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Accommodation of the Misfit Strain Energy in the BaO(100)/MgO(100) Heteroepitaxial Ceramic Interface using Computer Simulation Techniques

Dean C. Sayle,^{*†a} Stephen C. Parker^a and John H. Harding^b

^a School of Chemistry, University of Bath, Avon, UK BA1 7AY

^b AEA Technology, B424.4, Harwell Laboratory, Didcot, Oxfordshire, UK OX11 0RA

Static atomistic simulation techniques have been employed to investigate the accommodation of the misfit strain energy in the BaO(100)/MgO(100) interface. The materials return to their natural (bulk) lattice parameters a few planes from the interface, while maintaining expanded or contracted lattice parameters at the interface to ensure charge matching of counter ions. BaO also forms three-dimensional islands when grown on MgO(100), in accordance with molecular beam epitaxy results. This behaviour is attributed to the instability of a monatomic BaO layer on MgO compared with a BaO bilayer.

The formation and structures of thin film oxide interfaces have received much attention recently, particularly in the field of superconductivity. An understanding of the interfacial structure at the atomic level is critical to the development of thin films. For example, the modification of the thin film crystal structure as a result of the interface is important for the many applications of thin-film interfaces, which depend on the materials maintaining long range structural coherence.^{1,2}

The formation of a heteroepitaxial interface necessitates matching two incommensurate lattices. This can be achieved by compression or expansion of either or both of the component materials in order to accommodate the misfit. The resulting strain introduced into the interface will destabilise the interface. In this paper, we employ atomistic simulation techniques to investigate the accommodation of the misfit strain energy induced in forming a heteroepitaxial ceramic interface. The relaxation of ions can destroy the long-range coherence in the overlaying thin film, resulting in a deterioration of the material properties.

As an example, we investigate the BaO/MgO interface. This was chosen for its simplicity and because robust potentials (including a consistent oxygen potential for the component materials) are available. Furthermore, this interface has applications in the field of thin-film superconductors, where the BaO plane can terminate the YBa₂Cu₃O_{6.5} thin film at the YBa₂Cu₃O_{6.5} interface.³ Cotter *et al.*⁴ have investigated the BaO/MgO interface⁴ and, more recently, McKee *et al.*⁵ have investigated the stability and the growth of optical-quality perovskites on MgO with either BaO or TiO₂ terminating the BaTiO₃ at the interface plane.⁵

First, we investigate a bulk BaO(100)/MgO(100) interface. In particular, we investigate the behaviour of the interface when it meets a surface and thus allows interface edge effects to be included for the first time in our simulations. Second, we investigate a monolayer of BaO(100) on a bulk MgO(100) substrate. Finally we examine the formation of a 'BaO monolayer' on an MgO substrate.

Simulation Code and Potential Model

The simulations in this work were performed on a CRAY X-MP4/8 at the Atlas Division of the Rutherford Appleton Laboratory, using the energy minimisation codes MIDAS⁶

and CHAOS.⁷ The MIDAS program considers the crystal as a stack of planes periodic in two dimensions (Fig. 1). The stack is divided into two regions: region 1, where the ions are allowed to relax explicitly; and region 2, where the ions are held fixed relative to each other. Region 2 can, however, relax as a whole, enabling the crystal to either 'expand' or 'contract'. Region 2 is included to ensure that the potential for the ions at the bottom of region 1 are calculated correctly. The top of region 1 is the free surface, unless two such blocks are placed together, enabling the cohesive energy of the perfect crystal to be calculated. A heteroepitaxial interface is created if two dissimilar materials are placed together.

The CHAOS code was employed to study the sequential addition of isolated BaO units to the MgO substrate. The approach is to divide the crystal 'surrounding' the BaO units into two regions (Fig. 2): an inner region 1, where all the ions are allowed to relax explicitly; and an outer region 2, which extends to infinity and is treated using a quasi-continuum approximation.

