Transformation of cluster structure at initial stage

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ABSTRACT

The initial stages of cluster nucleation for Pd or Ir adatoms on a W (1 1 0) surface and in the vicinity of surface steps are directly imaged by a field ion microscope (FIM). Three types of structures are observed. One is a one-dimensional linear chain, which is parallel to the nearest neighbor-stacking directions of the substrate. Another is a two-dimensional compact island, which is a pseudomorphic structure like the substrate. The other is a three-dimensional cluster, which shows a structural transition from bcc (1 1 0) to fcc (1 1 1). Factors affecting the structural transformation include coverage of atoms or atom chains, temperature of heat treatments and boundary of the substrate terrace.

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1. Introduction

In the nano era, many efforts have been made to investigate the self-assembly of nanometer-scale clusters [1–3]. In order to control the growth structure, it is necessary to understand growth properties. A basic understanding of metal films on metal substrates is of interest not only in fundamental research, but also in technologically bimetallic applicable areas [4]. Transition metals of the platinum family adsorbed on the W (1 1 0) plane show interesting properties. For example, the adsorbed atoms prefer to form linear chains at the initial growth stage. The growth of these material systems has been investigated with various surface analysis techniques and has attracted continuing study for many years [5–11]. However, few studies have investigated the structural transformation between different dimensional clusters at initial growth.

Studying cluster surface structures using field ion microscopy (FIM) is an ideal way. First, it is possible to observe individual atoms and monitor their diffusion directly. Second, the symmetry of the problem can be reduced to two dimensions and the entropy of the system is negligibly small for the small ensemble of atoms [12–14]. In addition, the size limitation of the FIM samples causes nucleation in the vicinity of surface steps and the growth effect of the terrace boundary to be more obvious.

In the present paper, we report some FIM observations of structural transformation of Pd and Ir clusters on the W (1 1 0) surface. The transformation of one-dimensional (1D) linear chain to two-dimensional (2D) compact island with three-dimensional (3D) growth affected by surface steps, and a commensurate bcc

(1 1 0) to incommensurate fcc (1 1 1) structural phase transition in the Pd overlayer are shown. The important factors triggering structural transformation are discussed.

2. Experiment

All investigations were made with a home-built atomic resolution ultra-high vacuum-field ion microscopy (UHV-FIM), which has already been described in detail elsewhere [15–17]. A tungsten tip was prepared from a poly-crystal wire of 0.1 mm in diameter by electrochemical etching in aqueous KOH (concentration 2 M) and was cleaned in a UHV environment by a combination of thermal degassing, neon cathode sputtering, and field evaporation. Pd or Ir atoms were deposited from well-outgassed evaporation sources with high purity (99.995%) coil spot-welded with two potential leads. In this experiment, helium gas of 1×10^{-5} torr was admitted as the image gas. The number of atoms on the terrace was controlled by alternating with vapor deposition and field evaporation. Vapor deposition can increase the number of atoms on the sample terrace and field evaporation can reduce the number of atoms. Heating was done by electronic-controlled current power supply which can heat up the tip mounting loop in less than 0.5 s. The temperature was determined by a resistance measurement of the loop. The resistance was double calibrated with the thermocouple in the cooling and warming processes and checked with room temperature.

3. Results and discussions

3.1. Cluster structures at initial stage

At initial growth stage, a small cluster with more than three atoms can form a 1D linear chain, and various types of 2D or 3D

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structures. For palladium, previous observations reported that clusters containing as many as eight atoms formed chains [18], chains of nine Pd atoms were metastable [8], and structural rearrangements from 1D linear to 2D compact shapes were reversible for Pd_8 [19]. Our results are consistent with that of previous research. Fig. 1 shows the FIM images of Pd_x on W (1 1 0) surfaces. Fig. 1(a) shows the linear structure with seven Pd atoms. Fig. 1(b) shows the 2D compact shapes with eight Pd atoms. The most stable configurations for Pd_8 on W (1 1 0) surfaces transform from the 1D linear chain to 2D compact islands. As the number of Pd atoms increases, the growth goes to the upper layer forming a 3D structure, as shown in Fig. 1(c).

Some characteristics for the initial growth clusters are observed. First, linear chains are always oriented in a close-packed <1 1 1> direction on bcc (1 1 0) surfaces. Second, 2D compact islands usually follow the substrate structure to form a pseudo-morphic layer. Last, the structure of 3D islands usually transform from pseudomorphic bcc (1 1 0) to an incommensurate fcc (1 1 1) overlayer for fcc adsorbates at higher coverages.

Fig. 2(a) and (c) display FIM images which show the structure of the first layer of Pd and Ir compact islands on W (1 1 0) surfaces individually. Fig. 2(b) shows the schematic of possible atomic arrangement for clusters in (a) and (c). Because the Pd–W and Ir–W bonds are rather strong and the lattice mismatch between W (1 1 0) and Pd or Ir (1 1 1) is rather small, r/r_s is only 0.47% and −0.80% respectively. Both Pd and Ir atoms follow the substrate structure to form a pseudomorphic layer. This result is consistent with that of the LEED study on obtaining (1×1) refraction pattern at submonolayer coverages [20].

