Palladium diffusion and cluster nucleation on Ta(110)

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The surface diffusion and initial stages of cluster nucleation of Pd adatoms on Ta(110) are investigated by field ion microscopy (FIM). The results indicate that Pd atoms become mobile on Ta(110) at 180 K and diffuse with an activation energy of 0.49 ± 0.02 eV. The structure of small Pd clusters on the Ta(110) plane depends upon the number of Pd adatoms present on the plane. If fewer than nine Pd atoms are deposited on the plane, the stable configuration is a linear chain oriented along a close-packed direction of the substrate. Two-dimensional island clusters containing fewer than nine atoms are metastable. For nine or more adatoms, however, the stable configuration is a two-dimensional island cluster and the linear chain cluster is metastable. Field ion images of the two-dimensional island clusters indicate that the Pd overlayer is pseudomorphic up to, and including, approximate monolayer coverages. Two-dimensional Pd clusters migrate as a unit on Ta(110) at temperatures from $\sim$250 to 325 K. Above $\sim$350 K the clusters rapidly disappear from the plane. The results of this investigation are compared to other FIM data related to the nucleation of metal-adatom clusters.

I. INTRODUCTION

Nucleation and crystal growth have been a topic of interest for a number of years.[1,2] More recently, the atomic processes involved in the growth of metal overlayers on metal surfaces, which are closely related to single-crystal growth processes, have attracted considerable attention.[3] A basic understanding of metal overlayers is of interest not only in fundamental research, but also in such technologically applicable areas as bimetallic catalysis.[4]

Detailed studies of the initial stages of metal-adatom nucleation on metal surfaces are particularly well suited for investigation by field-ion microscopy (FIM), as it is possible to observe directly the diffusion of single atoms over a well-defined surface and study the formation of atom clusters. Of primary importance are the mobility of the surface atoms and the adatom-adatom interactions which lead to cluster formation. An overview of field-ion-microscope studies related to atom diffusion and clustering can be found in several recent review articles.[5-7]

In this paper, investigations of the diffusion and clustering of Pd atoms on the Ta(110) plane using field-ion microscopy are reported. The macroscopic structural and electronic properties of this overlayer system have been characterized previously,[8-10] but microscopic studies of atom mobility and cluster formation have been lacking. One aspect of the Pd-on-Ta(110) overlayer system which is particularly interesting is the proposed structural transformation which occurs at approximately monolayer coverage.[10] Thus, in addition to investigating the diffusion and nucleation characteristics of the Pd adatoms, the overlayer structure near monolayer coverage was examined.

A major portion of the present investigation focused on the initial stages of Pd cluster nucleation on Ta(110). Fundamental to the nucleation process of adatom clusters is the transition from one-dimensional to two-dimensional clusters. Experiments utilizing field-ion microscopy have shown that the configurations assumed by three or more adatoms depend on the adatom species for a given substrate.[5,11] On W(110), the most commonly used substrate for such experiments, growth of two-dimensional clusters of W, Re, and Ta begins with the addition of a third atom to the respective dimer; the stable configuration for the trimer is in the form of a triangle.[5,11] In marked contrast, the later transition metals such as Ni, Pd, Ir, and Pt preferentially form linear chains before two-dimensional clusters are preferred.[5,12] In addition, both metastable chains and clusters of various adatoms have been observed. Specifically, it has been shown that chains of Ni atoms composed of four to six atoms and Pd chains containing more than $\sim$10 atoms form two-dimensional clusters if heated to temperatures at which rearrangement can occur.[12] Similarly, two-dimensional clusters of Ir composed of twelve atoms, formed by the partial field evaporation of larger two-dimensional clusters, form a linear chain configuration upon heating.[13] To aid in the present study of Pd-cluster nucleation on Ta(110), additional observations of Pd-cluster nucleation on W(110) were performed.

II. EXPERIMENT

The experimental chamber was an all-metal FIM based on a liquid-nitrogen-cooled cold finger. With the pump valved off, pressures between 6×10^{-11} and 1×10^{-10} Torr could be maintained for approximately 2 h by titanium gettering. Helium and neon imaging gases were purified and admitted to the vacuum chamber by diffusion through heated Vycor bulbs. For field-ion imaging, pure helium or a mixture of $\sim$20 at. % Ne and 80 at. % He, at an absolute pressure of $\sim1\times10^{-3}$ Torr, was used. The tantalum and tungsten tips were formed from polycrystalline wire by anodic dissolution in 90% concentrated H_2SO_4+10% HF and 1 N NaOH, respectively. The tips were cleaned in the FIM by a combination of thermal flashing, neon cathode sputtering, and field evaporation. Pd was deposited on the emitter tip from resistively heated Pd coils and equilibrated on the tip surface at various temperatures in zero applied electric field.

III. RESULTS

Measurement of the activation energy for the diffusion of a single Pd adatom on the Ta(110) plane provided initial characterization of the Pd-on-Ta(110) system. The measured mean-square displacement and the calculated activation energy are shown in Table I for 45-s heating cycles at three temperatures. At each temperature the activation energy was calculated from the standard Arrhenius equation relating the mean-square displacement of the atom to the temperature.[5-7] An isotropic diffusivity (the Arrhenius prefactor) of 2×10^{-3} cm^2/s was assumed in our calculation of the activation energy because the temperature range which could be utilized in these diffusion experiments was too small to yield a meaningful slope in an Arrhenius plot. The value of 2×10^{-3} cm^2/s is consistent with essentially all other FIM data.[5-7] From the results shown in Table I, the average value of the activation energy was found to be 0.49±0.02 eV.

