Stoichiometry engineering of ternary oxide ultrathin films: Ba$_3$Ti$_2$O$_3$ on Au(111)

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(Technical report received 23 December 2014; revised manuscript received 1 April 2015; published 21 April 2015)

Ternary oxide Ba$_3$Ti$_2$O$_3$ ultrathin films on Au(111) substrates ($x \leq 2/3$) have been studied using a joint experimental and theoretical approach, including the use of scanning tunneling microscopy (STM), first principles calculations, and Monte Carlo simulations. The films are created by first covering the Au(111) substrate with a Ti$_2$O$_3$ (2 × 2) honeycomb (HC) network and then evaporating low concentrations of Ba atoms onto this film. STM imaging shows that the Ba atoms adsorb individually in the hollow sites of the HC network. Depending on the Ba coverage $x$, which ranges from 0 to 2/3, two ordered phases can be identified at $x = 1/3$ and $x = 2/3$. A disordered labyrinthlike phase is observed for values of $x$ between 1/3 and 2/3. Theoretical modeling shows that the structural character of these films is driven by the charge transfer that occurs between the electropositive Ba atoms and the electronegative Ti$_2$O$_3$/Au substrate. This results in a number of calculated effects including an increase in the film rumpling and a reduction of the film work function with increasing $x$. The evolution of the structure of the thin films as a function of Ba coverage can be described by a lattice gas model with first-, second-, and third-neighbor Ba-Ba repulsive interactions. The range of the dipolar interactions is a key factor in understanding the behavior of Ba ordering. The structural and electronic flexibility, which can be engineered through stoichiometry, temperature, or support control, makes these ultrathin films promising materials for applications related to adsorption or reactivity, or as template supports for the growth of size-selected clusters.

DOI: 10.1103/PhysRevB.91.155424 PACS number(s): 68.37Ef, 68.43.Bc, 68.43.De, 73.22.--f

I. INTRODUCTION

Spontaneous two-dimensional (2D) ordering of adspecies on surfaces has long been a subject of active research. These studies are motivated both by a development of an understanding of the fundamental nature of the adspecies-substrate interaction as well as a desire to create materials systems with novel properties that might lead to new applications. Over the years the focus has moved through very different systems, including alkali atoms on semiconductors [1], rare gas atoms on graphite [2–4], anions on metals [5], molecules on metals [6], etc. More recently, growth of ultrathin oxide films, usually on metallic supports, has been successfully performed, either with the aim of obtaining a patterned support for the formation of size-selected clusters for catalysis or magnetic recording purposes, or as an inverse catalyst system. When the film thickness is no more than one or two atomic layers, depending upon preparation conditions, these 2D films may display structures and stoichiometries that are not seen in bulk crystals as has been observed for example for the oxides of Al, Ti, V, Fe, Co, and Si [7–12].

Ordering of metal adspecies on ultrathin films may be driven by Moiré surface patterning due to the lattice mismatch [12–16] or by specific features, such as periodic holes [17]. Alternatively, repulsive adspecies-adspecies interactions may be involved, when charge transfer between the adspecies and the support takes place. It has been shown that the sign of the charge transfer is determined by the relative position of the adatom frontier orbitals with respect to the gap edges and/or the Fermi level of the supported film and that there is a coupling between the charge state of the adsorbate and the polaronic distortion of the film [18–22]. The importance of this charge transfer is reflected in the adatom-substrate and adatom-adatom interactions. This has a potentially significant effect on the adspecies morphology, with important consequences related to their catalytic properties. For this reason, transition and noble metal atoms have formed the focus of most studies [23–26], particularly within the context of single atom catalysis [27]. When adsorption of early transition metal or simple metal atoms is considered, a distinct situation arises. The charge state of the adsorbate is large and may be comparable with that of its corresponding oxide. These adsorbate systems, when ordered, should be considered as ternary 2D oxides with no equivalent in the bulk.

