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Low-energy electron-diffraction determination of the structure of successively deposited ordered layers of Cd on Ti(0001). I. The first layer

H. D. Shih and F. Jona
Department of Materials Science, State University of New York, Stony Brook, New York 11794

D. W. Jepsen and P. M. Marcus
IBM Research Center, P. O. Box 218, Yorktown Heights, New York 10598

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The successive stages of the deposition of Cd onto a clean Ti(0001) surface are studied by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Completion of successive layers of Cd up to the fourth is recognized by study of the AES and LEED spectra as a function of exposure. The atomic arrangement in the first layer is determined by the methods of LEED crystallography. The Cd atoms are not located in the hexagonal-close-packed positions that would be occupied by Ti atoms if the substrate were to grow, but are rather located in the face-centered-cubic positions with respect to the first two substrate layers. The distance between the Cd overlayer and the top Ti layer is 2.57 Å—somewhat more than the interlayer spacing in bulk Ti (2.34 Å) but less than the same in bulk Cd (2.81 Å) corresponding to a bond length of Cd to Ti of 3.08 Å.

I. INTRODUCTION

Studies of surface structures by means of low-energy electron-diffraction (LEED) crystallography have been almost exclusively concerned, so far, with chemisorption phases involving surface coverages of less than one monolayer and periodicities twice as large as those of the substrates.[1] Most of the problems in surface science, however, are considerably more demanding, both in terms of surface coverage and of structure type. The problems associated with the mechanisms of epitaxial growth, for example, deal with superstructures involving a variety of periodicities, and require information about the first full monolayer and, beyond that, about several of the atomic layers formed in the growing crystal.[2] We show here the capability of LEED crystallography to provide quantitative information about the structures of successively deposited layers.

The system studied here is the Cd-Ti system involving the deposition of Cd on the (0001) surface of Ti and eventually leading to the epitaxial growth of a single-crystal Cd film over the Ti substrate. This system was chosen because of the special relationship that exists between the bulk crystallographic data of the two materials: both Ti and Cd crystallize with the hcp (hexagonal close packed) structure and have almost equal a spacings (a_{Ti} = 2.950 Å, a_{Cd} = 2.979 Å) but markedly different c parameters[3] (c_{Ti} = 4.683 Å, c_{Cd} = 5.617 Å). The lattice "misfit" is therefore small within the basal plane, which suggests that a Cd monolayer on the Ti(0001) surface would probably be close packed with the same periodicities as the substrate. In Wood's notation,[4] such a resulting surface phase would be labeled Ti(0001)1 × 1-Cd. The geometry of the corresponding LEED pattern, i.e., the angular positions of the beams, would be indistinguishable from that of the clean Ti(0001) surface.

The questions that arise are the following: (i) Can one recognize the completion of the first Cd layer? (ii) Can the registry of the first Cd layer with respect to the first Ti layer be determined, in particular, can the two types of threefold sites be distinguished from each other? (iii) Can the interlayer spacing d_z^S of the first Cd layer with respect to the first Ti layer be determined? We show that these questions can be answered affirmatively. In addition, we show that not only can completion of the first layer be recognized but that upon prolonged deposition of Cd the completion of the second, third, and fourth atomic layer can also be recognized. Detailed discussion of the second, third, and fourth layers will be given in a following paper.[5]

Development of criteria for the recognition of *completed* 1 × 1 phases, i.e., for the identification of full monolayer coverage when the surface phase has the same symmetry and the same two-dimensional periodicity as the clean-surface structure is a difficult task. In the only published case in which a full structure analysis of a surface 1 × 1 phase was carried out, such an identification was made by examining the changes in both the Auger electron spectroscopy (AES) and LEED spectra as functions of exposure; completion of a layer was identified with an inflection point in the AES-exposure relationship.[6] In the present case, as we will show below, the AES studies are subject to many experimental difficulties, and must be supplemented with the information provided by the measurement of LEED intensities; taken together, these two sets of data provide a consistent description which clearly points toward the establishment and completion of stable 1×1 phases at specific exposure values. The confirmation is finally the demonstration given below that calculated LEED intensities with the 1×1 model fit the experimental spectra very well.

In the present report, we discuss, in Sec. II, details of the experimental procedures which are essential for an understanding of the results. In Sec. III, we describe the results of the AES experiments and, in Sec. IV, of the LEED observations. We discuss the structure analysis of the first Ti(0001) 1×1-Cd phase observed in Sec. V and show that the Cd atoms are not located on the "expected" sites. A preliminary account of this work has been published elsewhere.[7]

II. EXPERIMENTAL DETAILS

Two Ti samples, each of 99.999% purity, were used sequentially in the present investigation: sample *A*, with dimensions $20\times 5\times 0.3$ mm^3, was used predominantly for the LEED studies; sample *B*, with dimensions $17\times 8.5\times 0.5$ mm^3, was used predominantly for the AES studies, but all LEED results obtained with sample *A* were confirmed with sample *B*. The (0001) surfaces were prepared as described elsewhere.[8] The Cd source consisted of 99.9999% material enclosed in a cylindrical Pyrex capsule with outside diameter 8 mm and length 38 mm, which was sealed in a separate vacuum system at a pressure of approximately 10^{-8} Torr. A Ni ribbon was wrapped around the capsule, which could then be heated by an electric current. The capsule was provided with a break-off tip to be broken *in situ* at the appropriate time and was mounted in the LEED chamber in such a way that the extension of its cylinder axis would meet the Ti(0001) sample surface at a distance of 7.6 cm. After breaking the tip a suitable electric current through the Ni ribbon caused sublimation of the Cd charge and generated a beam of Cd atoms directed straight at the Ti(0001) surface. The Cd beam could be interrupted by a shutter and, in addition, the Ti sample could be turned to orient the (0001) surface either toward or away from the Cd source. Two capsules were used in the two runs involving samples *A* and *B*, sequentially. In all experiments, the Ti sample was not intentionally heated and was therefore expected to be at or near room temperature.

While room-temperature operations in the vacuum chamber were possible with the capsule open (the vapor pressure of Cd is about 10^{-11} Torr at 295 °K), the indirect heating by means of the Ni ribbon made it very difficult to establish and maintain a very slow and steady Cd sublimation rate. A slow and constant rate was necessary in order to observe the changes in the LEED and AES spectra with increasing coverage of the substrate surface by the Cd atoms. Two different methods were employed to achieve very slow exposure rates: the "direct" and "indirect" method, both described below.