The nucleation of Pd clusters was investigated by the deposition of dispersed atoms at 77 K and subsequent equilibration at temperatures above the onset of atom mobility (typically >200 K). The cluster configuration was examined as a function of the number of Pd atoms present on the Ta(110) plane and the surface temperature at which they were equilibrated. Following the deposition of between two and about eight Pd atoms on the Ta(110) surface at 77 K and their equilibration at 200 K,

TABLE I. Measured mean-square displacements and calculated activation energy for 45-s heating cycles for Pd adatom diffusion on a Ta(110) plane. T is the temperature, N is the number of diffusion intervals, $\langle r^2\rangle$ is the average mean-square displacement, and E_a is the activation energy for surface diffusion.

T (K)	N	$\langle r^2\rangle$ (Å^2)	E_a (eV)
178	40	6.6	0.48
187	40	15.9	0.49
197	40	33.1	0.51

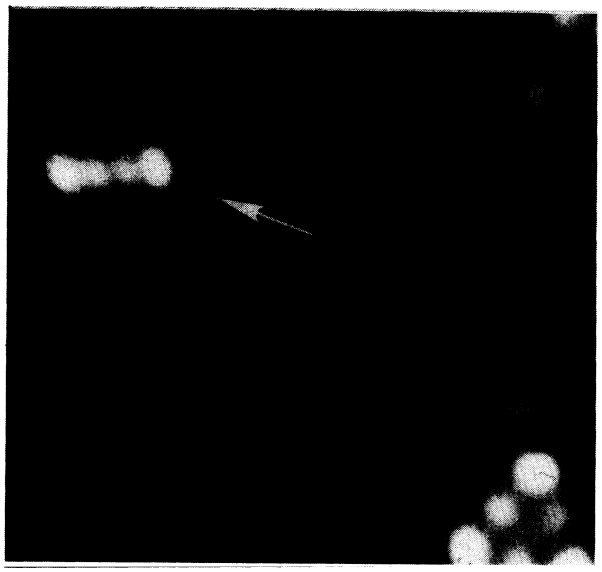


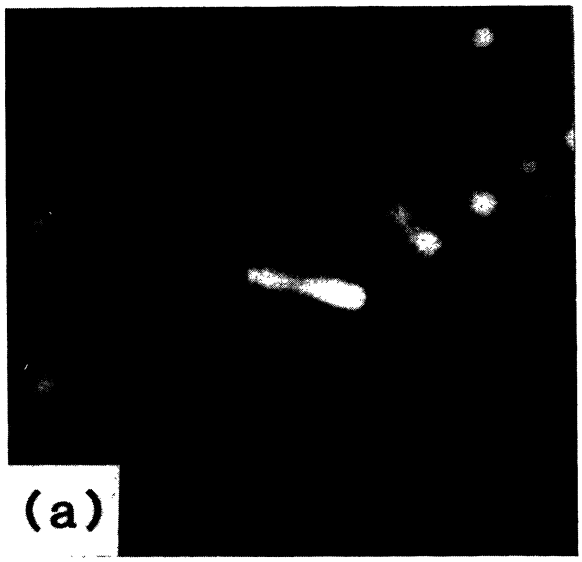
FIG. 1. Helium-neon field-ion micrograph of a Pd chain on Ta(110) oriented in the [111] direction. The atoms in the lower right-hand corner are the topmost layer of the (111) plane, which was used to obtain the orientation of the chain.

the Pd atoms were always seen to form a single chain oriented in a close-packed ⟨111⟩ direction on the surface. An example of a Pd chain oriented in the [111] direction on the Ta(110) plane is shown in Fig. 1. Although chains consisting of fewer than nine atoms, such as the one shown in Fig. 1, became mobile on the surface at $\sim$250 K, they maintained their configuration of a single chain oriented in a ⟨111⟩ direction (i.e., they did not reconfigure to a two-dimensional cluster). The preference of eight or fewer adatoms to form a single chain was observed up to temperatures of $\sim$350 K, at which point the Pd atoms left the surface by diffusing over the (110) plane edge.

