13. NANOLITHOGRAPHY ON SURFACES OF SiW_x AND ITO FILMS BY STM

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Abstract

Under a condition of $CHCl_3$ vapor injection into the chamber, the creation of local regions with sizes about 50-100 nm can be observed surrounding the scanning tunneling microscope (STM) points of action. The conductivity of these regions is 5-6 times lower than the conductivity of the starting SiW_x layer. Although different gaseous mediums have been explored, this effect was observed only in $CHCl_3$ vapor. This effect seems to be a metal-insulator transition caused by the locally stimulated adsorption of chlorine by the STM tip. The process of local STM-stimulated deposition of organic nano-sized objects on the ITO films was investigated. Under special conditions the process of deposition does not occur in the region under the tip of the STM. However, a nano-ring was created around the point of action. When the STM electric pulse action occurs along a straight line, two parallel nano-sized lines are formed. In both cases it appears as if the tip of the STM casts a shadow in the region beneath it and deposition does not occur in this region.

Part I: Stm-Induced Local Sensor Effect On The SiW_x Films (Ryjikov 1996)

Introduction

This work is the continuation of research into the local electric field stimulated processes of reactive adsorption and segregation on the surfaces of structures based on semiconductors, dielectric, and metal thin films. The STM was used as a source of local electric action. The general purpose of the research is to discover the qualitative dependencies between main parameters of the STM process and the resulting nano-structures. The first results have already been published (Gorelkin et al. 1994; Luskinovich et al. 1995), demonstrating the existence of processes on surfaces that lead to the formation of stable objects of nanoscale size. These objects were created as a result of the action of electromagnetic pulses delivered by the STM tip. The adsorbate was formed by injecting the gas mix in a well-controlled manner. Research was carried out on the following structures: (-C:H (thickness: 50 Å - 100 Å) on W in a medium of vaporous diethyl ether or chloroform; SiW_x in a medium of diethyl ether on W; (-C:H: on In_2O_3 γSnO_2 (thickness: 200 Å - 500 Å); and W in a medium of diethyl ether and chloroform. Only clear, pronounced, and stable effects will be discussed here. It has already been shown that initial contamination on the surface plays some role, but our results also show that the nanostructures are formed controllably through the control of the adsorbate—substrate interaction via STM tip.

Experimental Scheme

This study used He, N_2 and vapors of organic diethyl ether, chloroform, acetone, toluene, propanol-2 (isopropanol), ethanol, heptane, styrene, acetic acid, etc. The conditions of injection, the partial pressure of components, and the temperature values were varied. The STM image of the substrate was fixed for different conditions in the chamber. After that action, a series of electric pulses was provided in the system tip of the STM - adsorbate-thin film structure. The pulses' duration (1 (- 10( ), the pulses' numbers at the action point (1 - 1000), the distance between action points and regions, and the trajectory of the action were varied. The dynamic STM images were assumed to provide a record of the lithographic process itself: the appearance and disappearance of the different nano-sized objects on the thin film surface; their form, height, and depth; their lateral sizes; the time stability and stability for secondary actions; and their electric conduction. All these parameters were analyzed as a function of the controlled parameters of the experiment by using representative statistics (more than 104 experimental situations). In every stage of the experiment, only the parameters that produce small perturbations into the state of the system as a whole varied.

Experimental Equipment

The experimental equipment consisted of an STM with a large range manipulator, a vacuum chamber, a pumping system, a vapor-gas mix injection system, and an electric pulse generator.

Experimental Results

The study investigated processes of reactive adsorption and segregation stimulated by the local electric field action created by the STM on the surfaces of structures based on layers of SiW_x. With $CHCl_3$ vapor injection into the chamber, the local creation of regions with sizes about 50-100 nm was observed about the points of action of the STM. The pulse voltage was 18 V - 20 V. The conductivity of these regions was a factor 5-6 times lower than the conductivity of the starting SiW_x layer. Experiments were carried out in different gaseous media, but the effect was observed only in $CHCl_3$ vapor. Nano-sized dielectric regions were observed and secondary STM actions did not produce a return to a conductive state. Two interesting phenomena were observed when scientists attempted to create a new dielectric region near the earlier-formed non-conducting object. First, if the distance between the point of action and the dielectric cluster was less than 0.2 µm, the new object was formed and merged with the old one. The new cluster was created with a larger size. Formation of two dielectric regions with a distance less than 0.2 µm between them is impossible. Secondly, if the distance between the point of action and the dielectric cluster is more than 0.2 µm and less than 0.6 µm, the new non-conducting region is not formed at all. Only if the distance is more than 0.6 µm is the stable formation of new dielectric regions possible.

