

Photoelectron diffraction determination of the structure of ultrathin vanadium films on Cu(001)

G. D. Waddill,* D. P. Moore, and O. Ozturk

Physics Department, University of Missouri–Rolla, Rolla, Missouri 65409

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X-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) have been used to study the structural properties of V thin films on Cu(001). For room-temperature growth, submonolayer coverages result in (1×1) LEED patterns that evolve to exhibit very diffuse (2×1) structure at approximately 1 monolayer coverage. We do not observe any V forward-focusing enhancements for V films that exhibit either the (1×1) or (2×1) structure, suggesting that these structures are limited to the first 1–2 vanadium layers. At coverages above 1 monolayer, the V films display complex LEED patterns characteristic of four bcc(110) domains. This structure persists to V coverages as high as 100 ML, and the LEED and XPD angular scans suggest that V in these films retain the bulk V lattice constant. These results have important ramifications for predictions of magnetic order in vanadium thin films that typically assume pseudomorphic growth.

Recently two studies have reported on the structure of ultrathin vanadium films on Cu(001).^{1,2} Both studies report (1×1) low-energy electron diffraction (LEED) patterns for vanadium coverages below 1 monolayer (ML), and, for thicker films, both report the observation of additional spots in the LEED pattern known to correspond to the presence of four domains of bcc(110) vanadium. The reports differ, however, on the vanadium film thickness where the transition to four bcc(110) domains occurs. Pervan, Valla, and Milun¹ report the observation of the complex multidomain LEED patterns at 2–3 ML, while Tian, Jona, and Marcus² report that a body-centered tetragonal structure producing the (1×1) LEED pattern persists to vanadium coverages as high as 14 Å (or about 6–7 ML). Herein we report our observations on this system using x-ray photoelectron diffraction (XPD) and LEED. For the high photoelectron kinetic energies studied here (approximately 975 eV for the $V 2p_{3/2}$ core level), XPD polar angle scans are dominated by forward-scattering peaks that occur when a near-neighbor bond in the film lies along the photoelectron emission direction. This technique is therefore well suited for determining both the number of layers present in a thin-film structure, as well as any relaxation in the interlayer distances in the film.³ As such, we can use these results together with LEED observations to determine the number of vanadium layers present when the four-domain bcc(110) growth begins.

The V/Cu(001) system is of interest both as a test for the existence of metastable phases predicted by total energy calculations of tetragonal states of V and its resulting epitaxial Bain path⁴ and because of the possibility of magnetic order in either vanadium thin films or clusters. Bulk vanadium exhibits no long-range magnetic order; however, recent theoretical predictions and experimental observations have found the possibility of magnetic ordering in V thin films and clusters. Theoretical models^{5–12} of vanadium thin films on metals such as Ag, Au, Cu, Pd, and Fe have predicted the appearance of magnetic ordering. Although calculations have predicted both ferromagnetic and antiferromagnetic ordering, an antiferromagnetic configuration may be favored due to energy considerations. Studies by Stepanyuk *et al.*^{7–9} show that an antiferromagnetic configuration is preferred for V clusters

on Cu(001). In contrast to these predictions, Reddy, Peder-son, and Khanna¹³ found that V_2 dimers on Cu(001) are non-magnetic, although their results for low concentrations of V atoms on Cu(001) may not hold for higher concentrations such as monolayers or large clusters. Experimental studies^{14–23} of V thin films on various substrates have yielded conflicting results. Ferromagnetic, antiferromagnetic, and no magnetic ordering have all been found in the various experimental studies. It is important to note that all the monolayer calculations assume a square surface net for the V film with a lattice constant determined by the substrate. Because of the physical relationship between the structure and magnetic properties of these thin-film systems it is essential to have an accurate structure determination in order to understand any observed magnetic properties or lack thereof.