In contrast to the chains of eight and fewer atoms, chains comprised of nine or more atoms formed two-dimensional island clusters upon equilibration at temperatures exceeding $\sim$190 K. The existence of such metastable chains was first noted for Pd and Ni on W(110),[12] and our results are similar for Pd on both W(110) and Ta(110). An example of the transformation of a metastable chain to a stable cluster is shown in Fig. 2 for Pd on W(110). Figure 2(a) is a helium-ion micrograph of nine Pd atoms equilibrated at 190 K to a linear-chain configuration oriented in a ⟨111⟩ direction on the W(110) surface. Following equilibration at 225 K, this chain transformed to the two-dimensional cluster configuration shown in Fig. 2(b), where it is seen that the symmetry of the bcc (110) surface is reflected in the structure of the Pd overlayer. This suggests that the Pd atoms form a pseudomorphic overlayer as suggested in macroscopic studies by low-energy electron diffraction (LEED).[10]

Subsequent to the deposition of $\sim$10 or more Pd atoms, equilibration at a temperature of $\sim$200 K directly

results in the formation of two-dimensional Pd clusters on the Ta(110) plane. An example of a two-dimensional cluster formed in this way is shown in Fig. 3. This cluster is comprised of 15 atoms and is of sufficient size that only its edge atoms are clearly resolved at an emitter temperature of 77 K. The structure of the larger Pd clusters is clearly revealed by partial field evaporation of the cluster which allows high-resolution imaging of the interior structure. Figure 4 is an image of eight Pd atoms which composed the interior of a cluster of ~20 atoms, of which ~12 edge atoms were systematically field-evaporated. Again, the symmetry of the bcc (110) substrate is evident in the cluster.



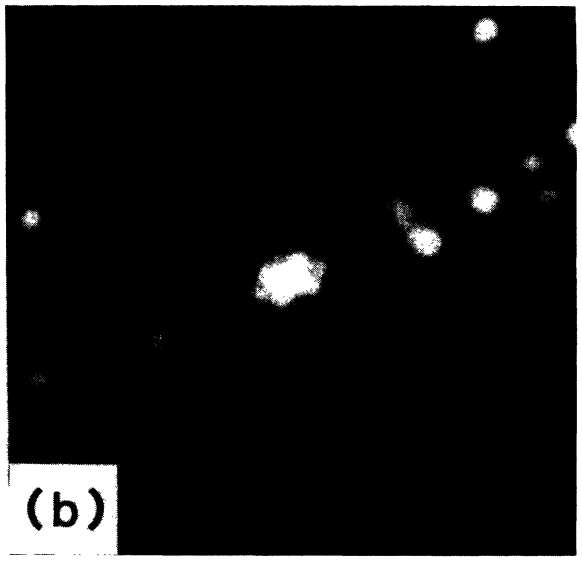


FIG. 2. Helium field-ion micrographs of the Pd linear-chain cluster of minimum length (nine atoms) to be metastable on Ta(110) and W(110) and its transition to a two-dimensional island cluster. (a) A linear-chain cluster of nine Pd atoms on W(110). (b) The two-dimensional island cluster of nine atoms formed by equilibrating the chain configuration in (a) at 225 K.

FIG. 3. Helium-neon field-ion micrograph of a two-dimensional cluster of 16 Pd atoms on Ta(110).

The two-dimensional Pd clusters were found to become mobile and diffuse as a unit on the Ta(110) plane at ~250 K. Cluster diffusion as a single unit was observed up to temperatures of ~325 K. An important question related to this type of cluster diffusion, which has been observed previously for Pd and Ni clusters on W(110),[12,14,15] is the mechanism by which the atoms disappear at these higher temperatures. Specifically, one would like to know if the clusters dissociate into single atoms which subsequently diffuse over the edge, or if the cluster diffuses over the

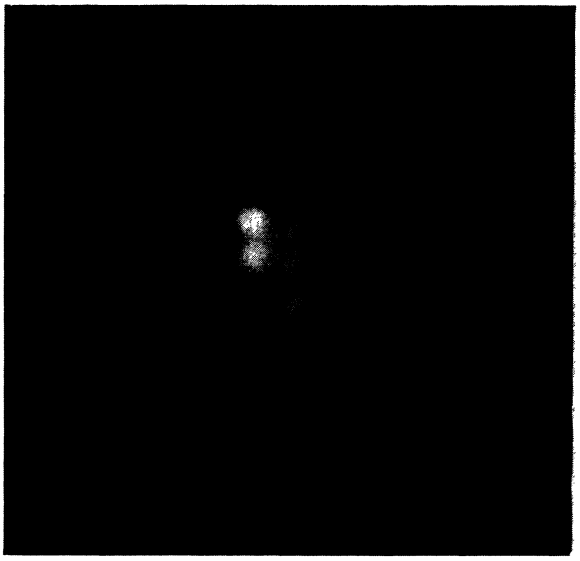


FIG. 4. Helium-neon field-ion micrograph of eight Pd atoms on the Ta(110) plane which comprised part of the interior of a two-dimensional cluster of ~30 atoms; imaged by the partial field evaporation of the original large cluster.

edge as a unit. At intermediate temperatures of ~250–300 K, the reduced diffusion rate of the cluster occasionally allowed its disappearance from the Ta(110) plane to be followed in some detail. Figure 5(a) is an ion micrograph of a cluster of 12 Pd atoms equilibrated at 200 K and located near the center of the Ta(110) plane. The edges of this cluster are aligned along the ⟨111⟩ directions of the tantalum substrate. Figure 5(b) is a micrograph taken after warming the tip of 250 K for 60 s. The cluster diffused to the edge of the (110) plane, at which point five atoms apparently diffused over the plane edge. The plane edge is not imaged in the micrograph since the imaging field required would result in the field evaporation of several or all of the Pd atoms. Its location, however, can be deduced from previous micrographs, which indicate that the atoms located at the 6-, 7-, 8-, and 9-o'clock positions of the cluster are at the Ta(110) plane edge. Additional heating at 250 K did not result in any change in the clusters shape or location. The result of heating to 300 K for 60 s is shown in Fig. 5(c). It is seen that two more Pd atoms have diffused over the edge, leaving a cluster of five atoms behind. In this micrograph the atoms located at 6-, ~8-, and 9-o'clock positions are in contact with the plane edge. An additional heating cycle to 300 K for 30 s resulted in the loss of one more atom. The remaining four atoms formed a linear chain which diffused to a location near the center of the (110) plane and oriented in a ⟨111⟩ direction as shown in Fig. 5(d). Further heating showed this to be an equilibrium configuration at 300 K. Thus, it appears that the loss of two-dimensional clusters at higher temperatures is due to the cluster diffusing as a unit over the plane edge.

