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Ab initio study of early stage Nb growth on MgO(001)

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ABSTRACT

Using density functional theory calculations we have examined the effects of cluster shape and a neutral O vacancy on the energetics and stability of Nb monomers and clusters on the MgO(001) surface. The relative stability of different monolayer structures is also examined. As found in other cases of metal adsorbates on MgO(001), our results indicate that an O site is the preferred adsorption site for a Nb atom. In addition, O-vacancy sites tend to increase the binding energy of small clusters and thus act as nucleation sites, while the effect of a nearby O vacancy on the binding energy of a Nb cluster is much weaker. In particular, we find that the binding energy for a Nb monomer at an O site (O-vacancy site) is 1.5 eV (2.2 eV) while the corresponding activation barriers for Nb monomer diffusion are 0.58 eV (0.80 eV). We also find that, in the absence of O vacancies, the preferred planar structure for tetramers and pentamers is an isotropic (100)-like structure. In contrast, the presence of an O vacancy transforms the isotropic tetramer into an anisotropic (110)-like structure. In addition, due to strain effects as well as strong Nb–Nb interactions, for large clusters (e.g. a complete monolayer) the anisotropic (110) structure is favored over the (100) structure. These results appear to explain recent experimental observations for the dependence of thin-film orientation on deposition conditions. However, we also find that for small (100)-like and (110)-like clusters, three-dimensional (rather than planar) structures are energetically preferred due to the strong Nb–Nb interaction. These results suggest that the pathway to form a coherent (100) or (110) structure during the growth of Nb films on Mg(001) may be relatively complex.

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1. Introduction

Recent interest in superconducting radio frequency (SRF) technology has stimulated a variety of experiments on the growth of Nb thin films on various substrates, including MgO, Cu, and amorphous and crystalline sapphire [1–5]. In particular, because of the shallow penetration depth of RF fields, it has been suggested that the performance of SRF cavity-based particle accelerators might be enhanced by replacing bulk Nb with thin-film Nb. As a result it is important to gain a better understanding and control of the structure and properties of Nb thin films.

One system which has been studied extensively is the growth of Nb on MgO(001) which has been found [1–8] to exhibit a complex dependence on substrate temperature and deposition flux. In particular, using a vacuum arc discharge for Nb deposition, Krishnan et al. [1] have shown that the orientation of Nb films changes from an anisotropic (110) structure with two different but equivalent orientations at low temperatures, to a mixture of the (110) and (100) orientations at intermediate temperatures (~500 °C), while at higher temperatures (T \approx 700 °C) a purely (100) orientation is observed [1]. This result suggests that in the absence of grain boundaries the Nb(110) structure

may be the energetically preferred phase. On the other hand, because of the existence of two different but equivalent phases — which may lead to a high density of grain boundaries — the single-phase Nb(100) structure exhibits better superconducting properties [2,4].

In contrast, in the case of sputter deposition [3,4] at 600 °C it was found that the orientation in Nb/MgO(001) thin-films depends on the initial condition of the substrate as well as on deposition conditions. In particular, deposition on MgO substrates which were only *in situ* annealed tended to lead to (110) films [4], while the (100) orientation was favored when a freshly deposited thin (~2 nm) seed layer of MgO was grown onto the substrate using reactive sputtering. In addition, an increase in the Argon vapor pressure from 1 mTorr to 5 mTorr was found [4] to lead to a change in orientation from (110) to (100). This sensitive dependence on deposition parameters as well as on the initial surface treatment suggests that defects observed on the MgO surface [9,10] may play a role.

Since the lattice mismatch $\varepsilon = (a_{MgO} - a_{Nb}) / a_{MgO}$ is significant (11% for Nb(110)/MgO(001) and 21.6% for Nb(100)/MgO(001)) we expect that strain may also play an important role. In this connection, it is interesting to compare Ni/MgO(001) growth with Pt/MgO(001) growth. In contrast to Ni/MgO(001) for which (110) and (100) films are observed, both (111) and (100) Pt films are observed depending on growth conditions and film thickness [11–16], while the degrees of lattice mismatch are 16.4% (Ni) and 6.9% (Pt) for (100) structure. On the other hand, both Ag and Cu (with strains of 2.9% and 14.1%,









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respectively) simply exhibit a (100) structure on MgO(001) [11]. These experimental results suggest that the magnitude of the strain may not be sufficient by itself to explain the observed metal overlayer structures on MgO(001) surfaces. In this regard, we note that while an O site is the preferred adsorption site for all of the cases above, the metal–O interactions for Ni and Pt are much stronger [17–20] than for Ag and Cu, while Cu–O bonding also exhibits some degree of mixing of Cu 3d/4s and O 2p orbitals [22,21]. We also note that the cohesive energies of Ni and Pt are significantly higher than those of Ag and Cu. These results indicate that the relative strength of the metal–oxygen and the metal–metal interaction also plays a key role. A similar conclusion was drawn in Ref. [23].