Fig. 3 provides an evidence of structural phase transition from pseudomorphic bcc (1 1 0) to an incommensurate fcc (1 1 1) overlayer at higher coverages. In this case, the transition occurs at monolayer coverage. This transition can be judged by the variety of the intersecting angles. The directions of atom arrangements along [−1, 1, 1] and [−1, 1, −1] of bcc (1 1 0) intersect at angle 70.5°; while the directions of atom arrangements along [−1, 1, 0] and [−1, 0, 1] of fcc (1 1 1) intersect at angle 60°. The transition can be indicated by the reduction in intersecting angle. A LEED investigation of Pd on Ta (1 1 0) indicates that the Pd overlayer is commensurate at submonolayer coverages, yet undergoes a
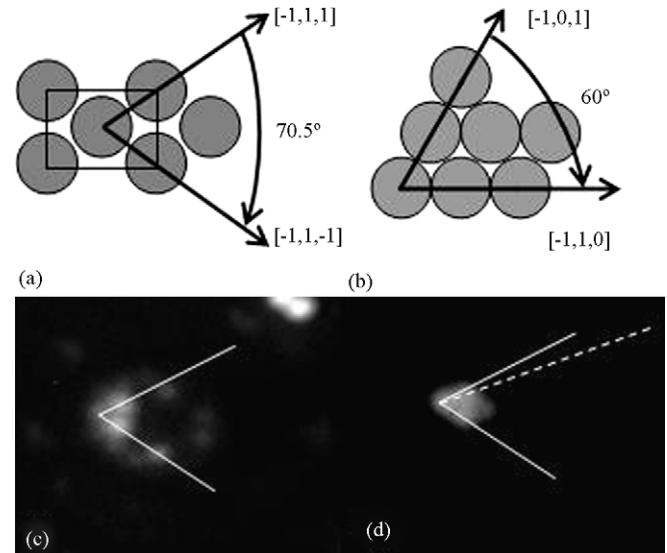
Fig. 3. (a) Schematic drawing shows the intersecting angle of bcc (1 1 0) structure is 70.5°, (b) fcc (1 1 1) structure is 60°, (c) FIM image shows the first layer of Pd cluster, the solid lines indicate the intersecting angle of the bcc pseudomorphic layer, and (d) the second layer of the Pd cluster, whose intersecting angle is smaller indicated by dashed line.

structural phase transition to become an incommensurate overlayer at approximately monolayer coverage [21].

In view of the interaction of adsorbate and adsorbate or adsorbate and substrate, the above-mentioned characteristics may exist in general cases. In other words, they are common characteristics. The oscillatory behavior has been proved in the interaction energy versus adsorbate separation curve [22]. For different adsorbate separations, the interactions may be attractive or repulsive. The curve which varies with the Fermi wave vector is different in different systems. In other words, the chemical nature of different elements plays a pronounced role. If the adsorbate prefers to form a linear chain, the interaction must be attractive in the nearest sites and repulsive or much less attractive in the next nearest sites. Therefore, the linear chain
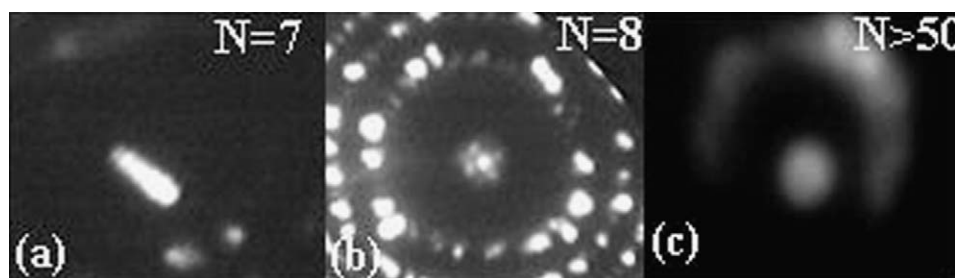
Fig. 1. FIM images show (a) 1D, (b) 2D, and (c) 3D Pd clusters on W(1 1 0) surfaces.
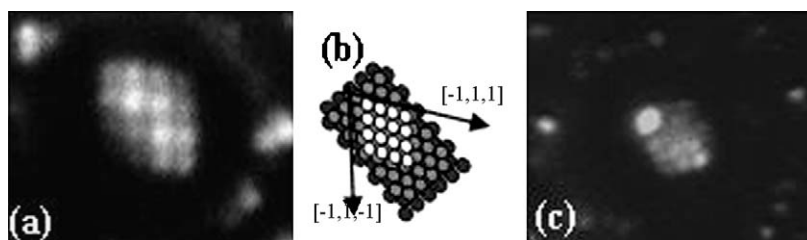
Fig. 2. FIM images with the schematic drawing showing the pseudomorphic structure. (a) The pseudomorphic Pd cluster on the W(1 1 0) surface, (b) schematic drawing showing the pseudomorphic cluster on the bcc (1 1 0) surface, and (c) the pseudomorphic Ir cluster on the W(1 1 0) surface.