

Monte Carlo simulation of growth of binary bcc structured layersRui-Qiang Zhang,¹ Xiao-Hong Xu,^{1,*} Shun-Yan Zhang,¹ and Gillian A. Gehring²¹*School of Chemistry and Materials Science, Shanxi Normal University, Linfen, Shanxi 041004, People's Republic of China*²*Department of Physics and Astronomy, The University of Sheffield, Hicks Building, Sheffield S3 7RH, United Kingdom*

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Pulsed laser deposition is a very promising experimental technique for growing layers of nanoscale thickness. In this paper, the growth of a perovskite structured film grown on a perovskite substrate is simulated using the Monte Carlo procedure and LaMnO_3 is taken as an example. In the model, we consider the motion of the La and Mn atoms, and assume the oxygen atoms follow the metal atoms. The quality of the film is controlled by three parameters: namely, the temperature of the substrate, the kinetic energy of the atoms, and the average coverage of each pulse. The simulated results show that the quality of the films is strongly dependent on the three parameters. We analyzed the composition of the films layer by layer and find an interesting phenomenon: if the deposition conditions are not optimal, the fraction of wrong atoms (fractional mismatch) presents odd-even staggering as the number of deposited atom layers increases.

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I. INTRODUCTION

Pulsed laser deposition (PLD) is used increasingly to grow thin oxide films,¹ which play an important role in the development of different materials and devices.^{2,3} It is suitable for the growth of complex materials because it reflects the stoichiometry of the target in the films well, and gives good adhesion between the layer and the substrate. These properties result mainly from the fact that atoms have a large kinetic energy (0.1–100 eV) when they impinge on the substrate, which promotes an increase in the diffusion rate of atoms on the surface.^{4–7} In PLD, the target material is ablated by a pulsed laser and then deposited in pulses on a substrate so that many atoms arrive at the surface simultaneously. Experimentally, each pulse lasts for a few nanoseconds and the time between two pulses is of the order of seconds. PLD is often used for oxides such as perovskites and the oxygen stoichiometry is controlled by the introduction of molecular oxygen into the growth chamber.

Some experimental and theoretical works have given strong evidence showing the superiority of PLD for layer-by-layer growth.^{8–12} Jenniches *et al.*¹⁰ observed that in some cases PLD leads to smoother surfaces than molecular beam epitaxy (MBE) for metallic layers. Blank *et al.*⁸ have shown that it is possible with PLD to impose a single level two-dimensional (2D) growth mode (or layer-by-layer growth mode) for SrTiO_3 by depositing every unit-cell layer at a very high deposition rate followed by a relaxation interval. It is usually found that the best oxide films are obtained for a narrow window of the deposition parameters.

Several papers have been devoted to the atomistic models of thin layer growth by PLD.^{12–18} Xu *et al.* simulated the growth of an elemental film and showed that the optimum conditions for a smooth film were obtained with a low substrate temperature, a low kinetic energy and suitable number of atoms per pulse. The Monte Carlo method has been used to simulate the grain growth and microstructure of polycrystalline system.^{19,20}

Very few papers reported the simulation of the growth of films containing two elements by the kinetic Monte Carlo

(KMC) method. Pyziak and co-workers^{6,7} simulated the CdTe layers growth on CdTe and Si substrates but they found that their films were randomized after a few (~ 5) layers.

In this paper, we simulate the growth of the perovskite LaMnO_3 on a LaMnO_3 substrate. In a single LaMnO_3 body-centered unit cell, La atoms lie in the body center site and Mn atoms occupy its eight vertices. Oxygen ions lie on the midpoint of the cube edges. This means that in the perfect structure MnO_2 and LaO layer alternate. We have chosen to simulate the arrival and diffusion of the Mn and La ions, and assumed that the oxygen ions will fit in between the heavier metal ions. It is a challenge to simulate such a material because, in any laser pulse, equal numbers of Mn and La ions arrive together. The perfect crystal has alternate planes that are occupied by either Mn or La so in each layer one of the species of ions should stay mobile and not get trapped in the “wrong” layer. We show explicitly why there is a competition between different effects that gives the most perfect films. The simulations provide a real understanding to the processes that occur.

