Discontinuous Gold Films for Nanocell Memories

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ABSTRACT

An important component to the nanocell, among other self-assembled networks, is the fabrication of a framework by which molecular elements can be interconnected. This framework must be nanometric in scale, created in a material suitable for attachment chemistries and remain electrically discontinuous until molecular attachment. Utilizing the Volmer-Weber mechanism by which gold grows on silicon dioxide surfaces, nanometric islands of gold are fabricated to provide this framework. Using standard photolithography techniques, the regions where these islands are located are well defined. A two-layer photoresist stack is developed that prevents edge shorting around the boundaries of each region. The discontinuous gold films fabricated in this study are repeatable, offer a fill factor of 63%, and are easily patterned down to the one-micron scale.

Keywords: molecular electronics, Volmer-Weber, self-assembled, integration

1 INTRODUCTION

Since a moleculer mechanism was first proposed as a basis for electronic circuits [1], self-assembly of these circuits has remained a primary goal for most molecular electronic technologies [2]. By utilizing specific chemical reactions, molecules can be attached to specific regions on a semiconductor or metal surface. Although photolithographic technologies limit lateral resolutions, molecular self-assembly, when combined with photolithography, offers the potential to scale circuit architectures below these limits. The nanocell [3] is a device that proposes to use chemical self-assembly followed by post fabrication training to realize electronic circuits. The post fabrication training step reduces the demand for nanometer-scale layout and integration.

An important component to the nanocell is the fabrication of a framework by which molecular elements can be interconnected. This network must be: 1) fabricated using gold, or some other material appropriate for sulfur attachment chemistry, 2) electrically discontinuous, 3) patternable to allow molecular self-assembly only in well defined areas, and 4) be repeatable and robust to the environment. Previous research [4] has shown that gold, when evaporated in thin layers, grows discontinuously according to the Volmer-Weber mechanism. Using this technique, a process was developed to repeatably grow and pattern discontinuous gold films as a backbone for molecular interconnection.

2 FABRICATION

As previously shown [4], a thin layer of gold can be sputtered onto a thermally grown silicon dioxide film, which results in the formation of discontinuous islands.

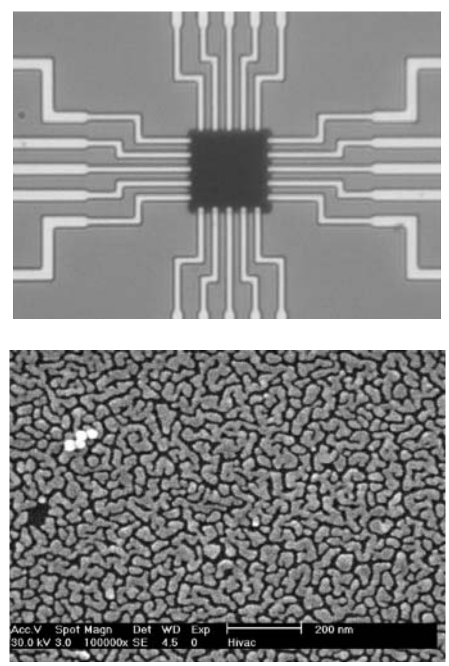

Figure 1: The nanocell device (top) and the center region of the discontinuous gold film (bottom).

Rather than growing as a continuous film, gold tends to exhibit three dimensional island formation during the initial stages of growth, known as the Volmer-Weber mechanism. This growth mechanism results from strong gold-gold interactions, coupled with relatively weak gold-silicon dioxide interactions [5].

2.1 Device Fabrication

The nanocell device (Figure 1) consists of a series of metallic leads that come into close proximity. Variations in numbers of leads and gap distances have been fabricated, including gaps under 1 micron. The substrate is a 1000 angstrom thick silicon dioxide film, thermally grown on a (100) p-type, 1-10 ohm-cm silicon wafer. The leads are formed by depositing 100 angstroms of titanium for adhesion, followed by 1500 angstroms of gold, patterned using a liftoff process.

2.2 Discontinuous Film Growth

The silicon dioxide surfaces, patterned with the Ti/Au leads, are first solvent cleaned with acetone followed by a methanol bath. Afterwards, the samples undergo a dehydration bake of 150^{o}C for 10 minutes prior to the photolithography step used to pattern the films. After the photoresist stack is patterned with the nanocell regions defined, the samples are quickly placed under vacuum in the E-beam system.

The discontinuous gold films are deposited using E-beam evaporation, and patterned using a liftoff photolithography process. The evaporation system uses a Thermionics, Inc. 5-position electron gun for evaporation, and a Sycon, Inc. STM-100 quartz crystal microbalance for measuring film thicknesses. The base pressures for all evaporations are $5*10^{-6}$ Torr, and rates are held constant at 1.0 angstrom/second during the evaporation for controllability. Evaporations were timed and the average thickness was monitored using the Sycon thickness monitor. Comparisons between samples evaporated with different measured thicknesses were made. Endpoints were determined by monitoring the average thickness on the Sycon monitor, which takes into account any small perturbations in the evaporation rate. Since the thickness reported by the monitor represents an average, rather than an absolute, these values are used only as a reference for experimentation.