We use an ionic model for the solid with full ionic charges. The long-range Coulomb interaction is treated by the standard Ewald summation. The short-range potentials between the

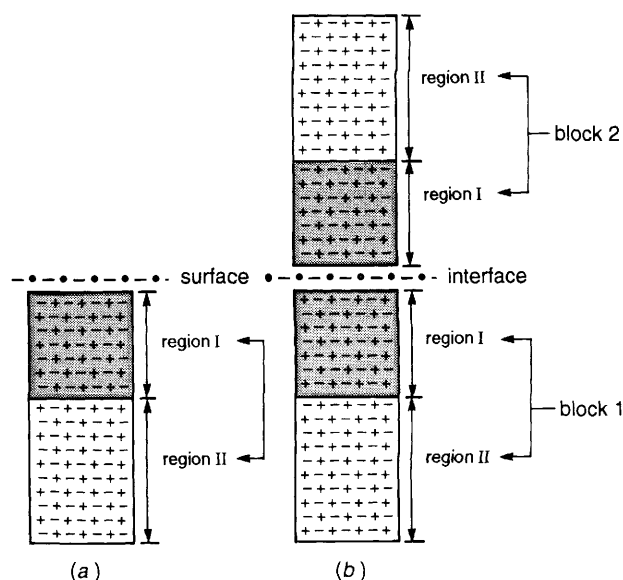


Fig. 1 Schematic representation of the crystal regions for interface and surface calculations employed in the MIDAS code

[†] Present address: Royal Institution of Great Britain, 21 Albermarle Street, London, UK W1X 4BS.

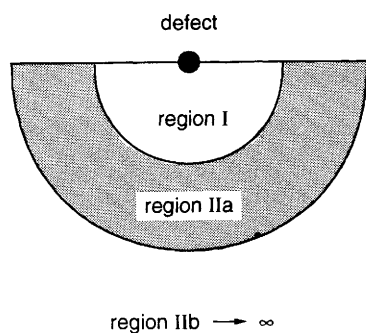


Fig. 2 Representation of the two-region strategy used in the CHAOS code

ions⁸ were obtained by fitting to the bulk crystal properties. The shell model⁹ was used to describe the electronic polarisability of the component ions. The potential parameters are given in Tables 1 and 2.

Epitaxial Constraints

The incommensurate relationship between the lattice parameters of BaO (2.77 Å) and MgO (2.10 Å) leads to a prohibitively large, two-dimensional interfacial unit cell. In a previous paper,¹⁰ we employed a near-coincidence site lattice theory to construct BaO/MgO interfaces of low misfit (less than 3%) and showed them to be more stable than interfaces of higher misfit. The misfit strain energy was alleviated by explicit relaxation of the interfacial ions, mainly perpendicular to the interfacial plane. Relaxation of these ions parallel to the plane of the interface was, however, restricted as the calculations were performed at constant surface or interfacial area. The relaxation behaviour is inevitably influenced by the constant surface area boundary conditions imposed on the simulation, which are necessary to ensure periodicity in neighbouring unit cells.

The obvious problem in simulating interfaces without this constraint is that the incommensurate lattices could lead to an infinitely large unit cell if the standard configuration for the calculation is used. However, we can perform this type of calculation by creating a surface perpendicular to the interface. Cotter *et al.*⁴ have experimentally examined BaO(100) layers on an MgO(100) substrate conforming to the $\sqrt{2}a_0(\text{MgO}) = a_0(\text{BaO})$ configuration or, more correctly, using coincidence-site-lattice notation,¹¹ $\Sigma_{\text{BaO/MgO}} = 1/2(\theta = 45^\circ)$. We employ this interfacial configuration as a basis for our studies. This configuration is the smallest interfacial primitive unit cell with

Table 1 Short-range parameters describing the short range potential energy terms between the component ions. The analytical function is of the form: $V(r) = A \exp(-\rho/r) - Cr^{-6}$.

species	A/eV	$\rho/\text{\AA}$	$C/\text{eV \AA}^{-6}$
$\text{Ba}^{2+}-\text{O}^{2-}$	905.7	0.3976	0.0
$\text{Mg}^{2+}-\text{O}^{2-}$	1428.5	0.2945	0.0
$\text{O}^{2-}-\text{O}^{2-}$	22764.3	0.149	27.879

Table 2 Shell-model parameters employed to describe the polarisability of the component ions. The analytical function is of the form: $\alpha = Y^2/k$.