II. MODEL OF FILM GROWTH

We use the kinetic Monte Carlo approach to study the film growth by PLD. The model treats a given number of atoms arriving in a pulse and all of the atoms on the surface diffuse by random hopping. The diffusion time is a strong function of the substrate temperature and the incident kinetic energy of the atoms. The atoms lose energy to the lattice^{18,21} and can be bound to favorable sites. Once they are buried (i.e., have an atom present in the site that is directly above them) their motion is not considered further. Blank *et al.*⁸ considered the interchange of a La and a Mn ion. This is an additional effect that has not been included here and leads to even better film quality. The model is controlled by three parameters: namely, the temperature of the substrate, T , the initial kinetic energy of the atoms, E_k , and the average coverage of each pulse N . The kinetic energy of the atoms as they arrive can be controlled experimentally as it depends on the separation of the target and substrate, and the amount of gas in the chamber.

The atoms from each pulse are instantaneously deposited at random sites on a $D \times D$ LaMnO₃ substrate; most of the results presented here were done for $D=50$ but simulations were done for other lattice sizes to check if our results were affected by finite-size effects. Periodic boundary conditions were imposed on the lattice. We assumed that an adsorbed atom is not stabilized until it is situated in a site where it has four nearest neighbors (NN) in the layer below, with which it forms bonds,²² otherwise the atom would select an empty site in the layer below according to the principle of lowest energy. An atom on the surface may have four next-nearest neighbors in the same layer. A free atom may diffuse on the surface by jumping at random in the x or y directions to a neighboring empty site in the same layer, or jump up to an empty site in the layer above provided that the new site is more favorable.

In the Monte Carlo method, the surface diffusion of atom is dependent on the probability of an atom jumping from one site to another one. This hopping rate is assumed to satisfy the Arrhenius relation $P_h = \nu_0 \exp(-E_{\text{eff}}/k_B T)$, where the vibration frequency is $\nu_0 = 2k_B T/h$ (assumed to be $10^{13}/\text{s}$), k_B is the Boltzmann constant, and T is the surface temperature. The effective barrier height is the difference between the actual barrier height, E_D , and the extra energy of the particle due to its kinetic deposition energy, $E_{\text{eff}} = E_D - E_K$. A significant value of E_K means that the adsorbed atom is in high vibrational state. Tunneling, rather than ballistic motion, occurs because in all cases $E_D - E_K > 0$. A particle may move to a neighboring site in the same plane but if the neighboring site is occupied, it can move up a step to the next layer. The values of these potential energies were calculated by the method suggested in Ref. 23. The interatomic potential between Mn and La atoms is taken to be 0.35 eV, between La-La is equal to 0.24 eV, and that for Mn-Mn is 0.25 eV. These are effective parameters because the oxygen atoms have been missed from our model and, in the actual film of LaMnO₃, there would be oxygen ions between the metal ions. In our case, the interaction energy between second neighbors, E_2 , is set to a quarter of the value of the corresponding E_1 .

In our model,¹⁸ the atoms transfer their kinetic energy to the substrate locally. We assume that the energy decays with time as

$$E_k(t) = E_k e^{-\Lambda t}, \quad (1)$$

where Λ is the decay constant and the characteristic time is the attempt frequency $\nu_0 = 10^{13} \text{ s}^{-1}$. We assume that a particle is most likely to lose energy to lattice vibrations when it is making a hop from one lattice site to another. This leads to an estimate,

$$\Lambda = \nu_0 e^{-E_{\text{av}}/K_B T}. \quad (2)$$

The energy E_{av} is a typical value of the barrier height. In our simulations we took $E_{\text{av}} = 2 \text{ eV}$, which leads to a value of $\Lambda \sim 10^2 \text{ s}^{-1}$. If we take the value of $E_{\text{av}} = 1 \text{ eV}$, we find a correspondingly larger value of Λ close to 10^7 s^{-1} . We found that the results were almost independent of the size of Λ provided that $\Lambda > 1$, which corresponded to a value of $E_{\text{av}} < 2.3 \text{ eV}$. Hence we are confident that our crude estimate of

the decay does not seriously impair our results. In an earlier work²¹ it was assumed that the particle kept all its kinetic energy for an initial time of 5 ps and then lost it all.

It is also possible to consider desorption, which occurs if the kinetic energy of the incident atoms is larger than the binding energy of the atoms to the substrate. We do not consider incident kinetic energies that are large enough for this to occur with any appreciable probability.