The "direct" method consisted in exposing the substrate surface perpendicularly to the atomic Cd beam emerging from the capsule. The procedure involved the following steps: (i) with the pressure in the chamber at its base value $[(5-6)\times 10^{-11}$ Torr$]$ the Ni ribbon was heated to 300 °C for a fixed time interval (4 min for the capsule used with sample *A*, 3.33 min for that used with sample *B*) with the shutter closed; (ii) after turning off the current through the Ni ribbon, the sample surface was turned toward the capsule, the shutter was open and exposure was allowed for 30 sec while the pressure in the chamber increased to a maximum of $(2-3)\times 10^{-10}$ Torr; (iii) the shutter was closed again and the pressure was allowed to return to its base value (requiring typically about 3 min.); (iv) the sample was set in position for LEED observations and the 00 spectrum was recorded (requiring typically about 6 min). Thus, with this procedure the exposure periods of 30 sec. each were set approximately 15 min apart. We will see below that in order to identify the completion of the first, second, third, and fourth Cd layer about 40 spectra of the 00 beam were recorded, a process that required in total approximately 15 h. Although the chamber was continually pumped during this period, it was reasonable to worry about possible contamination of the surface by residual gases. The AES spectra, however, revealed no increase in oxygen or carbon lines during the whole sequence of Cd exposures—a surprising result in view of the high reactivity of the clean Ti(0001) surface.[8] It appears that a Cd-covered Ti surface does not collect oxygen or carbon very rapidly.

The "indirect" method of surface exposure was a result of the accidental discovery that it was not necessary to turn the surface into a position in direct line of sight of the source in order to deposit Cd on the surface itself. It was found that with the open capsule hot (the actual temperature of the Cd source was roughly estimated to be of the order of 100 °C), the shutter closed and the Ti surface turned away from the heated capsule, the amount of Cd on the surface increased with time, as indicated by AES. (No increase in oxygen or carbon concentration was detected over periods of several hours.) The explanation for this fact is that Cd atoms originating at the source reached the Ti surface after collisions with the shutter and the vacuum chamber walls, i.e., that the sticking coefficient of Cd atoms on the oxidized stainless steel surfaces of shutter and walls is smaller than unity (see also Ref. 9). In fact, the ionization gauge measuring the pressure in the vacuum chamber (which was located near the Ti sample and was not in direct view of the Cd source) registered an increase in reading, under the above conditions, from the base value of $(5-6)\times 10^{-11}$ Torr to about $(6-7)\times 10^{-9}$ Torr. Analysis of the residual gases in the chamber under these conditions, done with a quadrupole mass spectrometer, revealed no increase of O_2, CO, CO_2, or hydrocarbons, but indeed the presence of Cd vapor. Thus, the pressure increase in the chamber was due to the Cd vapor generated at the source and reaching the gauge location after one or more collisions with the shutter or chamber walls.

The LEED observations and measurements were made with a commercial display-type instrument. The procedures for adjusting the sample position, measuring the incident and azimuthal angles, minimizing the residual magnetic field were described in an earlier publication.[10] The diffracted intensities were measured by recording the brightness of the corresponding spots on the fluorescent screen by means of a spot photometer. The latter's response was then converted to electron current by calibration with a Faraday cage.

The AES scans were done by the retarding-field method with the four-grid filter of the LEED optics. The energy of the exciting electrons was sometimes 3 keV, but most often 1.5 keV, as discussed below, while the modulating voltage varied between 1 and 5 V peak to peak.

III. AUGER ELECTRON SPECTROSCOPY

The use of AES in the present study was affected by two experimental difficulties. The first was that for high energies and large-current densities of the exciting electron beam the Cd concentration of the Ti surface was found to decrease. For example, with a 3-keV, 400-μA beam an amount of Cd equivalent to 3 atomic layers was observed to disappear from the surface in less than 1 min. This disappearance was detected by recording the changes in the 00 LEED spectrum, as discussed in the next section, and was due, we think, to electron-stimulated desorption of the Cd atoms. With an exiting beam of 1.5 keV and less than 100 μA no change in the Cd concentration was detected even after 150 min. All subsequent measurements were, therefore, made under conditions of relatively weak excitation (1.5 keV, less than 100 μA).

The second difficulty arose from partial overlap of the most pronounced Auger lines of Ti and Cd. We see from Fig. 1 that the 378-eV Cd line ($M_5N_{4,5}N_{4,5}$) overlaps the small Auger emission of Ti at 377 eV,[11] while the Cd line at 384 eV ($M_4N_{4,5}N_{4,5}$) practically overlaps the Ti line at 383 eV ($L_3M_{2,3}M_{2,3}$). In order to monitor the increasing concentration of Cd on the Ti surface during deposition we followed the Cd lines at 378 and 6 eV,[12] and the Ti lines at 419 and 28 eV.

Figure 2 depicts the intensities of these four lines as functions of surface exposure to the Cd vapor. The intensities are defined as the peak-to-peak heights of the doubly differentiated Augar lines. AES spectra were recorded during exposure of the surface by the "indirect" method described in the preceding section. The time zero on the abscissa axis corresponds to the moment at which an electrical current through the nickel strip wrapping the Cd source was switched on. After approximately 30 min. the pressure in the chamber was stabilized at the value $(6-7)\times 10^{-9}$ Torr, as des-

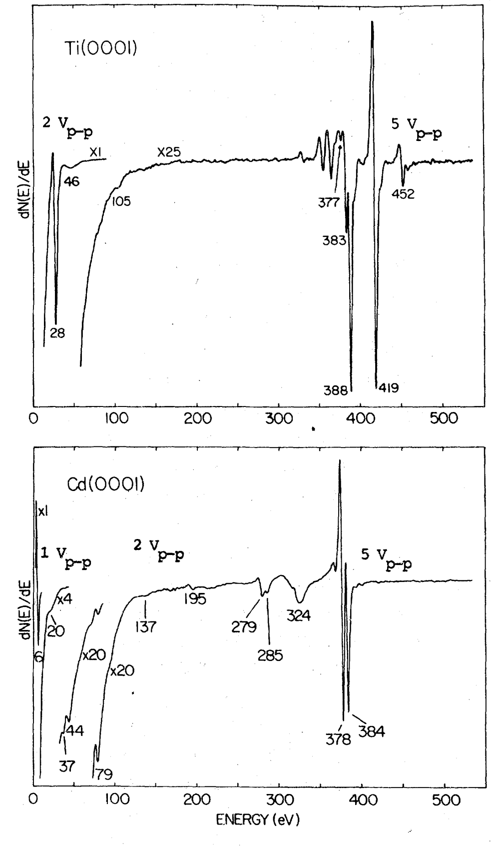

FIG. 1. AES spectra from a clean Ti(0001) surface (upper box) and a clean Cd(0001) surface (lower box). The latter was determined from a Cd film grown epitaxially on the Ti(0001) surface in the present work.

