FABRICATION OF MOLECULAR DEVICES

A Senior Scholars Thesis

By

KATHERINE WALTON

Submitted to the Office of Undergraduate Research Texas A&M University In partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2006

Major: Chemistry

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ABSTRACT

Fabrication of Molecular Devices (April 2006)

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This project focuses on the synthesis and attachment of metal nanoparticles to Au and GaAs surfaces using a combination of chemical self-assembly and scanned probe lithography. In this project self-assembled monolayers (SAMs) of alkanethiols and dithiols were prepared on Au and GaAs surfaces. There chemical assembly was investigated using a combination of Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The surface morphology and nanopatterning of these SAMs was investigated using atomic force microscopy. Lastly, as the final goal of the project was to create single electron tunneling devices by attaching metal nanoparticles to these surfaces, Au nanoparticles of varying sizes ranging from ca 2 - 12 nm were synthesized.

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CHAPTER I

INTRODUCTION

The concept of molecular devices opens an enormous area of technological application. The principle behind molecular devices is to utilize the unique properties of materials at the nanoscale level to control the physical characteristics of the device such as electron transport.

Molecular devices are being designed for many different purposes, for example wires, data storage, and molecular switches.¹ Molecular wires are ideally designed to carry a charge rapidly over long distances. In many of these wires, charge is transferred by a tunneling mechanism. Nanotubes and fullerenes (C_{60}) are also being used to produce data storage devices. Van der Waals forces within a nanotube junction produces an On and Off mode. This phenomenon is also observed when a fullerene is placed within a nanotube. The elements can then be utilized to form more complex data storage devices. Switches are formed from molecules, nanoparticles, or carbon nanotubes. These devices utilize the van der Waals interactions similar to the data storage devices producing an On and Off mode.

In the work presented here we have started investigations of the attachment of metal nanoparticles coated with SAMs to metal and semi-conducting surfaces as an approach to the construction of single electron tunneling devices.² The basic construction of these devices includes a substrate or surface, a self-assembling monolayer, and a conducting

This thesis follows the style of the Journal of the American Chemical Society.

nanoparticle. The principle substrates used in these types of studies have been evaporated gold on silica or mica, however in this project we are also interested in assembly on GaAs. GaAs is a narrow band-gap, 1.52 eV, III-V semiconductor.³ The use of a semiconductor as opposed to a metal surface affords the ability to tune the electron injection barrier by controlling the doping levels of the GaAs. GaAs also offers another advantage in transitioning such experiments from Au in that the same approaches used for the chemical assembly of alkanethiols on Au can also be applied to GaAs. This will allow for a ready comparison to devices constructed using both platforms as substrates.

Alkanethiols have been used in this work as they are known to assemble into well ordered monolayers on surfaces such as Au.⁴ In many of the studies presented herein, dodecanethiol was used to produce a resist monolayer on the surface of choice. On Au the terminal -SH "head group" attaches to the Au surface by forming a strong Au-S bond with removal of the H. The monolayers of long chain alkanethiol (> C10) can form condensed monolayers on Au with a close packed configuration with all of the molecules uniformly tilted with their molecular axis at an ~ thirty degree angle relative to the surface normal. This compact monolayer can then be used as the resistive layer and a pattern can be etched into the monolayer by utilizing scanned probe lithography. Self-assembly of thiols on GaAs has received far less attention. In general they have been found to exhibit far less short range order than on Au surfaces.⁵

Attachment of metal nanoparticles requires that a second solution of dithiol be introduced to the surface in a controlled environment. In principle the dithiol acts as a connector for the nanoparticles and the surface. Since the dithiol is only assembled where the pattern was impressed, then the particles should also appear in the pattern.

To create metal nanoparticles we have employed two main procedures, that of Brust and that of Turkevitch.^{6,7} Gold nanoparticles synthesized by the Brust method produce particles in the range of 1-3 nm and are thiol passivated to prevent aggregation. The basis of this method is the reduction of hydrogen tetrachloroaurate tribasic while rapidly stirring causing dissociated gold ions to convert to gold atoms. The increase in concentration of the reducing agent increases the concentration of the atoms causing them to precipitate as nanoparticles. The two-phase system was reduced with sodium borohydride and tetraoctylammonium bromide was added as a phase transfer catalyst. Dodecanethiol was added to the solution to stabilize the particles and prevent them from clustering.