Here we present the results of extensive density functional theory [24] (DFT) calculations of binding and adsorption energies for various sizes and shapes of mainly planar Nb clusters on the MgO(001) surface which we have carried out in order to understand the stability and energetics of both submonolayer two-dimensional (2D) islands as well as of single-layer Nb(100) and Nb(110) structures. We note that those small Nb clusters are representative 2D structures in order to have better understanding of the stability of 2D Nb(100) and Nb(110) structures formed at the Nb/MgO(001) interface presented in Refs. [3,4]. In our calculations, the effects of a neutral O vacancy were also examined. As found in other cases of metal adsorbates on MgO(001), our results indicate that an O site is the preferred adsorption site for a Nb atom. In addition, O-vacancy sites tend to increase the monomer and small cluster binding energies and thus act as nucleation sites, while the effect of a nearby O vacancy is much weaker. In particular, we find that the binding energy for a Nb monomer at an O site (O-vacancy site) is 1.5 eV (2.2 eV) while the corresponding activation barriers for Nb monomer diffusion are 0.58 eV (0.80 eV).

We also find that in the absence of O vacancies, for tetramers and pentamers an isotropic (100)-like structure is energetically favored. In contrast, the presence of an O vacancy transforms the isotropic tetramer into an anisotropic (110)-like structure. In addition, our DFT calculations indicate that for large clusters and/or a complete monolayer (ML), the anisotropic Nb(110) structure is more energetically favorable than the Nb(100) structure due to significant strain relaxation. This is consistent with experimental results for the case of energetic deposition [1], in which the (110) structure was observed at low temperature while the (100) structure was observed at high temperature.

This paper is organized as follows. In Section 2, we provide the details of our DFT calculations. In Sec. 3.1, we present our results for the binding energies and diffusion barriers for a Nb monomer on the MgO(001) surface along with an analysis of the density of states for Nb–O bonding. We then present results for the cases of Nb dimers, trimers, tetramers and pentamers in Sections 3.2 and 3.3, and discuss the stability of Nb(100) and Nb(110) ML structures in Section 3.4. Finally, we summarize our results in Section 4.

2. DFT calculation

In our DFT calculations, we have employed the Vienna ab initio simulation package (VASP) [25,26] with the projector-augmented wave (PAW) method [27]. Spin polarization effects were included, while relativistic effects are not considered. For Mg and Nb, the semicore p electrons were treated as valence electrons. The one-electron wave functions were expanded in a plane wave basis typically with an energy cutoff of $E_{cut} = 350$ eV. A higher value of $E_{cut} = 450$ eV was also used in some cases. However, our test results for Nb binding energy indicate that $E_{\text{cut}} = 350 \text{ eV}$ may be sufficient (see Table 1). For exchange and correlation, the Perdew-Becke-Ernzerhof (PBE) generalized gradient approximations (GGA) [28] was used. Our bulk calculations result in lattice constants of 4.25 Å and 3.32 Å for MgO and Nb, in good agreement with the experimental values $a_{MgO} = 4.21$ Å and $a_{Nb} = 3.30$ Å for MgO and Nb, respectively. The Monkhorst-Pack scheme [29] was used for **k**-point sampling, with a $5 \times 5 \times 1$ mesh, while higher k-point meshes were also used to check convergence. A change of the

Table 1

Binding energy (E_B), interlayer distance (d) between a Nb atom and its adsorption site, and the electron charge transfer $\Delta \rho_e$ to a Nb adatom. Here $d = 2.1^{\circ}$ (2.3^{Mg} or 2.14^{Mg}) represents the vertical distance between Nb and nearby O (Nb and nearby Mg), as shown in Fig. 1(a) and (c).

	$E_{\rm cut} ({\rm eV})$	E_B (eV)	d (Å)	$\Delta \rho_e \left(\mathbf{e} \right)$
O site—Fig. 1(a)	350	1.52	2.21	0.03
	450	1.52	2.21	
Mg site—Fig. 1(a)	350	0.32	3.05	0.03
	450	0.32	3.04	
Hollow site-Fig. 1(a)	350	0.94	2.1 ^o -2.3 ^{Mg}	0.06
	450	0.94	2.1 ⁰ -2.3 ^{Mg}	
O vacancy—Fig. 1(c)	350	2.19	2.14 ^{Mg}	1.32
	450	2.19	2.14 ^{Mg}	
O site-Fig. 1(d)	450	1.71	2.19	0.27
O site-Fig. 1(e)	450	1.5	2.23	0.02

mesh from $5 \times 5 \times 1$ to $8 \times 8 \times 1$ was found to result in a very small change (~0.01 eV) in the total energy of a Nb/MgO system that consists of one Nb atom on a 4 ML MgO substrate. For calculations of density of states (DOS), a $15 \times 15 \times 1$ **k**-point mesh was used, along with the tetrahedron method with Blöchl corrections implemented in VASP. In addition, we have also carried out a Bader analysis [30,31] in order to calculate the amount of electronic charge transfer between Nb and MgO substrate atoms. Our Bader analysis of the MgO(001) surface atoms yields a charge transfer of 1.72 *e* from Mg atoms to O atoms, which is in good agreement with the previous result in Ref. [31].