It is in this context that the present paper focuses on the model ternary system Ba$_3$Ti$_2$O$_3$ obtained by the deposition of Ba adatoms on (2 × 2) Ti$_2$O$_3$ honeycomb ultrathin film grown epitaxially on a Au(111) substrate [12,28]. This system is to some degree related to BaTiO$_3$ ultrathin films, which are currently the subject of intense activity [29–33]. However our Ba$_3$Ti$_2$O$_3$ system differs significantly due to its variable stoichiometry, and its distinct structure and electronic properties displayed for $x \leq 2/3$, which we have studied through scanning tunneling microscopy (STM), first principles modeling, and Monte Carlo (MC) simulations.

The paper is organized as follows. A description of the experimental and theoretical methods is given in Sec. II. The next part (Sec. III A) describes our STM results and ab initio modeling of isolated Ba adatoms on the bare Ti$_2$O$_3$/Au(111) substrate. We then calculate in Sec. III B the energetics of Ba-Ba interactions, followed by a section (III C) comparing STM images with MC simulations of Ba coverages up to the experimentally observed saturation limit of 2/3. The results of the calculations of the electronic structure of the Ba$_3$Ti$_2$O$_3$ system are presented in Sec. III D. A discussion follows (Sec. IV) before the conclusion.
II. METHODS

The present study makes use of STM measurements, first principles calculations, and MC simulations. These are described individually in the following three sections.

A. Experimental methods

The experiments were carried out in a JEOL JSTM4500xt instrument, operating at UHV base pressure of $10^{-8}$ Pa. Mica-supported Au(111) single crystals (Agilent Technologies, UK) were used as the substrates. The Au(111) surfaces are first Ar$^+$ ion sputtered and then UHV annealed for 1.5 hours at 600 °C which results in the familiar herringbone reconstruction. Ti is deposited onto the reconstructed Au substrates from an electron beam evaporator (Oxford Applied Research EGN4) and the samples are then annealed at 600 °C in an O$_2$ atmosphere of $10^{-6}$ Pa. This gives rise to epitaxial (2 × 2) Ti$_2$O$_3$ honeycomb ultrathin films as described in detail in Ref. [12]. Ba deposition is then performed from a getter wire (SAES Getters S.p.A.) installed in a dedicated Ba evaporation system that is further described in Refs. [28] and [34]. The samples are then annealed in UHV at 600 °C for 40 minutes, so that ordered Ba structures are created. STM imaging is carried out at room temperature in constant current mode using electrochemically etched W tips with the bias voltage applied to the sample. The Ba coverage is calculated by examining the STM images and counting the number of Ba adatoms occupying the threefold hollow sites of the honeycomb Ti$_2$O$_3$ structure. Full Ba coverage (1 monolayer (ML)) is defined as full occupation of all the hollow sites of the honeycomb structure.

B. Ab initio computational details

The computational part of the study relies on a plane waves density functional approach, with gradient-corrected PW91 exchange-correlation functional [35], and the projector augmented wave method [36] implemented in VASP [37]. The Ti$_2$O$_3$/Au(111) support is represented by a slab composed of four atomic Au layers with a Ti$_2$O$_3$ layer adsorbed on one side only. Periodic slab images are separated by at least 11 Å of vacuum, and dipole corrections are used to eliminate the remaining spurious interactions. The experimental gold lattice parameter of 4.08 Å is systematically used in the calculations. Atomic positions of Ba adsorbates of all ions in the Ti$_2$O$_3$ film and of the Au surface atoms are fully optimized, while the remaining Au atoms are relaxed only in the direction normal to the surface (threshold on forces = 0.01 eV/Å). Fine calculations on structural and electronic characteristics of the 1/3 ML coverage are performed with a (2$\sqrt{3}$ × 2$\sqrt{3}$R30°) surface unit cell and fine (6 × 6 × 1) Monkhorst Pack sampling of the Brillouin zone. With these settings the Ba adsorption energy converges to within 0.01 eV/Ba. Simulations of model ordered configurations for a wide range of Ba coverages from 1/12 to 1 ML are performed to estimate the Ba-Ba effective interactions, and these are performed in a larger (4$\sqrt{3}$ × 4$\sqrt{3}$R30°) surface unit cell with a (1 × 1 × 1) Monkhorst Pack grid. Atomic charges are estimated according to Bader’s prescription [38,39].