Interpretation of Results

The STM-induced local sensor effect may be explained by an interaction between ions of Cl^+ contained in the adsorbate and ions of W^- formed in SiW_x film as a result of the STM action. The results confirm the results published in Zaporozchenko et al. (n.d.) in that when the action energy to the SiW_x is 16 - 25 eV, a metastable state of the material was observed. The effect may be interpreted as a creation of W^- ions, which then interact with Cl^+ ions of the adsorbate, forming a new amorphous film in the region of this interaction. As a result, the percolation paths of the electrons are destroyed, and the transformed region becomes non-conducting. The Cl diffusion length is about 0.2 µm. Therefore, if the action region is nearer than 0.2 µm to the previously formed dielectric cluster, the new non-conducting object merges with the first cluster. The dielectric region formed in the SiW_x film creates an electric field around itself. The cause of this field is the zone curvature near the boundary between conducting and non-conducting regions. If the potential barrier created by the dielectric phase for the Cl^+ ions is high enough, the Cl^+ ions will be attracted to the conductor-nonconductor boundary. The Debye length for Cl^+ ions is about 0.4 - 0.6 µm. Therefore, there may not be enough Cl^+ ions to create the dielectric phase if the STM action region is nearer than 0.6 µm to a non-conducting cluster. Note that this is not the only possible interpretation. For a complete understanding of this interesting phenomenon, more detailed investigation will be necessary.

Part II. The Shade Effect on STM-Stimulated Local Deposition of Organic Nano-Objects
(Zaporozchenko Et Al. N.D.)

Introduction

This work is the continuation of the research into the local electric field stimulated processes of reactive adsorption and segregation on the surfaces of structures based on semiconductors, dielectric, and metal thin films. The STM was used as a source of local electric action. The general purpose of the research is to discover the qualitative dependencies between the main parameters of the structures, mediums, and actions and possible ways in which the processes might proceed.

The first results of this study were published earlier (Gorelkin et al. 1994; Luskinovich et al. 1995) and demonstrated the existence of rather pronounced processes on substrate surfaces, processes that lead to the formation of stable objects with nanoscale sizes. These objects were created as a result of the action of electromagnetic pulses in the system tip of the STM adsorbate - substrate. The adsorbate was formed by injecting a vapor-gas mix with controlled components into the chamber. Research was provided on various structures: (-C:H (thickness: 50 Å - 100 Å) on W in a medium of diethyl ether or chloroform vapors; SiWx on W in a medium of diethyl ether vapors; (-C:H on In_2O_3 γSnO_2 (thickness: 200 Å - 500 Å) and W in a medium of diethyl ether and chloroform vapors. Only the clear, pronounced, and stable effects will be discussed here. In this section, only recent results will be presented: the STM-induced local sensor effect on the SiW_x films and the shade effect on STM-stimulated local deposition of organic nano-objects.

Experimental Scheme and Equipment

The same as for Part I.

Experimental Results

The process of local STM-stimulated deposition of organic nano-sized objects on the (-C:H (50 Å) /xIn_20_3 γSnO_2 (ITO) (200 Å - 600Å) films and ITO (500 Å) films on W (1500 Å - 2000 Å) in a medium of chloroform and diethyl ether was investigated. It was shown that under special conditions (pressure of N_2: 10 Pa - 100 Pa, chloroform and ether: 1 Pa - 10 Pa, temperature equal to 300 K), the process of deposition is not observed in the region under the tip of the STM. However, nano-sized annular objects were formed around the point of action. When the points of STM electric pulse action traveled along a straight line, two parallel nano-sized lines were formed. In both cases, it appears as though the tip of the STM casts a shadow in the region under it, and the deposition process in this region is absent. Note that on the highly conducting substrates, the process of local deposition was observed only directly under the tip of the STM. The shadow effect was observed only on semiconductor surfaces.

Interpretation of Results

This effect seems to be a consequence of the interaction of the secondary electrons and the holes created in ITO as a result of the electron emission from the STM tip into states in the ITO. These states became charged and ready for interaction with adsorbate molecules. It may be a result of both electrostatic and chemical interactions. This point of view correlates with the scattering diagrams of secondary particles. The secondary holes migrate to the region under the STM tip through the action of electrostatic forces that lead to partial compensation for the electrons' charges. As a result, the region under the tip becomes nonactive for interaction with positively charged ions. The secondary electrons interact with the ITO surface traps that lead to the creation of the negatively charged regions around the tip. These regions play the role of adsorbate centers. The shadow effect was observed only on the ITO surface. In the other investigated semiconductors only deposition directly under the STM tip was observed. The special features of the ITO material may explain this phenomenon, but these special features have not yet been determined.

References

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