Another method we employed for the synthesis of gold nanoparticles utilized citrate ions as stabilizers. The synthesis developed by Turkevitch utilizes a one-pot synthesis with hydrogen tetrachloroaurate and sodium citrate. The synthesized particles have a radius of about ca. 12 - 14 nm. One of the advantages of this method is that the Au particles formed are soluble in water.

In order to pattern our surfaces, scanned probe lithographies such as nanoshaving and nanografting have been used. Using scanned probe nanolithography an AFM tip attached to a cantalever is used to remove surface bound alkanethiols from a substrate that contains a molecular layer to form a specific pattern. This procedure is done while the sample surface is immersed in pure ethanol (to make nanowells in the SAM) or in an ethanolic solution of a molecule of interest to graft that molecule into the resist SAM. We have employed this grafting approach to introduce dithiol patterns to the surface. Once the molecular pattern forms the dithiol solution is removed and the surface is again rinsed with ethanol. A concentrated solution of thiol functionalized gold nanoparticles can then be introduced into the system and again allowed to stand in order to assemble the Au particles on the desired pattern.

In this research, molecular devices were attempted to be formed with Au and GaAs surfaces. In Chapter 2, the basic details of SAMs on Au and GaAs surfaces are introduced. In Chapter 3, nanopatterning of the surface by AFM are discussed. In Chapter 4, the synthesis of nanoparticles is described. Lastly, in Chapter 5 the conclision of the project and future work is discussed.

CHAPTER II

SAMS OF ALKANETHIOLS ON Au AND GaAs

Introduction

Self-assembly of molecular layers is a natural phenomenon in which molecules self-organize themselves into well defined structures driven by thermodynamics. In nature for example, self-assembly is found in the formation of cell membranes. Phospholipids with nonpolar tails and polar heads have the polar heads oriented outward interacting with the aqueous phases. The nonpolar tails are drawn inward creating a bilayer. In our research polarity is not the key-determining factor of self-assembly, instead bond strength and molecular affinity are utilized to create structures of well ordered molecules on surfaces.

The fabrication of molecular devices is generally approached in two different ways, bottom up or top down.⁸ In this project, our research utilizes a bottom-up technique by applying self-assembled monolayers. This is then combined with a top-down approach by nanolithography to control patterning in these molecular layers. The formation of theses layers on gold occurs in transitional steps.⁹ The initial structure of the layer has the alkanethiols adsorbed and laid parallel to the surface. As more molecules come in contact with the surface the attached molecules start to become more perpendicular as it becomes more favorable to increase the number of chain-chain interactions over chain-surface interactions. Ultimately, the layer of molecules forms a surface at a 30 degree angle to the normal due to the bond formed by the sulfur with the

Au surface. This is shown in Figure 1: Projection of a monolayer of dodecanethiol on Au.



Figure 1: Projection of a monolayer of dodecanethiol on Au.

Self-assembled monolayers have been shown to form well ordered structures on Au surfaces and to form dense layers on semiconductor surfaces such as GaAs. A procedure by Allara¹⁰ has the SAMs formed at elevated temperatures (100-200 °C). Infrared spectroscopy studies by Allara have shown that films of alkanethiols on GaAs(100) can form dense layers with reasonably long range order.⁵ Research done by Uosaki¹¹ showed that the formation of SAMs on semiconductor materials was much harder to obtain than for metals. To produce similar layers of SAMs on GaAs a small amount of ammonium hydroxide was added to the solution of ethanol and alkanethiol. This addition leads to a more ordered monolayer. Unlike the formation of selfassembled monolayers on gold, the SAMs on GaAs do not form layers with short range order. This is due to the tendency of the surface to form oxide layers. In order to counteract this problem harsh cleaning techniques are required to remove the majority of the oxide layer. In this chapter we have compared the structures of SAMs formed on Au and GaAs surfaces.