species	Y/eV		$k/\text{eV \AA}^{-2}$
Ba^{2+}	9.203		443.46
Mg^{2+}		rigid ion	
O^{2-}	-3.0		51.836

a lattice misfit of less than 10% and requires the BaO overlayers to be rotated 45° with respect to the MgO substrate. Three distinct configurations arise (Fig. 3); first, with the barium and oxygen of the BaO lattice constrained to sit above the magnesium sublattice of the MgO crystal surface; second, with the barium and oxygen constrained to sit above the oxygen sublattice; third, with the BaO sited above the interstitial sites of the MgO lattice. The most stable configuration is the first. We therefore use this interfacial configuration as a starting point for the calculations. Our method is to construct this interface and then create a surface perpendicular to the interfacial plane (Fig. 4). The relaxation perpendicular

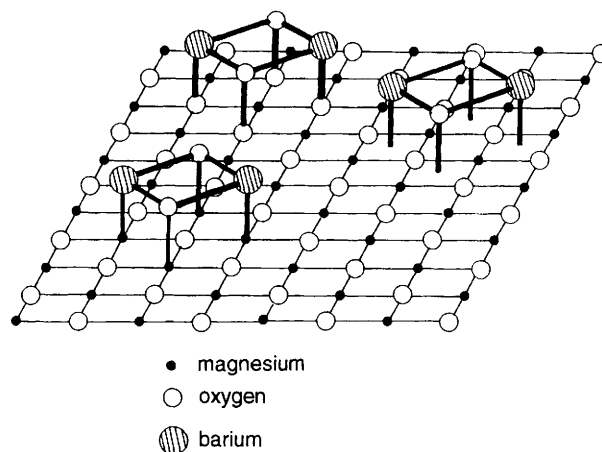


Fig. 3 Representation of three configurations of BaO overlayers on an MgO(100) substrate. The BaO is constrained to adopt positions above the oxygen sublattice of the MgO, above the magnesium sublattice and also at interstitial positions.

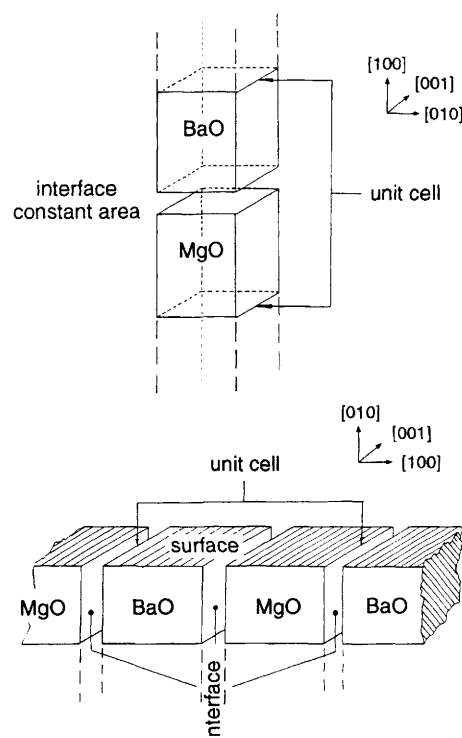


Fig. 4 (a) Original MIDAS interface construction constrained to constant interfacial area. Relaxation unconstrained only in the [100] direction. Relaxation in [001] and [010] directions restricted to maintaining constant interfacial area. (b) Modified interface construction enabling unconstrained relaxation in the [010] direction and hence allowing for an interfacial area change. Relaxation in [001] and [100] directions restricted to maintain constant area.

to the surface ([010] direction) or in the plane of the interface is now not restricted by the constant surface area constraint and therefore relaxation in the [010] direction can also be associated with a change in the interfacial area. However, in order to ensure periodicity in neighbouring unit cells, the constant surface area boundary condition must still be imposed. This results in undesirable interface–interface interactions. It is therefore essential to have the [100] direction of the unit cell as large as possible to minimise these interactions.