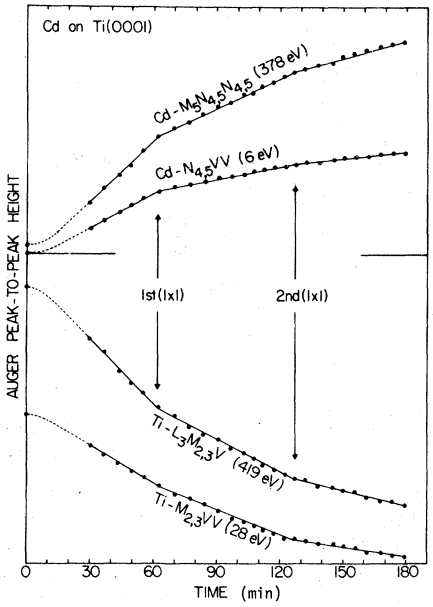

FIG. 2. Dependence of AES lines intensities (defined as the peak-to-peak heights of the doubly differentiated Auger lines) upon coverage of the Ti(0001) surface by Cd. The top two curves represent the growth of the Cd lines at 378 and 6 eV, respectively, the bottom two curves, the decay of the Ti lines at 419 and 28 eV, respectively. The abscissa is the time of exposure of the surface to Cd vapor as described in the text. The arrows indicate the exposures at which the LEED observations reveal the formation of the 1st (1×1) and 2nd (1×1) phases.

cribed above. The recording of each Auger line, i.e., every point plotted in Fig. 2, required approximately 30 sec, and each point was plotted at the time at which the measurement was started. At time zero, the Ti lines have the intensities characteristic of the clean surface, while the Cd lines have zero intensities—the fact that the plot of the 378-eV line starts at a nonzero value is due to the existence of a Ti line at the same energy.

All data in Fig. 2 indicate continuing increase of the Cd concentration on the surface—the substrate lines decrease, while the adsorbate lines increase, in intensity with surface exposure. The slopes of all lines change discontinuously at approximately the same exposures, a fact that has been demonstrated earlier in other systems[13-15] to correspond to completion of well-defined surface phases. Here, studies of the LEED intensities observed at the surface coverages which correspond to the discontinuous slope changes (to be discussed below) revealed that the latter do indeed correspond to completion of what in Sec. IV we call the 1st (1×1) and the 2nd (1×1) phases (indicated by arrows in Fig. 2).

IV. LEED OBSERVATIONS

If, as mentioned in Sec. I, the deposited Cd atoms were to arrange themselves on a close-packed net with the same orientation and the same periodicity as the substrate surface, the geometry of the LEED pattern would not be expected to change from that of the clean surface. However, the intensities of the diffracted beams would indeed be expected to change, reflecting a different scattering power and a different registry and elevation of the adsorbed atoms over the substrate surface. The observations of the LEED pattern from clean Ti(0001) and its changes upon adsorption of Cd fulfilled the above expectations. In addition, the pattern background remained low and the contrast high, whereas if the Cd atoms had been distributed at random over the Ti surface, the background would be expected to increase and the contrast to decrease with increasing Cd concentration.

These qualitative observations were sufficient to establish that the arrangement of the deposited Cd atoms on the surface was ordered and epitaxial. The next question, already asked in the Introduction, was: can we tell when the formation of the first Cd monolayer is completed? Since the geometry of the LEED pattern did not depend upon the Cd concentration it was obvious that the answer to the question had to be sought in the changes of the *intensities* of the diffracted beams. We concentrated our attention on the 00 beam and examined carefully the changes that occurred in the intensity-versus-energy curve (LEED spectrum) of this beam with increasing deposition of Cd on the initially clean surface. The exposures were done with the "direct" method described in the Introduction, the substrate surface being directly exposed to the Cd beam with the shutter open for 30 sec—an operation that we arbitrarily defined as a "unit exposure." The 00 spectrum was recorded for the clean surface, after one unit exposure, after two units of exposure, etc. The corresponding normalized curves are depicted in Fig. 3 for the exposure range from 0 (clean surface) to 26 units of exposure, and in Fig. 4 for the range from 26 to 90 units of exposure.

Careful scrutiny of the family of curves led us to conclude that the change from any one curve to the next was minimum around curve 7, then again around curve 17, around curve 42 and finally curve 90. We chose to label the first minimum as the 1st (1×1) phase, the second minimum as the 2nd (1×1) phase, the third minimum as the 3rd (1×1) phase, the fourth minimum as the 4th (1×1) phase. These extrema can be recognized from a number of details. For the 1st

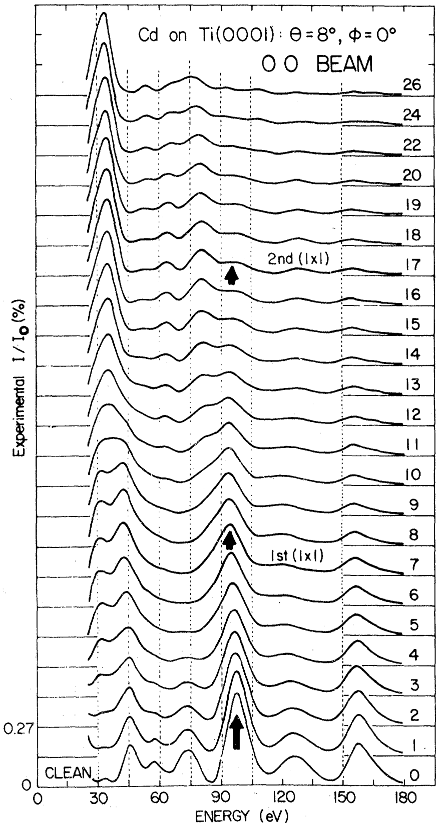

FIG. 3. Evolution of the 00 spectrum at $\theta = 8°$, $\phi = 0°$ with increasing exposure of the initially clean Ti(0001) surface to Cd vapor. The numbers on the curves represent units of exposure as defined in the text. The arrows indicate the peaks whose intensities are plotted in Fig. 5.