The laser pulses once each second and the Monte Carlo procedure is applied 100 times between pulses; hence the time between Monte Carlo sweeps is $t_0 = 10^{-2} \text{ s}$. In a given sweep each atom may or may not make a move so the maximum number of moves that any atom may make in the time between pulses is 100. However a given atom may continue to move for several seconds. At each step the hopping rate, $P_h = \nu_0 \exp(-E_{\text{eff}}/k_B T)$, is evaluated for each atom that does not have another atom directly above it. The kinetic energy that is used to evaluate E_{eff} is determined using Eqs. (1) and (2) where time is taken as the time since that particular atom was deposited. The dimensionless quantity $p_0 = t_0 P_h$ determines the likelihood of an atom moving. The probability that an atom has made a move in time t_0 is given by

$$f(t_0) = 1 - e^{-p_0}. \quad (3)$$

If $p_0 > 1$ we assume the atom moves, $f(t_0) = 1$, to a site that is chosen at random if more than one site is available; if $p_0 < 1$ then the atom is assumed to move only if $p_0 > r$, where r is a random number $0 < r < 1$. After a given Monte Carlo cycle, the kinetic energy is updated according to Eq. (1) and the process is repeated until the 100 cycles are complete. At this point another pulse of atoms arrives and the procedure is repeated.

The chemical composition of the layer was characterized by introducing the fractional mismatch of the layer parameter C_L defined as: $C_L = N_{\text{La}}/N_T = N_{\text{Mn}}/N_T$, where N_{La} and N_{Mn} are the numbers of Lanthanum atoms in a Mn Layer, and the number of Manganese atoms in a La layer, respectively, and $N_T = D \times D$ represents the total number of atoms in a layer. The parameter C_L indicates the mismatch of the deposited Mn or La layers; for a deposition such that sufficient atoms have been deposited to complete ten layers, i.e., a ‘‘ten layer film,’’ we calculate the average value of C_L (C_{av}) averaged over eight layers in which the simulation starts with a perfect layer. If the deposition conditions are far from optimal ones, the value of the mismatch increases with thickness, as was found for CdTe.^{6,7} However for the best conditions, it remains at a low value for all layers. In principle we should allow for the possibility that a given layer contains vacancies; however in our model this has a much higher energy than a wrong atom and so does not occur.

III. RESULTS AND DISCUSSION

The simulations were performed to find the deposition parameters that gave the best films with the least number of defects. We considered the following variables: the temperature of the substrate ($T = 300 - 1000 \text{ K}$), the kinetic energy of the atoms as they arrive ($E_k = 0 - 1.2 \text{ eV}$), and the number of atoms in each pulse, expressed as the fractional coverage f

=0.1–1.3 C. In previous published papers, the substrate temperature was not considered by some authors^{13,14} and others¹¹ neglected the initial kinetic energy of the atoms. The average coverage of each pulse was considered by all previous authors as this is a characteristic feature of PLD. For each variable we find the values of the defect parameter C_L for the ten layers and also the average C_{av} . The best value of each parameter is chosen as that which minimizes C_{av} .

We considered ten layers as we expect that the results found for ten layers would be a good guide for thicker films. We found that the film quality depended strongly on the deposition parameters. The set of parameters that gave the most perfect films was termed the optimal set. If the conditions are not optimal, then the quality of the layers deteriorates rapidly after a few layers. For the optimal conditions the fraction of atoms in the wrong layers becomes essentially independent of the thickness. This means that a wrong atom in one layer does not automatically nucleate additional wrong atoms in the layers above it.

The homogeneity of the LaMnO_3 films depends strongly on the substrate temperature, as is shown in Fig. 1(a). It is important that the atoms have enough mobility so that they can move to their correct sites. When the substrate temperature is below 700 K, the hopping probability of the deposited atoms is too low to give good mobility so that most of the ablated atoms stay on the site where they first arrive on the film. In this situation the crystal has a high density of defects. When the temperature of the substrate is raised, the single atoms become more mobile so the film quality increases. Good self-organization phenomena occur for the substrate temperature higher than 700 K. The average of C_L is taken over the first eight layers in a ten layer film and is shown because the subsequent layers are not completed. The results are shown in Fig. 1(b). An odd-even staggering is very clear in the results, which are due to the fact that a unit cell covers two layers.

The homogeneity of the film also depends on the kinetic energy of the incident atoms, as shown in Figs. 2(a) and 2(b). When the kinetic energy lies within the range 0–0.8 eV, the value of C_{av} decreases for increasing values in the kinetic energy of the atoms, and then C_{av} increases with the increase in the value of E_k when E_k is higher than 0.8 eV and the film quality deteriorates rapidly when E_k is higher than 1.2 eV.

