

# THEORETICAL STUDY OF THIN NOBLE-METAL FILMS ON THE NIOBIUM SURFACE\*

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## Abstract

Recent experiments suggest that noble-metal deposition on niobium metal surfaces can remove the surface oxide and ultimately improve superconducting radio-frequency (SRF) cavities performance. In this preliminary study, we use density-functional theory to investigate the potential for noble-metal passivation of realistic, polycrystalline niobium surfaces for SRF. Specifically, we investigate the stability of gold and palladium monolayers on niobium surfaces with different crystal orientations and evaluate the impact of these impurities on superconducting properties. In particular, our results suggest that gold can grow in thin layers on the niobium surface, whereas palladium rather tends to dissolve into the niobium cavity. These results will help inform ongoing experimental efforts to passivate niobium surfaces of SRF cavities.

## INTRODUCTION

Recent experiments suggest that modifications to the niobium native oxide can substantially improve RF performance by reducing the thickness of the oxide. In particular, it has been found that noble-metal deposition can passivate the surface and completely remove the oxide. However, experiments on noble-metal layers have only been performed so far on small single-crystal samples under highly controlled conditions [1]. To shed further light on the potential for noble-metal layers, here we use first principles density-functional theory electronic structure software [2] to investigate the potential for noble-metal passivation of realistic, polycrystalline niobium surfaces for SRF. Specifically, we investigate the stability of gold and palladium monolayers on niobium surfaces with the most common, low-index crystal orientations. The preliminary results that we present here help inform and extend ongoing experimental efforts, which so far have shown a modest but significant benefit from sub-monolayer gold deposition on niobium.

## BACKGROUND

### Density-Functional Theory

Density Functional Theory (DFT) is a highly adaptable tool that can compute and predict a diverse array of fundamental material properties, ranging from electronic structures to formation energies to superconducting characteristics, with an accuracy within a few percent and without the necessity of experimental input. This positions DFT as an

immensely beneficial complement to experimental investigations of advanced materials, like those utilized in SRF cavities. In this paper, we employ DFT to predict the effects of thin noble-metal films of Au and Pd on the Nb surface. In particular, we estimate the number of monolayers that can form a coherent interface, study the stability of these atoms on the surface, and calculate the effects of impurities on the superconducting transition temperature  $T_c$  [2].

### Coherent Interfaces with Nb

In nature, niobium forms a body-centered cubic structure (bcc), with a lattice constant of approximately  $a_{\text{Nb}} = 3.30 \text{ \AA}$ , whereas Au and Pd typically form face-centered cubic structures (fcc), with lattice constants  $a_{\text{Au}} = 4.16 \text{ \AA}$  and  $a_{\text{Pd}} = 3.95 \text{ \AA}$  respectively (values obtained from our *ab initio* relaxation calculations). Nevertheless, for a small number of monolayers (ML), we expect the noble metal to occupy bcc lattice sites. As the number of MLs grows, we expect the formation of misfit dislocations, and finally a transition of the material to its preferred fcc geometry. Our goal is to estimate how many MLs it is possible to deposit on the Nb surface before this final phase transition occurs.

It is not straightforward to directly predict the lattice constant of an element in its bcc phase given its lattice constant in the fcc phase, as the change in the structure can involve physical changes due to different atomic packing, bonding characteristics, and potential energy minima. We can roughly estimate the lattice constant by relating it to the atomic radius  $r$  through the equations  $a_{\text{fcc}} = \sqrt{2} \cdot 2r$  and  $a_{\text{bcc}} = \sqrt{3} \cdot 2r$ . Using these relations and the above fcc lattice constants, we estimate  $a_{\text{Au,bcc}} \approx 3.39 \text{ \AA}$  and  $a_{\text{Pd,bcc}} \approx 3.22 \text{ \AA}$ . The proximity of these values to the niobium lattice constant of  $a_{\text{Nb}} = 3.30 \text{ \AA}$  make Au and Pd potential candidates for having a smooth coherent interface with Nb.