C. Monte Carlo simulations

The energetics of Ba adsorption and Ba-Ba interactions are mapped onto a lattice gas model of the form

$$E = \frac{1}{2} \sum_{i,j} J_{ij} n_i n_j. \quad (1)$$

The sites $i$ represent the Ba adsorption sites, i.e., the hollow sites of the honeycomb structure. The sum of pair interactions is restricted to first, second, and third neighbors, with respective values $J_1$, $J_2$, and $J_3$. Occupation numbers $n_i$ are either 0 or 1.

Standard importance sampling MC simulations are carried out at given parameter values $k_B T / J_1$, $J_2 / J_1$, and $J_3 / J_2$ and constant Ba concentrations on a two-dimensional hexagonal lattice of 36 × 36 sites with periodic boundary conditions. The Metropolis algorithm is applied to trial exchanges between filled and empty sites, with 500 000 Monte Carlo steps per site. Neglecting the first 10% of the steps in each run, the average numbers $\overline{N}_1$, $\overline{N}_2$, and $\overline{N}_3$ of first, second, and third neighbors around each occupied site are evaluated and snapshots of the final configurations are kept.

III. RESULTS

A. The Ti$_2$O$_3$ monolayer and adsorption of single Ba adatoms

Figure 1(a) shows an STM image of the clean (2 × 2) Ti$_2$O$_3$ lattice grown on Au(111) as described in Ref. [12]. Ti atoms appear bright in the STM image and form a honeycomb pattern where the O atoms sit on the bridge sites between

![STM image of the bare honeycomb Ti$_2$O$_3$ monolayer on Au(111)](image)

![STM image of a single Ba atom adsorbed on the honeycomb lattice](image)

![Top view ball and stick representation of a single Ba atom adsorbed on the Ti$_2$O$_3$/Au support](image)
two neighboring Ti atoms. This structure is similar to the
$k$-TiO$_2$/Pt(111) phase previously reported [40]. However, in
the present case the Ti$_2$O$_3$ lattice is fully commensurate with
a (2 × 2) Au(111) surface unit cell.

Additional information is provided by *ab initio* calculations
for the experimentally determined registry of the Ti$_2$O$_3$
film with respect to the Au (111) surface. It is found that the
Ti$_2$O$_3$ film develops significant rumpling $δ_{CTi-O} \sim 0.70$ Å, with
the anions relaxing outwards and the cations approaching the
Au(111) surface. This rumpling is much larger than in the un-
supported film (0.28 Å) and likely arises from the in-plane
compression of the oxide film, necessary for maintaining the
preferential registry with Ti in hollow sites at the interface.
Indeed the strong adsorption energy of the oxide layer on
the gold surface (3.8 eV/Ti$_2$O$_3$) enforces pseudomorphism
at the interface. This is associated with significant electron
transfer towards the gold support (0.94 electrons per Ti$_2$O$_3$
unit) and an increase of the work function of the surface
by about $ΔW \sim 0.40$ eV. In the unsupported film, the cations
bear a magnetic moment of about 0.7 $μ_B$, suggesting a formal
Ti$^{3+}$ oxidation state, consistent with the Ti$_2$O$_3$ stoichiometry.
When the film is supported on the Au(111) substrate, these
magnetic moments are entirely quenched, which is in line
with the increased positive charge of the film.