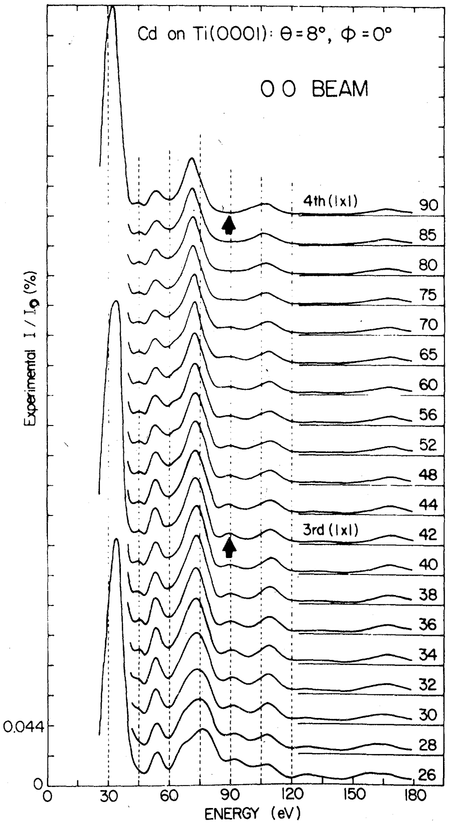

FIG. 4. Continuing evolution (after Fig. 3) of the 00 spectrum at $\theta = 8°$, $\phi = 0°$ with increasing exposure to Cd vapor. The numbers on the curves represent units of exposure as defined in the text. The arrows indicate the peaks whose intensities are plotted in Fig. 5.

(1×1), e.g., the evolution of the peak at 32 eV and the decay of that at approximately 74 eV are stabilized around curve 7. For the 2nd (1×1), the peaks around 65 eV and around 130 eV are most pronounced in the vicinity of curve 17. For the 3rd (1×1), the features between 50 and 75 eV are stabilized around curve 42, and the broad peak around 110 eV, which is shifted toward higher energies from curve 26 on, reaches its highest-energy position around curve 42. Finally, toward the top of Fig. 4 the positions of the peaks at approximately 70 and 110 eV are stabilized at curve 90, and the spectra recorded after longer exposures to Cd vapor (not shown) no longer change in a perceptible way.

The key point in the LEED analyses that follow was the assumption that each one of the phases identified above represented a *complete* layer of Cd atoms. Full justification and proof of this assumption was to be provided ultimately by the agreement with experiment of calculations done for models based just on that assumption. A possible explanation is as follows. The deposition of only a few atoms on a flat surface is likely to cause negligible changes in the LEED spectrum of the surface. These changes become larger as soon as the deposited atoms aggregate to form islands with lateral dimensions comparable to the coherence length of the probing electrons. When the islands coalesce to form a complete (or almost complete) layer then the changes in the observed LEED spectrum are again expected to be small. Another possibility for explaining the extrema referred to above is a decrease of the sticking coefficient in the vicinity of the completion of a layer.

However, whatever the interpretation of a minimum change between curves, we need to recognize first that such a minimum indeed exists, and then to show that the corresponding LEED spectra agree with calculations for complete layers. Recognition of the minima is not easy for an untrained eye on the basis of Figs. 3 and 4 alone, despite the details that we have described above. For this reason, we

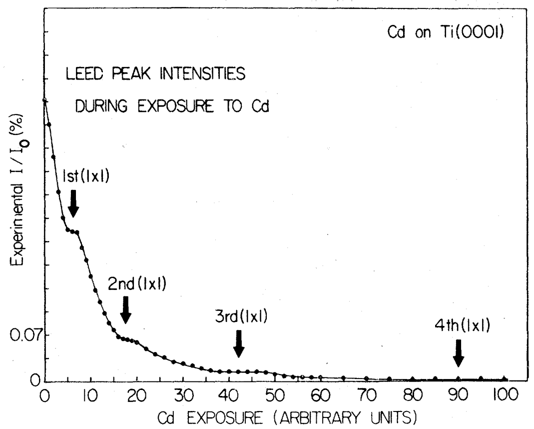

FIG. 5. Decay of the LEED peak at 98 eV in the 00 spectrum of clean Ti(0001) with increasing exposure to Cd vapor. The minima in the slope are identified with the 1st, 2nd, 3rd, and 4th (1×1) phase, respectively, as discussed in the text.

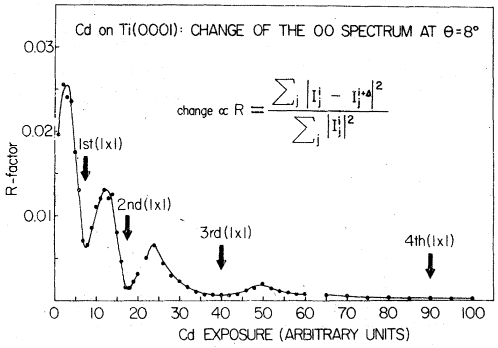

FIG. 6. Change of the 00 spectrum at $\theta = 8°$, $\phi = 0°$ with exposure of the initially clean Ti(0001) surface to Cd vapor. The interruptions in the curve are due to the fact that up 20 units of exposure the spectra were recorded after every unit; from 20 to 60, they were recorded after 2 units; and after 60, they were recorded after 5 exposure units (see Figs. 3 and 4).

give more obvious evidence in two additional figures. The peak that is located at 98 eV in the spectrum of clean Ti(0001) (see the arrow in the bottom curve of Fig. 3) undergoes shifts, splits and changes in magnitude with increasing exposure to Cd vapor and is completely absent in the spectrum that, as we shall see, corresponds to a clean Cd (0001) surface (top curve in Fig. 4). In Fig. 5, we plot the intensity of this peak as a function of Cd exposure in the units defined above. Minima in the change of the intensity with exposure are recognizable at the exposure values, indicated by arrows, that correspond indeed to what we have defined as the 1st (1×1), the 2nd (1×1), the 3rd (1×1), and finally the 4th (1×1) phases.

