# Low-Energy-Electron-Diffraction Determination of the Atomic Arrangement in a Monatomic Underlayer of Nitrogen on Ti(0001)

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The importance of recognizing a 1 × 1 structure preceding a superstructure in a chemisorption experiment is demonstrated by the system N-Ti(0001). Low-energy-electron-diffraction analysis of the 1×1 structure reveals that the N atoms are located in the octahedral holes 1.22 ±0.05 Å *below* the first layer of Ti atoms. Interatomic distances are such as to justify the view of the surface structure as a single double-layer of TiN.

The present Letter reports the first successful structure analysis by low-energy electron diffraction (LEED) of an *underlayer* of chemisorbed atoms on a clean metal surface. All structures of chemisorbed species on metal surfaces investigated so far are of the overlayer type, i.e., with the adatoms located *above* the outermost layer of the substrate.[1] The present note discusses the case of a 1× 1 room-temperature structure of nitrogen on Ti(0001), in which the atomic arrangement reflects very closely the structure of the bulk compound TiN, the N atoms being located *underneath* the top layer of Ti atoms in what are usually called octahedral interstitial positions.

The reaction of a clean Ti(0001) surface with nitrogen gas at room temperature goes through the following stages as observed by LEED and Auger electron spectroscopy (AES). With increasing concentration of nitrogen on the surface, the LEED pattern of the clean surface maintains its geometry but exhibits changes in the intensities of the diffracted beams. We interpret this observation as indicative of the formation of a Ti(0001)-1× 1-N structure. Completion of the 1× 1 structure, at 4–5 L (1 L ≡ 1 langmuir ≡ $10^{-6}$ Torr sec), is associated with minima in the rates of changes of LEED spectra on adsorption[2]; with an inflection point in the rate of the plasmon-decay Auger line at 12 eV [3]; and with a maximum in intensity of the interfacial Auger peak at 23 eV.[4] After completion of the 1× 1 structure, the nitrogen concentration on the surface as revealed by AES keeps increasing until, around exposures of 8–9 L, a $\sqrt{3}\times\sqrt{3}$-30° structure is observed which is completed at approximately 15 L. The nitrogen AES signal remains constant after about 9 L.[4] It is clear, in the light of these observations, that the $\sqrt{3}\times\sqrt{3}$-30° structure cannot be a low-coverage structure of the type reported, e.g., by Forstmann, Berndt, and Büttner[5]—we have carried out intensity calculations that indeed confirm this fact.

In all experiments carried out so far, both the 1× 1 and the $\sqrt{3}\times\sqrt{3}$-30° phases appeared to be reproducibly well crystallized. The background in the LEED patterns remained at least as low for the 1× 1 phase as it was for the clean substrate surface, then increased slightly in the early stages of formation of the $\sqrt{3}\times\sqrt{3}$-30° phase but finally dropped again to a very low level after completion of the latter structure. Reproducibility of peak shapes, peak positions, and peak intensities in LEED spectra of both the 1× 1 and $\sqrt{3}\times\sqrt{3}$-30° phases was excellent, not only with a given Ti sample in a first run but also with a different Ti sample in a second run.[3]

Intensity data were collected for nine LEED beams of the Ti(0001)1× 1-N structure at three different incidence angles. Corresponding LEED intensity calculations were carried out with the layer–Korringa-Kohn-Rostoker method described elsewhere.[6] Thirty-one beams and eight phase shifts were used to describe the electron wave function. For all structural models described below the assumption was made and tested that the two types of domains made possible by the two different terminations of an hcp (0001) surface[7] were equally represented on the surface.