Figure 1(b) is an STM image of a single Ba adatom
occupying the hollow site of the honeycomb Ti$_2$O$_3$ structure.
The Ba atom is not mobile on the surface over multiple STM
scans indicating a strong chemical bond between the Ba and
the hollow site. *Ab initio* calculations confirm that the Ba
atom located in the hollow site of the honeycomb lattice is
the energetically most favored atomic arrangement, with an
associated adsorption energy of $E_{ads}^0 = 6.22$ eV. Six Ba-O
bonds are formed with the neighboring anions [Figs. 1(c)
and (d)], with Ba-O bond lengths of 2.80 Å, close to those
obtained for bulk BaO in the rock-salt structure (2.81 Å).
Upon adsorption, the Ba adatoms become fully oxidized. From
Bader analysis ∼1.65 electrons are transferred towards the
support, from which roughly one electron is accommodated
by the oxide film, and the remaining electrons by the Au(111)
substrate.

B. Energetics of Ba-Ba interactions from *ab initio* simulations

To determine effective Ba adatom-adatom interactions, a
variety of model ordered configurations were simulated with
various Ba concentrations and ordering. *Ab initio* modeling
enabled us to calculate the energetics of the different Ba
arrangements. Table I summarizes the Ba adsorption energies
$E_{ads}$ as a function of Ba coverage and also lists the changes
in adsorption energy $ΔE_{ads}$, with reference to the lowest
Ba coverage under consideration ($x = 1/12$ ML). Table I
also gives the first $N_1$ (Ba-Ba distance 5.76 Å), second
$N_2$ (Ba-Ba distance 9.98 Å), and third $N_3$ (Ba-Ba distance
11.52 Å) neighbor coordination numbers for the different
configurations.

Assuming that the change of adsorption energy $ΔE_{ads}$ (per
Ba adatom) due to interaction between the adsorbates can be
written as

$$ΔE_{ads} = \frac{1}{2} [N_1 J_1 + N_2 J_2 + N_3 J_3],$$

with $J_{1,2,3}$ the first-, second-, and third-neighbor effective
Ba-Ba interactions, respectively, the data reported in Table I
provide an estimate of $J_{1,2,3}$. Moreover, since at low coverage
(1/6 ML) we have considered three different configurations
(A, B, C) with Ba adatoms only in respectively first-, second-, and third-neighbor positions, we can extract separately the low
coverage ($x = 1/6$) values of $J_{1,2,3} = 0.46, 0.09$, and 0.06 eV,
and the high coverage ($1/2 \leq x \leq 1$) values of $J_{1,2,3} = 0.39,
0.09$, and 0.06 eV. We note that, while $J_2$ and $J_3$ vary very
little with $x$, $J_1$ is noticeably reduced at higher coverage.
The best fit across the range of configurations we have considered
is achieved with $J_1 = 0.43$ eV, $J_2 = 0.09$ eV, and $J_3 = 0.06$
eV. This results in values of $J_2/J_1 = 0.21$ and $J_3/J_2 = 0.667$.

C. STM and MC structural determination of Ba$_x$Ti$_2$O$_3$/Au

The structure of the Ba$_x$Ti$_2$O$_3$ films on Au(111) was
investigated through a combined STM and MC approach.
Figure 2 shows a series of six STM images (upper panels)
of the Ba adatom distributions for coverages ranging from
low values of $x = 0.07$ up to close to the maximum observed
coverage of $x = 0.62$. STM images for coverages exceeding
$x = 2/3$ indicate that a completely different type of atomic
ordering takes place where Ba no longer adsorbs on the
Ti$_2$O$_3$ honeycomb hollow sites. For this reason our analysis
is restricted to Ba coverages of $0 < x < 2/3$.

The lower panels in Fig. 2 show MC snapshots at the
same coverages as indicated in the STM images. In order
to obtain the best agreement between the experimental STM
images and the MC snapshots, certain values of the MC
parameters $k_BT/J_1$, $J_2/J_1$, and $J_3/J_2$ had to be selected.
The calculations showed that reproducing the STM images
over the full range of coverages implied strong constraints
on the fitting parameters. The best agreement was obtained
for $k_BT/J_1 = 0.1 - 0.2$, $J_2/J_1 \approx 0.666$, and 0.2 $< J_2/J_1 < 0.25$. These results strikingly confirm the validity of the $J_1,$
$J_2$, and $J_3$ values extracted from the independent *ab initio*
calculations (see Sect. III B).