Experimental

Au

The gold surfaces were cleaned in an ozone cleaner, NovaScan PSD-UV, for twenty minutes to remove the metallic oxide. To remove the remaining oxide the surfaces were rinsed for one minute with deionized water and dried under nitrogen. A 1 mM solution of dodecanethiol in ethanol was prepared in a sealable container. The cleaned surface was immersed in the solution and allowed to rest for eight hours. When the sample is not being viewed under AFM or FTIR it remains in solution. However, when it is time to perform nanolithography the surface is rinsed with ethanol to remove any excess dodecanethiol and dried under nitrogen.

<u>GaAs</u>

In order to prepare SAMs on GaAs, the surfaces were washed in pure ethanol and then cleaned in an ozone cleaner for 20 minutes. The cleaned surfaces were exposed to concentrated HCl to produce an arsenic layer and rinsed with ultra pure water. The surface was then immersed in a 1 mM solution of dodecanethiol.

Atomic force microscopy was used to view the topography of the monolayers on both gold and GaAs. FTIR was used to determine the order of the layers of the gold surfaces. Atomic force microscopy is a technique that allows scientists to explore the topography of a surface and etch patterns into monolayers.¹² The main component of the AFM consists of a tip comprised of silicon nitride a few nanometers in size, and attached to a cantilever. When the tip is brought into contact with the surface Van der Waals forces occur between the tip and the surface causing a deflection of the cantilever. The tip follows the profile of the surface maintaining a constant lever deflection (constant force). Forces acting on the tip provide the signal. This deflection is measured by a laser that is reflected off the cantilever and onto a detector. The detector records these measurements and converts them into images of the topography or friction of the sample. A diagram of the instrument is given in Figure 2.



Figure 2: Diagram of an AFM illustrating the primary components, including a cantilever-tip assembly, a laser and quadrant photodiode for measuring tip deflection, a feedback loop to control force and a piezoelectric translator to control the tip position. (Diagram produced by James Batteas)

The other form of characterization of these monolayers is Fourier Transform Infrared Spectroscopy. FTIR measures the vibrational transitions of different bonds when a molecule is excited into different energy levels.

Results and Discussion

SAMs on Gold



Figure 3: FTIR spectrum of dodecanethiol SAMs on Au substrates

The FTIR spectrum produced bands shown in Figure 3, and values given in Table 1, correspond to an ordered dodecanethiol monolayer on gold.¹³ The band values

for the symmetric and asymmetric stretching of the CH_2 groups can be used to determine the order of the SAMs. The bands that determine the order appear at 2850 cm⁻¹ for CH_2 symmetric stretch (d+), and 2920 cm⁻¹ for asymmetric stretch (d-). The spectrum was taken on a Nicolet 6700 FT-IR. The IR spectra are collected at an angle of incidence of 80° .

Wavenumber (cm ⁻¹)	Assignment
2965	CH ₃ asymmetric stretch
2938	CH ₃ symmetric stretch
2919	CH ₂ asymmetric stretch
2878	CH ₃ symmetric stretch
2850	CH ₂ symmetric stretch

Table 1: Vibrational transitions corresponding to ordered dodecanethiol monolayers on Au.

The order of the SAM could also be confirmed by AFM. As seen on the AFM image the dodecanethiol layer on gold produces an ordered layer. The attachment of the thiol is shown in Figure 4.



Figure 4: AFM image (7 nm x 7 nm) of an ordered dodecanethiol monolayer and corresponding diagram

The sulfur head attaches to the surface of the gold in the grooves made by three gold atoms, this is shown in Figure 4. The AFM images were taken on a Molecular Imaging AFM.

SAMs on GaAs

So far no FTIR spectra were taken for the dodecanethiol monolayers on GaAs, however, AFM images show that the monolayers were not very ordered as shown in Figure 5.



Figure 5: Topographic AFM image of a dodecanethiol monolayer on GaAs (1 $\mu m \ x \ 1 \ \mu m).$

Though GaAs does not produce well-ordered monolayers further studies will be done to try to reproduce similar monolayers as seen on Au. For the purposes of our experiment however, our main concern is to have a dense packed monolayer, which indeed seems to be the case given the relatively uniform AFM images found for thiol SAMs on GaAs. This is further confirmed by nanopatterning of the SAMs on GaAs as described in

Chapter III.

