

## Oblique-incidence reflectivity difference (OI-RD) and LEED studies of adsorption and growth of Xe on Nb(110)

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### ABSTRACT

We studied adsorption, growth and desorption of Xe on Nb(110) using an in-situ oblique-incidence reflectivity difference (OI-RD) technique and low energy electron diffraction (LEED) from 32 K to 100 K. The results show that Xe grows a (111)-oriented film after a transition layer is formed on Nb(110). The transition layer consists of three layers. The first two layers are disordered with Xe-Xe separation significantly larger than the bulk value. The third monolayer forms a close packed (111) structure on top of the tensile-strained double layer and serves as a template for subsequent homoepitaxy. The adsorption of the first and the second layers are zeroth order with sticking coefficient close to one. Growth of the Xe(111) film on the transition layer proceeds in a step flow mode from 54K to 40K. At 40K, an incomplete layer-by-layer growth is observed while below 35K the growth proceeds in a multilayer mode.

### INTRODUCTION

Most heteroepitaxy studies have been focused on a pseudomorphic growth of materials with a lattice constant close to that of the substrates (roughly within 10 to 15%). The pseudomorphic growth persists up to a critical thickness beyond which the accumulated strain in the film due to mismatch becomes too large to further sustain such a growth [1 - 5]. Less has been done on heteroepitaxy on highly mismatched substrates where the critical layer is less than one monolayer thick. The issue becomes whether one can still grow high-quality crystalline films with a transition layer of a few monoatomic layers to release the strain.

In this regard, heteroepitaxy of rare gas on metals and semiconductors serves as a useful model. Due to the distinct difference in atomic configuration, rare gas atoms do not intermix with metallic or semiconductor substrates. Since rare gas atoms on a flat surface tend to form a close-packed structure with a fcc (111) orientation, by choosing the lattice constant or the terminating plane of a substrate, one can study how the effect of a large lattice mismatch alone is overcome.

### EXPERIMENTAL PROCEDURES

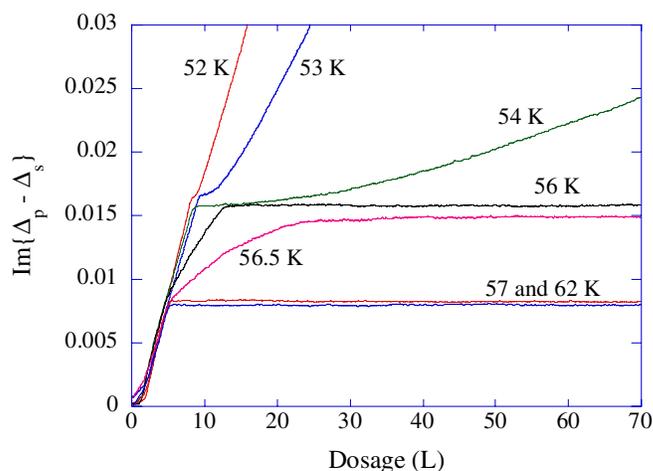
The experiment is performed in an ultrahigh vacuum chamber with a base pressure below  $1 \times 10^{-10}$  torr. The chamber is equipped with an Omicron rear-view LEED/AES system. The LEED screen is imaged onto a 16-bit CCD detector so that the LEED intensity can be measured quantitatively. The Nb(110) substrate is cleaned by sputtering at room temperature with a 50%-50% mixture of Ar-ion/Ne-ion at 1 keV and subsequent thermal annealing at 900 °C for 10 minutes [6]. The AES measurement indicates that the Ar-Ne mixture is effective for removing both carbon and oxygen from the Nb(110) surface. We monitor the temperature with a type-K

thermocouple spot-welded to the side of the Nb(110) substrate. For Xe deposition, we back fill the chamber with a 99.999%-pure Xe gas and the partial pressure is monitored with the ionization gauge.