In Fig. 6, we follow a procedure that was proven useful in a recent study of another 1×1 phase.[16] We define a factor R that is meant to quantify the change exhibited by the entire 00 spectrum corresponding to i units of exposure when the latter is increased by Δ units to $i+\Delta$. The definition is

$$R = \left(\sum_j |I_j^i - I_j^{i+\Delta}|^2 \right) \Big/ \sum_j |I_j^i|^2 ,$$

where I_j^i is the intensity of the 00 beam at energy j in the spectrum measured after i units of exposure to Cd vapor, and the summation extends over the energy range from about 30 to 180 eV. The R factor was calculated for all curves depicted in Figs. 3 and 4, and is plotted in Fig. 6 as a function of Cd exposure. Minima, indicated by arrows, are found indeed at the exposure values at which they were first revealed by the visual examination of the family of curves depicted in Figs. 3 and 4—and which were identified with the 1st, 2nd, 3rd, and 4th (1×1) phases, respectively.

We believe, therefore, that the case for the existence of minima in the rate of change of the LEED spectra with exposure to Cd vapor has been made. When added to the results of the AES study (Fig. 2), this information makes it indeed plausible to assume that those minima announce the completion of ordered monoatomic layers of Cd in the same orientation as the Ti substrate. In accordance with this assumption, we have collected for all 1×1 phases thus defined intensity spectra for a number of beams (about ten) at two angles of incidence, for the purpose of carrying out LEED structure analyses, i.e., determinations of the relative atomic arrangements. Unambiguous definitions of the incidence angles θ and ϕ have been given before.[16,17] Indexing of the beams and sketches of the LEED patterns observed have been given explicitly in the paper reporting the structure analysis of the clean Ti(0001) surface.[8]

V. DETERMINATION OF THE ATOMIC ARRANGEMENT IN THE FIRST (1 × 1) PHASE

The small misfit of the a parameters of Ti and Cd structures leaves little doubt that the first monolayer of Cd on Ti(0001) is very probably close packed and epitaxial. What remains to be determined are the registry and the interlayer spacing of the Cd layer with respect to the Ti(0001) substrate. Figures 7 and 8 are concerned with the registry, and depict models in which the bare Ti(0001) surface [Fig. 7(a)] is covered with Cd atoms located directly above each Ti atom [so-called top-atom model, Fig. 7(b)]; or in the threefold symmetrical hollows that would harbor substrate atoms if the substrate were to grow [so-called hcp model, Fig. 7(c)]; or in the other three-

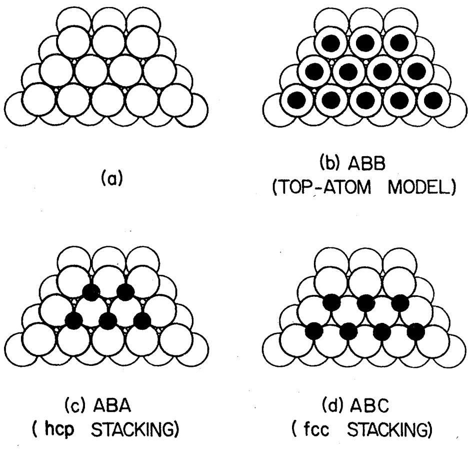

FIG. 7. Schematic model of (a) the clean Ti(0001) surface; (b) monolayer of Cd (black circles) in the top-atom positions; (c) monolayer of Cd in the sites that correspond to hexagonal-close-packed stacking; (d) monolayer of Cd in the sites that correspond to face-centered-cubic stacking.

fold symmetrical sites that correspond to fcc stacking [so-called fcc model, Fig. 7(d)]; or finally, in the bridge positions across two adjacent substrate atoms (so-called bridge-site model, of which Fig. 8 depicts the three possible types of domains).

We carried out LEED-intensity calculations for each of the structural models just described, using the layer-KKR (Kohn-Korringa-Rostoker) method described elsewhere,[18] 8 phase shifts and 31 beams for the description of the electron wave function. The nonstructural parameters pertinent to the substrate were taken from the successful analysis of the clean Ti(0001) surface[8] (i.e., self-consistent band-structure potential for Ti; imaginary part $\beta^B = 3$ eV; inner potential $V_0^B = 11$ eV; mean amplitude of lattice vibrations $\langle u_B^2 \rangle^{1/2} = 0.198$ Å). The corresponding parameters for the surface overlayer were chosen accordingly (i.e., self-consistent band-structure potential for Cd; $\beta^S = \beta^B$, $V_0^S = V_0^B$, $\langle u_B^2 \rangle = \langle u_S^2 \rangle$).

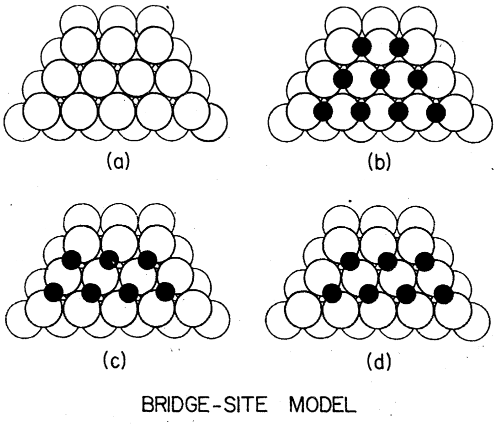

FIG. 8. Schematic models of (a) the clean Ti(0001) surfaces; (b)–(d) the three possible configurations of a Cd monolayer in the bridge sites.