Finally we varied the numbers of atoms arriving in each pulse; this was expressed in terms of the average coverage from each pulse. We found that if f is low, $f < 0.2$ C, most of the Mn and La atoms stay on the same layer, which hinders

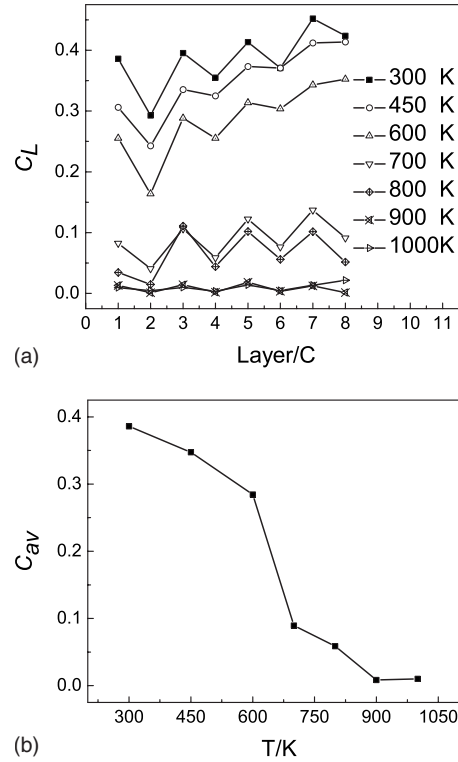


FIG. 1. The displacement parameter (a) C_L and the average displacement parameter (b) C_{av} as a function of the substrate temperature. Here, the incident kinetic energy is $E_k=0.8$ eV and the average coverage per pulse is $f=0.2$ C.

the MnO_2 and LaO alternate layer growth, as can be seen from Figs. 3(a) and 3(b). However, the value of C_{av} begins to increase after $f=0.2$ C, which can be understood that the motion of the atoms on the substrate is blocked when too many atoms are deposited simultaneously. Hence if we want to obtain both smooth and great homogeneity film, we need T higher than 700 K, E_k near to 0.8 eV, and f between 0.1–0.5 C, if possible. Combining these results and taking into account experiment conditions, we chose $T=900$ K, $E_k=0.8$ eV, and $f=0.2$ C as the optimal parameters.

We also looked at the way in which the values of C_L differed for the last layers that are not yet complete by calculating the values of C_L when A ($1 < A < 10$) layers had been deposited using the optimal parameter set defined above. The results are shown in Table I, which gives the results for $A=5, 6, 7, 8, 9$, and 10. Several interesting features are apparent from this table. First we see that the values

TABLE I. The displacement parameter C_L ($L=1-10$) for the coverage $A=5-10$ under the optimal parameters $T=900$ K, $E_k=0.8$ eV, and $f=0.2$ C.

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
A=5	0.0124	0.0012	0.0248	0.0249	0.5515					
A=6	0.0124	0.0012	0.0216	0.0048	0.1638	0.1494				
A=7	0.0124	0.0012	0.0216	0.0036	0.0216	0.0302	0.5439			
A=8	0.0124	0.0012	0.0216	0.0036	0.0188	0.004	0.1589	0.1739		
A=9	0.0124	0.0012	0.0216	0.0036	0.0184	0.0004	0.0172	0.0285	0.5319	
A=10	0.0124	0.0012	0.0216	0.0036	0.0184	0.0004	0.0148	0.0044	0.1501	0.1638

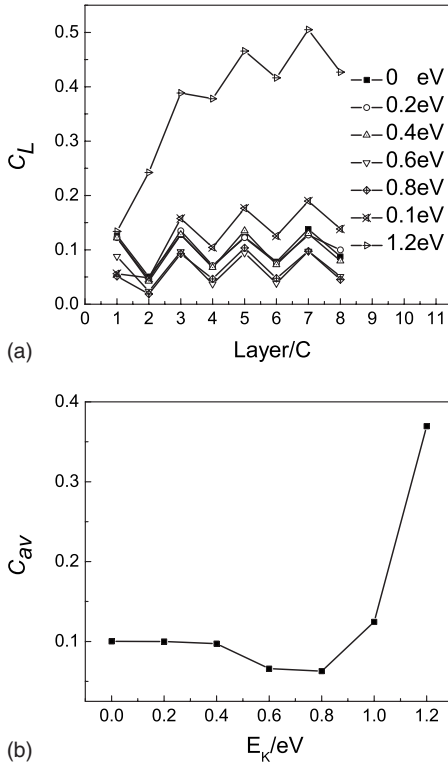


FIG. 2. The displacement parameter C_L and the average displacement parameter C_{av} as a function of the kinetic energy. Here, the substrate temperature is $T=800$ K and the average coverage per pulse is $f=0.2$ C.