We used supercells of size 3×3 or 4×4 which contain 9 (16) oxygen atoms and 9 (16) Mg atoms per layer for a 3×3 (4×4) system, along with a slab of three to four layers and six vacuum layers (~ 12.8 Å). We have allowed full ionic and electronic relaxations of Nb adatoms (adsorbed only on one side of a slab) and substrate atoms in the top two substrate layers, while the bottom two (or one) layers were fixed. All geometries were optimized until the remaining forces were smaller than 0.01 eV/Å. Finally, the energy barriers for Nb monomer diffusion and the detachment barrier for a Nb dimer were calculated using the climbing-image nudged elastic band (NEB) method [32] with a number of images $N_{image} = 5$ and spring constant equal to 5 eV/Å².

In order to characterize the strength of Nb adatom and Nb cluster binding at the MgO(001) surface, we have used the following expressions to obtain the (per atom) cluster binding energy (E_B), adsorption energy (E_A), and intracluster binding (E_{IB}) energies,

$$E_B = -\left(E_{\rm Nb/MgO} - E_{\rm MgO} - nE_{\rm Nb}\right)/n \tag{1}$$

$$E_A = -(E_{\rm Nb/MgO} - E_{\rm MgO} - E_{\rm Nb-n \ cluster})/n$$
⁽²⁾

$$E_{\rm IB} = E_B - E_A,\tag{3}$$

where *n* is the number of Nb atoms adsorbed on the MgO(001) substrate. In Eqs. (1) and (2), $E_{Nb/MgO}$ and E_{MgO} are the total energies of Nb/MgO system and MgO substrate, respectively, and E_{Nb} is the energy of a single Nb atom. On the other hand, $E_{Nb-n \ cluster}$ is the total energy of a floating Nb cluster of size *n*, obtained by using its minimized configuration on the MgO substrate. Thus, E_{IB} in Eq. (3) measures the net strength of Nb–Nb interactions in a Nb cluster.

3. Results and discussion

3.1. Monomer adsorption and diffusion on MgO(001)

Several previous studies of metal adsorption on MgO(001) surfaces [19–21,33–37] have found that the preferred adsorption site for a metal adatom is directly above an oxygen atom (O site) while other possible adsorption sites, such as on a Mg atom or at a fourfold hollow site are less preferred. To determine if this is also the case for Nb, we have calculated the binding energy at these three adsorption sites, marked



Fig. 1. Binding energy E_B of a Nb atom on three adsorption sites—O, Mg, and hollow sites, marked as '+'. (b) Binding energy E_B for bcc metals on an O site as function of the cohesive energy E_o where the GGA values of E_B for Cr, Fe and V are from Ref. [33]. (c)–(e) show the effects of a neutral O vacancy on E_B : (c) Nb on an O vacancy site and (d) and (e) Nb on an O site with a nearby O vacancy marked by 'x'. For clarity, only the (minimized) uppermost layer of MgO(001) substrate along with an adsorbed Nb atom is shown in (c)–(e), where white, yellow, and blue circles represent O, Mg, and Nb atoms, respectively.

by a '+' in Fig. 1(a). As expected, we find that the binding energy at an O site ($E_B^O = 1.52 \text{ eV}$) is significantly higher than the corresponding values ($E_B^h = 0.94 \text{ eV}$ and $E_B^{Mg} = 0.32 \text{ eV}$) at fourfold hollow and Mg sites, respectively (see Table 1). These results indicate that the O site is the preferred adsorption site for a Nb atom on MgO(001).

As shown in Fig. 1(b), this result may be compared with previous results for bcc metals, Cr, Fe and V which indicate that the binding energy tends to increase with increasing cohesive energy. In addition, it is worth noting that E_B for Nb is much larger than the value we have obtained for Ag ($E_B^O = 0.43$ eV) but is comparable to values previously obtained for Ni ($E_B^O = 1.33 - 1.45$ eV [19,33]) and Pt (1.50 eV [20]).

As indicated in Table 1, the significantly higher binding energy at an O-site compared to a Mg-site is not due to a difference in the amount of electronic charge transfer $\Delta \rho_e$ mainly from below an O-site since in both cases it is negligibly small (0.03 *e*). Instead, as shown in Fig. 2, the strong hybridization between the Nb s and d orbitals and the O p orbital leads to primarily covalent bonding. A similar hybridization has also been observed for Ni/MgO(001) at an O-site with a similarly large value of the binding energy [19].

We now consider the effect of an O vacancy on MgO(001) surfaces. A recent experiment [9] has shown that there are several types of defects on the MgO(001) surface, while the estimated defect density has been found [9] to be of the order of $10^{-2}-10^{-1}$ defects/nm². One defect of particular interest is a neutral O vacancy (F-center) which appears to be much more stable than an ionic O vacancy (and is also more stable at the surface than in the bulk)[38–41]. Our DFT calculation of the formation energy of a neutral single O vacancy on the MgO(001) surface yields $E_F^O = 9.46$ eV in good agreement with a previous result (9.5 eV) reported in Ref. [38]. It is interesting to note that the charge transfer ($\Delta \rho_e \approx 0.7 e$) of the Mg atom below a surface O vacancy is significantly smaller than the value ($\Delta \rho_e \approx 1.7 e-1.78 e$) for a Mg atom in the MgO substrate.