Taking into account the experimental value for the an-
nealing temperature $T = 600^\circ$C, the snapshots shown in
Fig. 2 were obtained for $k_BT/J_1 = 0.17$, $J_2/J_1 = 0.21$, and
$J_3/J_2 = 0.666$, which are very close to the *ab initio*


\[ \begin{array}{cccccc}
\hline
x & E_{ads} (eV/Ba) & ΔE_{ads} (eV/Ba) & N_1 & N_2 & N_3 \\
\hline
1/12 & 6.22 & -0.00 & 0 & 0 & 0 \\
1/6 A & 5.99 & -0.23 & 1 & 0 & 0 \\
1/6 B & 6.13 & -0.09 & 0 & 2 & 0 \\
1/6 C & 6.14 & -0.08 & 0 & 0 & 3 \\
1/3 & 5.97 & -0.25 & 0 & 6 & 0 \\
1/2 & 5.56 & -0.66 & 2 & 2 & 6 \\
2/3 & 5.27 & -0.95 & 3 & 6 & 3 \\
1 & 4.91 & -1.31 & 6 & 6 & 6 \\
\hline
\end{array} \]
predictions. As is clear from Fig. 2, the MC simulations account qualitatively well for the Ba atom distributions which are observed experimentally. At very low coverage ($x = 0.07$), randomly distributed Ba atoms are observed on the surface. With increased Ba deposition ($x = 0.29$), the configurations with first nearest neighbor (1nn) atoms are strongly suppressed, confirming 1nn repulsion, i.e., $J_1 > 0$. Aside from small thermal fluctuations, two ordered phases are found at $x = 1/3$ and $2/3$, with the same $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ unit cell with respect to the gold surface. At $x = 1/3$, all second nearest neighbor (2nn) sites of a given Ba atom are occupied by another Ba atom, and all 1nn sites are empty. Empty and filled sites are interchanged in the $x = 1/3$ and $x = 2/3$ configurations. For coverages intermediate between $1/3$ and $2/3$ ($x = 0.35$, $0.43$, and $0.49$), the 1nn sites start to become occupied as well as the 2nn sites. This results in a disordered phase with a labyrinthlike pattern. Similar configurations have been found in other contexts, for example, in some 2D magnetic structures [41,42].

More quantitatively, Fig. 3 displays a comparison between the MC simulation results and an experimental measurement of the mean number of occupied 1nn and 2nn sites, $N_1$ and $N_2$, respectively, as a function of Ba coverage. $N_1$ is close to zero up to $x = 1/3$ and then increases monotonically, while $N_2$ presents two maxima at $x = 1/3$ and $x = 2/3$ and a minimum for $x \approx 1/2$. Such very good quantitative agreement between experiment and simulation shows that the theoretical analysis encompasses all the critical microscopic mechanisms that form the basis of the Ba-Ba interactions on the $\text{Ti}_2\text{O}_3/\text{Au}(111)$ substrate.

### D. Electronic structure of $\text{Ba}_x\text{Ti}_2\text{O}_3/\text{Au}$ from ab initio simulations

Table II summarizes the evolution of the main structural and electronic characteristics of the $\text{Ba}_x\text{Ti}_2\text{O}_3$ ordered configurations ($x = 0$, $1/3$ and $2/3$), as determined from ab initio calculations. Regardless of the coverage, Ba adatoms transfer their electrons towards the support, giving rise to a positively charged $\text{Ba}_x\text{Ti}_2\text{O}_3$ film. The Ba positive charge slightly decreases as $x$ grows, tending towards values comparable with either bulk BaO (+1.45) or bulk BaTiO$_3$ (+1.52). The overall positive charge density of the films increases rapidly with $x$, and the negative charge density of the Au substrate increases proportionally.

