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Nucleation, Formation, and Stability of Benzene Islands on Cu(111)

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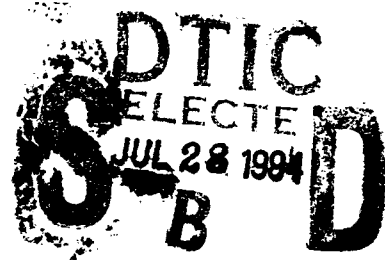
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NUCLEATION, FORMATION, AND STABILITY OF BENZENE ISLANDS ON Cu{111}

S. J. Stranick, M. M. Kamna, and P. S. Weiss*

We have imaged stable islands of benzene molecules on the surface of Cu{111} at 77K using a low temperature ultrahigh vacuum scanning tunneling microscope. The islands consist of a small number of benzene molecules and nucleate into straight lines on the Cu{111} surface. The ordering and stability of these clusters are discussed in terms of the molecular interactions with the substrate surface state electrons and the intermolecular interactions.

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1. Introduction

The creation and stability of nanometer scale structures has become increasingly important. This is due in large part to the forthcoming technological need to engineer and to construct devices on the nanometer scale as well as the rapid current development of techniques to study them. To this end, we have conducted studies on the structure and stability of nanometer scale adsorbate/substrate systems of widely varying complexity. These range from phase separated mixed composition self-assembled monolayers of alkanethiols on Au{111}¹ to the simpler systems discussed here — the nucleation of small benzene islands at and near step edges of the Cu{111} surface at dilute coverage and low temperature.

We have previously studied adsorption sites and their effects on STM images of isolated benzene molecules on Pt{111} at 4K.^{2,3} At such a low temperature the benzene is frozen in place both on Pt{111} and on Cu{111} and no motion is observed.^{2,3} Benzene molecules have also been imaged at room temperature when held fixed in various ordered overlayers by coadsorbed CO on Rh{111}.⁴ On these surfaces benzene molecules lie flat, *i.e.* with the molecular plane parallel to the surface plane. Wolkow has used a low temperature STM to observe the diffusion and perhaps desorption into the vacuum of isolated benzene molecules on the Si{111} surface.⁵

Studies by Bent and coworkers have shown that benzene adsorbs and desorbs molecularly on the Cu{111} surface.⁶ From temperature-programmed desorption (TPD) of perdeutero (d_6 -) benzene on Cu{111} it is known that multilayer and monolayer coverages of benzene desorb from the surface below 250K. A high-temperature tail in the TPD spectrum extending to 300K is attributed to desorption from surface defect sites. Therefore, by dosing the Cu{111} crystal at room temperature with benzene, we preferentially populate defect sites on the surface. By controlling the extent to which we saturate the surface, we can control the resulting surface coverage of benzene over a limited range. In our previous experiments we have worked with densities on the Cu{111} terraces of as low as 0.002 monolayers as measured by surveying the surface at 4K with our STM.³

The studies described here were carried out using a low temperature ultrahigh vacuum (UHV) scanning tunneling microscope (STM) described previously.⁷ By working at low temperature we are able to look at simple nanometer scale structures which might not be stable relative to translation, desorption, or even reaction at room temperature. At low coverages of benzene on Cu{111} at 77K, the mobile molecules on the atomically flat terraces are rapidly trapped at substrate step edges where they are tightly bound and form a narrow two-dimensional molecular solid.³ A small fraction of molecules remain mobile on the Cu{111} terraces. These molecules adsorb and desorb at the two-dimensional gas-solid interface.³ At somewhat higher coverages, as shown here, molecules nucleate near step edges to form islands.

Electrons in the surface states of close-packed noble metal surfaces have been observed by STM to be scattered by steps, defects, and adsorbates.⁸ The scattering leads to interferences and thus modulates the surface local density of states (LDOS).⁸ Here we find that the interactions of the adsorbate molecules with this modulated LDOS determine the nucleation sites equidistant from the substrate step edges. The additional stability afforded by intermolecular interactions freezes the motion of molecules in order to form these small islands. We have previously shown how a single adsorbed benzene molecule can perturb the LDOS of the surrounding Pt{111} substrate surface.² It is the perturbing effects of the steps *and* the adsorbates in concert which lead to the formation and stability of the benzene islands.