The transformation to a chain configuration from a two-dimensional cluster configuration, as seen in Figs. 5(c) and 5(d), demonstrates that two-dimensional clusters of a few atoms are a metastable configuration, and the linear-chain configuration is stable. Actually, for eight or fewer Pd atoms a two-dimensional cluster configuration was found to be metastable, as heating to 225 K would result in conversion to a linear-chain cluster on Ta(110). This was also found to be the case for Pd on W(110). An example of this reconfiguration on W(110) is shown in Fig. 6. Figure 6(a) is a helium-ion micrograph of a two-dimensional cluster of five Pd atoms formed by the partial field evaporation of a two-dimensional Pd cluster

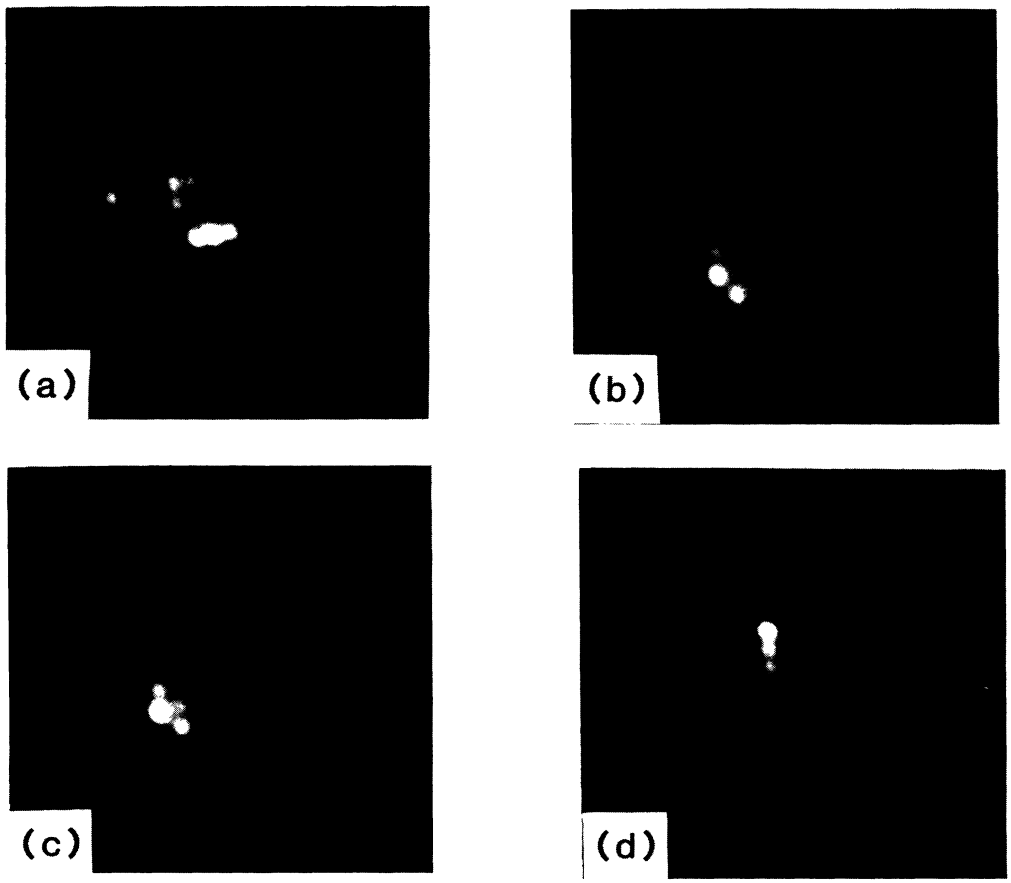


FIG. 5. A series of helium-neon field-ion micrographs of the diffusion of a two-dimensional cluster of Pd on Ta(110) as a single unit, the formation of a metastable cluster by the loss of Pd atoms over the plane edge, and the cluster's equilibration to a linear-chain cluster. (a) A cluster of 12 Pd atoms. (b) Appearance subsequent to heating the original cluster of 12 at 250 K for 60 s. (c) The appearance following an additional heating cycle at 300 K for 60 s. (d) The final configuration, stable at 300 K.

comprised of ~30 atoms. An additional Pd atom, disjoint from the two-dimensional cluster of five, was also left on the plane and is located to the right of the Pd cluster as seen in Fig. 6(a). During equilibration at 225 K, the cluster of five Pd atoms assumed a linear-chain configuration in which the lone sixth Pd atom was also incorporated, as shown in Fig. 6(b).