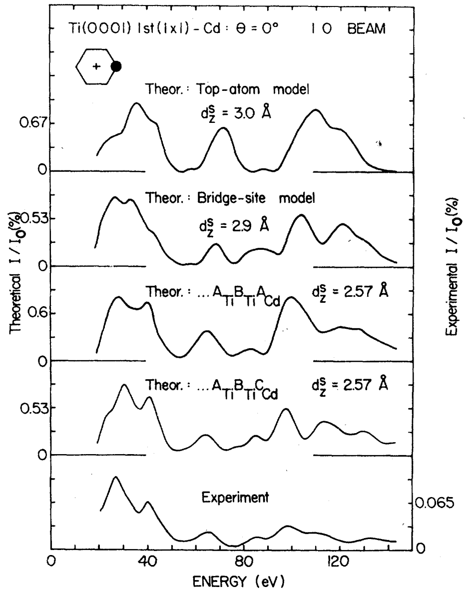

FIG. 9. Structure analysis of the Ti(0001) 1st (1×1)-Cd phase: 10 spectra at normal incidence calculated for the four models depicted in Figs. 8 and 9. The bottom curve is experimental.

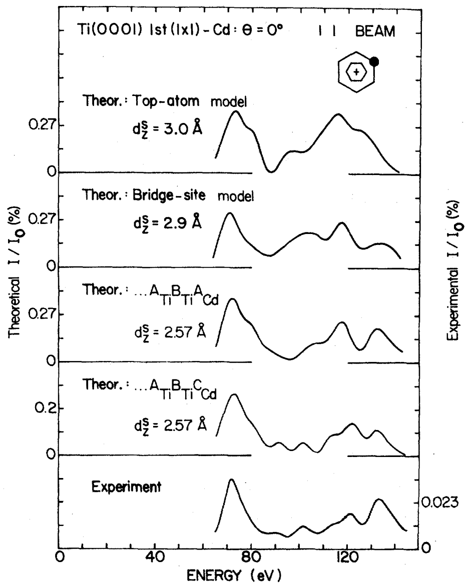

FIG. 10. Structure analysis of the Ti(0001) 1st (1×1)-Cd phase: 11 spectra at normal incidence calculated for the four models depicted in Figs. 8 and 9. The bottom curve is experimental.

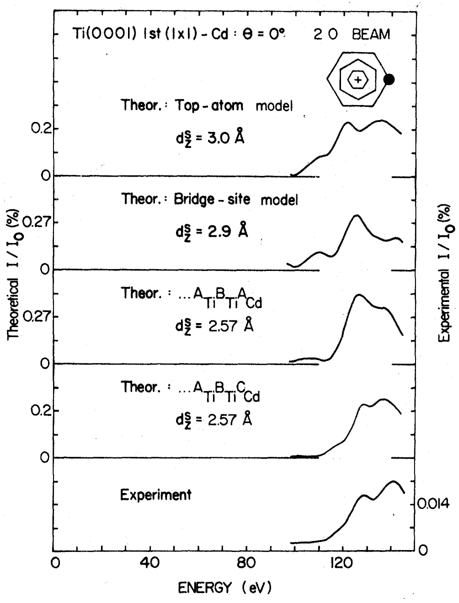

FIG. 11. Structure analysis of the Ti(0001) 1st (1×1)-Cd phase: 20 spectra at normal incidence calculated for the four models depicted in Figs. 8 and 9. The bottom curve is experimental.

For all models, the intensity calculations were done for an ideally flat surface with a given termination. The results were then averaged over both terminations that are possible at hcp (0001) surfaces[8] by assuming equal representation of the two terminations in the region of the surface interrogated by the primary beam.

Figures 9–11 compare with experiment the spectra of the 10, 11, and 20 beams at normal incidence, respectively, as calculated for all overlayer models described above. There is little doubt that only the models labeled$\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}A_{\mathrm{Cd}}$ and $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}C_{\mathrm{Cd}}$, in which the Cd atoms are located on the threefold symmetrical sites of the surface net, produce spectra similar to the observed ones. Detailed comparison of peak positions, peak shapes and relative intensities clearly discriminates in favor of the model in which the Cd atoms are located in the so-called fcc sites $(\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}C_{\mathrm{Cd}})$.

This trend is consistently confirmed by the comparison with experiments of the spectra of beams calculated for nonnormal incidence. Figures 12–15 depict the results for the 00, 10, 01, $\bar{2}1$, 22, $1\bar{2}$, and $\bar{2}1$ beams at $\theta = 7°$ and $\phi = -30°$. The 00 and the $\bar{2}2$ beams particularly strongly favor the $\ldots A_{\mathrm{Ti}}B_{\mathrm{Ti}}C_{\mathrm{Cd}}$ model. Thus, the question about the registry of the Cd layer with respect to the Ti(0001) net is answered: the Cd atoms are located in the threefold symmetrical hollows that correspond to fcc continuation of the substrate. Implicit

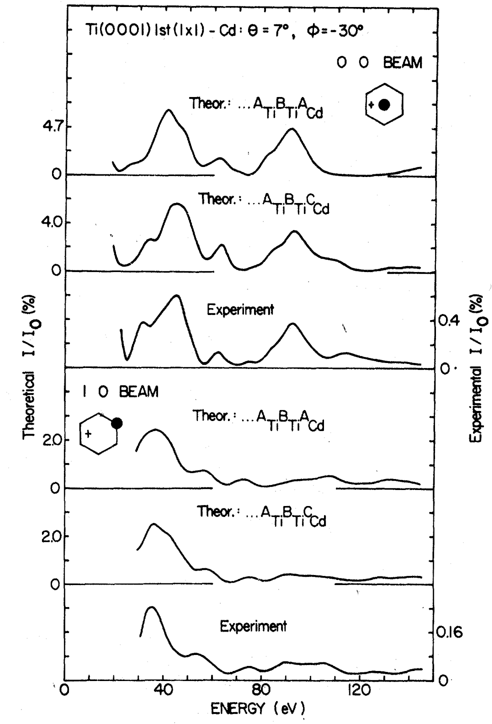

FIG. 12. Structure analysis of the Ti(0001) 1st (1×1)-Cd phase: two model calculations and experiment for the 00 and 10 beams at $\theta = 7°$, $\phi = -30°$.

