,12]. As a time saving feature, two successive deposition steps occurred in a time-scale of a *ps*, which means that the deposition rates calculated by the MD model were several orders of magnitude higher than the experimental deposition rates. Despite this fact, the structural results from the simulations were in good agreement with the data from X-rays diffraction (XRD) and transmission electron microscopy (TEM) analyses of the experimentally deposited films [11,12]. Our simulations showed that when energetic atoms are deposited in a manner similar to that of the magnetron-sputter deposition process it is safe to assume that the thermal diffusion does not play a significant role in the simulation of the film growth when the substrate temperature is low compared to the activation energy barriers for surface diffusion [11]. It was observed that the

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incident ion energy is dissipated in the first few *ps* and that this is the time-scale in which the ion-induced displacement events are completed. This observation is in agreement with the study of the atomistic processes induced by normally incident energetic Pt atoms in metal film growth by Adamovic et al. [10]. Hence, the fast deposition simulated by MD can be justifiable in the low-temperature deposition regime, where thermally activated processes are exponentially suppressed, if the energetic deposition flux, which enhances the surface diffusion, plays a dominant role for the film growth compared to that of the thermal surface diffusion.

Therefore, in this Letter we focus on the importance of the other limitation of the MD model, i.e. the inter-atomic interaction potential. Potentials can be derived from first principles by electron-structure methods, empirically by fitting to experimentally measured crystal properties or by semi-empirical procedures. However, potentials derived by fitting to bulk have poor performance in describing surface interactions. Furthermore, the empirically fitted potentials represent well the energy at typical inter-ionic distances in the crystal because their parameters are fitted to perfect lattice distances. However, the reliability of this type of potentials is uncertain at other distances. For this reason there have been considerable efforts in developing theoretical methods for deriving inter-atomic potentials. A good review on the ionic potentials, ways of deriving their parameters and a discussion about the difficulties to produce high-quality transferable potentials can be found in Refs. [13,14]. In this Letter we show that the particular ionic potential, although simple and fitted to the bulk structure could be used also to describe the surface interactions.

The methodology used to simulate the deposition of thin films by the MD model is described in detail in our previous work [11]. The MD package DL_POLY [15] is used to simulate the deposition of atoms. A driving program is written, which automates the deposition and relaxation. The size of the initial substrate was chosen in a way that each dimension would be at least twice the cut-off, which is set to 8 Å [11]. We found that such a small system can be used for fundamental prediction of the structure, while a larger system can be used to study details. The simulated films on a larger substrate showed polycrystalline columnar structure, presence of defects and grain boundaries, in agreement with the experimentally deposited films [11]. However, the crystallinity predicted by the study of the small system was also found back in the larger system. The advantage of studying a smaller system is the comparatively short CPU time needed to complete the simulation. Indeed, deposition on the small substrate as described in this Letter took 2 weeks, while if we increased the substrate surface four times, the CPU time for deposition of the same thickness thin film increases to 4–5 months.

In the present study a classical pairwise ionic potential [16] describes the interactions between atoms:

$$V_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A\exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}$$

where q_i, q_j are the charges of atoms i and j, r_{ij} is the distance between the atoms, and A, ρ and C are parameters fitted for each pair of ions. The first term is the Coulombic interaction, the exponential term represents the short-range repulsion and the dispersion term $(-r_{ij}^{-6})$ accounts for van der Waals attraction. The electrostatic interactions were evaluated by the Ewald summation technique [17], which was applied to three-dimensional (3D) periodic boundary conditions [11]. The MD package DL_POLY implements the Smoothed Particle Mesh Ewald method of Essmann et al. [18], which is a modification of the standard Ewald method.

The present ionic model was tested by applying two potential sets, i.e. with formal charges (FC) [19] and partial charges (PC) [20] to investigate the growth and structure of $Mg_xAl_yO_z$ thin films at different metal content $x/(x+y)$ of x Mg and y Al; z is defined from the electro-neutrality requirement of the system. Mg, Al and O ions in different ratios are deposited one by one on a crystalline MgO (1 0 0) surface. The parameters for the cation–anion and anion–anion interactions and the charges of the ions of the two potential sets are presented in Table 1. In the FC potential set the cation–cation interactions are assumed to be purely Coulombic, i.e. the short-range parameters are 0 [16]. The short-range cation–cation parameters in the PC set are presented in Table 1. It should be noted however, that the contribution of the cation–cation short-range interaction is very weak and close to 0 at inter-atomic distances above 1.2 Å.