2.3 Edge Defects

One observation made during early experiments is the tendency for the gold islands to agglomerate against the edges of the photoresist used to pattern the regions of discontinuous film within the nanocell. Easily seen using SEM microscopy (Figure 2), this agglomeration against the step edges results in the formation of electrical shorting paths between any two patterned leads. These shorting paths render a device useless, since they cannot be corrected and the low-resistive path prevents the measurement of any current passing through the highly resistive paths within an assembled nanocell. The frequency of devices that exhibit edge shorts is related to the perimeter of the nanocell region in which the discontinuous film is patterned, and the orientation of the sample in the evaporation system. This makes reasonable sense, because the tendency of the gold to agglomerate into the resist edges should be greater in the direction of the evaporation flux.

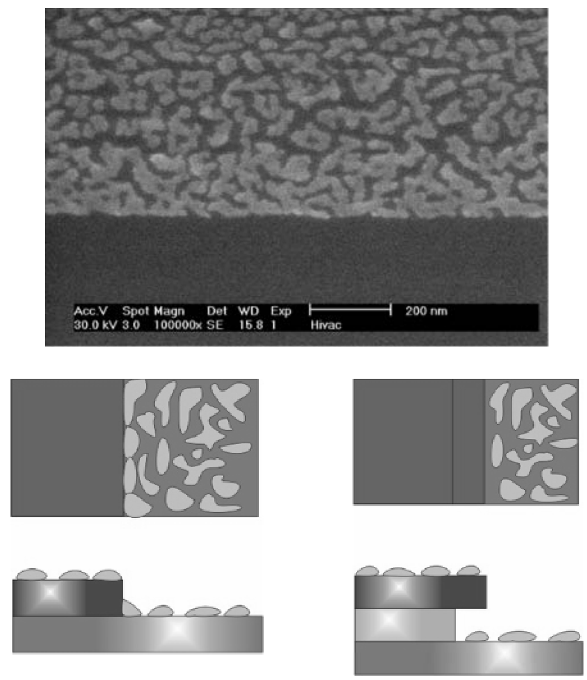

Figure 2: Edge shorts (top) and photoresist process to minimize them (bottom).

3 CHARACTERIZATION

3.1 Morphology

It is understood that the evaporation method used to deposit the gold films significantly contributes to the morphology of the gold islands themselves. Previous studies using sputter deposition [4, 5] result in small, more colloidal gold island formation. Using E-beam evaporation, the average area and perimeter of each gold island tends to be greater, an effect that might be explained by the lower mobility of evaporated gold versus sputtered gold. A study is planned that will experimentally compare sputtered verses evaporated gold targets, and derive a quantitative analysis of island area, perimeter and fill factor.

To statistically study the discontinuous gold films, a custom image analysis software routine was developed using LabVIEW (National Instruments, Inc.) Shown below (Figure 3) is a portion of an SEM image taken of a Sycon measured 40 angstrom thick film, evaporated in approximately 40 seconds. The scale bar was separated from the image to remove any inconsistencies during analysis. By correlating the scale bar to the number of pixels, the resulting image area was determined to be 1200nm x 707nm, or 848,588nm^2. A summary of the data collected is shown below (Table 1). Calculations to determine the average gap distances are underway, but the average is estimated to be on the order of 10nm.

Island Analysis	
Image Area	848,588 nm^2
Number of Particles	196
Average Size	2713 nm^2
Fill Factor	0.63

Table 1: Island analysis for 40 angstrom measured deposition condition, image from Figure 3

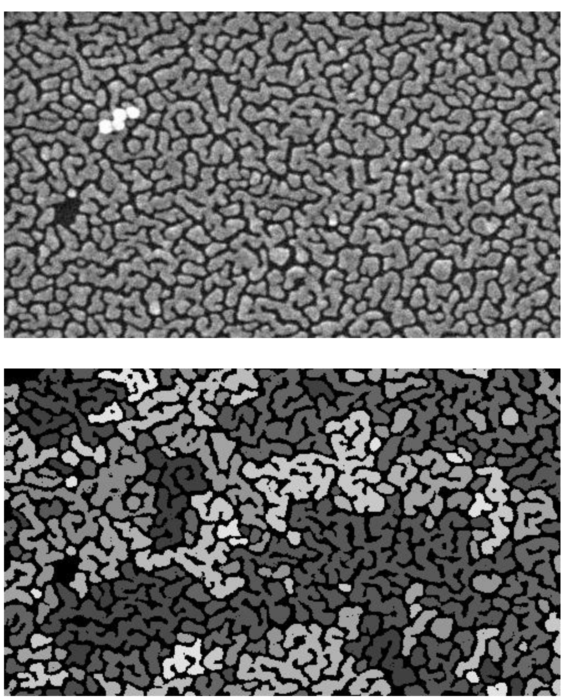

Figure 3: A section (504x297 pixels, or 1200x707nm) of the SEM image (above), and after analyzed using the particle counter routine (below)

Although the average particle size was determined to be 2713 nm^2, gold islands ranged in size from 50nm^2 to just over 10,000nm^2. The majority of the particles (72%) however, were determined to be in the 225nm^2 to 1700nm^2 range. The presence of only a few large area particles contributes to the resulting average area calculation.