Given that the above lattice constants are not perfect matches, to compensate for the resulting interfacial strain energy, the material must lower the total energy by replacing the surface energy of niobium with an energetically favorable interface. We call this energy difference  $E_{\text{gain}}$ , and it is given by the sum of the energy of the interface and the surface of the film, minus the energy of the original niobium surface,

$$E_{\text{gain}} = E_{\text{interface}} + E_{\text{surface film}} - E_{\text{surface Nb}} \quad (1)$$

On the other hand, for a coherent interface (which we assume for a low number of MLs), there is a strain energy cost per atom per ML due to the lattice-constant mismatch, of

$$E_{\text{strain}} = E_{\text{bcc}} - E_{\text{fcc}}, \quad (2)$$

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where  $E_{\text{bcc}}$  and  $E_{\text{fcc}}$  are the energies of the noble metal in the bcc phase with lattice constant  $a_{\text{Nb}}$  and in the fully relaxed fcc phase of the noble metal, respectively. Finally, combining  $E_{\text{gain}}$  and  $E_{\text{strain}}$  above, we can determine the total energy difference associated with adding several monolayers to be

$$\Delta E_{\text{total}} = E_{\text{gain}} + ML \cdot E_{\text{strain}}. \quad (3)$$

### Impurities in Nb and Superconductivity

When forming surface layers of noble-metal atoms it is possible that the noble metal will dissolve into the underlying niobium material. Specifically, this will happen when the energy to add one atom on the surface is greater than the energy to replace an atom in the bulk of the niobium. Below, we evaluate these energies to predict whether surface layers of noble metals will generate substitutional impurities in the niobium.

The presence of such substitutional impurities in the Nb bulk will result in changes in the superconducting properties of the material. To determine the impact on the superconducting transition temperature  $T_c$ , we compute the electronic density of states at 12.5% concentration of Au and Pd in Nb. Then, to estimate the impact on the transition temperature, we use the well-known BCS formula [3],

$$T_c \approx \Theta_D e^{-1/N(0)V}, \quad (4)$$

where  $N(0)$  is the density of states at the Fermi level,  $V$  is the electron-phonon coupling potential and  $\Theta_D$  is the Debye temperature, both of which we assume to be approximately constant.

## COMPUTATIONAL METHODS

For all *ab initio* density-functional theory (DFT) calculations below, we use the JDFTx density-functional theory software package [2] with the PBE exchange-correlation functional [4] and ultrasoft pseudopotentials from the GBRV library [5]. Finally, all calculations below are performed with a plane-wave energy cutoff of 20 Hartree and an effective electron temperature of 4 mH.

For the surface energy calculations, we employ 1x1x8 slabs with the two layers in the middle being frozen during the ionic-position optimization. We use a 12x12x1 k-point mesh and periodic boundary conditions along the surface. For the interface energy calculations we use 1x1x12 slabs with periodic boundary conditions in all directions along with a 12x12x4 k-point mesh, allowing relaxation of all atomic coordinates and of the lattice the direction perpendicular to the interface. Bulk energies are calculated using 1x1x1 primitive unit cells, with periodic boundary conditions and 12x12x12 k-point mesh. Finally, for the impurity calculations, we use 2x2x2 supercells with a 6x6x6 k-point mesh and periodic boundary conditions along all directions. Although the supercells employed for this preliminary study are somewhat small, we believe that the trends we find are significant.