The FC potential yielded a structure of the $Mg_xAl_yO_z$ films in very close agreement with the structure of the experimentally deposited films as was discussed in detail in Ref. [11]. The crystallinity of the simulated films was analyzed by the calculated pair radial distribution functions (RDFs) for the bulk film, i.e. the layers close to the substrate and the free surface were excluded. The snapshots of the deposited films at different Mg metal content using the FC and PC potential sets are compared in Fig. 1a and b, respectively.

Fig. 2 presents the calculated pair Mg–O and Al–O RDFs for the films presented in Fig. 1. The Al–O RDF in a $MgAl_2O_4$-spinel crystal is also presented in Fig. 2b for comparison. The deposited MgO film had a structure identical to the structure of the MgO (cubic, S.G. $Fm\bar{3}m$), which was used as a reference. The RDF of a crystal structure has a profile with several peaks corresponding to the lattice positions of the atoms while the RDF of an amorphous structure has a profile typically consisting of one peak at the bond length between the two atoms and smoothing down to the value of one further away.

The simulation results with FC potential set (Figs. 1a and 2a) showed a transition in the film from a crystalline to an amorphous structure, when the Mg metal content decreases below 50%. Furthermore, the crystalline $Mg_xAl_yO_z$ films have a structure of MgO with Al in solid solution. Indeed, the RDFs of the films with 80%, 60% and 50% Mg have a profile very similar to the profile of the MgO film, which represents the MgO crystal (Fig. 2a). Only the intensity of the peaks decreases with a decrease of the Mg concentration. Both of these simulation observations were confirmed by XRD and TEM analyses of the experimentally deposited films [11].

The simulation results with the PC potential set (Fig. 1b and 2b), on the other hand, show that all deposited films have a crystalline structure in contrast with the simulation results using the FC potential. Hence, although the PC potential was used successfully to simulate the structure and bulk moduli of a number of crystals [20], it seems not to be appropriate for the simulation of deposition especially when ionic crystals are considered. We think that the reason for the poor agreement with the structure of the experimentally deposited films may be due to the fact that the PC poten-

Table 1
Potential parameters of cation–anion and anion–anion interactions for the two potential sets with formal [19] and partial charges [20].

i–*j*	*A* (eV)	*ρ* (Å)	*C* (Å^6 eV)
Mg^{2+}–O^{2-}	1279.69	0.29969	0.0
Al^{3+}–O^{2-}	1374.79	0.3013	0.0
O^{2-}–O^{2-}	9547.96	0.21916	32.0
$Mg^{0.945+}$–$O^{0.945-}$	32 586	0.178	27.32
$Al^{1.4175+}$–$O^{0.945-}$	28 480	0.172	34.63
$O^{0.945-}$–$O^{0.945-}$	6463.4	0.276	85.22
$Mg^{0.945+}$–$Mg^{0.945+}$	17 650 254	0.080	8.76
$Mg^{0.945+}$–$Al^{1.4175+}$	22 981 293	0.074	11.10
$Al^{1.4175+}$–$Al^{1.4175+}$	31 574 470	0.068	14.07