In these calculations, the accommodation of misfit strain is partitioned between the BaO and MgO, on the basis of their respective bulk moduli, so as to introduce as little strain energy into the system as possible. Only 1.7% of the total 7% mismatch is therefore assigned to be accommodated by the MgO and the remaining 5.3% to the BaO lattice (MgO is expanded and BaO compressed).

Results

Bulk BaO(100)/MgO(100) Interface

Plate 1 shows the behaviour of the ions at the interface region after full relaxation. It is a side view of the interface; a thin slice is shown for clarity. A contraction of the BaO lattice away from the interface is clearly evident. The driving force for this relaxation is to relieve the strain in the system with the MgO and BaO crystals adopting their natural lattice parameters away from the interfacial plane. The BaO returns to its natural (bulk) lattice parameter five planes away from the interface region, while maintaining an artificially expanded lattice parameter at the interface. It is therefore apparent that the local interfacial strain is more than compensated for by

the favourable cation–anion interactions across the interface. The contraction follows a smooth progression from the +5.3% mismatch at the interface. The MgO exhibits similar behaviour with the MgO planes away from the interface region adopting their natural lattice parameter while MgO planes at the interface region remain artificially compressed. However, MgO was compressed by only 1.7%; the behaviour is therefore less obvious from the figure. These findings are consistent with the results of McKee *et al.*⁵ who write 'the BaTiO₃ lattice parameter relaxes to its strain free bulk value within 10 unit cells from the interface.'

Relaxation of the magnesium ions towards the BaO anions and away from the BaO cations (in the [100] direction) is clearly seen (in accordance with the results of Cotter *et al.*⁴). It is reassuring to see this behaviour as the relaxation is

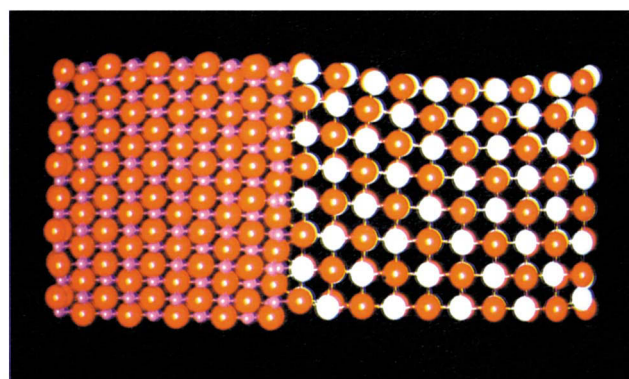


Plate 1 Behaviour of the ions at the interface region after full relaxation for a system with 10 BaO and 10 MgO planes explicitly relaxed in the [100] direction. Oxygen is coloured red, barium white and magnesium purple.

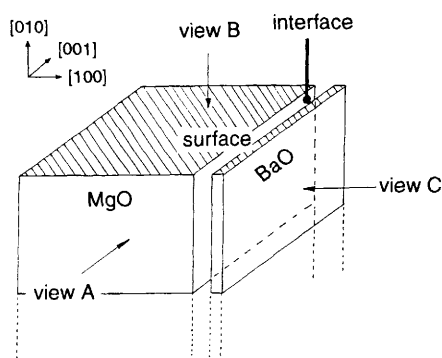


Fig. 5 Construction of the interface allowing for relaxations in the plane of the interface [010] direction, for monolayer coverage. Views A, B and C are indicated on the figure.