Fig. 1(c)-(e) and Table 1 illustrate the effects of a surface O vacancy on the binding energy of a Nb atom. If a Nb atom is placed directly above

an O vacancy site on the MgO surface (Fig. 1(c)), then the binding energy ($E_B \approx 2.2 \text{ eV}$) is almost 0.7 eV higher than above an O atom. This higher binding energy on F-center is consistent with the DFT results [37,38,42–45] obtained for other metals on the defect on the MgO(001) surface. In addition, there is a significant amount of electron charge transfer ($\Delta \rho_e \approx 1.32 e$, where a contribution of 1*e* originates from the Mg atom right below the surface O vacancy and the rest is from nearby O atoms). This large amount of charge transfer indicates the



Fig. 2. Site-projected density of states (PDOS) for a Nb atom directly above an O atom on MgO(001) surface. (a) Nb on a surface O atom, and (b) surface O atom with and without Nb bond and bulk O atoms in MgO(001). PDOS for bulk O is shifted in energy for comparison with the PDOSs for surface O atoms. The PDOS is obtained using a Gaussian smearing of 0.1 eV.

ionic nature of the Nb–O vacancy interaction. However, for a nearby O vacancy the effect is significantly decreased. In particular, the binding energy is increased by only 0.18 eV compared to the case without a nearby vacancy (see Fig. 1(d)). In this case, there is a small amount of charge transfer $\Delta \rho_e = 0.27 e$ from the Mg atom right below the surface O vacancy, which implies a relatively weak ionic interaction of the Nb atom with a nearby O vacancy. Due to the interaction, the adsorbed Nb atom moves toward the nearest-neighbor O vacancy site with a lateral displacement of 0.35 Å, as can be seen in Fig. 1(d). On the other hand, the effect of a next-nearest neighbor O vacancy on E_B is negligible (Fig. 1(e)). These results suggest that the interaction between a Nb atom and a nearby O vacancy is rather short-ranged.

The interlayer spacings measured for different adsorption sites shown in Fig. 1 are also summarized in Table 1. As can be seen, the interlayer spacing for a Nb atom above a Mg site is $d \approx 3.0$ Å, while it is much smaller ($d \approx 2.1-2.2$ Å) due to the enhanced bonding for an O vacancy site or an O site. This trend is in good agreement with other DFT results obtained for different metal atoms [19–21,33–37].

Since the fourfold hollow site is the saddle point for Nb adatom hopping from an O-site to another O-site, the diffusion barrier for a Nb monomer on the defect-free surface ($E_a = 0.58 \text{ eV}$) is given by the difference between the binding energy at the fourfold hollow site and at the O-site. We have also calculated the corresponding Vineyard prefactor v_0 [46] for monomer diffusion and obtained $v_0 = 3.1 \times 10^{12} \text{ s}^{-1}$, which is a typical value of v_0 that one might expect for monomer diffusion with the rate $D = v_0 \exp[-E_a/k_BT]$, where k_B is Boltzmann's constant and *T* is the temperature. Due to the computational cost associated with Vineyard calculations, the prefactor was measured using the same supercell of size 3×3 but with a smaller slab of one moving and two fixed layers (1 M + 2 F).

To understand the effects of an oxygen vacancy on the energy barrier for Nb monomer diffusion, we have also carried out NEB calculations for two other cases. The first case corresponds to Nb adatom hopping from an O vacancy site (Fig. 1(c)) to a nearby O site (Fig. 1(d)) while the second case corresponds to a move from a nearby O site (Fig. 1(d)) to another O site (Fig. 1(e)) which is further away from the O vacancy site. As shown in Fig. 3, the energy barrier for transition (c) \rightarrow (d) is $E_a \approx 0.8$ eV, and is only slightly higher (0.82 eV) for transition $(d) \rightarrow (e)$. The small difference between these two activation barriers is most likely due to a tendency of a Nb atom to "lean" toward a nearby O vacancy site (see Fig. 1(d)). On the other hand, the energy barriers for the reverse moves are $E_{rev} = 0.32 \text{ eV}$ for (d) \rightarrow (c) and $E_{rev} = 0.59 \text{ eV}$ for $(e) \rightarrow (d)$. In contrast, the diffusion barrier for a neutral O vacancy on the MgO(001) surface, $E_a \simeq 2 \text{ eV}$ [39], is significantly higher. These results imply that a Nb monomer tends to stay at an O vacancy site and thus a Nb cluster is more likely to be nucleated there. We note that our result is consistent with the other experimental and DFT results that point



Fig. 3. Energy measured from initial state along the diffusion path for transitions $(c) \rightarrow (d)$ and $(d) \rightarrow (e)$, shown in Fig. 1(c)–(e). O vacancy site is denoted by 'x'.

defects play a crucial role in the nucleation of metal clusters on MgO(001) [37,43,45,47–49].