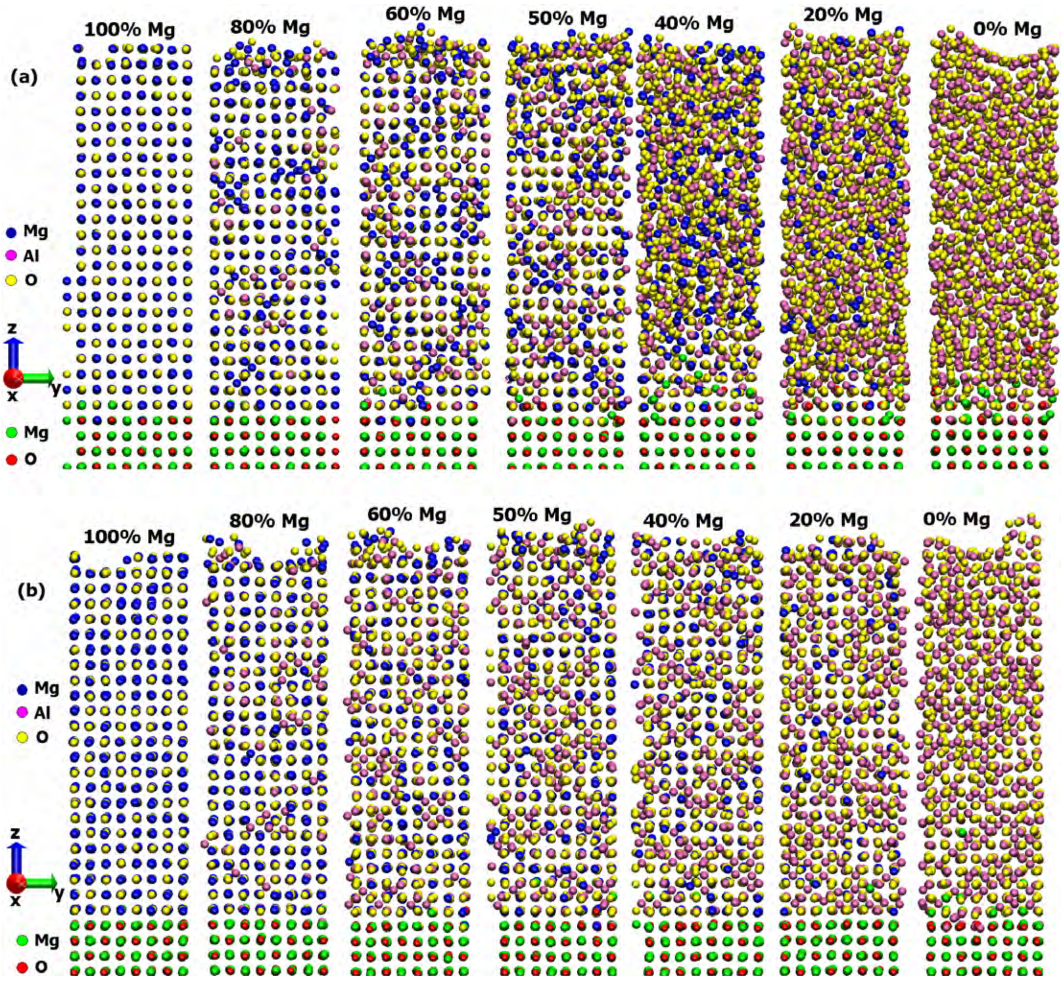

Fig. 1. Snapshots of simulated $Mg_xAl_yO_z$ thin films grown on a MgO (1 0 0) substrate by a MD method with FC (a) and PC (b) potential sets. The snapshots presented in (a) are reproduced from Ref. [11] with kind permission of IOP Publishing.

tial does not represent the ionic and covalent bonds in correct proportions, as will be discussed below.

Fig. 3a presents the total Mg–O, Al–O and O–O pair potentials calculated using the FC and PC models as a function of inter-ionic distances. It is clear that the energies calculated by the PC potential set (dashed lines) are four times lower than the corresponding energies calculated by the FC potential set (solid lines) at the typical inter-ionic distances of 2 Å. Indeed, this is attributed to the fact that the partial charges in the PC model are almost half of the corresponding formal charges and keeping in mind that the Coulomb energy contribution for ionic systems is an order of magnitude greater than the short-range energy contribution at the bond length distances [21].