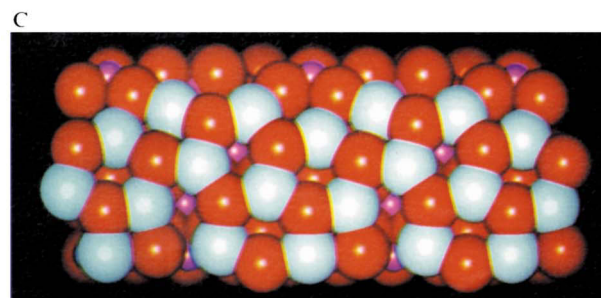
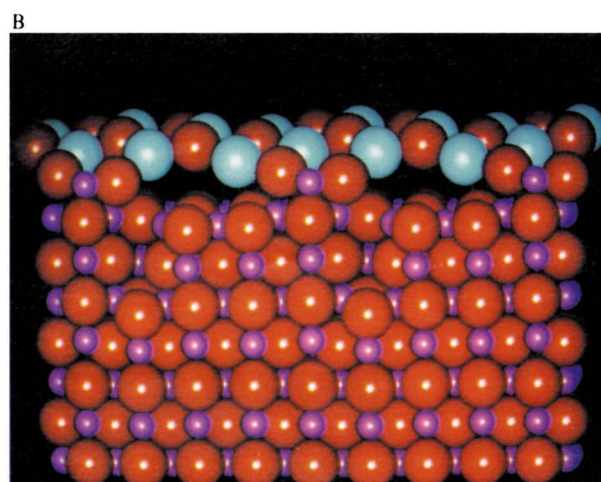
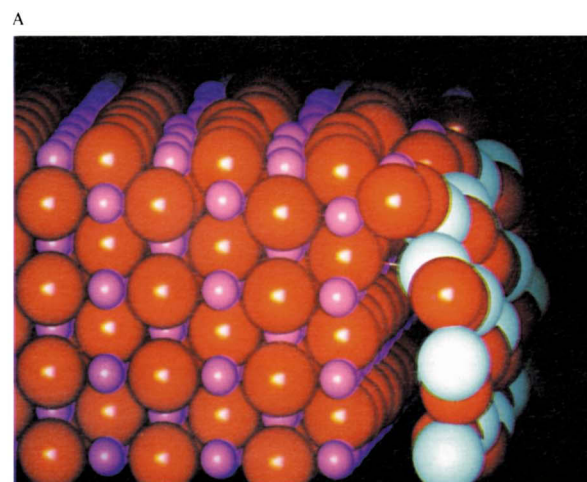


Plate 2 Three projections of the BaO monolayer on MgO after relaxation. Oxygen is coloured red, barium white and magnesium purple. Projections A, B and C are indicated in Fig. 5.

constrained by the constant surface area boundary condition perpendicular to the interfacial plane ($[100]$ direction). A more subtle point to note is that the surface relaxation of the BaO and MgO lattices remains consistent with experimental observations of the ions at the surfaces, *i.e.* the oxygens relax out of the surface and the cations relax towards the bulk of the crystal.^{12,13}

BaO(100) Monolayer on MgO(100) Substrate

The calculations above have shown the relaxation of a bulk BaO/MgO interface when the constant interfacial area boundary conditions have been partially removed. We now investigate the relaxed structure of a BaO monolayer on an MgO substrate, again with the boundary conditions partially lifted. Fig. 5 shows the construction of the BaO monolayer on the MgO substrate. The BaO monolayer is not constrained by

further BaO layers and is therefore free to relax in both the $[010]$ and $[100]$ directions. Of course, as with the bulk interface, any relaxation in the $[010]$ direction might also be associated with an interfacial area change. The constant-area condition must again be imposed and will result in the interface being repeated in the $[100]$ direction.

Plate 2 shows three projections of the structure of the monolayer interface after relaxation. Substantial reconstruction occurs at the interface region. Furthermore, the BaO monolayer has resulted in a perturbation of the MgO substrate as far as 7 interatomic spacings from the interface. View A shows the BaO overlayer to be attached or 'pinned' to the top of the MgO substrate. In view B, magnesium and oxygen ions have migrated from the MgO crystal to the top of the BaO monolayer. View C suggests a substantial modification of the BaO cubic structure after relaxation to an almost hexagonal symmetry. These relaxations enable the BaO to