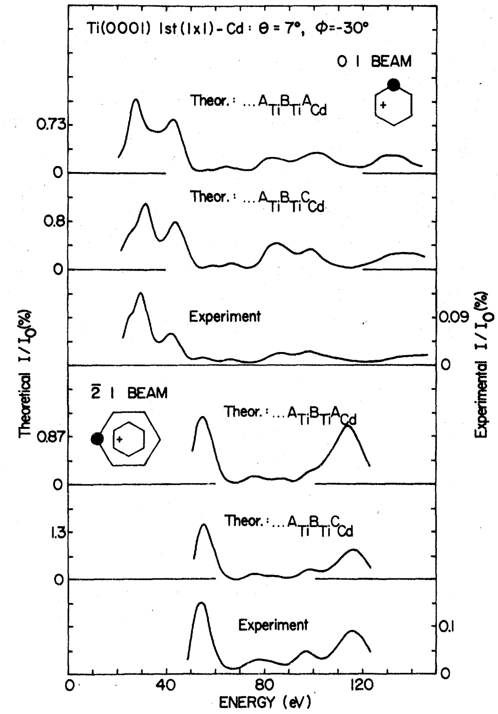

FIG. 13. Structure analysis of the Ti(0001) 1st (1× 1)-Cd phase: two model calculations and experiment for the 01 and $\bar{2}1$ beams at $\theta = 7°$, $\phi = -30°$.

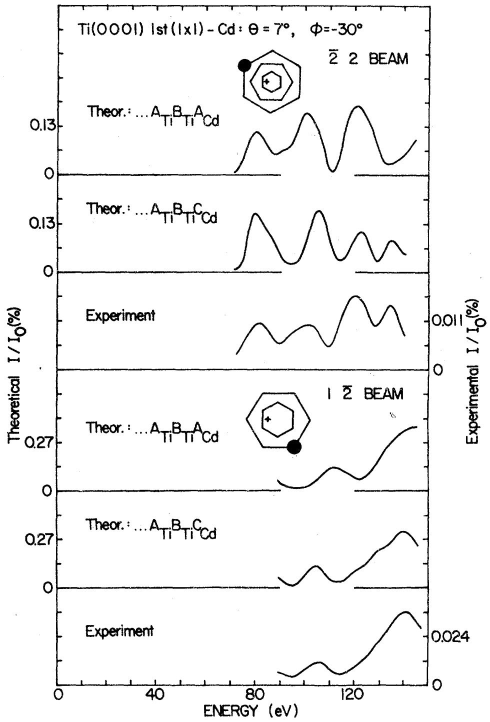

FIG. 14. Structure analysis of the Ti(0001) 1st (1× 1)-Cd phase: two model calculations and experiment for the $\bar{2}2$ and $1\bar{2}$ beams at $\theta = 7°$, $\phi = -30°$.

in these results is the answer to the question about the spacing between the Cd layer and the top Ti layer. For each beam, the spectrum is calculated over a range of different values for the distance d_z^S between the plane of Cd atoms and that of the first Ti layer. Figure 16 shows, as an example, the effect of a variation of d_z^S from approximately 2.8 to 1.4 Å, in steps of approximately 0.1 Å, on the 11 spectrum. The experimental curve (dotted in the figure) is best matched by the curve calculated with $d_z^S = 2.574$ Å. It is with this value that all curves for this model presented in the previous figures were calculated. For the other models, the d_z^S values quoted in Figs. 9–11 were chosen as those that produce closest *overall* agreement with experiment, even if such agreement is very poor.

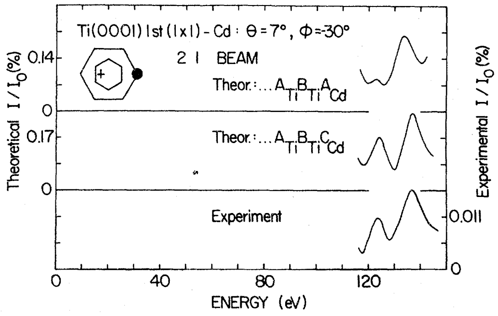

FIG. 15. Structure analysis of the Ti(0001) 1st (1× 1)-Cd phase: two model calculations and experiment for the 21 beam at $\theta = 7°$, $\phi = -30°$.

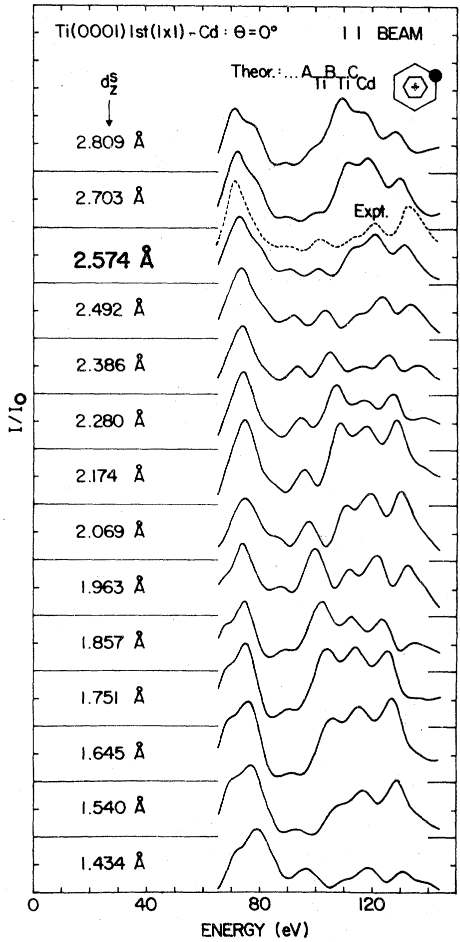

FIG. 16. Ti(0001) 1st (1×1)-Cd phase: effect of the distance d_z^S between the plane of Cd atoms and that of the top Ti layer on the calculated spectra of the 11 beam at normal incidence. The dotted curve is experimental. Although the theory-experiment correspondence is best for $d_z^S = 2.574$ Å, it is again acceptable around 2.069 and 1.540 Å, respectively.

It may be of interest to note, in Fig. 16, how the correspondence with experiment seems to vary almost periodically with varying d_z^S—a fact already pointed out some time ago by Andersson and Pendry[19] for the Ni(001)$c(2\times 2)$-O structure. We see in Fig. 16 that the agreement with experiment is good not only for $d_z^S = 2.574$ Å but also, although somewhat less good, for $d_z^S = 2.069$ Å and then again $d_z^S = 1.540$ Å. The choice of the correct value of d_z^S is made on the basis of *all* beams available for comparison.