The effect of limiting the possible chain length by the plane edge was also investigated. That is, the effect of equilibrating the Pd-on-Ta(110) planes having an insufficient diameter to accommodate all of the Pd adatoms in a single chain was examined. Under these conditions the Pd was seen to cluster in multiple chains. These chains either intersected or formed parallel to one another lying in a ⟨111⟩ direction and separated by one row.

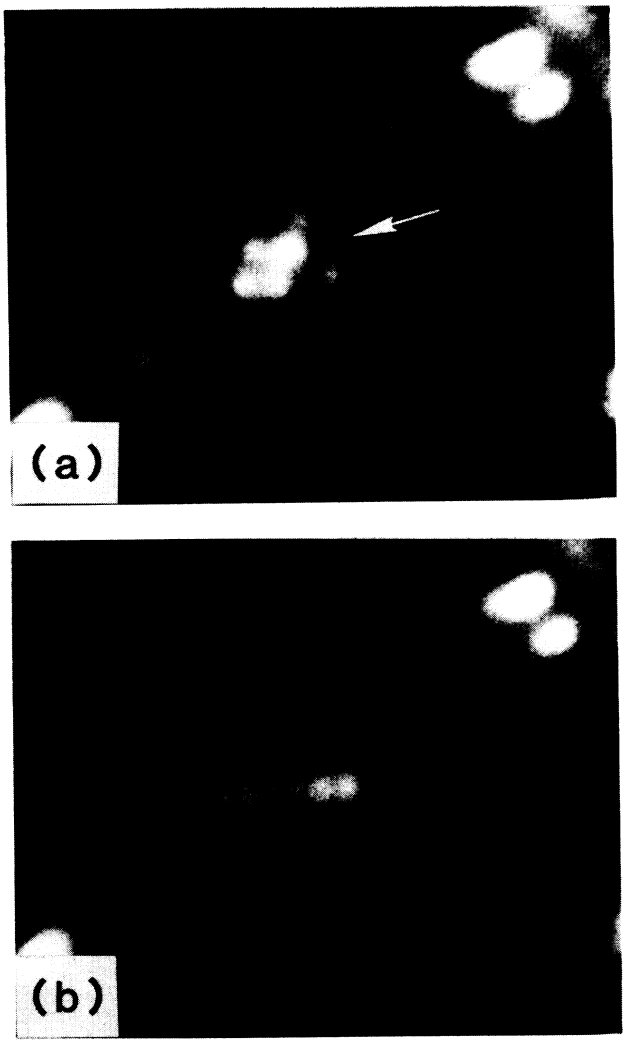


FIG. 6. Helium field-ion micrographs of a metastable two-dimensional island cluster of Pd on W(110) and its transition to a stable linear-chain cluster. (a) A two-dimensional cluster of five Pd atoms formed by the partial field evaporation of a large two-dimensional island cluster. A sixth Pd atom, disjoint from the cluster of five, was also left on the plane. (b) The linear-chain cluster of six atoms formed by equilibrating the configuration in (a) at 225 K.

An example of an intersecting-chain configuration is shown in Fig. 7 for seven Pd atoms on a Ta(110) plane having a diameter which would be spanned by six Pd atoms in a single chain. The Pd was observed to change back and forth between the intersecting and parallel configurations upon equilibration at gradually increased temperatures.

IV. DISCUSSION

Our measured activation energy of surface diffusion for Pd on Ta(110) is close to the previously measured value for Pd diffusion on W(110).[12] It is interesting to note, however, that the results of a recent photoemission study[16] indicate that the heat of adsorption for Pd on Ta(110) is -0.4 eV/atom, a value less than the measured activation energy for surface diffusion. Since activation energies for surface diffusion are typically ~10% of the atom binding energy, there is apparently a large discrepancy between the two results. Part of this discrepancy can be attributed to the fact that the heat of adsorption was measured for a monolayer of Pd atoms, in which the Pd adatom-adatom interactions will result in a Pd adatom-substrate binding energy which is lower than that associated with a single atom. However, it is unlikely that this interaction would reduce the binding energy by an order of magnitude. Unfortunately, direct measurements of the binding energy by thermal desorption are not possible for this system since the Pd atoms diffuse into the Ta substrate below the Pd desorption temperature.

The field-ion images of the Pd linear chain and two-dimensional island structures show conclusively that Pd overlayers on Ta(110) and W(110) have a bcc (110) structure. However, field-ion micrographs do not allow an exact determination of the relative atomic positions be-