As discussed above, two investigations of the structure of V films on Cu(001) at room temperature have been reported.^{1,2} The initial report by Pervan, Valla, and Milun¹ reported a (1×1) LEED pattern for coverages to 1 ML, and patterns consistent with four domains of bcc(110) for V coverages ≥ 2 ML. However, Tian, Jona, and Marcus² report highly disordered films with a (1×1) LEED pattern for coverages up to about 6 ML. For higher coverages the pattern evolved into that consistent with four domains of bcc(110) V. The structure associated with the (1×1) LEED pattern was determined to be a metastable body-centered-tetragonal structure with $c/a = 1.72$. Here, $a = 2.556$ Å and is dictated by the Cu substrate, and $c = 4.40 \pm 0.10$ Å as determined using quantitative LEED measurements. In both studies the film thickness was determined either by monitoring the attenuation of a Cu Auger signal by the vanadium films,¹ or by comparing the relative intensities of a V and Cu Auger signal for the same V film.² While the latter method is often more accurate for lower film thicknesses, both methods rely on knowledge of electron mean free paths and on assumptions about the growth morphology of the V films. In our studies we have determined the V film thickness using both the attenuation of Cu core-level photoemission intensities by the V film, and by comparing Cu and V photoemission intensities for a given film. While these methods suffer the same shortcomings of those in Refs. 1 and 2, both give consistent re-

sults and, most critically, are complemented by x-ray photoemission angular distributions for the $V 2p_{3/2}$ core level. In the kinetic energy regime examined here these XPD scans are dominated by forward scattering from near-neighbor atoms, and these data are therefore quite sensitive to the number of V atomic layers present and to V interlayer lattice parameters.³ This serves as a consistency check for the vanadium coverages determined by core-level attenuation methods.

Vanadium films were prepared in an ultrahigh-vacuum chamber with base pressure of $\leq 1 \times 10^{-10}$ Torr. The Cu single crystal was cleaned by cycles of Ar-ion sputtering followed by annealing to 450 °C. X-ray photoelectron spectroscopy (XPS) showed no contamination to detectable limits and the LEED showed a sharp (1×1) pattern. Vanadium thin films were deposited at room temperature by thermal evaporation from a tungsten basket. A quartz-crystal thickness monitor, in conjunction with XPS $Cu 2p_{3/2}$ and $V 2p_{3/2}$ intensities, monitored vanadium coverage with vanadium evaporation rates between 0.2 and 0.5 ML per minute. For thickness determinations using XPS signals we compared both the $Cu 2p_{3/2}$ attenuation as a function of V exposure and the $V 2p_{3/2}$ to $Cu 2p_{3/2}$ intensity ratio for a given film. In converting these to V thickness we used electron mean free paths calculated according to the method given in Ref. 24. Both methods agreed to within better than 10% for all coverages investigated.

Photoelectron diffraction data were taken using $Al K\alpha$ radiation ($h\nu = 1487$ eV) and a hemispherical energy analyzer of mean radius 125 mm and angular acceptance of $\pm 1^\circ$. The sample was mounted in a holder capable of 360° polar rotation and $\pm 100^\circ$ azimuthal rotation. Both polar and azimuthal rotations had an angular resolution of better than $\pm 0.5^\circ$. Angular scans were obtained for $V 2p_{3/2}$ (binding energy of 512 eV) and $Cu 2p_{3/2}$ (binding energy of 932 eV) core levels. The integrated area of these peaks, after background subtraction, was used to generate the photoelectron diffraction curves. XPD and LEED studies were performed on V films of thickness ranging from < 1 ML up to > 100 ML. We report herein only on films of thickness ≤ 5 ML.

Figure 1 (right side) shows the LEED pattern progression with increasing coverage. In the uppermost pattern a (1×1) pattern for a vanadium coverage less than 1 ML is observed. Progressing down the figure we see that increasing the coverage to approximately 1 ML results in a very diffuse (2×1) pattern. At coverages ≥ 2 ML additional spots characteristic of the multidomain bcc(110) vanadium structure are observed. In addition, at this coverage we still observe the (1,1) Cu-substrate-derived LEED beams. Finally, by 5 ML vanadium coverage only the multidomain pattern remains and there are no substrate-derived beams present. The 2.6- and 5.0-ML LEED patterns are shown for an incident energy of 150 eV, but we note that for 5 ML and thicker films the (1,1) Cu substrate beams were not observed at any incident energy. At all coverages the LEED beams are rather broad and the background is high, indicating the formation of a large number of small V domains with a significant degree of disorder. We note that a similar LEED pattern progression has been observed for Fe/Cu(001), which displays a more complicated progression of low coverage fcc Fe reconstructions prior to the transition to a four-domain