The chamber has the optical access so that we can perform the oblique-incidence optical reflectivity difference (OI-RD) measurement to monitor the epitaxy *in situ* [7]. This method was used in an earlier study of Xe growth on a commensurate Ni(111) surface where the transition from a three dimensional island growth at or below 35 K to a layer-by-layer growth at and above 40 K was observed[8]. The details of the oblique-incidence optical reflectivity difference set-up with a polarized He-Ne laser as a probe have been described elsewhere [7 - 9].

## RESULTS AND DISCUSSIONS

In figure 1, we show the imaginary part of optical reflectivity difference as a function of Xe dosage measured at a set of substrate temperatures. The real part of the OI-RD signal behaves qualitatively the same. The Xe partial pressure during the deposition is  $p = 1.4 \times 10^{-7}$  torr. Between 57 and 60 K, the coverage of Xe on Nb(110) increases linearly with dosage and reaches a plateau after a dosage of 3.5 L ( $1 \text{ L} = 1.0 \times 10^{-6} \text{ torr} \cdot \text{sec}$ ). This corresponds to the formation of one "full" monolayer of Xe. From the dosage, we deduce the sticking probability of Xe monomers on Nb(110) to be  $S_1 \sim 0.8$ . The first monolayer begins to desorb significantly at 75 K. When the substrate temperature is dropped below 57 K and yet still above 54 K, the second monolayer forms on top of the first monolayer. At 54 K or below, the second layer is formed after a dosage of 3.5 L. This means that the sticking probability onto the first monolayer is also close to unity. The change in the *apparent* adsorption rate between 54 and 57 K is due to a concurrent thermal desorption. Since the *actual* adsorption rate is the sum of the *apparent* adsorption rate and the desorption rate, we find the sticking probability on the first Xe monolayer is roughly a constant between 54 and 57 K,  $S_2 \sim 0.8$ .



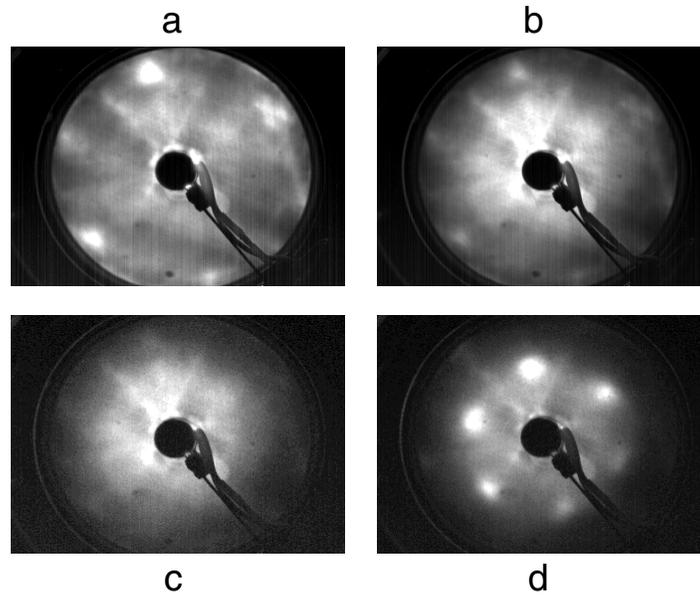
**Figure 1.** Imaginary part of the optical reflectivity difference signal vs. dosage during Xe growth on Nb(110) from 52 K to 62 K.

Below 54 K, Xe begins to grow continuously on top of the first two monolayers. Initially the "sticking probability" on the second layer appears nearly zero, and thus the "growth" rate of the third monolayer is very small. Once the third monolayer is formed, the growth of the subsequent layers is again a linear function of the dosage.