VI. CONCLUSIONS

We have demonstrated that in the course of very slow deposition of Cd atoms on a clean Ti(0001) surface there exist extrema and/or discontinuities in the changes of various quantities as determined by LEED and AES. We have identified those extrema with the completion of Cd monolayers, and accordingly, we have defined a 1st (1×1), a 2nd (1×1), a 3rd (1×1), and finally a 4th (1×1) phase, the latter being final, i.e., invariant with respect to further deposition of Cd atoms.

We have carried out a LEED intensity analysis of ten beams at two different angles of incidence for the 1st (1×1) phase, and found excellent agreement with experiment for intensity calculations based on the model of a complete close-packed monolayer of Cd atoms. Each of these atoms resides in a threefold symmetrical site of the Ti(0001) surface that corresponds to fcc stacking of the atomic layers—if the stacking is thought of as starting from the second layer of the Ti substrate. Thus, the Cd atoms are *not* located on the sites that would be occupied by Ti atoms if the substrate were to grow. The structure of the 1st (1×1) phase is accordingly labeled $\ldots A_{\mathrm{Ti}} B_{\mathrm{Ti}} C_{\mathrm{Cd}}$, the distance between the Cd layer and the top Ti layer being 2.57 Å. Hence, the interplanar spacing in the z direction is larger than that of bulk Ti (2.34 Å) but not yet as large as that of bulk Cd(2.81 Å). The Cd-Ti bond length is 3.08 Å—only slightly smaller than the sum 3.09 Å of the out-of-plane radii of Ti and Cd, 1.448 and 1.646 Å, respectively.

In general discussions of layer-by-layer epitaxial growth the statement is often made that the formation of new layers is expected to begin even before the preceding layers are completed.[20] We may ask why, therefore, in the present experiment we do not find that the Cd atoms are distributed in islands with heights greater than one layer, separated by regions of bare surface. We believe that the answer lies in the fact that our experiments were carried out very slowly, so that surface diffusion of the Cd atoms favored the formation of a single continuous atomic layer covering the whole surface. This result seems to lend support to the method for surface-coverage analysis developed by Argile and Rhead.[21] The same argument can explain the formation of a continuous second, third, and fourth layer. The structure analyses of these additional layers will be the object of a subsequent paper.[5]

The data plotted in Figs. 5 and 6 contain some implications about the sticking coefficient of Cd atoms. Complete cadmium layers occurred, as we can see from the figures, after 7, 17, 42, and 90 units of exposures, so that the ratios of the time periods required to achieve such complete layers go as 7 : 10 : 25 : 48. The implication is clearly that the sticking coefficient decreases by a factor of 4–5 in going from a single Cd layer to a three-layer Cd film on Ti(0001). At first sight, this result may appear surprising and therefore calls for a critical discussion of our Cd-dosing technique.

The main questions, of course, are concerned with possible experimental errors. Were the results reported in Figs. 5 and 6 reproducible? The answer is yes. First, data were reproduced more than twice with the same Ti sample and the same Cd source. Second, as mentioned in Sec. II, the data were reproduced with a different Ti sample and a different Cd source. Could the temperature of the source have varied from exposure to exposure? Although the temperature of the Ni ribbon heating the source was reproduced very well for each exposure, minor undetectable fluctuations were indeed possible. Such fluctuations, however, are expected to produce scatter of the experimental results, not the kind of systematic error that would lead to the data of Figs. 5 and 6. Could the temperature of the substrate have been substantially deviating (in particular, increasing) from room temperature in successive exposures? We believe that the answer is no. The only "hot" object that the substrate could have "seen" during the exposure series was the Cd source (the Ni ribbon was at 300 °C). The distance between substrate and source was about 8 cm and the two were in view of one another for only 30 sec at intervals of about 15 min. During data collection with the "indirect" method, substrate and source did not "see" one another at all. Could the surface of the Cd source have been progressively "poisoned" in such a way as to reduce its sublimation rate? The reproducibility of the data, mentioned above, seems to deny this possibility. Could there have been more pronounced desorption of Cd atoms (by the electron beams used for testing) from multilayer as opposed to single-layer deposits? As discussed in Sec. III, for relatively weak excitations no changes were observed in AES or LEED spectra. In particular, after collection of LEED intensity data for, say, a sequence of 11 beams (a procedure requiring 2–3 h with the electron beam on), the first beam was found to be unchanged.

It appears therefore that there were no serious flaws in our Cd dosing technique. We have not been able to find literature data on the Cd-Ti system that can be compared with our results. We can, however, compare the implications of our Figs. 5 and 6 with the careful work that Wagner and Voorhoeve[9] have done for the case of Cd on polycrystalline tungsten. These authors found, among other things, that (i) for the first 3–4 layers, Cd grows in the layer-by-layer mode; (ii) the sticking coefficient of Cd decreases with increasing coverage (Fig. 6 of Ref. 9 shows that at 108 °C the sticking coefficient decreases by a factor of about 3 when the coverage increases from 1×10^{15} cm^{-2} to about 4×10^{15} cm^{-2}); (iii) for thick Cd layers the sticking coefficient is about 0.6, very nearly independent of temperature. If growth had occurred exclusively on the basal plane it is probable that the sticking coefficient would have been found to be lower yet.

We conclude that the implications of our Figs. 5 and 6 about the sticking coefficient of Cd are not inconsistent with the results of other workers. It would be interesting, of course to test our results with other techniques. Unfortunately, however, most of the experiments reported in the literature having relevance to the sticking coefficient involve polycrystalline substrates and are, therefore, not quite comparable with the work described in this paper. We believe that critical experiments ought to be carried out on well-characterized *single-crystal* substrates and, eventually, a truly microscopic theory of sticking should be developed.

Note added in proof. After submission of this article we found an error that affects the energy scale of all LEED spectra. To correct for this error, each number on the energy scale of each LEED spectrum must be increased by 3 eV (i.e., instead of 0, read 3 eV; instead of 40 eV, read 43 eV, etc.). Accordingly, the values of V_0 and V_0^S quoted in the text should be decreased by 3 eV. The conclusions of the paper are otherwise not affected.

ACKNOWLEDGMENTS

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[12] Extreme caution is advised for repetitive measurements of Auger line intensities. Since particularly the low-energy lines have strongly angle-dependent intensities the incidence angle of the primary electrons must be reproduced exactly.

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