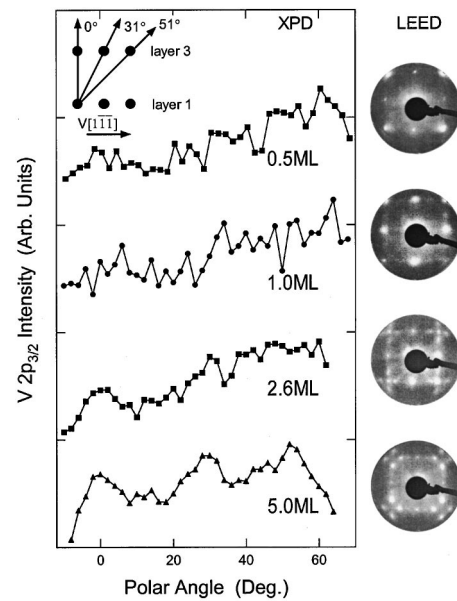


FIG. 1. Right panel: LEED patterns observed for 0.5 ML (110 eV), 1 ML (100 eV), 2.6 ML (150 eV), and 5 ML (150 eV) V. The structure progresses from (1×1) at submonolayer coverages to (2×1) with very diffuse fractional order beams near 1 ML to the four-domain bcc(110) structure with the Cu substrate beams at 2.6 ML to only the four-domain bcc(110) structure at 5 ML and higher. Left panel: XPD polar-angle scans for the Cu(110) azimuthal plane corresponding to the V coverages in the right panel. Note the absence of forward-scattering enhancements for films that do not produce the multidomain LEED pattern. The absence of forward-scattering enhancements indicates that the vanadium film contains two or fewer layers. The inset shows a cross section through the vanadium film with expected forward-scattering directions indicated.

bcc(110) Fe structure. Importantly, the reconstruction observed immediately prior to the appearance of the bcc(110) multidomain structure is the (2×1) structure similar to what we observe here for vanadium films.²⁵ The primary difference is that the Fe film does not collapse to the multidomain bcc(110) structure until it reaches a thickness of approximately 10–12 ML while this transition occurs for the vanadium films at about 2 ML. Finally, detailed investigation of the LEED patterns we observe for the four-domain structure indicates that the vanadium film growth is not pseudomorphic, but rather the vanadium films grow with the bulk bcc vanadium lattice constant. This is in contrast to the findings of analogous LEED studies for bcc or bcc-like Cr films on the Cu(001) surface where Cr films > 3 ML have the bulk Cr bcc(110) structure, but thinner films show pronounced distortions due to pseudomorphic growth.²⁶

The bulk bcc(110) films and the pseudomorphic films produce similar, but distinguishable, LEED patterns. The $V(110)$ reciprocal lattice is generated by two vectors of length $2\pi/(a_v \sin \alpha)$ with an angle of α between the two vectors. Here $a_v = 2.62 \text{ \AA}$ and $\alpha = 70.5^\circ$. The ratio of the lengths of the reciprocal-lattice vectors for $V(110)$ and $Cu(001)$ is then $b_v/b_{Cu} = a_{Cu}/(a_v \sin \alpha) = 1.037$ ($a_{Cu} = 2.56 \text{ \AA}$). For the LEED patterns this means that a line connecting the vanadium derived beams near fractional order positions referenced to the Cu substrate actually lie along a line that is closer to the (0,0) beam than a line connecting the

Cu (1,1) beams by a factor of $a_{\text{Cu}}/a_{\text{V}}=0.977$. For pseudomorphic vanadium growth all these spots would all be aligned. In addition, the vanadium (1,0) beam is 3.7% further from the (0,0) beam than the Cu (1,0) beam. We cannot actually resolve the separate vanadium and copper (1,0) beams due to the disorder in the vanadium films and the rather diffuse LEED beams that result (in addition, it is also likely that vanadium grows in rectangular domains, producing streaking of the LEED spots along the Cu [110] and $[\bar{1}\bar{1}0]$ directions for the different domains due to greater misfit in the [110] direction for two domains and in the $[\bar{1}\bar{1}0]$ direction for the other two domains). However, measurement of the perpendicular distance to the lines through the vanadium beams near the fractional order positions referenced to the Cu substrate compared to the lines through the Cu (1,1) beams gives a determination of $a_{\text{Cu}}/a_{\text{V}}=0.97\pm 0.02$, or $a_{\text{V}}=2.64\pm 0.05$ Å. This suggests that even the thinnest vanadium films retain the bulk bcc vanadium lattice constant, but this determination is difficult and the difference between the bulk vanadium structure and pseudomorphic growth structure is small. A further example of bulklike bcc(110) growth may be found in a LEED study of Fe films on Cu(001) following the transition from fcc-like Fe films to the multidomain bcc(110) structure, which determined structural parameters consistent with those of bulk bcc(110) Fe.²⁷