2. Experimental

The layout of our system for preparing, dosing, analyzing, transferring, and imaging our sample is shown schematically in Fig. 1. The details of the design and operation of the low temperature ultrahigh vacuum scanning tunneling microscope has been described elsewhere.⁷ Briefly, we have two room temperature ultrahigh vacuum chambers. One UHV chamber (SP) contains surface analysis equipment and a long stroke vertical transfer mechanism (VT) to transport our sample into the low temperature ultrahigh vacuum chamber containing the STM (LT STM). This entire cryogenic chamber is immersed in liquid cryogen (He or N₂) and held at low temperature for days at a

time. The other room temperature UHV chamber serves as a load lock and also contains a room temperature STM. Both STMs are compatible with tunable microwave frequency operation.⁷ The system contains various levels of vibration isolation (T, VP, B) as indicated in the figure. The two stages — cryogenic and sample preparation — are mounted on separate platforms (VP) and are vibrationally decoupled by an interconnecting welded bellows (B). The cryogenic and sample preparation platforms are each isolated from the main vibration isolation platform (a custom laser table with pneumatic legs, T) by air-filled pneumatic vibration dampers.

After initial electrochemical polishing and repeated sputtering and annealing cycles we obtained a clean flat Cu{111} crystal surface. The freshly cleaned crystal was dosed with several Langmuirs at room temperature by bleeding a small amount of benzene gas into the spherical sample preparation chamber (SP). The purity of the benzene was checked *in situ* using mass spectroscopy to verify that impurities and undesired wall reactions were negligible. After dosing, the room temperature Cu{111} sample was then rapidly lowered 1.4m into the cryogenic STM chamber (LT STM) using the vertical translator (VT).

Since benzene desorbs from Cu{111} terraces well below room temperature, this method of dosing the surface results in low surface coverages of benzene. Much of the benzene at steps and defects remains on the surface and results in an overall surface coverage of benzene of a small fraction of a monolayer.⁶ This coverage can be determined by cooling the sample to 4K and surveying the surface with the STM.³ In our initial low coverage studies we found the benzene coverage on Cu{111} terraces to be as low as 0.002 monolayers.³ Here, by saturating the surface prior to cooling we have obtained somewhat higher coverages which we estimate to be at most a few percent of a monolayer of benzene.

3. Results and Discussion

Our initial studies of benzene on Cu{111} showed transient molecules favoring sites equidistant from step edges at low coverage.³ In this study, higher coverages of benzene result in lines of small adsorbate islands. We attribute these observations to interactions between the molecules and the

modulated surface LDOS due to electrons scattering from the step edge and from other molecules. This scattering leads to interference patterns and dispersion curves for close-packed noble metal surfaces that have been mapped using STM by Avouris and Eigler and their coworkers.^{8,9}

The interactions of the mobile single molecules with the substrate electrons will be treated elsewhere.¹⁰ Here, under the same conditions, except at higher benzene coverage, we find small islands of benzene nucleated near step edges as shown in Figs. 2 and 3. Individual features in the clusters correspond to distinct benzene molecules. At this coverage, the islands range in size from three to nine molecules. As there are no significant protrusions other than the peaks due to each molecule, we infer that the islands are all one molecule thick. As seen in the figures, islands on a terrace form lines parallel to nearby substrate step edges. Lines of islands near *isolated* step edges are usually on the upper terrace relative to the step edge. Note that it is above the step riser (*i.e.* on the upper terrace) where the electronic perturbation due to the step is always the largest.^{8,10}

At 77K and at such low coverages, single benzene molecules remain highly mobile on terraces.³ Formation of stable benzene islands on Cu{111} implies that there are significant interactions between molecules. Recall that mobile benzene molecules on the Cu{111} terrace at this temperature adsorb and can desorb (in two dimensions) from the lines of molecules decorating the step edge.³ The islands formed here apparently bind the component molecules more strongly than do the step-bound rows. The unusual positions of the islands indicate that the substrate and particularly the nearby steps play an important role in the island formation process and their subsequent stability.

The observed islands are reminiscent of a number of other observations of nanometer scale patterns in thin films on metal surfaces. Chambliss *et al.* have found that Ni islands form at the "elbow" of the herringbone reconstruction on the Au{111} surface.¹¹ This site preference can be assigned as due to stress effects related to the uneven atomic distribution in this reconstruction. As with benzene, C₆₀ films on the Cu{111} surface grow out from step edges.¹² Islands form in the growth of the second layer of C₆₀. These overlayer islands are more indicative of

adsorbate–adsorbate attractions as no site preferences have been observed in island position. For Xe on Pt(111) at 4K after step edges are saturated the Xe forms islands on the surface, but the Xe islands have been shown to nucleate and grow at surface defects.¹³

What differentiates the islands found here from those described above is the striking position of the benzene clusters and the lack of a special site in the “geometric” surface structure. We note that the length scales of separation from island to island and from island to step are comparable to electronic spatial period in the charge modulation due to electron scattering from the steps and from adsorbates.⁸

At 77K benzene molecules are mobile on Cu(111) terraces.³ The islands are stabilized and immobilized. We attribute this to two effects. First, the clusters nucleate at favorable (high) charge density by two–dimensional collisions of mobile adsorbates. The nucleating islands modulate the surrounding charge density to make nearby (but not adjacent) sites more favorable. This apparently occurs along the same period of the charge density modulation from the nearby steps that nucleated the first island. We speculate that additional clusters grow out sequentially thus forming the line of islands that we observe.