## RESULTS

We begin by computing surface energies for Nb, Au, and Pd for the three surface orientations (100), (110), and (111), as illustrated in Fig. 1. We find, as is commonly found for bcc

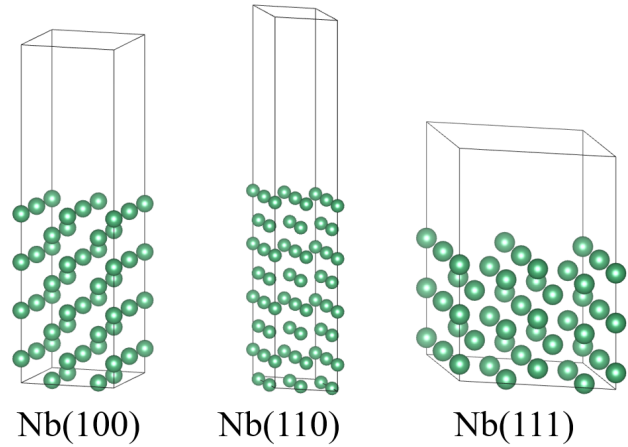


Figure 1: Nb surfaces used to calculate (100), (110), (111) orientations.

metals, that the (110) surface orientation has the minimal surface energy among the three, while the (111) surface orientation exhibits the maximum.

Next, for the same three orientations, we calculate interfacial energies for Nb/Au and Nb/Pd assuming continuation of the Nb bcc structure, as illustrated in Fig. 2. Figure 3 summarizes all of our surface and interfacial energies. Finally, combining Eqs. (1) and (2) yields the results shown in Table 1 for the number of ML that can be grown before the noble metal reverts to its ground-state fcc structure.

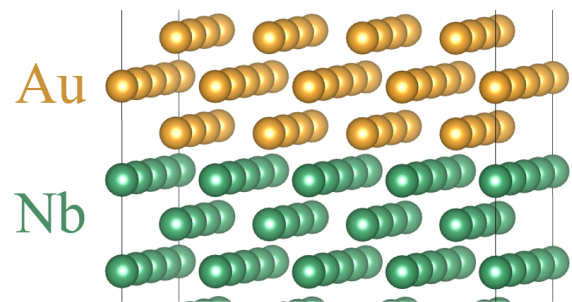


Figure 2: Coherent bcc interface utilized in calculating the interface energy for Au/Nb(100). The interfaces for Other orientations appear similar.

Next, we investigate the possibility that the noble metal would prefer to dissolve into the Nb bcc structure. We begin by calculating the energy of a noble-metal atom substitutional impurity in a 2x2x2 supercell of bulk bcc Nb material, as illustrated in Fig. 4. Comparing the results to the energy per atom of the noble metals in their respective fully-relaxed materials, we obtain  $\Delta E(\text{Au}_{\text{Nb}}) = -0.28$  eV for Au, and  $\Delta E(\text{Pd}_{\text{Nb}}) = -0.55$  eV for Pd, with the negative values indi-

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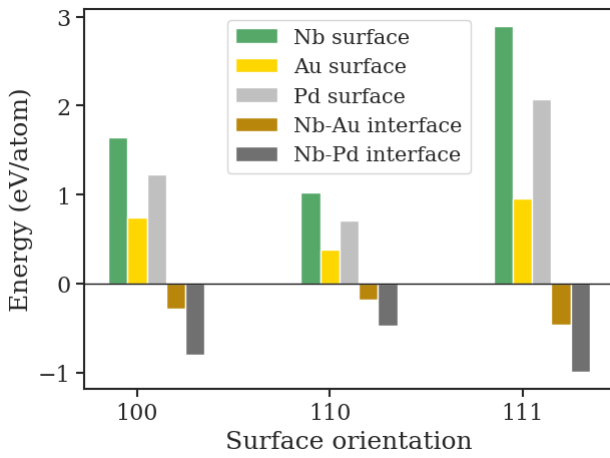


Figure 3: Calculated surface energies for Nb, Au, and Pd for different orientations. Energies for the interfaces of Nb/Au and Nb/Pd are also shown for the same orientations.