CHAPTER III

NANOPATTERNING

Introduction

Forming nanoscale patterns on surfaces can be accomplished in many different ways, some examples are nanolithography and microcontact printing. Formation of nanopatterns on surfaces by microcontact printing utilizes a stamp pad technique where a nanopattern of a SAMs of alkanethiol is stamped onto the surface.¹⁴ Microcontact printing can be used to generate structures ranging from 1 to 10's of microns in lateral dimension, while nanolithography focuses on structures < 1000 nm.

In order to generate patterned SAMs by microcontact printing a polydimethylsiloxane (PDMS) stamp was prepared by molding it to a pattern formed by photolithography on oxidized silicon wafers, such as grafting structures. After forming the stamp it "inked" by contact with an ink pad (also made of PDMS, but saturated with thiols) or by soaking the stamp in a 10 mM ethanolic solution of the desired SAMs. The "inked" thiols can then be patterned onto a surface such as Au by contacting the stamp to the surface for 1-2 minutes.

The nanolithography technique was generally used to position nanoparticles directly onto surfaces by shaving a pattern into a monolayer. Two methods of nanolithography are the shaved matrix approach and the NanoPen Reader and Writer method.¹⁵ In the shaved matrix method the AFM tip is used to remove some of the monolayer in the presence of a solution of either nanoparticles or a second molecule. As

the monolayer is shaved off the second molecule or particles assemble in the etched pattern. The NanoPen Reader and Writer method is accomplished by placing a droplet of a solution of particles or a second molecule on to an inverted AFM tip. As the AFM tip removes the monolayer the droplet of solution fills in the impressions forming a layer of either particles or molecules. In both methods, a program that inputs a script of movements to produce a specific pattern into the monolayer automated the lithography.

In this research nanolithography was used to form patterns into which a dithiol layer was grafted. Figure 6 is a diagram of the shaved method nanolithography.



Figure 6: Diagram of nanolithography. 1) A monolayer is formed on a surface. 2) An AFM tip shaves a pattern into the thiol layer. 3) A dithiol monolayer is then grafted into the etched pattern.

Experimental

SAMs were formed on gold or gallium arsenide by procedures reported in Chapter I. Patterns were etched into these surfaces by AFM. Two thin plastic tubes were fed into the AFM sample well with the ends attached to plastic syringes. Ethanol was injected into the well to rinse out the etched thiol (dodecanethiol). A 1 mM solution of dithiol (octadecanedithiol) in ethanol was then injected into the well and allowed to sit for 30 minutes to form a dithiol layer into the etched pattern. Ethanol was again injected to rinse out the unreacted dithiol.

Results and Discussion

The AFM was used to form the patterns in the surface utilizing a lithography program with prewritten scripts that control the AFM tip position and force. These scripts are able to complete the surface patterns shown typically in less than a few minutes. This allows for easy modification of the patterning conditions to optimize feature formation.

<u>Au</u>

Figure 7 shows an image of the topography of a pattern etched in a dodecanethiol monolayer on gold.



Figure 7: An AFM image of the topography of a dodecanethiol monolayer on gold with a series of squares nanoshaved into the surface. The "scribbles" indicate that the writing force was too high in this case.

A pattern can be etched into dodecanethiol as seen is the above figure. However, the figure also shows that the formed patterns are not very uniform

Grafting octadecanedithiol onto gold

Nanowells were formed in a dodecanethiol monolayer on gold and octadecanedithiol solution was introduced into the system forming the observed dithiol pattern. In Figure 8 the topography of the grafted dithiol is shown.



Figure 8: Grafted octadecanedithiol into a dodecanethiol monolayer on gold.

In Figure 8, the white line that bisects the square pattern corresponds to the topography shown in the graph to the right. The large peak shows that the dithiol did in fact graft onto the pattern, since the height of the pattern is greater than the height of the

surrounding monolayer. The other peaks correspond to the monolayer of dodecanethiol, and discrepancies in these peaks may be due to the roughness of the gold surface.

<u>GaAs</u>

Formation of nanowells:

In Figure 9 nanowells about 1.5 nanometers deep, which correspond with the length of dodecanethiol, are formed in GaAs.



Figure 9: Nanowells formed in a dodecanethiol monolayer on GaAs.

Octanedithiol was grafted into the nanowells as shown in Figure 10.