Under our normal tunneling conditions the single benzene molecules on the terraces are not imaged in full. Instead they appear as points or as streaks within single or multiple line scans. Here, we are able to image the individual molecules within clusters of three or more molecules. This is further evidence of the stability of the islands. Most of the clusters we find have four to six benzene molecules, although we have found clusters as large as nine molecules under these conditions at 77K. The upper limit in cluster size may be a result of the LDOS modulation. If the spatially oscillating LDOS is reduced below some threshold value at the edge of the island, the molecules at the periphery of the island may be unstable relative to desorption back into the two–dimensional molecular gas on the Cu(111) terraces. These molecules are then available for collision and nucleation or growth of other islands.

4. Conclusions

In summary, we have observed small islands of three to nine benzene molecules on Cu(111) which line up on the terraces above substrate steps. We attribute the unusual positioning of these islands to electronic effects due to the step edges on this surface. The LDOS is sufficiently modulated by the step edge and by adsorbates so that island formation becomes possible and the stability of such small clusters is enhanced. This result is promising in terms of using natural or man-made modulations of the surface electronic structure to form controlled nanometer scale patterns of thin or low-dimensional films on surfaces.

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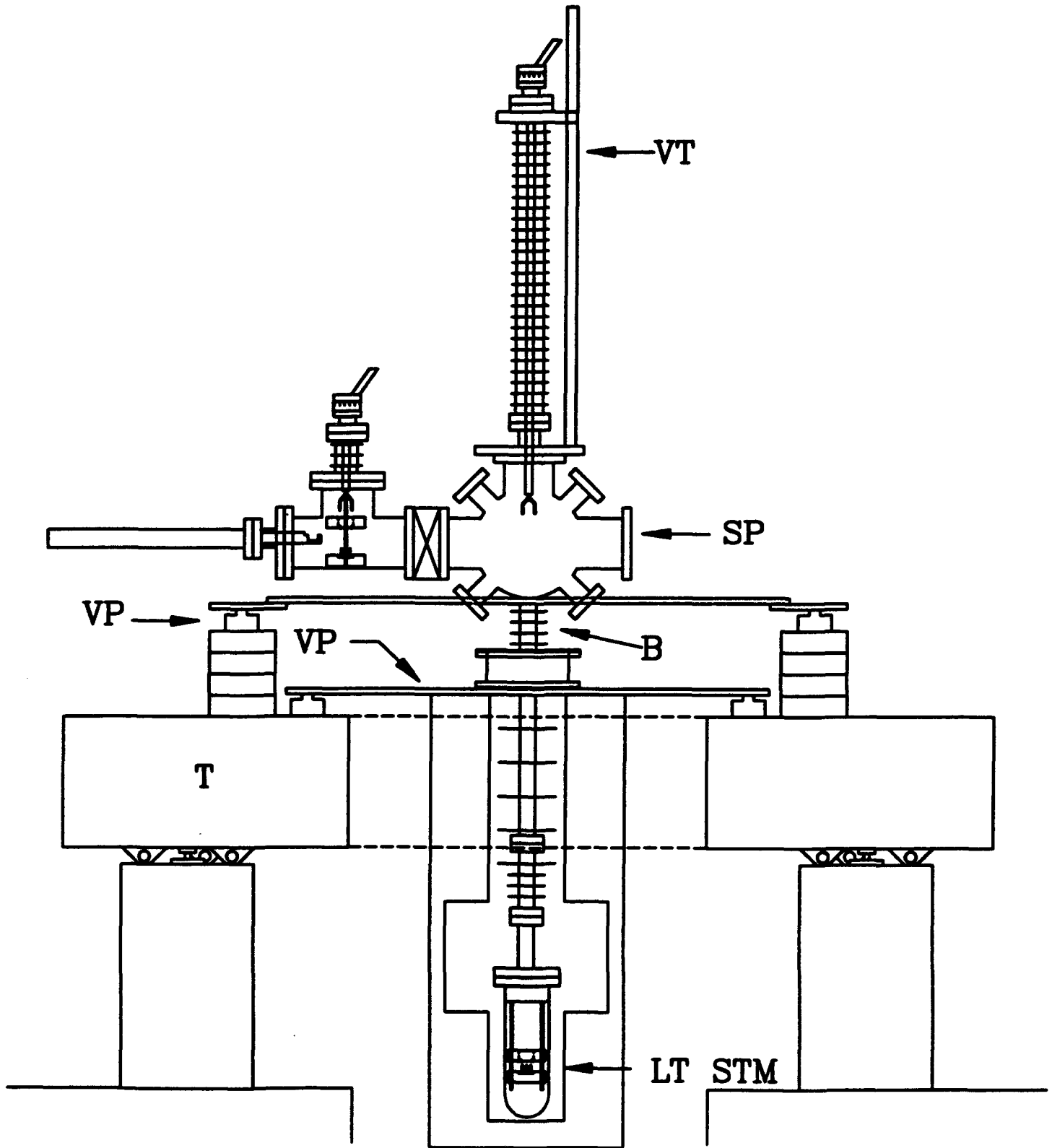
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FIGURE CAPTIONS

