



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

Yunsic Shim, Jacques G. Amar\*

Department of Physics & Astronomy, University of Toledo, Toledo, OH 43606, USA



## ARTICLE INFO

### Article history:

Received 17 April 2015

Accepted 16 November 2015

Available online 22 November 2015

### Keywords:

Nb/MgO(100)

Nb overlayer structure

Adsorption sites

Binding energy

Diffusion barriers

## 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 = 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  $\varepsilon = (a_{\text{MgO}} - a_{\text{Nb}}) / a_{\text{MgO}}$  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%,

\* Corresponding author at: Department of Physics & Astronomy, MS 111 University of Toledo Toledo, OH 43606.

E-mail addresses: [yshim@physics.utoledo.edu](mailto:yshim@physics.utoledo.edu) (Y. Shim), [jamar@physics.utoledo.edu](mailto:jamar@physics.utoledo.edu) (J.G. Amar).

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  $E_{\text{cut}} = 350$  eV. A higher value of  $E_{\text{cut}} = 450$  eV was also used in some cases. However, our test results for Nb binding energy indicate that  $E_{\text{cut}} = 350$  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  $a_{\text{MgO}} = 4.21$  Å and  $a_{\text{Nb}} = 3.30$  Å for MgO and Nb, respectively. The Monkhorst–Pack scheme [29] was used for  $\mathbf{k}$ -point sampling, with a  $5 \times 5 \times 1$  mesh, while higher  $\mathbf{k}$ -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  $d = 2.1^\circ$  ( $2.3^{\text{Mg}}$  or  $2.14^{\text{Mg}}$ ) represents the vertical distance between Nb and nearby O (Nb and nearby Mg), as shown in Fig. 1(a) and (c).

	$E_{\text{cut}}$ (eV)	$E_B$ (eV)	$d$ (Å)	$\Delta\rho_e$ (e)
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	$2.1^\circ$ – $2.3^{\text{Mg}}$	0.06
	450	0.94	$2.1^\circ$ – $2.3^{\text{Mg}}$	
O vacancy—Fig. 1(c)	350	2.19	$2.14^{\text{Mg}}$	1.32
	450	2.19	$2.14^{\text{Mg}}$	
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 ( $\sim 0.01$  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  $15 \times 15 \times 1$   $\mathbf{k}$ -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  $3 \times 3$  or  $4 \times 4$  which contain 9 (16) oxygen atoms and 9 (16) Mg atoms per layer for a  $3 \times 3$  ( $4 \times 4$ ) system, along with a slab of three to four layers and six vacuum layers ( $\sim 12.8$  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  $N_{\text{image}} = 5$  and spring constant equal to 5 eV/Å<sup>2</sup>.

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 ( $E_{\text{IB}}$ ) energies,

$$E_B = -(E_{\text{Nb/MgO}} - E_{\text{MgO}} - nE_{\text{Nb}})/n \quad (1)$$

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

$$E_{\text{IB}} = E_B - E_A, \quad (3)$$

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

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