The critical information contained in Fig. 1 is the correlation between the polar-angle XPD data and the observed LEED patterns. The left side of Fig. 1 shows the $V 2p_{3/2}$ polar-angle scans in the Cu(110) azimuthal plane that correspond to the LEED data on the right side. Also shown is a cross section of an ideal bcc(110) domain along $[\bar{1}\bar{1}\bar{1}]$. For two of the four vanadium domains this direction is parallel to the Cu [110] azimuth. The inset shows that for this orientation we should expect forward-scattering enhancements for V at polar angles of 0° , 31° , and 51° , but that these enhancements require the presence of at least three vanadium layers. Figure 1 shows forward-scattering enhancements at 0° and 31° for a 2.6-ML film, and the 5-ML film shows additional enhancement near 51° . There are no forward-scattering peaks observed for the 0.5- and 1-ML films. We do observe some intensity asymmetry at normal emission for 2-ML films, but it is much reduced in asymmetry from the 2.6-ML film. Note that the coverages cited herein are determined in the manner previously discussed, but are consistent with the XPD data of Fig. 1. In fact, the presence of forward-scattering enhancements at coverages slightly below 3 ML (where they are expected for layer-by-layer V growth) may indicate that the vanadium films exhibit some three-dimensional cluster growth.

Figure 2 shows a comparison between a cross section of the vanadium films with the bcc(110) structure and with the bct(100) structure observed in Ref. 2. For the bct cross section we have assumed the calculated c/a value of 1.78. For the Cu(110) azimuthal plane, the similarities in the angles for expected forward-scattering enhancements for the two structures is apparent. In fact, Tian, Jona, and Marcus² observe a c/a ratio somewhat lower than the theoretically predicted value, and this would bring the forward-scattering angles for the two structures into even closer agreement. The close agreement between the XPD expected for the two structures

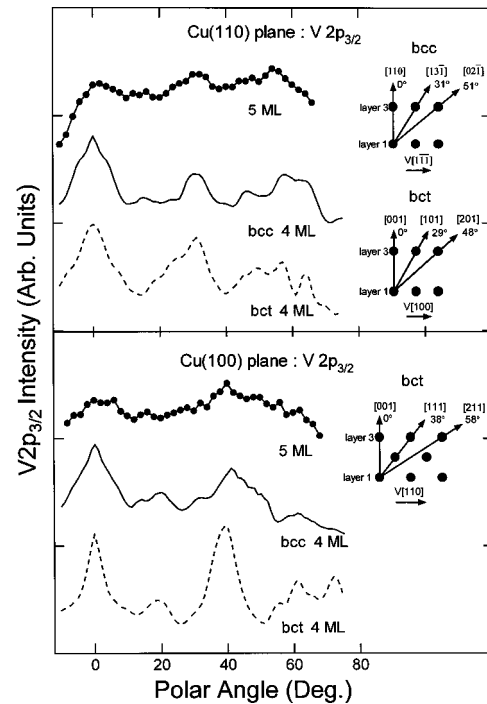


FIG. 2. Comparison of the experimentally observed and calculated XPD polar-angle scans for the Cu(110) (upper panel) and (100) (lower panel) azimuthal planes. The experimental data are shown with data points connected by solid lines, the calculation for 4-ML bcc(110) as a solid line and for bct with $c/a=1.78$ as a dashed line. The insets also show cross sections through the different vanadium film structures for the two azimuths. Calculations for the bcc structure are averaged over the four different domain orientations.

is apparent in our multiple scattering simulations also shown in Fig. 2.²⁸ Note that for the bct structure we should expect forward-scattering enhancement for 3-ML or thicker films. This suggests that if the (1×1) bct LEED pattern persists to 6–7 ML as reported² we should see forward-scattering peaks for films exhibiting this (1×1) LEED pattern. From Fig. 1 it is clear that we only observe any appreciable forward-scattering enhancement for films that produce the multidomain bcc(110) LEED pattern, suggesting that this structure begins with the growth of the second vanadium layer. This observation also rules out the presence of more than two vanadium layers that possess the symmetry of the Cu(001) surface.