Table 1: Net Change in Surface Energy due to Film (per Atom)  $E_{gain}$ , Strain Energy (per Atom per Monolayer)  $E_{strain}$ , Number of Monolayers (ML) at Point of Crossover

	$E_{gain}$ (meV/atom)	$E_{strain}$ (meV/atom·ML)	ML
Au(100)	-1200	10	120
Au(110)	-800	20	40
Au(111)	-2400	60	40
Pd(100)	-1200	50	24
Pd(110)	-800	120	6
Pd(111)	-1800	80	22

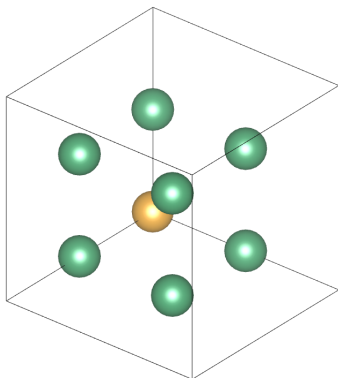


Figure 4: Nb 2x2x2 supercell with Au impurity.

indicating that these materials prefer to dissolve into the niobium from their respective bulk phases.

To ascertain whether the noble metal atoms prefer to dissolve into the Nb bulk or aggregate at the surface, we next consider the energy of adatoms as a function of coverage on the (100) niobium surface, as illustrated in Fig. 5. Figure 6 summarizes the resulting energies, defined as the energy change when removing an atom from its bulk phase and adding it as an adatom to a surface of a given monolayer

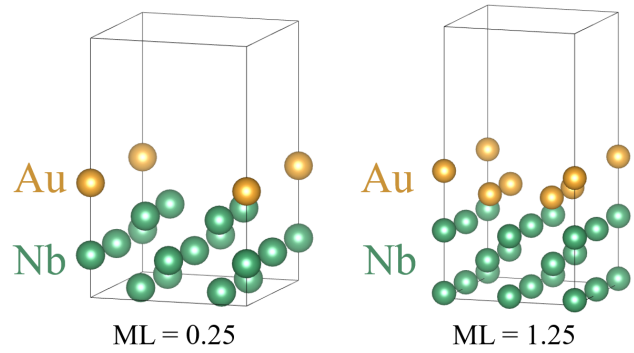


Figure 5: Nb(100) supercell slab with 0.25 and 1.25 monolayers of gold.

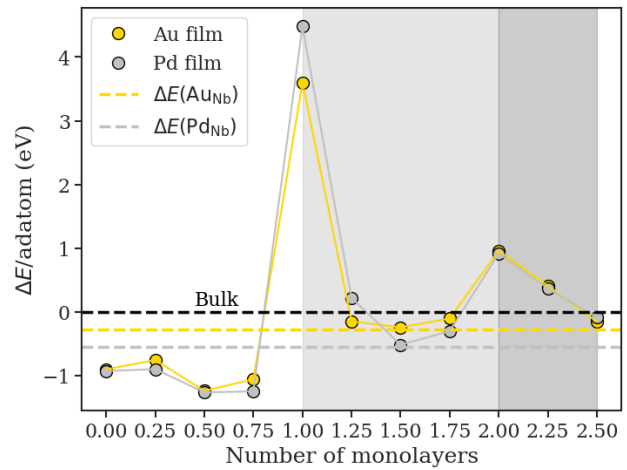


Figure 6: Energy difference per adatom at different number of MLs for Au and Pd for Nb(100) surface relative to bulk phase of each noble metal and compared with the corresponding substitutional impurity energies.

(ML) coverage as computed in our  $2 \times 2$  surface supercell. For comparison, the figure also includes the substitutional impurity energies computed above. Our results indicate that, although substitutional impurities are lower in energy than atoms in the corresponding bulk phase, the energy for adatoms is even lower, at least until completion of the first monolayer. This indicates that, below 1 ML of deposition of the noble metal, the metal will prefer to segregate to the surface. We note, however, that the preference for the surface over the bulk is much stronger for gold than for palladium, suggesting that gold would be a better candidate for use as a surface layer in these systems. We note also, that the results suggest that nucleation of the second ML is actually unfavorable until a coverage exceeding 1.25 ML is obtain, and that we observe a similar pattern as the second monolayer is nucleated.