Figure 10: Grafted octanedithiol into nanowells formed in a dodecanethiol monolayer on GaAs.

The depth of the nanowells has changed to about 1 nanometer. This experiment proves that the dithiol could be grafted onto a semiconducting surface in a specific pattern.

CHAPTER IV SYNTHESIS OF NANOPARTICLES

Introduction

Formation of colloidal gold is accomplished in one of two different ways.¹⁶ One approach includes a gold rod disintegrated by an electric arc in a liquid medium. The more conventional approach occurs by reducing gold salts to form particles. The process by which gold nanoparticles are formed occurs in three steps; nucleation, growth, and coagulation. In the nucleation step gold nuclei are formed by a polymerization step, which reduces the metal ions when a critical mass is achieved. The growth step occurs once a substantial amount of gold is nucleated. Compared to the nucleation step, multi-step polymerization, the growth step, occurs in one step. This process is catalyzed by the reduced nuclei. The coagulation step determines the ultimate size and shape of the particles, and can be affected by the addition of a molecular stabilizer.

The Brust method utilizes a two-phase system:

 $AuCl_{4}^{-}(aq) + Br^{-}N^{+}(C_{8}H_{17})_{4} + (C_{6}H_{5}Me) \rightarrow Br^{-}N^{+}(C_{8}H_{17})_{4} + AuCl_{4}^{-}(C_{6}H_{5}Me)$ $mAuCl_{4}^{-}(C_{6}H_{5}Me) + nC_{12}H_{25}SH(C_{6}H_{5}Me) + 3me^{-} \rightarrow 4mCl^{-}(aq) + (Au_{m})(C_{12}H_{25}SH)_{n}(C_{6}H_{5}Me)$

The gold source, hydrogen tetrachloroaurate tribasic, was dissolved in water and tetraoctylammonium bromide (TOAB) was dissolved in toluene. The TOAB functioned as a phase transfer catalyst to draw the gold ions into the organic phase. The sodium borohydride was added in the presence of dodecanethiol and reduced the gold ions. Particles are formed by the vigorous stirring of the system, which increases the interactions of the atoms. The dodecanethiol stabilized the size and shape of the particles.

In the Turkevitch synthesis, sodium citrate was used as a reducing agent to produce gold atoms. The citrate ions oriented around the particle give the particle a negative charge stabilizing the particles. The citrate also serves to prevent large clusters of particles from forming.

Experimental

Brust Method

The two-phase system was prepared by mixing an aqueous solution of hydrogen tetrachloroaurate tribasic (30 mL, 30 mmol dm⁻³) with a solution consisting of tetraoctylammonium bromide in toluene (80 mL, 50 mmol dm⁻³) in a beaker. The system was stirred until the organic layer turned a yellow orange color indicating that the tetrachloroaurate was transferred from the aqueous phase. Dodecanethiol (170 mg) was added to the organic layer. An aqueous solution of sodium borohydride (25 mL, 0.4 mol dm⁻³) was prepared and slowly added to the stirring solutions. The solution turns to a

dark red or black color and stirs for 3 hours. After such time the organic phase is separated from the aqueous phase and evaporated in a rotovap until the volume of the solution is 10 mL. The concentrated solution was then stirred with 400 mL of ethanol to precipitate the particles and remove any unreacted thiol. The solution was left for 4 hours in a -18° C environment. A dark brown precipitate formed and was filtered off, washed with ethanol, redissolved in toluene, and the process was repeated. The average size distribution was determined by TEM to be ~ 1-3 nanometers.

Turkevich Method

An aqueous solution of tetrachloroaurate (1mM, 250 mL) is brought to a boil and 25 mL of 38.8 mM aqueous solution of sodium citrate was rapidly added. The mixture was boiled for ten minutes and then removed from the heat and stirred for an additional fifteen minutes. The average size distribution determined by TEM showed a diameter of ~ 13 nanometers.

Results and Discussion

UV-visible absorption spectroscopy

The UV-vis technique utilized the ability for some compounds to absorb radiation in the ultraviolet visible range. A beam of light passes through a monochromator causing the light to separate into wavelength ranges. This is done to isolate a specific range. The separated light passes through the sample and onto a detector. The detector compares the measured light from the light source, and forms peaks based on wavelength versus absorption.¹⁷ The UV-visible spectra were taken on an Ocean Optics ISS UV-VIS and are shown in Figure 11.