Whenever possible, to describe a model, we use the notation that specifies the *ABAB* ... stacking sequence of close-packed atomic layers, bulk Ti being thereby denoted by $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}A_{\mathrm{Ti}}B_{\mathrm{Ti}}\ldots$. Since the first, and simplest, models for the 1× 1 nitrogen structure involved nitrogen *over*layers, we assumed that nitrogen atoms would be located, in turn, in the three-fold sites (hcp sites) that would be occupied by Ti atoms if the substrate grew $(\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}A_{\mathrm{N}})$; in both the hcp and the fcc sites, thereby doubling the surface adatom population $[\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}(A_{\mathrm{N}}+C_{\mathrm{N}})]$; directly on top of the surface substrate atoms $(\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}B_{\mathrm{N}})$; and on the bridge sites across two adjacent surface atoms (three types of domains of this structure are possible for each termination). None of these overlayer models (and their molecular counterparts) produced acceptable agreement with the observed intensity spectra for any reasonable distance between the plane of the adsorbed atoms and the top substrate plane. In order to give an idea about the extent of the disagreement produced by the "wrong" models we present in Fig. 1 the intensity spectra of the 11 beam at normal incidence as calculated for two of the models described above, together with the corresponding experimental spectrum for the Ti(0001)1× 1-N structure.

The failure of all simplest *overlayer* models led us to consider the possibility that the N atoms could penetrate below the first layer of Ti atoms and build what we may call, by contrast, an *underlayer* of chemisorbed atoms. This thought was considerably helped by the knowledge that bulk TiN is an "interstitial" compound in which, just as in the nitrides of many other transition metals, the metal atoms are almost exactly close packed.[8] The compound TiN crystallizes with the NaCl structure with lattice parameter[9] $a_{\mathrm{TiN}} = 4.240$ Å, so that the closest Ti-Ti distance within any (111) plane is $a_{\mathrm{TiN}}/\sqrt{2} = 2.998$ Å—only 1.6% different from the closest Ti-Ti distance within the (0001) plane of Ti metal, 2.950 Å. Furthermore, the interplanar distance between two successive Ti planes along a ⟨111⟩ direction of the TiN lattice is $a_{\mathrm{TiN}}/\sqrt{3} = 2.448$ Å—about 4.7% different from the spacing between two successive Ti layers along [0001] in Ti metal, 2.339 Å.

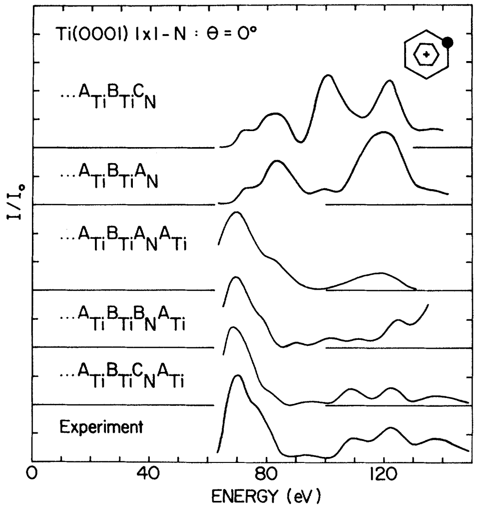

FIG. 1. Comparison between calculated and observed 11 spectra. The top five curves were calculated for the models indicated in the figure and discussed in the text. The bottom curve is the experimental 11 spectrum from the Ti(0001)1×1-N structure. The second curve from the bottom is the calculated spectrum for the correct model. The hexagon reproduces schematically the LEED pattern, the black dot represents the diffraction spot measured, and the cross the electron-gun position.

It is well known that in a close-packed array of atoms such as Ti metal, there are interstitial holes of two kinds; tetrahedral and octahedral holes.[8] If all octahedral holes are occupied throughout the bulk, the resulting atomic arrangement is that of the NaCl structure, as is the case for bulk TiN. In developing structure models for a single underlayer of N on Ti(0001) we must, however, allow for the possibilities of nitrogen occupying either the octahedral or the tetrahedral holes. We therefore arrive at the following three simple models for the N underlayer, in our notation: $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}C_{\mathrm{N}}A_{\mathrm{Ti}}$ (N in the octahedral holes, as in bulk TiN); $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}B_{\mathrm{N}}A_{\mathrm{Ti}}$ (N in one type of tetrahedral holes); and $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}A_{\mathrm{N}}A_{\mathrm{Ti}}$ (N in the other type of tetrahedral holes). We calculated LEED intensity spectra for all three models and found that only the first (the one with N in the octahedral holes) gives satisfactory agreement with experiment. The calculated 11 spectra at $\theta = 0°$ for all three underlayer models investigated here are also depicted in Fig. 1. Two more LEED spectra calculated for the first underlayer model (N in the octahedral holes) are compared with experiment in Fig. 2. We find the agreement very satisfactory, particularly in view of the fact that one of the spectra displayed in Fig. 2 belongs to a high-order beam $(\bar{2}2)$—usually more difficult to match accurately. The remaining spectra collected experimentally (not shown here) are also in satisfactory agreement with the corresponding ones calculated for the same model. We conclude, therefore, that this model is the correct one.