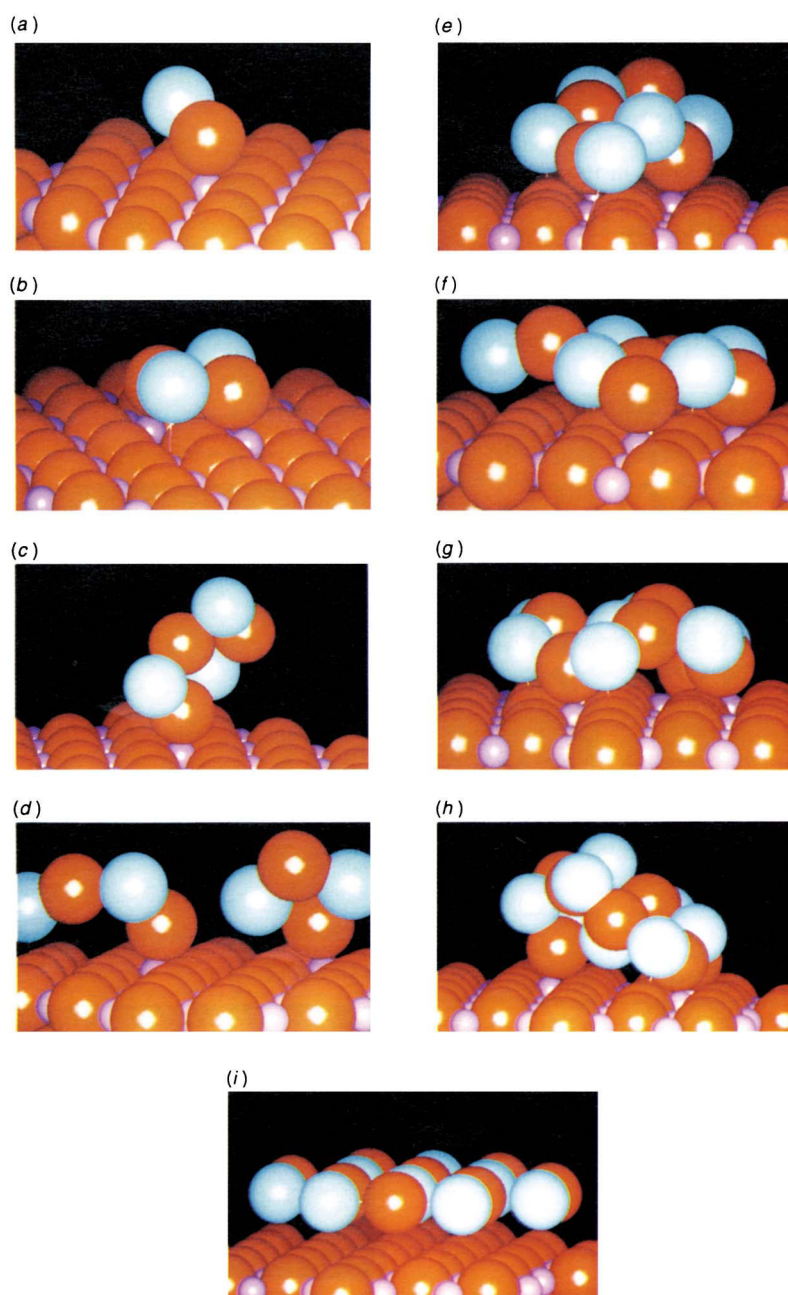


Plate 3 Representations of the relaxed configurations of from one to eight BaO units [(a)–(h)] placed on the MgO(100) surface. (i) illustrates the unrelaxed starting configuration of eight BaO units placed on the MgO(100) substrate.

relieve the high strains induced at the interface. The BaO achieves a higher surface area compared with its natural (bulk) value by changing to hexagonal symmetry, *i.e.* the barium and oxygen ions are then three coordinated instead of four coordinated within the monatomic BaO plane.

The removal of the constant-area constraint was developed using the BaO(100)/MgO(100) system because both BaO and MgO are relatively simple structures. It can also be used to model more complex interface systems. The application of this methodology to such systems must therefore wait for increases in computer size and speed, as these types of calculation are very computationally demanding.

BaO Monolayer Formation on MgO(100) from BaO Sub-units

In this section, we adopt a different approach by allowing the BaO monolayer to form from sequential additions of BaO units on the surface. The CHAOS code is employed for these calculations. This code can investigate isolated BaO clusters and hence there are no interactions between neighbouring BaO clusters. Furthermore, the calculations are not subject to constant surface area boundary conditions.