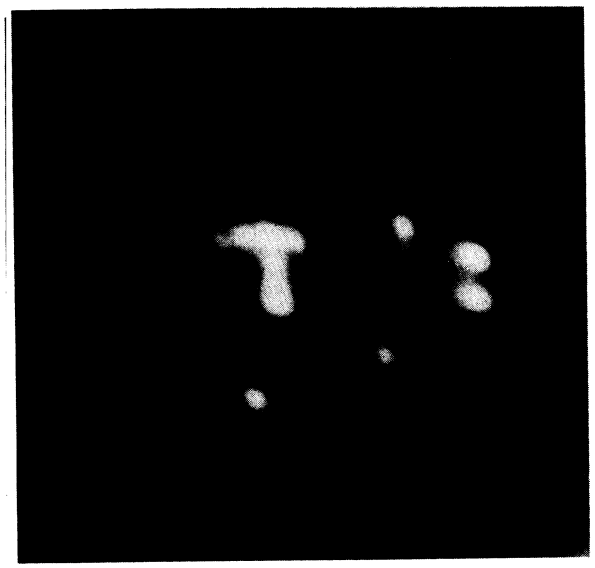


FIG. 7. Helium-neon field-ion micrograph of a configuration assumed by seven Pd atoms on a Ta(110) plane having a diameter sufficient to accommodate only about six Pd atoms in a single chain in a ⟨111⟩ direction.

tween the overlayer and substrate and therefore it is not possible to determine definitively whether or not the overlayer is commensurate. A LEED investigation of Pd on Ta(110) (Ref. 10) indicates that the Pd overlayer is commensurate at submonolayer coverages, yet undergoes a structural phase transition to an incommensurate overlayer at approximately monolayer coverage. Our field-ion images of the two-dimensional Pd clusters are consistent with the presence of a pseudomorphic, Pd bcc (110) overlayer from submonolayer to approximately monolayer coverage, but show no evidence of a structural phase transition to an incommensurate, Pd fcc (111) overlayer at higher coverages.

The existence of stable linear chains or two-dimensional island clusters depending on the number of atoms is an interesting special case of nucleation phenomena. On W(110) Bassett[12] has observed metastable linear Ni chains (for to six atoms in length) and metastable Pd chains (approximately nine or more atoms in length). Our observations show that linear-chain clusters of Pd on Ta(110) also become metastable beyond a length of eight atoms and, in addition, show that two-dimensional clusters comprised of fewer than nine Pd atoms on either W(110) or Ta(110) are metastable.

V. CONCLUSION

The activation energy for the diffusion of a Pd adatom on Ta(110) has been determined to be 0.49 ± 0.02 eV, similar to Pd and Ni on W(110).[12,14] Two-dimensional island clusters of Pd have been observed to diffuse as a single unit on the Ta(110) plane at temperatures of 250 to $\sim$325 K. The mechanism by which the clusters disappear at these temperatures has been shown to involve the cluster diffusing over the edge as a unit, not island dissociation on the flat surface.

Two-dimensional Pd clusters were observed to have the same symmetry as the Ta(110) substrate, indicating a pseudomorphic structure. No evidence of a commensurate bcc (110) to incommensurate fcc (111) structural phase transition in the Pd overlayer was observed up to and including monolayer coverages.

Concerning the nucleation of small Pd clusters, this investigation has shown that two-dimensional island clusters of Pd comprised of fewer than nine atoms are metastable on Ta(110) and W(110). While similar observations to those presented in this paper regarding the existence of metastable chains of Pd on W(110) have previously been made by Bassett,[12] no rationale has yet been advanced to describe the various transitions in the fundamental form of small nuclei. We are therefore in the process of developing a phenomenological model to provide a framework within which the existence of either a linear-chain or a two-dimensional cluster can be rationalized. In this model the fact that linear-chain clusters are stable below a certain number of atoms, and beyond this, two-dimensional clusters are stable, is considered and will be the subject of a planned future report.

ACKNOWLEDGMENT

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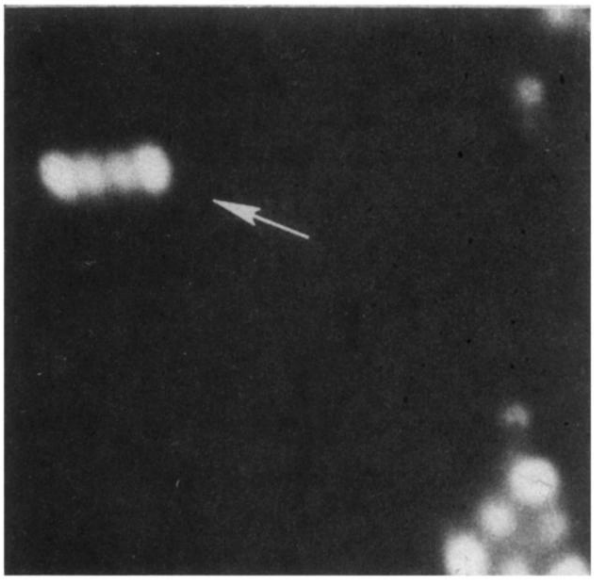
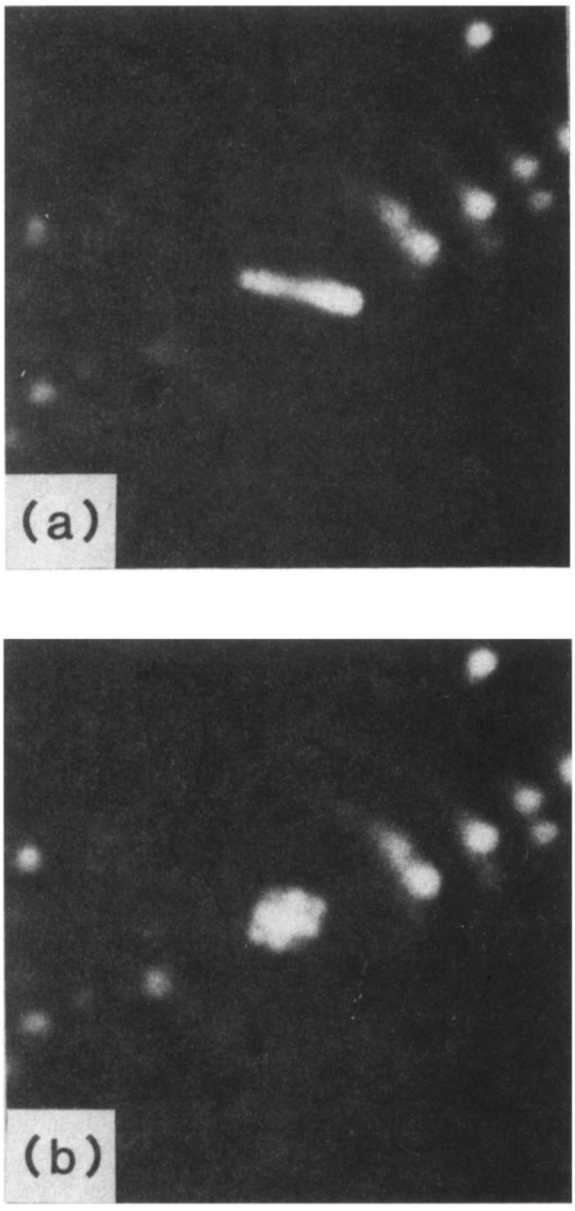