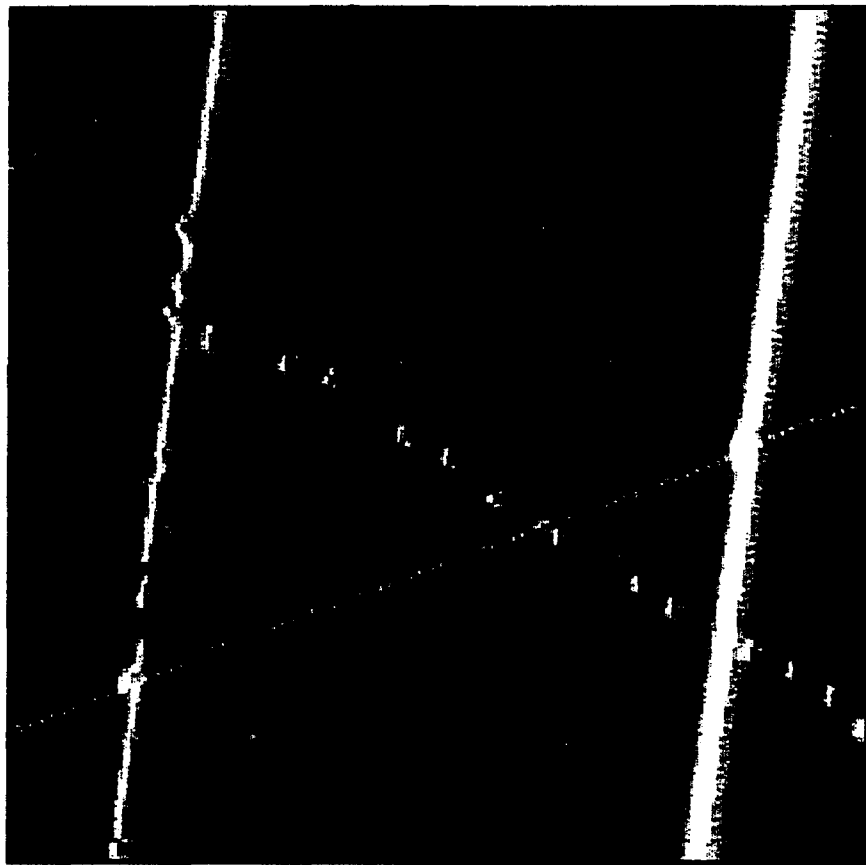
1. Schematic view of the ultrahigh vacuum low temperature scanning tunneling microscope (LT STM) chambers, the vibration isolation platform, and the LT STM. The system is supported on a pneumatic laser table (T) and the ultrahigh vacuum and low temperature chambers are decoupled by a welded bellows (B) and independently mounted on vibration isolation platforms (VP). The vertical translator (VT) is used to transfer the sample from the sample preparation chamber (SP) to the LT STM.
2. A scanning tunneling microscope image showing a $400\text{\AA}\times 400\text{\AA}$ area of a Cu{111} surface with adsorbed benzene molecules. The molecules decorate the step edges. In addition, molecules nucleate and form islands near substrate steps. The individual features within the islands correspond to individual molecules. The interference patterns due to scattering of the Cu{111} surface state electrons by the substrate steps are visible on the central terrace in the image. The image was recorded at 77K in constant current mode at a tunneling current of 100 pA and a tip bias voltage of ~ 0.1 V. Derivative along the fast scan direction (horizontal in the image) is displayed. Images are shown unfiltered.
3. A scanning tunneling microscope image of a $80\text{\AA}\times 80\text{\AA}$ area of a Cu{111} surface with adsorbed benzene molecules formed into small islands at 77K as in Fig. 2. The tunneling conditions are the same as for Fig. 2. Topography is displayed.



Stranick et al.

Fig. 2

Up^



Stranick et al.

Fig. 3

Up[^]