3.2. Nb dimer and trimer adsorption

We now discuss the binding, adsorption, and intracluster binding energies for Nb dimers and trimers as well as the effects of a surface O vacancy on these energies. For Nb dimers, we have considered five different cases as shown in Fig. 3(a)–(e). In the first case (Fig. 4(a)), two Nb atoms form a dimer atop two nearest-neighbor (NN) O sites, with a significant binding energy per Nb atom ($E_B = 3.46$ eV). Due to the Nb–Nb interaction, the lateral bond length of the NN dimer ($l_b = 2.15$ Å) is significantly smaller than the separation between two O sites ($l_o \approx 3.0$ Å) while the (per atom) intracluster binding energy ($E_{IB} = 2.35$ eV) is relatively large (see Table 2). In addition (see Fig. 4(c)), the NN dimer binding energy is not affected by the existence of a nearby O vacancy since the enhanced bonding to the O vacancy appears to be compensated by a slightly weaker Nb–Nb interaction which results in a slightly larger separation between Nb atoms. However, the binding energy for a NN Nb dimer in which one of the Nb dimer atoms is placed directly above



Fig. 4. Top views of minimized configurations of Nb dimers (a)–(e) and trimers (f)–(h), along with their binding energy E_B and their lateral bond length.

Table 2

Summary of (per atom) Nb dimer and trimer binding (E_B), adsorption (E_A) and intracluster binding (E_{IB}) energies for the cases shown in Fig. 3(a)–(h), where l_b is the Nb dimer lateral bond length and d is the interlayer spacing measured between Nb and O atoms.

	$E_B(eV)$	E_A (eV)	E_{IB} (eV)	l_b (Å)	d (Å)
Dimer-Fig. 4(a)	3.46	1.11	2.35	2.15	2.2
Dimer–Fig. 4(b)	1.98	1.85	0.13	3.1	2.1
Dimer–Fig. 4(c)	3.46	1.13	2.33	2.17	
Dimer–Fig. 4(d)	3.80	1.44	2.36	2.15	
Dimer-Fig. 4(e)	2.16	1.62	0.54	2.92	
Trimer–Fig. 4(f)	3.82	0.86	2.96		
Trimer–Fig. 4(g)	3.94	0.87	3.07		
Trimer-Fig. 4(h)	4.1	1.12	2.98		

an O vacancy site (Fig. 4(d)) is moderately higher ($E_B = 3.8 \text{ eV}$) than for the case without an O vacancy in Fig. 4(a) ($E_B = 3.46 \text{ eV}$). This is reflected in the higher adsorption energy, as can be seen in Table 2.

In contrast, the intracluster binding energy ($E_{IB} = 0.13 \text{ eV}$) for the case of Fig. 4(b) in which two Nb atoms are initially placed at nextnearest neighbor (NNN) O sites, is much smaller due to the very weak Nb–Nb interaction which occurs as a result of the large separation distance ($I_b = 3.1 \text{ Å}$). We note that if the O atom labeled as '1' in Fig. 4(b) is replaced by an O vacancy (not shown), then the NNN dimer binding energy increases only slightly (from 1.98 eV to 2.1 eV) due to the moderate effect of a nearby O vacancy. A similarly small increase in the NNN dimer binding energy (compared to the case without an O vacancy) is also observed for the case of Fig. 4(e).

Additional NEB calculations also indicate that the less stable NNN dimer configuration in Fig. 4(b) either corresponds to a very shallow local minimum or may even be a metastable configuration which is close to the saddle-point for a transition from the NN dimer configuration in Fig. 4(a) to an equivalent NN dimer state in which the "upper" Nb atom in Fig. 4(a) has moved to the site labeled '1' in Fig. 4(b). This implies a value $E_a \approx 3.0$ eV for the activation energy for NN dimer 'hopping' as well as a lower bound of 3.0 eV for the activation energy for NN dimer break-up. For the case of Fig. 4(d) in which one of the Nb atoms is atop an O vacancy, we expect similar but slightly higher values of the corresponding activation energies for the same type of NN dimer break-ing process. These results imply that a NN Nb dimer is very stable, while the NNN dimer configurations shown in Fig. 3(b) and (e) are either metastable or are not stable except at very low temperature.

Also shown in Fig. 4 are our results for the stability and binding energies of different NN trimers with and without an O vacancy. As for the case of a dimer, we find that the (per atom) binding energy is significantly larger for a trimer when one of the atoms is atop an O vacancy rather than an O-site, while there is a relatively small increase in the binding energy when two atoms of the trimer are next to but not on top of the O vacancy site. Taken together, these results strongly support the existence of enhanced stability for dimers and trimers when one of the atoms is atop an O vacancy. In addition, we note that the total dimer binding energy relative to two isolated monomers is very high and approximately the same (3.88 eV) in both cases. This is in contrast to the case of Pd/MgO(001) for which the corresponding dimer binding energy (0.57 eV [43]) is much weaker.