Given the possibility of the introduction of some amount of impurities, we next consider the impact of such substitutions on the superconducting properties. As a guide to this, Fig. 7 compares the electronic density of states (DOS) for bulk niobium and niobium with gold and palladium impuri-

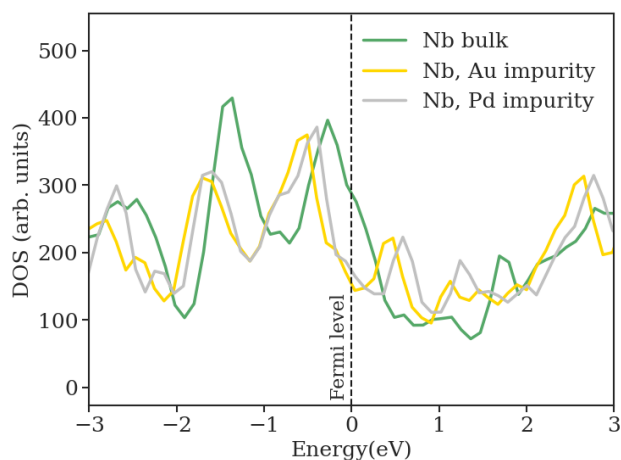


Figure 7: Electronic density of states (DOS) for pure Nb and with 12.5% concentration of Au and Pd impurities. Zero energy is set to the Fermi-level, which controls the superconducting properties.

ties, respectively, at a concentration of 12.5%, as calculated in a  $2 \times 2 \times 2$  supercell. We note that there is a substantial decrease in the Fermi-level density of states as such impurities are introduced. The DOS appears to mostly shift rigidly to the left with the increase in the number of valence electrons, as expected. Finally, using Eq. (4), we can estimate  $T_c$  from the Fermi-level DOS  $N(0)$ , using the known value for Nb [6],  $T_c = 9.2$  K, and the niobium Debye temperature  $\Theta_D \approx 270$  K [7], which yields values of  $T_c \approx 0.4$  K and  $T_c \approx 1.0$  K, respectively, for Au and Pd impurities at 12.5% concentration. We thus find a strong impact on  $T_c$ , but would expect a significantly lower impact for lower impurities concentrations, which can be estimate readily from the expected rigid shift in the DOS.

## CONCLUSION

Although the above conclusions are preliminary due to the size of the supercells employed for this initial study, we believe that the above trends are correct and useful to direct future research. Work is currently underway to repeat these calculations in larger supercells and to explore the adatom energies for surfaces beyond Nb(100) to include the other low-index surfaces (110) and (111). Moreover, full Eliashberg equation calculations of the superconductivity, instead of simple BCS density of states calculations, are also underway, as well are more detailed statistical mechanics

calculations of the final surface and bulk noble-metal atom densities.

From this study, nonetheless, we have drawn an important set of preliminary conclusions regarding the surface treatment of Nb with noble metal atoms. We find that Au and Pd layers can grow coherently with underlying low-index Nb surfaces to significant thicknesses, with Au being more favorable for a greater number of monolayers. We also find that there is a tendency for these noble metals to dissolve into the Nb bulk material, with the very important exception of a surface layer of one or two monolayers. In this regard, we also find gold to behave more favorably than palladium. Finally, we considered the impact of these noble metal impurities on the superconducting properties of bulk niobium and find that, in this case, palladium behaves more favorably.

From the impurities calculations, we check that it is energetically favorable the presence of impurities in the Nb bulk. The formation of a first monolayer of noble-metal film on top is even more favorable, which is good for its stability but for  $ML \geq 1$  we can expect atoms to start diffusing into the bulk.

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