Fig. 3b compares the Coulomb and short-range (van der Waals) attraction terms for the Mg–O and Al–O pairs using the PC model. The short-range repulsion term for the same pairs using the FC and PC models is compared in Fig. 3c. The Coulomb contribution in the FC model is about four times as large as the corresponding contribution in the PC model and is therefore not presented in Fig. 3b. Next, the short-range attraction term in the cation–anion interaction in the FC model is zero, i.e. the van der Waals or dispersion term is neglected [16] and the parameter C is 0 (see Table 1). When partial charges are assigned to ions, the contribution of the dispersion term assumes unphysical values at low inter-atomic distances (Fig. 3b) [22]. Therefore, the short-range repulsion term increases too (Fig. 3c) and the total potential is more repulsive in case of the PC model as is shown in Fig. 3a, i.e. the surface diffusion is expected to be hindered. We calculated the energy barriers for MgO dimer diffusion for the two potential sets using a temperature accelerated dynamics (TAD) code. The TAD method [23] accelerates the diffusion by heating the system for a short time and studies possible diffusion paths. The energy barriers are calculated with the nudged elastic band method, using a dimmer approach [24,25]. We found, for example, that the Mg and O interlayer exchanges have energy barriers of 0.48 and 1.6 eV, respectively if the PC set is used. If the FC set is used, the Mg interlayer exchange happens into two stages each of which has energy barriers of 0.32 and 0.46 eV, respectively. In the first stage, the Mg adion moves to a hollow site and pushes the Mg ion below the O adion. In the second stage, the Mg adion moves further below the O adion and the pushed Mg ion moves half hop. The O exchange follows similarly two stages with energy barriers of 0.49 and 0.3 eV, respectively. Hence, the energy barriers calculated by the FC set are indeed smaller than the corresponding values calculated by the PC set. In addition, the exchange processes observed in case of the FC set occur in two stages similar to the results found in the DFT study of MgO dimmer diffusion [26]. The energy barriers calculated by the FC set are also found to be in reasonable agreement with the energy barriers calculated by the DFT study [26].

An ionic model with partial charges can be used to handle some degree of covalence in systems such as silicates [27] or transition metal oxides [28]. However, MgO is known to exhibit a high degree of ionicity as it was found by Phillips definition [29] as well as by detailed HF calculations [30]. Although there is an inherent prob-