Figure 3 presents a perspective view of the model. The spacing between the two Ti ($A$ and $B$) layers sandwiching the N layer is 2.45± 0.05 Å and the spacing between the N layer and the top

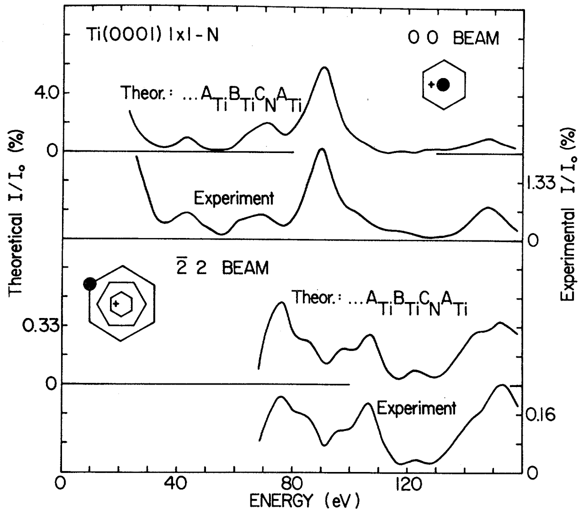

FIG. 2. Comparison between observed and calculated (for the correct model) 00 and $\bar{2}2$ spectra at $\theta = 8°$ and $\varphi = 30°$.

Ti (*A*) layer is 1.22 ± 0.05 Å. Both spacings are equal within the experimental accuracy to corresponding distances found in bulk TiN (2.448 and 1.224 Å, respectively), and the former distance is very close to the $c/2$ spacing in Ti metal (2.339 Å). Hence, the underlayer does not represent a strong distortion of the clean Ti surface and yet it is essentially identical to one (111) double-layer of the TiN crystal.[10] It is also worth noting that the underlayer structure reported here, insofar as it allows for the outermost layer exposed to vacuum to be yet a layer of Ti atoms, is consistent with the experimental fact that more nitrogen can be adsorbed on the surface, at least until completion of the $\sqrt{3}\times\sqrt{3}$-30° structure.

In conclusion, the novelties in the results reported in this paper may be condensed in two points: (i) Recognition and demonstration of the importance of 1× 1 structures in chemisorption processes. This recognition may be obvious when the 1×1 structure is the only (or the last) structure observed in a chemisorption experiment[2,11,12] but is considerably more difficult when the 1×1 *precedes* a clearly recognizable superstructure involving fractional-order beams, as in the present case. Occurrence of 1×1 structures in such cases may, in fact, be more common than heretofore recognized. (ii) Whereas overlayers have been almost exclusively found to form on metal surfaces,[1] the present is the first report of an underlayer structure.