of C_L are independent of the total number of layers, A , in the film provided that $L < A - 2$. Second we note that the values of C_L depend strongly on whether L is an even or an odd number. If A is odd, then the value of C_L ($L=A$) is very high (about 50%); however, if L is even, then the value of C_L ($L=A$) is less than 18%. We can see that the value of C_L for odd layer is always larger than that of next even layers in the film. The odd/even staggering is very clear here; the even layer corresponds to a situation in which the terminating layer consists of complete unit cells.

We have checked the sensitivity of the results to the lattice size by calculating C_{av} for the optimal parameter set. The results for $D=40, 50, 80,$ and 100 are shown in Table II. It is seen that the effect of changing the lattice size is within the errors. This confirms that the simulations run for all the other parameter sets for $D=50$ are reliable. We also checked for

TABLE II. The average displacement parameter C_{av} for the different substrate size of $D=40, 50, 80,$ and 100 , with coverage $A=10$, under the optimal parameters $T=900$ K, $E_k=0.8$ eV, and $f=0.2$ C.

Substrate size D	C_{av}
40	0.0082 ± 0.0006
50	0.0081 ± 0.0008
80	0.0083 ± 0.0006
100	0.0080 ± 0.0007

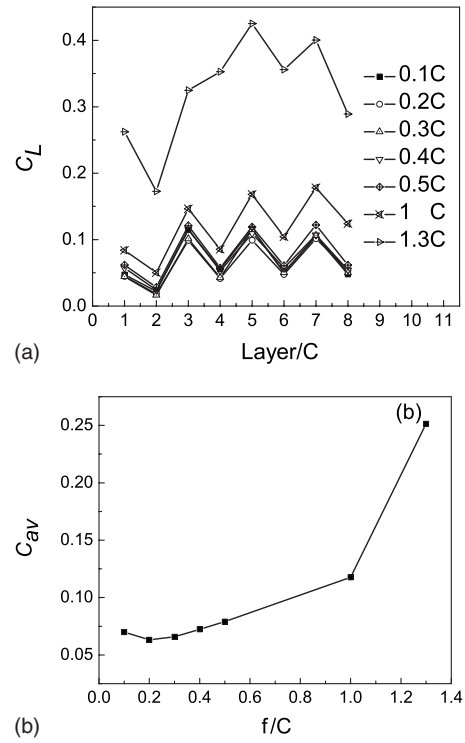


FIG. 3. The displacement parameter C_L and the average displacement parameter C_{av} as a function of the average coverage per pulse. Here, the substrate temperature is $T=800$ K and the incident kinetic energy is $E_K=0.8$ eV.

the dependence on the decay constant of the kinetic energy, Λ , by recalculating the values of C_L for the optimal parameter set. We found that there was no marked dependence on Λ unless it was less than one. We also simulated the growth of films of various thicknesses, $L=20, 30, 40,$ and 50 . The value of C_{av} for different highnesses using the optimal growth parameters is almost independent of L , as shown in Table III. We have confidence that the simulations that have run different conditions for ten layer films is representative of the films with any thickness.

In Fig. 4, we show the two-dimensional profile picture for deposition on substrates at $T=600$ K and $T=900$ K. This shows how the film quality deteriorates with thickness for the film grown on a substrate at 600 K. For the case of the optimal temperature, 900 K, the fraction of atoms in the wrong layers is very small and is essentially independent of the thickness.

TABLE III. The value of C_{av} for the different film thicknesses of $A=10, 20, 30, 40,$ and 50 , with substrate size $D=50$, under optimal parameters $T=900$ K, $E_k=0.8$ eV, and $f=0.2$ C.