The $\text{Ti}_2\text{O}_3$ film rumpling $\delta_{\text{Ti-O}}$ also displays a strong variation as a function of $x$. Starting from a large positive value at $x = 0$, $\delta_{\text{Ti-O}}$ increases in a quasilinear way with coverage, which correlates with the quasilinear increase of the total substrate charge density.

The combined effect of the interfacial charge transfer and of the Ti-O rumpling leads to large modifications $\Delta W$ of the...
work function of the bare Au support. While positive at \( x = 0 \), \( \Delta W \) becomes negative and its absolute value increases with \( x \).

### IV. DISCUSSION

We have shown that the ternary oxide ultrathin films consisting of \( \text{Ba}_x \text{Ti}_2 \text{O}_3/\text{Au}(111) \) display flexible structural and electronic characteristics which can be finely tuned through control of the Ba coverage \( x \). The structural configurations are determined by the strength and range of the effective Ba-Ba repulsion induced by the oxidation of Ba upon deposition. From the \( J_{1,2,3} \) values determined by \textit{ab initio} calculations, as well as the values yielding the best agreement between MC simulations and STM images, the Ba-Ba interactions appear to be noticeably screened by the substrate. The \( J_{1,2,3} \) values (\( J_1 = 0.43 \) eV, \( J_2 = 0.09 \) eV, and \( J_3 = 0.06 \) eV) scale roughly as the inverse third power of nearest neighbor site distances (\( d_1 = 5.76 \) Å, \( d_2 = 9.98 \) Å, \( d_3 = 11.52 \) Å), which is typical of dipole-dipole interactions, rather than as the inverse of atomic distances, which would be expected from unscreened Ba-Ba Coulomb repulsion. The strong electron transfer between the Ba adatoms and the support, which occurs upon adsorption, is responsible for this effect, since it results in a negative charge in the support, which counterbalances the positive charging of the Ba adsorbates.

While strong enough to stabilize the two ordered phases at \( x = 1/3 \) and \( x = 2/3 \), these interaction values do not succeed in overcoming the entropy term associated with thermal disorder in the labyrinth configurations when \( 1/3 \leq x \leq 2/3 \) and in particular at \( x = 1/2 \). As shown in Fig. 4(b), by keeping the same \( J_2/J_1 \) and \( J_3/J_2 \) ratio values but lowering the temperature (\( k_B T/J_1 = 0.02 \) instead of 0.17), an ordered phase is found at \( x = 1/2 \) which consists of stripes in which each atom has two 1nn, four 2nn, and two 3nn. Small portions of such stripes may be recognized in the labyrinth patterns obtained when \( 1/3 < x < 2/3 \) in Fig. 2. It is interesting to note that longer range interactions would also induce an ordered stripe phase at \( x = 1/2 \) [Fig. 4(c)], but with a periodicity different from the previous one, Fig. 4(b). The configuration shown in Fig. 4(c) was obtained with the same \( k_B T/J_1 = 0.17 \) value as the labyrinth phase, Fig. 4(a), but with effective unscreened Ba-Ba repulsions, decreasing as the inverse of distances (\( J_2/J_1 = 0.57 \) and \( J_3/J_2 = 0.87 \)). In the ordered regions of this phase, each atom has three 1nn, two 2nn, and two 3nn. Due to the increased relative weight of 2nn and 3nn interactions, 1nn occupation is less inhibited and 3nn occupation more heavily penalized, compared to the stripe phase obtained with effective dipole-dipole interactions. This discussion highlights the structural flexibility present in this ultrathin film, which can be engineered through stoichiometry, temperature, or support control.

From the point of view of electronic properties, the various ordered phases also display very different characteristics. In particular, the presence of the oxide film, with or without Ba adatoms, strongly modifies the Au work function \( W \), with expected consequences on the film reactivity. While the presence of the bare Ti2O3 film increases \( W \), further deposition of Ba adatoms lowers it substantially and in a quasilinear way with respect to \( x \). On general grounds, it is well established that the change of work function due to the presence of an oxide ultrathin film on a metal has three contributions which come from the compression of the metal electrons at the interface (negative contribution), the interfacial charge transfer, and the change in the oxide film rumpling [43–45]. In the present case, the large Au electronegativity always results in interfacial electron transfer from the film towards the support, which lower \( W \), while the oxide film rumpling with the oxygen moving outwards increases \( W \).