3.3. Nb tetramer and pentamer adsorption

As shown in Fig. 5, we now consider a few representative 2D Nb tetramer and pentamer island structures as well as one 3D Nb tetramer (Fig. 5(h)) for comparison with 2D tetramers which we have examined in order to compare their relative stability. We note that the tetramer configurations except the one in (h) correspond to a highly-compressed Nb(100)/MgO(001) structure (Fig. 5(a)) and a similarly highly compressed rotated Nb(100)/MgO(001) structure (Fig. 5(b)). The pentamer structure shown in Fig. 5(e) is also isotropic and is similar to the nonrotated tetramer structure shown in (a) since the Nb atoms are on top of O sites. However, it may also be thought of as a compressed version of the Nb(110) structure shown in Fig. 5(i). While for the cases of Fig. 4(a), (b) and (h) a supercell of size 3×3 with a slab of 2 M + 2 Fwas used, for the cases of Fig. 4(c)–(g) we have used a larger supercell of size 4×4 with a slab of 2 M + 1 F to avoid finite-size effects due to the extended Nb island structures. In these calculations, all the Nb atoms were initially placed directly above O sites, except for the cases of Fig. 5(b), (f) and (g) where one Nb atom (middle atom) was placed above an O vacancy site, while for the case of Fig. 5(h) where the Nb atom marked '2' was placed above the Mg atom marked '+' in Fig. 5(a). In particular, the initial configuration of Fig. 5(g) corresponds to that of (f) without the Nb atom marked '1'.

As indicated in Fig. 5 and also summarized in Table 3, the Nb(100) tetramer in Fig. 5(a) has a higher (per atom) binding energy than the rotated Nb(100) tetramer (Fig. 5(c)) as well as the two Nb(110) pentamers shown in Fig. 4(e)–(f). In addition, in all cases the presence of an O vacancy increases the binding energy. The minimized configurations in Fig. 4(b) and (g) also indicate that for tetramers the presence of O vacancy sites also leads to a significant morphological change (anisotropy). We also find that the 3D tetramer in Fig. 5(h) has a slightly higher binding energy than the 2D Nb (100) tetramer in Fig. 5(a) due to strong Nb–Nb interactions, as can be seen in Table 3. However, this 3D tetramer has a lower binding energy than the Nb tetramer at F-center in Fig. 5(b) due to the lack of strong Nb–O vacancy interactions along with slightly weaker Nb–Nb interactions.

We note that the lattice mismatch ($\varepsilon = (a_{MgO} - a_{Nb})/a_{MgO}$) for Nb(100)/MgO(001) is +21.6%, but it is about -11% for the [110] direction in Nb(110)/MgO(001), where +(-) sign denotes tensile (compressive) strain on Nb films exerted by the MgO(001) substrate. In this regard, it is worth considering the degree of lattice misfit ε_{Nb} for compact Nb tetramers and pentamers with respect to the corresponding Nb bulk unit cell structures (Fig. 5(i)), defined as

$$\varepsilon_{\rm Nb} = \left(a_{\rm Nb(100),(110)} - l_b\right) / a_{\rm Nb(100),(110)},\tag{4}$$

where l_b is the lateral bond length of a Nb cluster on MgO(001) while the corresponding Nb bulk unit cell values are $a_{\text{NB}(100)} = 3.3$ Å and $a_{\text{NB}(100)} = 3.3$ Å and 4.67 Å in the [010] and [100] directions, respectively. Using the values of l_b shown in Fig. 5 we find that $\varepsilon_{\text{NB}(100)} = 24-25\%$ for the tetramer configurations shown in Fig. 5(a) and (b). Similarly, while the strain in the [010] direction $\varepsilon_{\text{Nb}(110)}^{[010]}$ for the pentamer configurations shown in Fig. 5(e) and (f) is only 0.6–2.7% the corresponding strain in the [100] direction ($\varepsilon_{\text{Nb}(110)}^{[100]} = 27 - 29\%$) is much larger. These high values of ε_{NB} suggest that the minimized cluster configurations shown in Fig. 5 are the result of a competition between strong intracluster and interlayer bonds and large misfit strain. However, these large amounts of strain must be released in a growing Nb film on the MgO(001) surface to form the coherent Nb overlayer structures, such as Nb(100) and Nb(110), observed in various experiments [1–4,6–8].

3.4. Nb monolayer adsorption

We now discuss the stability of 2D ML Nb(100) and Nb(110) structures. Due to its simplicity, it is straightforward to model a Nb(100) overlayer structure in which the Nb atoms are placed directly above O sites as suggested in Ref. [3], although a somewhat different Nb(100) overlayer structure grown by electron-beam evaporation has been suggested in Ref. [8]. Fig. 6(a) shows the corresponding minimized Nb(100) ML structure, which has interlayer spacing d = 2.24 Å and (per atom) binding energy $E_B = 4.96$ (5.0) eV for a supercell of size 4×4 (3×3) with a slab of 2 M + 1 F. This value is significantly higher than the corresponding value ($E_B = 3.97$ eV) found for the compact Nb(100) tetramer (Fig. 5(a)). This may be explained by the fact that, although the Nb–Nb bond strength is reduced due to the larger Nb–Nb distance, the Nb coordination number is doubled while the resulting



Fig. 5. Top views of minimized configurations of tetramers (a)–(d), (g) and (h) and pentamers (e) and (f), along with their binding energy E_B and their lateral bond length l_b . In (c) and (d) the initial positions of Nb atoms are denoted by '+'. (g) is the minimized configuration after removing the Nb atom labeled '1' in (f). Here, Δ is the height difference between the middle Nb atom and four surrounding Nb atoms in (e) and (f). In (h) the initial position of the Nb atom labeled '2' is denoted by '+' in (a). (i) shows the unit cell structures of Nb(100) and Nb(110) in a Nb bulk single crystal.