Coverage	C_{av}
10	0.0081 ± 0.0008
20	0.0075 ± 0.0008
30	0.0065 ± 0.0005
40	0.0063 ± 0.0008
50	0.0063 ± 0.0007

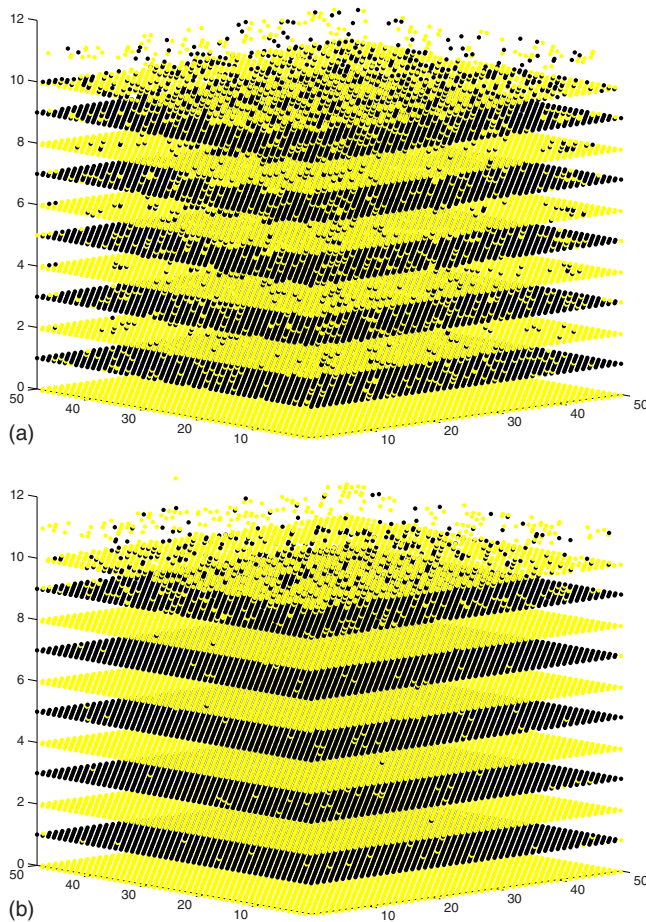


FIG. 4. (Color online) The simulated result at coverage $A=10$, $E_k=0.8$ eV, and $f=0.2$ C monolayers with the substrate temperature: (a) $T=600$ K and (b) $T=900$ K; the yellow dot represents the Mn atoms and the black dot represents the La atoms.

When the film is deposited at the optimal deposition conditions, it is a good example of self-organization during the film growth. This phenomenon results from the different bonding energies between different atoms. When a set of Mn and La atoms is deposited on the LaMnO_3 surface (we assumed that the substrate is terminated by Mn atoms), Mn and La atoms begin hopping on the surface and form the small islands. The hopping probability (P_h) of Mn atoms is higher than that of La atoms in the first layer because the attractive potential between La-Mn is higher than that of Mn-Mn (in our model). Most of La atoms that stayed in the first layer and meet each other form the small La atom islands. Mn atoms are more likely to jump up to the islands that are composed of La atoms, according to the principle of lowest

energy, and stay there to start forming the second layer. Then that process will be repeated and realize the self-organization growth: La atoms form an ordered layer on the top of a Mn layer and vice versa.

The results presented here were all done assuming that the allowed hopping time that appears in Eq. (3), t_0 , was 1 s—the time between pulses. However we repeated the calculations for $t_0=10^{-2}$ s and in this case found that the results for the optimal set of parameters was unchanged when the temperature of the substrate was changed to from 800 to 990 K. Therefore we believe that this procedure is valid, and changing the assumptions only changes the details of the optimal set of parameters and not the conclusions we made about self-organization.

IV. CONCLUSION

In this paper, we present the results of our simulation of a LaMnO_3 film deposited on a LaMnO_3 substrate. The substrate temperature, the kinetic energy of deposited atoms, and the average coverage of per pulse are all very important factors. The simulated results show that the ablated atoms are self-organized into a LaMnO_3 film provided that the deposition parameters lie in a special range. The parameters are reasonable and compare well with those normally used. The self-organization is due to the different interaction energy between different atoms, and can be explained by the principle of lowest energy. Another interesting phenomenon is that the displacement parameter C_L shows odd/even staggering, which can be explained by the fact that only even layers correspond to complete unit cells. The Monte Carlo simulations described here give a quantitative prediction on the range of the parameters of self-organization so our results would be a good guide for other PLD deposited films. The important result of our work is that, for optimized deposition parameters, very good quality films are obtained even without allowing for deposited atoms to interchange after they have initially come to rest.

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