The Xe film structure as a function of the dosage are monitored with low energy electron diffraction (LEED). Figure 2(a) shows the LEED pattern of a clean Nb(110) substrate. Figure 2(b) displays the completion of the first monolayer of Xe on the Nb(110) surface. The further *change* due to the deposition of the second monolayer is very similar to Figure 2(b). Figure 2(c) shows the formation of the third monolayer on top of the first two monolayers. Figure 2(d) shows after additional 10 layers are grown on top of the third monolayer. The first two monolayers of Xe on Nb(110) clearly lack long-range crystalline order. Beyond the third monolayer, the intensity of the diffraction pattern corresponding to a (111)-oriented bulk-phase structure increases, indicating that a good-quality Xe(111) film grows on top of the third layer. The widths of the LEED spots were dominated by the limitation of our LEED setup instead of the domain sizes in the (111)-oriented Xe film. The azimuthal orientation of the film is of Nishiyama-Wassermann (NW) type where the fcc  $[0\bar{1}1]$  row in the film is parallel to the bcc  $[001]$  row on Nb(110)  $[10]$ .

The apparent disorder in the first monolayer indicates that Xe monomers, in the absence of Xe-Xe interaction, have preferred adsorption sites on Nb(110). We have performed a first-principle calculation of the binding energy for Xe on a frozen Nb(110) surface. We find that Xe monomers prefer to adsorb on-top sites with a binding energy of 247 meV. The binding energies at the short bridge site and the long bridge site are 196 meV and 177 meV, respectively [11]. It shows that an adsorbed Xe atom prefers the least coordinated site on Nb(110). The surface corrugation of the binding energy varies in the range of 50 ~ 70 meV and is comparable to that of two to three Xe-Xe bonds. This is consistent with the observation that the first layer is disordered instead of forming a close-packed structure if the Xe-Xe interaction were dominating. Comparing figure 2(d) with figure 2(b), we find that the LEED intensity from the first two monolayers is more concentrated towards the center than the diffraction pattern for the subsequent Xe(111) film. This means that the averaged Xe-Xe separation in the first two monolayers is larger than 4.34 Å by roughly 20% so that the film is under tensile stress.

The tensile-stressed double layer has a profound effect on the growth of the third monolayer at the initial stage. On top of a Xe double-layer with the nearest neighbor Xe-Xe separation being 20% larger than that in a bulk Xe crystal, the binding energy of a Xe adatom is reduced by 20 meV from 103 meV, a reduction equivalent to the energy for a single Xe-Xe bond in the bulk. At 54 K, this binding energy reduction makes the desorption rate of a Xe monomer two orders of magnitude larger than that on a closed-packed Xe(111). As a result, the steady-state density of Xe monomers on the tensile-strained double layers is much less than a monolayer. This explains why the initial growth rate at around 54 K is almost zero or very small. The subsequent adsorption rate appears to increase almost exponentially until a significant fraction of the third monolayer is present on the double layer. This can be understood as follows. Though Xe monomers on the tensile-strained Xe surface are short-lived, Xe adatoms in the form of two dimensional clusters such as dimers, trimers, or larger clusters are stable against desorption.

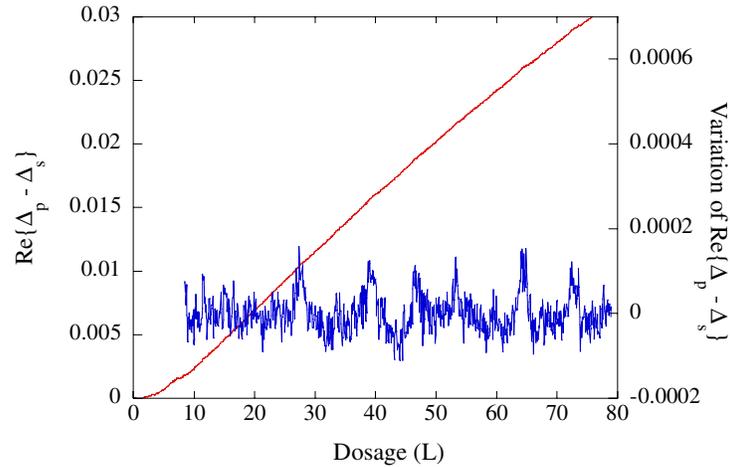


**Figure 2.** LEED pictures (a) from a clean Nb(110); (b) when a monolayer of Xe is on Nb(110); (3) when the third monolayer is formed on top of the second monolayer; (d) when 10 layers of Xe are deposited on top of the third monolayer.