In the bare Ti2O3 film, the rumpling is very large (0.7 Å) due to the strong binding to the gold surface which induces large epitaxial compressive strains. Its associated dipole overcomes the charge transfer and electron compression dipoles, which results in a positive \( \Delta W \). A similar situation was discussed in relation to the Moiré pattern produced by MgO islands on Au(111) [46].

At variance, in the Ba,Ti2O3 films (\( x \neq 0 \)), increasingly large electron transfer to the support takes place as more and more Ba is deposited. Via the electrostatic coupling mechanism by which the electrostatic field exerted by this interfacial dipole distorts the film in such a way as to produce an opposing dipole [47,48], the film rumpling increases, but not enough to counterbalance the large negative contribution to \( \Delta W \) of the charge transfer.

### V. CONCLUSION

Ternary oxide Ba,Ti2O3 ultrathin films with variable Ba coverage \( x \) were created on Au(111) substrates and studied using an approach involving both experiment and theory. STM was able to provide experimental evidence of the film structure, and first principles calculations and MC simulations accurately

<table>
<thead>
<tr>
<th>( x )</th>
<th>( Q_{Ba} ) (e)</th>
<th>( \sigma_{Ba} ) (e/Å²)</th>
<th>( z_{Ba} ) (Å)</th>
<th>( \delta_{TiO} ) (Å)</th>
<th>( \Delta W ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-8.2</td>
<td>+0.70</td>
<td>+0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/3</td>
<td>+1.61</td>
<td>-15.0</td>
<td>3.77</td>
<td>+0.79</td>
<td>-1.5</td>
</tr>
<tr>
<td>2/3</td>
<td>+1.55</td>
<td>-21.3</td>
<td>3.68</td>
<td>+0.86</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) Comparison of MC configurations at \( x = 1/2 \) obtained with different sets of parameters: (a) \( k_B T/J_1 = 0.17 \), \( J_2/J_1 = 0.21 \), and \( J_3/J_1 = 0.666 \); (b) \( k_B T/J_1 = 0.02 \), \( J_2/J_1 = 0.21 \), and \( J_3/J_1 = 0.666 \); and (c) \( k_B T/J_1 = 0.17 \), \( J_2/J_1 = 0.57 \), and \( J_3/J_2 = 0.87 \) (see text).
modeled the results. Depending on \( x \) several ordered phases were identified as well as a disordered labyrinthlike phase. The structural evolution as a function of \( x \) is rationalized using a lattice gas model with first-, second-, and third-nearest-neighbor Ba-Ba repulsive interactions \( J_{1,2,3} \). MC simulations using \( J_{1,2,3} \) values produced by the first principles calculations show an excellent agreement with STM images at all coverages \( (0 \leq x \leq 2/3) \).

The physics underlying the structural characteristics of these films is driven by the charge transfer which occurs between the electropositive Ba atoms and the highly electronegative support. This gives rise to interfacial dipole moments which result in effective dipole-dipole Ba-Ba interactions, whose range is a key factor in understanding the Ba ordering. The dipoles also induce an increasingly large film rumpling with increasing \( x \), through an electrostatic coupling mechanism. An efficient reduction of the gold work function with increasing \( x \) results. This will significantly affect the film reactivity. Our results suggest that, due to their structural and electronic flexibility, these ultrathin films are promising materials for various types of applications related to adsorption and reactivity, or as patterned supports for the growth of size-selected clusters.

**ACKNOWLEDGMENTS**

We acknowledge support from the COST Action CM1104 *Reducible oxide chemistry, structure and functions*, from the CNRS-Oxford collaboration scheme, from the John Fell OUP research fund, and from the EPSRC.

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