FIG. 1. Helium-neon field-ion micrograph of a Pd chain on Ta(110) oriented in the [111] direction. The atoms in the lower right-hand corner are the topmost layer of the (111) plane, which was used to obtain the orientation of the chain.



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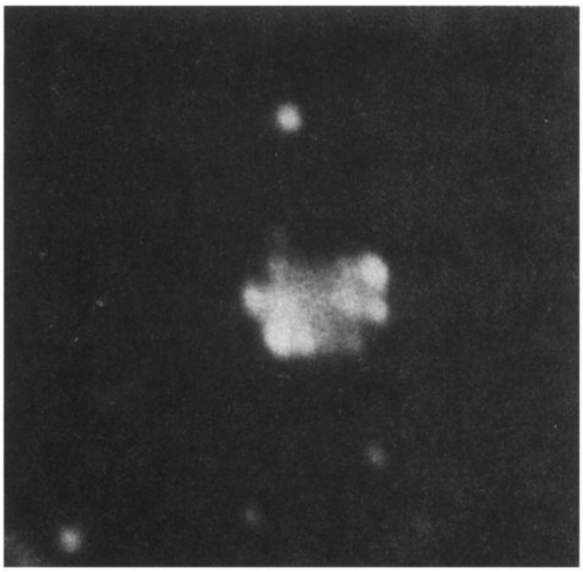

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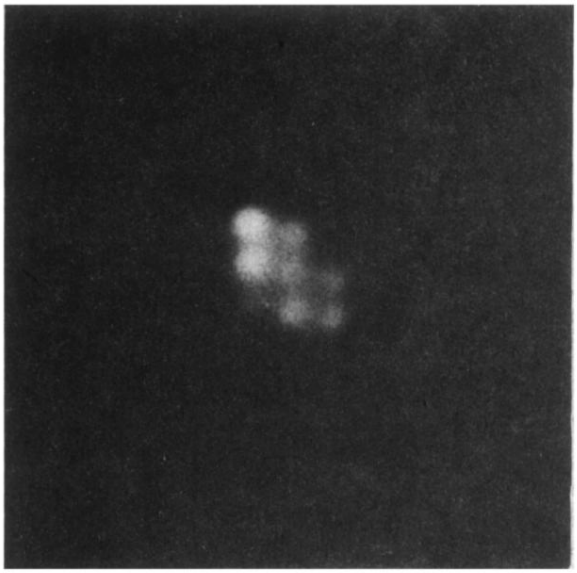