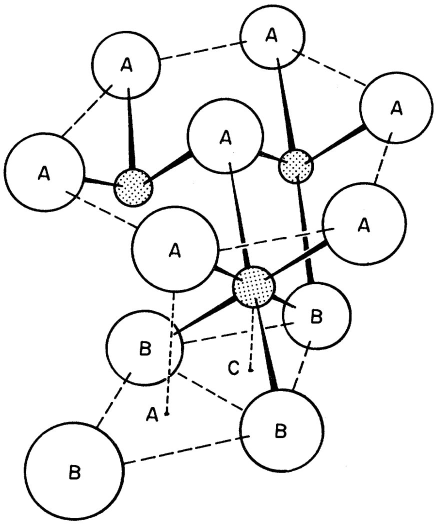

FIG. 3. Perspective view of the Ti(0001)1×1-N structure. The circles marked *A* represent close-packed Ti atoms in the top atomic plane; the circles marked *B*, close-packed Ti atoms in the second plane. The smaller dotted circles represent N atoms sandwiched between the two Ti planes. Only for the nearest N atom is the full octahedral coordination indicated by bond lines. The dotted vertical lines indicate the registry of the *A* Ti atoms and of the N atoms relative to the close-packed *B* plane.

There may be several by-products of the knowledge of surface structures. One of these, in the present case, is the fact that since TiN is a superconducting compound, the Ti(0001)1×1-N structure may offer the unique opportunity of studying the electronic properties of a well-defined *single* atomic double-layer of TiN "deposited" onto a metallic (Ti) substrate.

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[10] Earlier photoemission results by D. E. Eastman, Solid State Commun. 10, 933 (1972), seem to confirm the TiN character of nitrogen sorbed on Ti.

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# Neutron Inelastic Scattering Study of Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ)*

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Neutron inelastic scattering techniques have been used to measure the phonon dispersion curves along the chain direction in TTF-TCNQ. Most of the branches are rather flat and probably stem from excitations within the TTF or TCNQ molecules. Longitudinal and transverse acoustic modes were also measured and a large Kohn anomaly that seems to stem from the longitudinal branch was observed at $0.295\,(2\pi/b)$.

Reports of high conductivities[1-2] found in the charge-transfer salt TTF-TCNQ have stimulated a great deal of interest in this material. Various measurements of the physical properties[3] of TTF-TCNQ prove that it is not a simple metal and it has been suggested[2] that the high conductivities are associated with a Peierls instability in which a phonon mode is driven soft by a very strong interaction with the electrons at a wave vector equal to 2 times the Fermi-surface wave vector, $2k_F$. Recent x-ray and neutron scattering measurements have shown that a superstructure exists in TTF-TCNQ at low temperatures.[4-6] As the temperature is increased above 55°K the scattering measurements showed that three-dimensional ordering disappears and at higher temperatures one expects that any one-dimensional scattering observed by x-ray diffuse measurements would result from a Kohn anomaly in one of the phonon branches. Such one-dimensional x-ray diffuse scattering was observed up to room temperature using counter detection techniques[6] but no sensitive energy analysis is available with x rays and neutron inelastic scattering measurements are needed for detailed examination of the Kohn anomaly.

Unfortunately neutron scattering measurements on TTF-TCNQ can only be performed with considerable difficulty. Only small crystals can be obtained of this material, the largest being about $2\times0.4\times0.02$ cm$^3$. A single crystal is, therefore, not large enough for neutron inelastic scattering measurements and an assembly of crystals must be constructed. A sample was thus constructed in the following manner. Several batches of crystals were grown from solution using very highly purified starting material in order to obtain the largest possible crystals. A series of slots were then milled in thin aluminum plates about $3\times4$ cm$^2$ in size and the largest crystals positioned in the slots. Around fifty crystals were mounted on a plate and five of these plates were stacked together to make the complete sample, giving a sample weight of about 300 mg of TTF-TCNQ. Despite the fact that the crystals were slightly irregular the rocking curve of the whole assembly of about 250 crystals was on the order of 1° in all directions. After cycling the sample through the transition at 55°K a few times it was found that the alignment had decreased to about 2.5°, but this is still sufficient alignment for good phonon measurements especially in the region of the Kohn anomaly where the scattering is limited to a one-dimensional sheet.

The fact that TTF-TCNQ is monoclinic creates additional problems.[7] The crystals have their long dimension along the $\vec{b}$ direction which is the chain direction and are widest along the $\vec{a}$ direction; thus the sample consisted of stacks of crystals lying on the $\vec{c}^*$-axis face. This means that