Table 3

Summary of (per atom) Nb tetramer and pentamer binding (E_B) , adsorption (E_A) and intracluster binding (E_{IB}) energies for the cases shown in Fig. 4(a)–(h), where l_b is the lateral bond length and d is the interlayer spacing between Nb and O atoms.

	E_B (eV)	E_A (eV)	E_{IB} (eV)	l_b (Å)	d (Å)
Tetramer-Fig. 4(a)	3.97	1.10	2.87	2.52	2.19
Tetramer—Fig. 4(b)	4.55	1.06	3.49		
Tetramer-Fig. 4(c)	3.46	0.58	2.88	2.51	2.28
Tetramer-Fig. 4(d)	3.98	1.05	2.93	2.47	2.29
Pentamer—Fig. 4(e)	3.58	0.95	2.63		
Pentamer—Fig. 4(f)	3.77	1.04	2.73		
Tetramer—Fig. 4(g)	4.30	0.83	3.47		
Tetramer-Fig. 4(h)	4.18	0.79	3.39		

9% strain is much smaller than the value (~24%) obtained for the tetramer. While the 4×4 slab system does not exhibit any fluctuation in the interlayer spacings between pairs of Nb and O atoms, there is a small fluctuation (~0.03 Å) in *d* for the 3×3 slab system, thus suggesting weak supercell-size effects.

Unlike the Nb(100) overlayer structure, it was not easy to find minimized Nb(110) overlayer structures due to their complexity and the high computational cost for minimization. Fig. 6(b) shows a possible Nb(110) overlayer structure based on a schematic diagram presented in Ref. [3]. Unfortunately, such a Nb structure requires a very large supercell size due to its large Nb unit cell structure. Thus, we did not consider that case here. Instead, based on our findings in Figs. 5 and 6(a), we have considered the two different anisotropic Nb(110) ML



Fig. 6. Top views and binding energies for (a) minimized Nb(100) structure and (b) possible large-scale Nb(110) structure. Two slightly different smaller scale initial Nb(110) structures are shown in (c) and (e) along with the corresponding minimized structures in (d) and (f).

structures shown in Fig. 5(c) and (e). We note that these initial structures are similar to the bulk Nb(110) unit cell structure shown in Fig. 5(h) and are based on small (red) rectangular (110) unit boxes which have dimensions of 3 Å × 4.5 Å and 3 Å × l_u where $l_u = 4.5$ Å or 4.77 Å. However, in one case (Fig. 6(c)) a row of Nb atoms is initially located directly above a row of Mg atoms while in the other case (Fig. 6(e)) a row of Nb atoms is initially located directly above a row of O atoms. It is important to note that with 90° rotation symmetry one might construct an equivalent Nb(110) initial unit cell structure. As a result, for Nb(110) two possible phases may coexist, unlike the single phase for Nb(100).

A coincidence site lattice (CSL) analysis indicates a moiré period of $\Lambda = a_f \times a_s/(a_f - a_s)$, where a_f and a_s denote the lattice constants of film and substrate, respectively. This implies that the minimum supercell size corresponding to the rectangular (110) unit structure is 3 Å × 9 Å (*i.e.*, 1 × 3 system) along the [110] direction where $a_s = 3$ Å and $a_f = 3$ Å or 4.5 Å. In particular, in this initial unit structure the strain along the *elongated* direction is significantly reduced with $\varepsilon_{Nb(100)} = 3.6\%$.

Fig. 6(d) shows the minimized Nb(110) ML structure corresponding to the initial configuration in Fig. 6(c) which was obtained using a 3×3 MgO supercell with a slab of 2 M + 1 F and $E_{cut} = 450$ eV. As can be seen, the resulting rectangular unit structure (black rectangular box) is slightly modified due to the complex Nb–MgO interaction, and

there are some visible distortions in the Nb atom positions which suggests possible supercell size and/or slab thickness effects. However, the overall Nb(110) unit cell structure is maintained. Surprisingly, we find that the binding energy $E_B = 5.46$ eV is 0.5 eV higher than that of the Nb(100) structure in Fig. 6(a). For an initial single unit structure with $l_u = 4.5$ Å, we have found a very similar result with $E_B = 5.42$ eV and almost the same minimized configuration, as shown in Fig. 6(d), but with slightly less distortions. We have also minimized the shifted Nb(110) structure is very similar to that in Fig. 6(f), the resulting minimized structure is very similar to that in Fig. 6(d), with almost the same binding energy ($E_B = 5.43$ eV). These results indicate that while the Nb(100) structure may be more stable for small clusters (see Section 3.3), as a result of strain relaxation the Nb(110) structure is energetically preferred for large islands and/or at monolayer coverage.