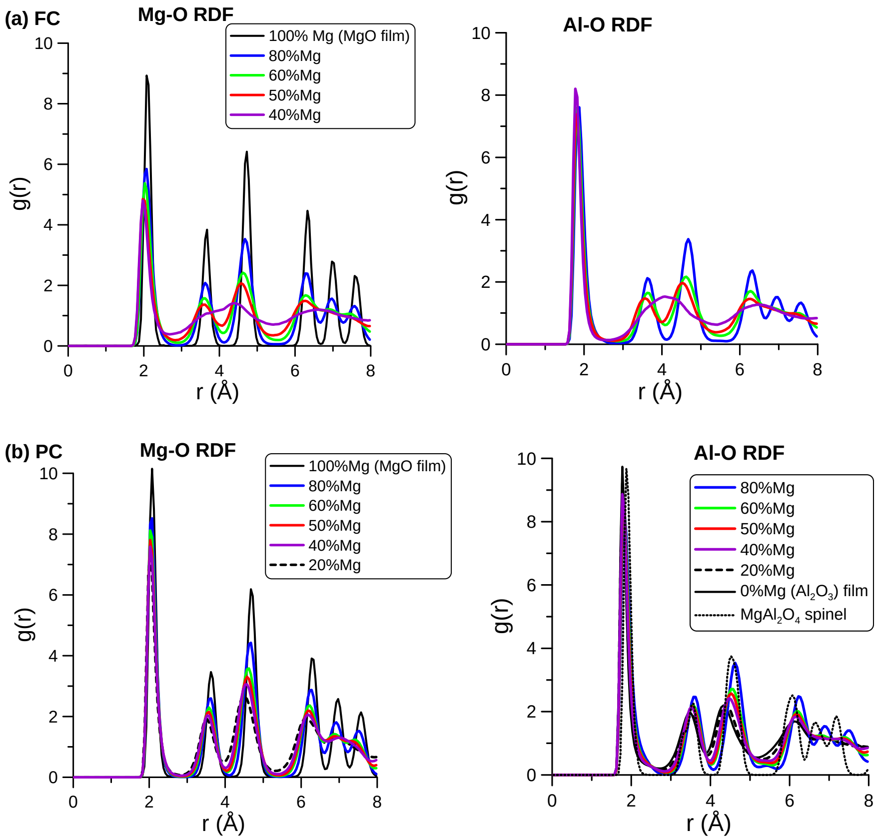

Fig. 2. Calculated Mg–O and Al–O RDFs of the simulated thin films presented in Fig. 1 by the MD method with FC (a) and PC (b) potential sets. The RDFs in (a) below 40% Mg were found to be the same as the RDFs at 40% Mg, i.e. an amorphous structure is observed, and therefore they are not shown in the figure for the sake of clarity. The Mg–O RDF of the MgO film is identical to the corresponding RDF in a MgO crystal.

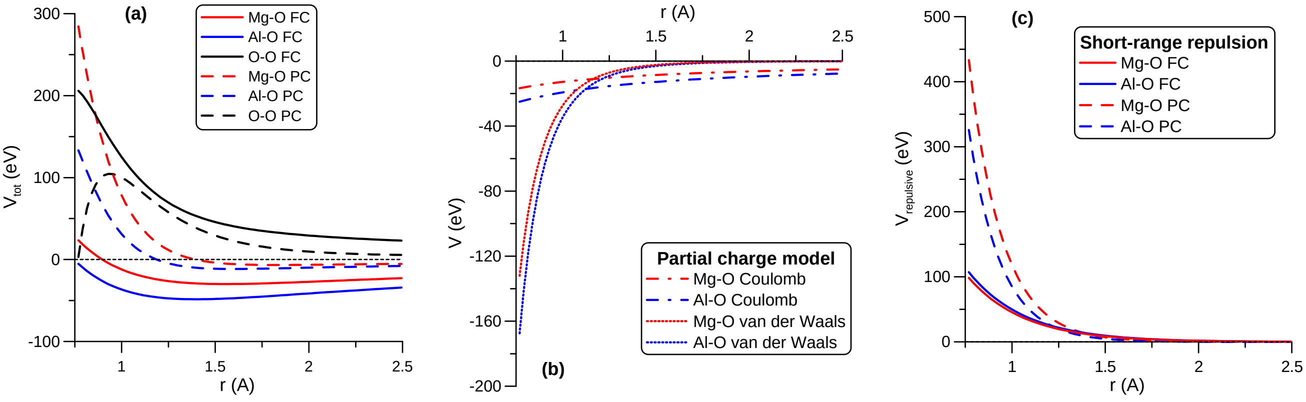

Fig. 3. Total pair Mg–O, Al–O and O–O potential energy calculated applying the FC and PC potential sets (a); Coulomb and dispersion terms of the Mg–O and Al–O potential energy calculated by the PC potential set (b); and short-range repulsion term of the Mg–O and Al–O potential energy calculated by the FC and PC potential sets.

lem in a clear definition of ionicity and covalency because of the several distinct forms that appear in such ideas [30] and because of the difficulty to transform a qualitative concept to a quantitative, mathematical formula [29], we could conclude following either Phillips [29] or Pauling [31] definition of ionicity of a single bond, that both Mg–O and Al–O exhibit a high degree of ionicity. Therefore, considering the partial charge to be only half of the formal charge (see Table 1) would not be a good approximation when the Coloumb contribution to the total configurational energy is essential as in the case of ionic crystals.

It is clear that an accurately calculated energy surface is crucial for the simulation of thin film deposition. In this sense, DFT calculations of MgO addimer diffusion on a MgO surface [26] showed that partial charge models with parameters calculated from DFT could give a better representation of *ab initio* energy surfaces than those using the formal charges expected from simple chemical valence considerations. However, the calculated charges of Mg and O ions of +/−1.7*e* in Ref. [26] are not very different from the formal charges of +/−2*e* in comparison to the charges in the PC potential set adopted from Ref. [20].

In conclusion, two potential sets, i.e. based on PC and FC models, were used to study the growth of $Mg_xAl_yO_z$ thin films by a classical MD method. The importance of the potential for the simulation results was demonstrated. We found that the ionic model with formal charges is successful in the simulation of thin film growth by magnetron sputtering.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.12.067.