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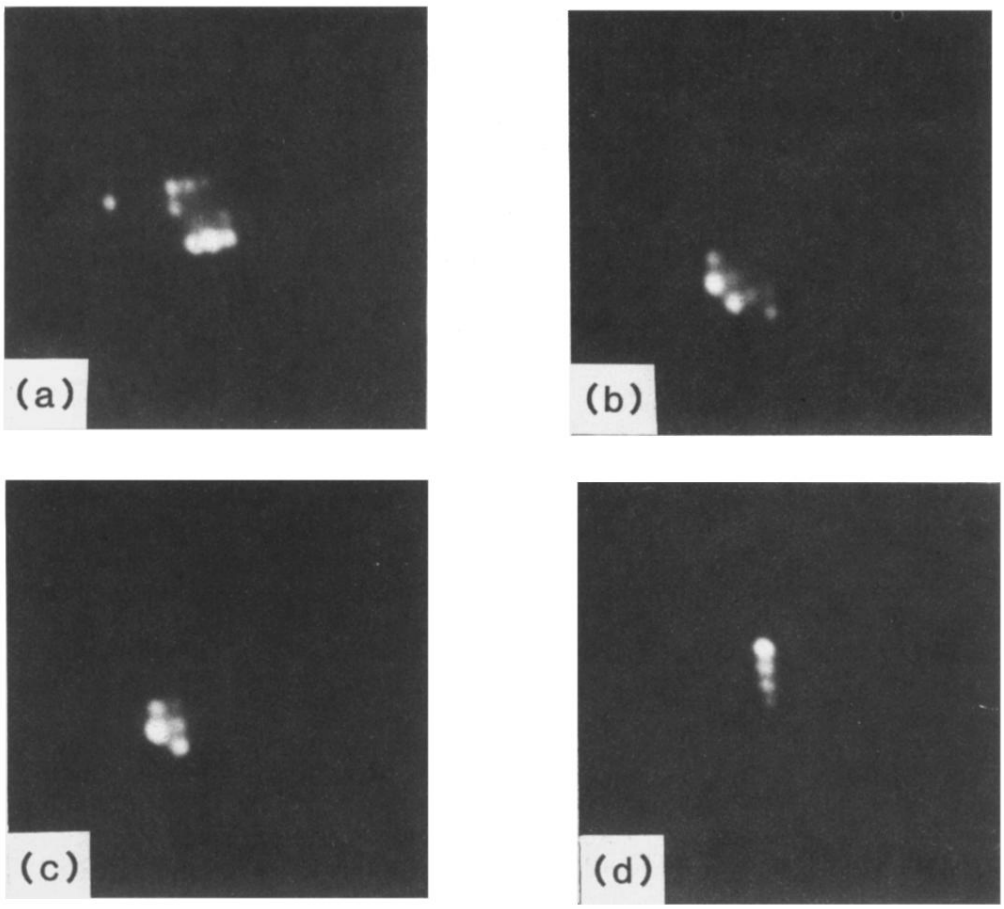

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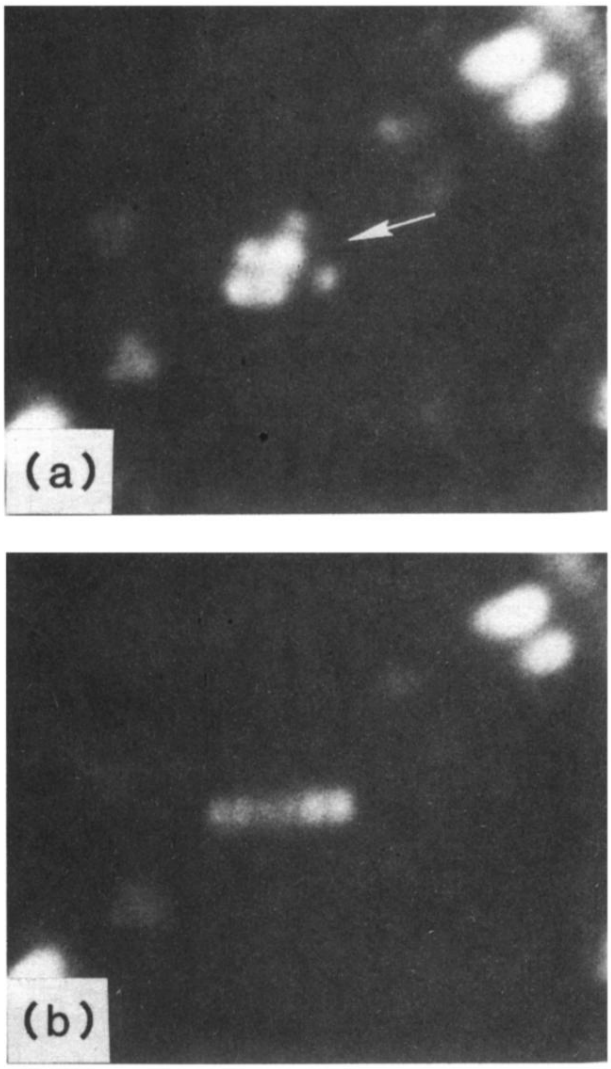

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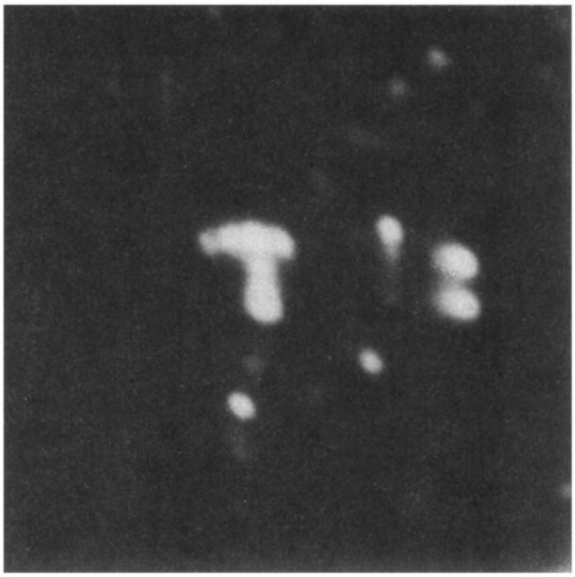

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