We have also examined the stability of an isolated Nb(110) structure which corresponds to the unit rectangular box considered in Fig. 6(c) but which does not span the whole substrate – *e.g.*, using the 12 Nb-atom unit cell structure in Fig. 6(c) on a MgO supercell of size 4×4 with a slab of 2 M + 1 F. In this case, the initial unit cell structure was not well maintained. In particular, edge Nb atoms that miss a lateral bond with Nb atoms tend to go up and form a stronger bond with neighboring Nb atoms since this has a higher binding energy than a Nb–O bond, as seen in Table 2. This leads to a "clumped" 3D Nb structure (not shown). This result implies a complex pathway to form a coherent Nb(110) monolayer structure during the growth of Nb multilayer films on MgO(001). This result is also consistent with an analysis which we have carried out based on the calculated surface energies for Nb(110) [51] and MgO(100) [50] which indicates that for thick-films on defectfree MgO(001), Volmer–Weber (3D) growth mode is favored.

4. Summary and conclusion

Motivated by recent experiments on Nb/MgO(001) growth we have performed extensive DFT calculations to understand the stability of various 2D dimer, trimer, tetramer, and pentamer clusters as well as of complete monolayer Nb(100) and (110) structures. As was found in other cases of metal adsorption on MgO(001), our results indicate that an O site is the preferred adsorption site for a Nb atom, while the binding energy (1.5 eV) is relatively large due to the strong hybridization between Nb 4d/5s states and the O 2p state. In addition, we find that the Nb–Nb bonds in Nb clusters are typically stronger than either Nb–O bonds or Nb–O vacancy bonds, while the Nb–Mg interaction is much weaker.

Due to the existence of strong Nb–Nb interactions, we also find that the (per atom) binding energy for small compact clusters is quite large, ranging from 3.5 eV for a dimer to 4.0 eV for a compact tetramer. However, for compact pentamers the (per atom) binding energy (3.6 eV) is slightly reduced due to a decrease in the number of nearest-neighbor Nb–Nb bonds per atom. These results indicate that in the absence of O vacancies, for small clusters (*e.g.* tetramers and pentamers) a (100)-like structure, in which the Nb atoms all sit atop O atoms, is energetically favored.

Our DFT calculations also indicate that the presence of a surface O vacancy increases the binding energy of small compact clusters. These results imply that O-vacancy sites may act as nucleation sites for Nb clusters. In addition, our results indicate that the presence of an O vacancy may transform the stable (100)-like tetramer structure into an anisotropic (110)-like structure.

In addition to energetics calculations for small clusters, we have also calculated the energy barriers for a few key Nb diffusion processes. The energy barrier for Nb monomer diffusion on defect-free MgO(001) is 0.58 eV, while the barrier for a Nb monomer to diffuse away from a surface O-vacancy site is approximately 0.8 eV. Our NEB calculations also indicate that in the absence of an O vacancy, the barrier for detachment of a Nb atom from a dimer is larger than 3.1 eV. These results are

consistent with our energetics results which indicate that small clusters are stable while O vacancies may act as nucleation sites.

We have also studied the stability of monolayer Nb(100) and Nb(110) structures. In contrast to our results for tetramers and pentamers, which indicate that in the absence of vacancies a (100)like structure is preferred, for the case of a complete monolayer we find that an anisotropic (110) structure is energetically favorable. This result is consistent with the experimental results of Ref. [1] in which it was found that at low substrate temperature the (110) structure was favored. It is also consistent with the increased number of nearestneighbor Nb-Nb bonds for the (110) structure as well as the expectation that with increasing cluster size the effects of strain, which are reduced for the (110) structure, will be dominant. While it is possible that due to finite-size effects, the (110) structures shown in Fig. 6 may not be the lowest energy structures, since they are already lower in energy than the (100) structure (for which finite-size effects are expected to be minimal) our results clearly demonstrate that the (110) structure is energetically more favorable than the (100) structure.

It is also interesting to try to relate our results for the effects of O vacancies on the cluster morphology with the dependence of the preferred film orientation on deposition conditions observed in recent sputter deposition experiments [4]. For example, it was found [4] that deposition on MgO substrates which were only in situ annealed tended to lead to (110) films, while the (100) orientation was favored when a freshly deposited MgO seed layer was grown. Similarly, an increase in the Argon vapor pressure from 1 mTorr to 5 mTorr was also found to lead to a change in orientation from (110) to (100). Both of these observations appear to be consistent with our DFT results which indicate that the presence of an O vacancy may transform the stable (100)-like tetramer structure into an anisotropic (110)-like structure. In particular, we expect that a freshly deposited MgO seed layer will have a decreased density of O vacancies, thus favoring the nucleation of isotropic (100) clusters. Similarly, an increase in the Argon vapor pressure is expected to lead to a decrease in the kinetic energy of sputtered Nb atoms, thus decreasing the formation of O vacancies, which again may favor the nucleation and growth of (100) structures.

Finally, we note that while our calculations have been restricted to the monolayer and submonolayer regime, the experiments in Refs. [1-4] correspond to multilayer growth. In addition, our DFT calculations for an isolated 12-atom Nb cluster on Mg(100) suggest that the pathway to form a coherent (100) or (110) structure during the growth of Nb films on MgO(001) may be relatively complex. Accordingly, it would be of interest to carry out additional calculations in order to study the multilayer growth behavior.

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