Plate 3[(a)-(h)] shows the relaxed structures of from one to eight BaO units added to the MgO substrate. Plate 3(i) shows the unrelaxed starting configuration of eight BaO units placed on the MgO(100) substrate. The initial structures before relaxation were constructed by placing BaO units flat on the substrate adopting the $a_0(\text{BaO}) = \sqrt{2}a_0(\text{MgO})$ configuration. For one BaO unit on the MgO substrate [Plate 3(a)], the barium ion is seen to move away from the surface to reduce the unfavourable Ba-Mg interaction. The magnesium directly below the oxygen of the BaO unit has migrated out of the surface towards the oxygen, resulting in an increased energy contribution to the system because of the close proximity of the oppositely charged ions. For two BaO units on the surface [Plate 3(b)] the $a_0(\text{BaO}) = \sqrt{2}a_0(\text{MgO})$ configuration is still apparent after relaxation (the BaO remains directly above the magnesium sublattice of the MgO, see Fig. 3). The magnesium ions directly below the oxygens of the BaO units are again seen to move out of the MgO surface thereby decreasing the Mg-O distance. The barium ions are seen to move away from the magnesium ions, above which they are constrained to sit, because of unfavourable Ba-Mg interaction. For three BaO layers the BaO units appear to have moved from the MgO surface. For four BaO units, the BaO has split into two sets of two BaO units; however, the units do not adopt the configuration observed for two BaO units. This may be because the interaction between the two units pushes the structure towards an alternative local energy configuration. With five or more BaO units, cluster formation of BaO is observed on the MgO substrate. For eight BaO units a three-dimensional island structure is observed. In previous work,¹⁴ we have found that two layers of BaO on MgO are more stable than a monatomic layer. We tentatively suggest therefore that the formation of a 'bilayer' of BaO is facilitated by three-dimensional clustering of the originally monatomically flat BaO.

Fig. 6 shows the calculated energies of adding BaO layers to the MgO substrate per BaO unit. The calculated energy of one BaO unit is lower than the energy of a BaO cluster containing two or more BaO units. We would therefore expect single BaO units to be observed rather than clusters at low concentrations of BaO on the MgO surface. At higher BaO loadings (*i.e.* monolayer coverage) the BaO does not form a coherent monatomically flat epitaxial film but instead BaO clusters form. Recent molecular beam epitaxy results⁵ suggest that BaO grown on an MgO(100) surface does not grow monatomically flat epitaxial films but forms three-dimensional

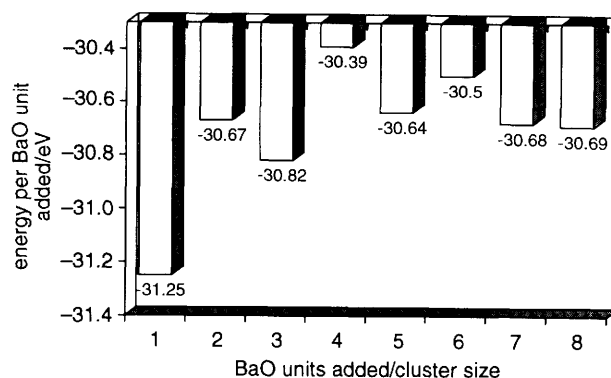


Fig. 6 Calculated energies of from one to eight BaO units placed on the MgO(100) surface after relaxation

islands, in accordance with our results. The molecular beam epitaxy results are for a monatomic loading on the MgO substrate, equivalent to 50% monolayer coverage based on the MgO surface.

Conclusion

The methodology devised for the partial removal of the constant-area boundary condition has enabled the strain energy imposed on the interface to accommodate the misfit to be dissipated by interfacial area changes as a direct consequence of interfacial relaxation.

For the bulk BaO(100)/MgO(100) interface, the BaO and MgO crystals relax to their strain-free bulk values within 5 planes of the interface. The planes at the interface remain artificially lengthened (BaO) or compressed (MgO) to accommodate the mismatch. We attribute this relaxational behaviour to the excellent charge matching across the interfacial plane, more than compensating for the strain energy induced into the system to accommodate the misfit between the two materials.

Finally, we have identified that BaO forms three-dimensional islands when grown on MgO(100), in accordance with molecular beam epitaxy results. This behaviour is attributed to the instability of a monatomic BaO layer on MgO compared with a BaO bilayer.

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