Finally, in the lower panel of Fig. 2 we show the same information for the Cu(100) azimuth. For the bct structure, we expect forward-scattering enhancements at 0° (requires three V layers) and at 38° (requiring only two V layers). The Cu(100) plane does not correspond to any low index plane for any of the four bcc(110) V domains so no cross-sectional diagram is produced for it. Again, the differences in the calculated XPD scans for the two structures is not dramatic, but the experimental data at 5 ML agree better with the bcc(110) calculation. We note that for the bcc(110) structure we performed calculations for the four-domain orientations independently and averaged the results. Multiple-scattering calculations for all structures involved 165-atom clusters with four vanadium layers. In this plane, as in the Cu(110) plane, we do not observe any intensity asymmetry in the V XPD

polar-angle scans for films exhibiting (1×1) LEED patterns. This again argues against the presence of a multilayer tetragonal structure for the vanadium films and suggests that the vanadium film growth proceeds as follows: (1) (1×1) structure below 1 ML with the vanadium adopting the Cu surface net, (2) nearing the completion of the first ML the vanadium film undergoes a (2×1) reconstruction similar to that seen for Fe/Cu(001) at higher coverages (this reconstruction involves relative displacements of adjacent V atomic rows²⁹ along $[110]$), and (3) multidomain bcc(110) vanadium growth for coverages above 2 ML.

With the exception of our observation of the (2×1) reconstruction prior to the onset of the multidomain bcc(110) vanadium growth, our findings are consistent with those of Pervan Valla, and Milun.¹ The (2×1) reconstruction is very diffuse and is only evident for a very narrow range of vanadium coverages. The similarities between this (2×1) reconstruction and both a fcc(111) close-packed surface and a weakly sheared bcc(110) surface have been discussed previously.^{30,31} It is therefore not surprising to observe this reconstruction that apparently serves as a precursor to bcc(110) growth.

The discrepancies among the different investigations, particularly among those of Pervan, Valla, and Milun¹ and this study and those of Tian, Jona, and Marcus,² of the V/Cu(001) system are likely due to minor differences in film preparation. Similar differences have been observed in several thin film epitaxial systems,³⁰ and they have often led to significant controversy and conflicting results in the studies of these systems. We have examined the results of annealing and elevated temperature V deposition for the V/Cu(001) system and found that deposition at slightly elevated tem-

peratures or gentle annealing of room-temperature deposited films leads to significant V/Cu interdiffusion and V agglomeration.³¹ The required temperatures depend upon the vanadium film thickness, but the results dramatically impact the observed LEED and XPD data. Similar results for annealed films were reported in Ref. 1. The minimum temperature required to produce significant interdiffusion and vanadium agglomeration, either for room-temperature deposited and annealed films or for films grown at elevated substrate temperatures, has not been determined, but it is clear that these processes produce markedly different structures.

In summary, we have combined LEED and XPD angular scans to determine the structure of vanadium thin films on Cu(001). Our results indicate that for room-temperature deposited films submonolayer coverages produce (1×1) LEED patterns with a diffuse (2×1) reconstruction apparent at approximately 1 ML. Thicker films produce a complex pattern characteristic of four bcc(110) vanadium domains. Our XPD results demonstrate that this multidomain bcc(110) structure initiates in the second vanadium layer. Detailed investigation of the LEED patterns we observe for the four-domain structure coupled with the angular locations of the forward-scattering enhancements for these films indicate that for coverages above 2 ML the vanadium films grow with the bulk bcc vanadium lattice constant of 2.64 ± 0.05 Å. This suggests that we should not expect any magnetic ordering for these films, as bulk vanadium has no magnetic order, and all calculations of magnetic ordering in vanadium thin films assume pseudomorphic growth.

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*Author to whom correspondence should be addressed.

FAX: 573-341-4715. Electronic address: waddill@umr.edu

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