Figure 11: UV-visible absorption spectrum of Au nanoparticles

The UV-visible absorption spectrum of the citrate-stabilized particles corresponds to the dark red peak, and the UV-vis spectrum of the Brust dodecanethiol stabilized particles corresponds to the light red peak. The citrate particles absorb more light at 525 nm showing that these particles are more optically active at that wavelength. The Brust particles are observed to be more active at around 300 nm. This spectrum is similar to that obtained by Duff.¹⁸ The peak that formed from the citrate particles was attributed to "weak surface plasmon extinction." The Brust particles produced a broad peak due to greater dispersion and decreased size. The general way the transmission electron microscope functions is to produce an image from a beam of unscattered electrons bombarding the sample. The source of the electrons is an electron gun at the top of the TEM which produces a beam of electrons that are focused onto the sample. Once the beam reaches the sample some of the electrons scatter, secondary electrons reflect off the sample, and some pass through.¹⁹ Figure 12 shows the interaction between the sample and the electron beam.



Figure 12: Interaction between sample and electron beam

The two main techniques used to determine size and shape of the particles are UV-visible absorption spectroscopy and transmission electron microscopy.

The electron beam is aligned by a gun-aligning coil and focused by condenser lenses. All TEM images were taken on a JEOL JEM-2010.

Using TEM we could confirm the particle size distribution of our synthesized Au nanoparticles. The two images are of two different synthesized particles utilizing methods to stabilize Au in organic (Brust) or aqueous (Turkevich) media. Figure 13a is a TEM image of gold nanoparticles synthesized by the Brust method, and Figure 13b is a TEM image of gold nanoparticles synthesized by the Turkevich synthesis. Comparing the size of the two particles to the 20nm scale the Brust particle range about 1-3 nm in size while the Turkevich particles range form 12-13 nm in size.



Figure 13: Left (a) Gold nanoparticles synthesized by the Brust method. Right (b) Gold nanoparticles on silica particles synthesized by the Turkevich method.

Attachment to dodecanethiol

The Brust particles were diluted in a solution of ethanol (approximately 1mM) and injected into the sample well of the AFM with a grafted sample of dithiol. An image could not be obtained due to drifting of the AFM laser caused by it reflecting off of the particles. The same procedure was conducted in toluene, in which the particles were more dispersed, and the same results were observed. Another procedure was conducted to try to attach the particles to dithiol in solution. The sample was introduced into the sample well to try to form a monolayer in the pattern, but the gold failed to attach to the dithiol. They may have failed to attach for two reasons: 1) the particles perhaps were not allowed enough time to attach to the dithiol molecules, as the attachment process is diffusion limited, or 2) the stabilizing alkanethiol layer may have been too thick to allow for sufficient access by the dithiol to bond to the Au nanoparticle surface. In our next attempts we will vary both thiol chain length and attachment time.

CHAPTER V

CONCLUSION AND FUTURE WORK

Though each component of the device was formed successfully, building the final device proved to be difficult and has yet to be completed. Thiol layers were assembled on both Au and GaAs surfaces and dithiol was grafted into etched patterns. However, thus far in the project gold nanoparticles were unable to be attached to the dithiol patterns. When a concentrated solution of gold nanoparticles was introduced into the AFM sample well, the laser was lost due to changes in the dielectric constant of the medium and an image could not be generated. This means that the laser no longer was oriented on the cantilever and was not reflecting onto the detector. In the future less concentrated solutions will be used to try to create conditions optimal to observing nanoparticle attachment.

Future work will include a surface study of GaAs to try to form the most ordered monolayer. GaAs surfaces have in general not been found to form well-ordered monolayers. This problem could be remedied by varying the temperature and solvent in the formation procedure, as well as by tying to find a means to generate more atomically smooth GaAs surfaces prior to attachment. Once the final test devices are formed, the capacity of these devices to transfer a charge will then be measured by passing a current through the surface-molecule-nanoparticle junction and measuring the output with a metallized AFM tip. This paper is a precursor for the progression of this type of technology. Studies on both the surfaces and the devices themselves can be further applied to other areas of nanotechnology.

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