This is because that the loss in the binding energy to the tensile-strained "substrate" is compensated for by forming at least one additional Xe-Xe bond with neighboring Xe adatoms. The adsorption or growth rate of the third monolayer increases as more stable clusters are formed and available, and is proportional to the probability of an incident Xe atom to strike a neighboring position of a cluster or a residence monomer.

In an earlier study of heteroepitaxy of a strain-free Xe(111) film on a commensurate Ni(111), the growth beyond the third monolayer (where the influence of the Ni substrate is negligible) goes through a transition from a three-dimensional island mode at 35 K to a layer-by-layer mode at 40 K [8]. Park and coworkers observed similar growth behaviors of Xe on Cu(111) using scanning tunneling microscope [12]. The transition was attributed to a dramatic increase in the critical radius ( $R_c$ ) of two dimensional Xe islands for second layer nucleation.

In our present study, we have also observed the evidence of such a transition at around 40 K. In figure 3, we display the real part of the optical reflectivity difference signal taken at 40 K. If we examine the optical signal more closely, we notice small peaks that ride on top of the envelope, almost periodically with the dosage. These peaks become more obvious if we subtract the envelope portion of the signal (as also shown in figure 3). The average amplitude of these peaks is about 5% of that for a full monolayer. These peaks indicate that the growth at 40 K and thus up to 54 K is predominantly a step flow growth; at 40 K, it is accompanied by a small component of layer-by-layer growth. At 33 K, we can no longer observe any periodic features above the noise. At 49 K, though the peaks are still noticeable, the average amplitude is reduced by more than one half. This means that as the temperature is lowered through 40 K, the growth partly crosses over from a step flow mode to a layer-by-layer mode and then quickly into a three-



**Figure 3.** The real part of the optical reflectivity difference signal vs. dosage during the Xe growth on Nb(110) at 40 K. The difference between the original signal and the envelope part of the signal (also shown) reveals peaks that are roughly periodic with the dosage.

dimensional island mode at 33 K. Based on the result of a kinetic Monte Carlo simulation, the incomplete transition from a step flow mode to a layer-by-layer mode is expected on the  $0.1^\circ$ -miscut Nb(110) substrate with an average terrace width of  $L_t = 1300\text{\AA}$  if the homogeneous nucleation dominates [8].

## CONCLUSION

To summarize, Xe heteroepitaxy on Nb(110) is a case where the critical thickness of a pseudomorphic overlayer is effectively zero. Unlike the epitaxy of rare gas (Xe, Kr, Ar) on the basal plane of crystalline graphite where an ordered close-packed monolayer is formed and the misfit is compensated for by a rotation of the superlattice with respect to the substrate lattice [13], Xe on Nb(110) represents a different way that a large lattice mismatch is accommodated through the formation of a transition layer so that a subsequent homoepitaxy can be sustained without the ill effect of the lattice-mismatched substrate. In this case the transition layer consists of two "disordered" monolayers, followed by an ordered close-packed monolayer. The first two "disordered" monolayers are strongly influenced by the substrate. The fact that the epitaxy proceeds in a Nishiyama-Wassermann configuration indicates that the crystalline substrate plays a useful role of pinning down the orientation of the overlayer lattice through the "disordered" double layer. It remains to be explored whether such a pinning effect applies to growth of other rare gases on Nb(110), or to heteroepitaxy of fcc metals on (110) planes of a bcc metal substrate in general. With the transition layer being only three-monolayer thick, our result shows the feasibility of growing epitaxial multilayer structures on highly mismatched crystalline materials.

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