References

[1] D. Frenkel, B. Smith, Understanding Molecular Simulation, Academic Press, 2002.
[2] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1989.
[3] R. Dreizler, E. Gross, Density Functional Theory, Plenum Press, New York, 1995.
[4] C.R.A. Catlow, E. Kotomin (Eds.), Computational Material Science, NATO Science Series III, vol. 187, IOS Press, Amsterdam, 2003.
[5] C.R.A. Catlow, W.C. Mackrodt (Eds.), Computer Simulation of Solids, Lecture Notes in Physics, Spinger-Verlag, Berlin, 1982.
[6] R. Iftimie, P. Minary, M.E. Tuckerman, Proc. Natl. Acad. Sci. 102 (2005) 6654.
[7] N. Baguer, V. Georgieva, L. Calderin, I.T. Todorov, S. VanGils, A. Bogaerts, J. Cryst. Growth 311 (2009) 4034.
[8] A. Hasnaoui, O. Politano, J.M. Salazar, G. Aral, R.K. Kalia, A. Nakano, P. Vashishta, Surf. Sci. 579 (2005) 47.
[9] D.C. Sayle et al., Mol. Sim. 28 (2002) 683.
[10] D. Adamovic, V. Chirita, E.P. Munger, L. Hultman, J.E. Greene, Phys. Rev. B 76 (2007) 115418.
[11] V. Georgieva, M. Saraiva, N. Jehanathan, O.I. Lebedev, D. Depla, A. Bogaerts, J. Phys. D: Appl. Phys. 42 (2009) 065107.
[12] M. Saraiva, V. Georgieva, S. Mahieu, K. Van Aeken, A. Bogaerts, D. Depla, J. Appl. Phys. 107 (2010), in press.
[13] C.R.A. Catlow, C.M. Freeman, M.S. Islam, R.A. Jackson, M. Leslie, S.M. Tomlinson, Phil. Mag. A 58 (1988) 123.
[14] J.H. Harding, Rep. Prog. Phys. 53 (1990) 1403.
[15] <www.ccp5.ac.uk/DL_POLY/>.
[16] G.V. Lewis, C.R.A. Catlow, J. Phys. C 18 (1985) 1149.
[17] P. Ewald, Ann. Phys. 64 (1921) 253.
[18] U. Essmann, L. Perera, M.L. Berkowitz, T. Darden, H. Lee, L.G. Pedersen, J. Chem. Phys. 103 (1995) 8577.
[19] D. Bacorisen, R. Smith, J.A. Ball, R.W. Grimes, B.P. Uberuaga, K.E. Sickafus, W.T. Rankin, Nucl. Instrum. Methods Phys. Res. B 250 (2006) 36.
[20] M. Matsui, Phys. Chem. Miner. 23 (1996) 345.
[21] J.D. Gale, Philos. Mag. B 73 (1996) 3.
[22] A. Pedone, G. Malavasi, M.C. Menziani, A.N. Cormack, U. Segre, J. Phys. Chem. B 110 (2006) 11780.
[23] M. Sorensen, A. Voter, J. Chem. Phys. 112 (2000) 9599.
[24] G. Henkelman, B.P. Uberuaga, H. Jónsson, J. Chem. Phys. 113 (2000) 9901.
[25] G. Henkelman, H. Jónsson, J. Chem. Phys. 111 (1999) 7010.
[26] G. Henkelman, B.P. Uberuaga, D.J. Harris, J.H. Harding, N.L. Allan, Phys. Rev. B 72 (2005) 115437.
[27] B.W.H. van Beest, G.L. Kramer, R.A. van Santen, Phys. Rev. Lett. 64 (1990) 1955.
[28] B.S. Thomas, N.A. Marks, B.D. Begg, Nucl. Instrum. Methods Phys. Res. B 228 (2005) 288.
[29] J.C. Phillips, Bonds and Bands in Semiconductors, Academic Press, New York, 1973 (Chapter 2).
[30] C.R.A. Catlow, A.M. Stoneham, J. Phys. C 16 (1983) 4321.
[31] L. Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry, Cornell University Press, Ithaca, NY, 1973.