The contribution of these relatively few, large islands is also important to the performance of the nanocell network. The gap distances between gold islands formed under the above conditions are too large for direct molecular attachment. When used as a seed layer, however, these islands can be bridged using molecularly passivated gold colloids (Figure 4) or nanorods [6]. The larger islands can allow for low attachment densities, requiring only a few connections be made to complete a circuit between two leads [6]. Although the nature of these connections is not conclusively determined, nanometallic filament formation is suspected between the gold nanorods and the gold islands. More experimentation is under way using islands fabricated from refractory metals, such as palladium, to minimize electromigration and isolate the current path within the nanocell.

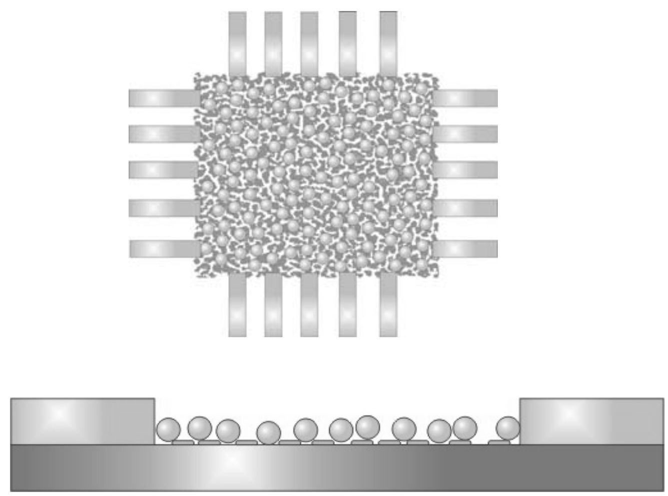

Figure 4: Representation of an assembled nanocell using metallic colloids attached to a discontinuous gold film.

3.2 Electrical Characterization

Three separate experiments were used to determine the electrical discontinuity of the gold films. First, electrical measurements were taken using a Magne-tron Instruments M-700 4-point probe system. For the sample analyzed above, the sheet resistance was out of range, indicating a >10 G-ohm sheet resistance. This is the expected result for a discontinuous film. Second, a series of 1500 angstrom thick gold pads were shadow masked on an unpatterned discontinuous film sample, formed using the above conditions. Distances between the pads ranged from 100 microns to 1 millimeter. Currents measured were in the pA range at 20V, also indicating open circuits. Finally, the discontinuous gold films were patterned on a substrate containing patterned gold probes, with gap distances from 10 microns down to under 1 micron in length. Currents measured from these devices indicated either open circuits (pA range at 20V) or direct shorts (approximately 100 ohm resistances.) The shorts were much more prevalent in the gap distances less than 5 microns. After SEM analysis, it was determined that the cause of these shorting paths was from the edge defects previously explained (Figure 2). Using the two-layer photoresist process, the number of shorts was greatly reduced, and confined to the gaps less than 3 microns.

4 CONCLUSION

Discontinuous gold films have been fabricated and patterned, resulting in a large fill factor and average gap distances of approximately 10nm. The perimeter and area of these islands make this technique desirable as a seed layer for molecular attachment, using gold colloids or nanorods passivated with thiol-terminated molecules. This process offers an alternative to previously researched seed layers fabricated from the self-assembly of gold colloids, which often suffer from lack of density, patternability and reproducibility. The discontinuous gold films fabricated in this study are repeatable, offer a fill factor of 63%, and are easily patterned down to the one-micron scale.

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REFERENCES

[1] A. Aviram, M. A. Ratner, “Molecular Rectifiers,” Chem. Phys. Lett., **29**, pp277-283, 1974.

[2] R. StanleyWilliams, P. J. Kuekes, “Molecular Nanoelectronics,” IEEE Int. Sym.On Circuits and Systems, pp. 5-7, 2000.

[3] J. M. Tour, W. L. V. Zandt, C. P. Husband, L. S. Wilson, P. D. Franzon, and D. P. Nackashi, “Nanocell Logic Gates for Molecular Computing,” IEEE Transactions on Nanotechnology, **1**, pp100-109, 2002.

[4] F. Parmigiani, G. Samoggia, G.P.Ferraris, “Optical Properties of sputtered gold Clusters,” J. Appl. Phys., **57**, pp. 2524-2528, 1985.

[5] Paulson, C.G., Friedberg, A.L., “Coalescence and Agglomeration of Gold Films,” Thin Solid Films, **5**, p47, 1970.

[6] James M. Tour, Long Cheng, David P. Nackashi, Yuxing Yao, Austen K. Flatt, Sarah K. St. Angelo, Thomas E. Mallouk and Paul D. Franzon, “Nanocell Electronic Memories,” **125**, pp.13279-13283, 2003.