Patterning of Carbon Nanotubes on Nitride

Undergraduate Researcher
Pooja Shaw
Columbia University

Faculty Mentor
Horacio Espinosa
Department of Mechanical Engineering,
Northwestern University

Graduate Student Mentor
Owen Loh
Department of Mechanical Engineering,
Northwestern University

Abstract

Carbon nanotubes (CNTs) are highly promising in the miniaturization of electronic devices. However, there are currently many limitations in mass producing devices that involve the application of CNTs, one of which is the ability to physically pattern CNTs in specific locations on a wafer, which is what this study aims to address. Typically, dip-pen nanolithography (DPN) or microcontact printing is used to pattern CNTs (16-mercaptohexadecanoic acid [MHA]) on a gold substrate; however, this gold adds an additional conductive layer in the design of circuits. This study demonstrates that it is possible to pattern MHA, and thus CNTs, directly on a silicon nitride substrate (this method should in theory work similarly on other hydrophilic substrates such as silicon dioxide). This shows that there is the potential to use photolithographic methods such as liftoff to pattern CNTs directly on nitride, eliminating the need for the conductive gold layer and potentially simplifying the circuit design process.

Introduction

In 1965, Gordon Moore, cofounder of Intel, predicted that the transistor density of semiconducting chips would double roughly every 18 months.[1] To date, "Moore's Law" has proven to be a good indicator of the steady advances in computer processing technology. But the industry is realizing the limits of silicon, the materials that serves as the basis of transistor technology. It has become clear that in order for circuits to continue to shrink in size while increasing in computing power, entirely new materials and assembly processes must be used.[2] It appears that researchers may very well have found this new material in the form of carbon nanotubes. Given their high Young's Modulus, tensile strength, and semiconducting abilities, carbon nanotubes show the potential to overcome silicon in pursuit of the continued miniaturization of electronic devices.[3]

Currently, there are still limitations to mass production of devices that involve the application of carbon nanotubes. One major hurdle is the ability to physically pattern (i.e., place) the nanotubes on specific locations on a wafer.[2] A current method used in directed assembly of carbon nanotubes is the patterning of 16-MHA. This is based on the discovery that nanotubes are attracted to COOH-terminated self-assembled monolayers (SAMs), such as MHA.[4] When CNTs are brought close to the MHA patterns, Van der Waals attractions between the two provide the basis for assembly. Previous studies have determined that an individual nanotube can be stabilized on a surface even if only 19% of its surface is in contact with the MHA.[4] Thus, one can pattern a template of MHA on a substrate, and the carbon nanotubes will selectively assemble directly on the patterns. This study aims to pattern MHA directly on a nitride substrate, allowing for the directed assembly of carbon nanotubes in specified locations.

Background

Currently a widely used technique to pattern the MHA is dip-pen nanolithography (DPN). DPN is a nanopatterning technique in which molecules, in this case MHA, are delivered to a substrate via an AFM (atomic force microscope) tip.[4] While this method is effective and offers sub-100 nm resolution, there are two main drawbacks when looking at the larger goal of mass production of devices that use carbon nanotubes for commercial applications. The first is that the process is slow; it could take a very long time to pattern the potentially millions of devices on a single chip. The second major limitation is that DPN patterning of MHA is primarily done on an Au substrate, as the MHA molecules bind and stick to this substrate. Au is a conductive metal, which means that when designing electronics using carbon nanotubes, this conductive layer must also be incorporated into the fabrication process.

Another possible method for patterning MHA is microcontact printing. In this procedure, a silicone stamp is made with a relief pattern on it. The stamp is then "inked" in MHA and pressed against the surface to be patterned (in this case, Au). When the stamp makes contact with the substrate, the "ink" is transferred via diffusion from one surface to the other, patterning the MHA.[5] Although this method is capable of patterning an entire wafer with a single stamp, it still requires

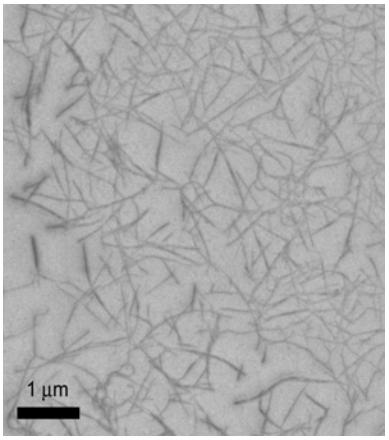

Figure 1. SEM image of SWNTs assembled on an MHA-coated nitride substrate.

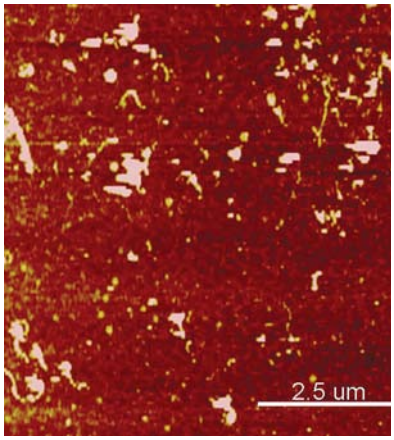

Figure 2. AFM image of MWNTs assembled on an MHA-coated nitride substrate.

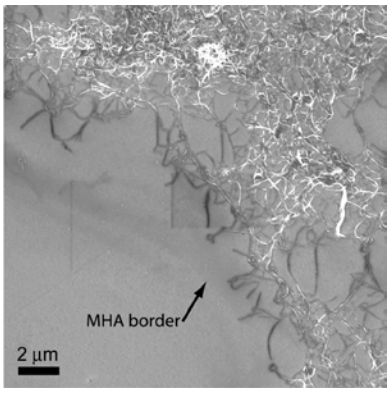

Figure 3. CNTs selectively assembled on MHA on a nitride substrate.

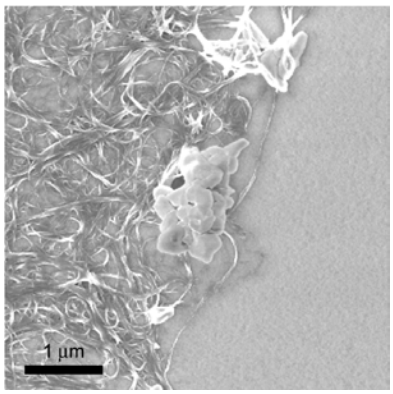

Figure 4. Large clumps of dried MHA formed along the edge of the dried MHA spot.

patterning onto a Au layer, and the resolution is typically lower than that of DPN. Thus, this study proposes a technique of patterning MHA directly onto nitride, eliminating the Au layer while also speeding up the process.

Approach

This research seeks to find out whether MHA will adhere to a bare silicon nitride substrate. To do this, drops of a saturated solution of MHA in ethanol were placed directly onto a nitride substrate and allowed to dry. A solution of carbon nanotubes suspended in dichlorobenzene by sonication was then dispersed across the nitride surface. Excess CNT solution was rinsed from the substrate, leaving nanotubes assembled selectively on the areas coated with dried MHA. Given that this fundamental step worked, the next step would be to pattern MHA, using the common photolithographic method of liftoff, beginning with a nitride-coated silicon wafer.

In this technique, the wafer is spin-coated with a layer of photoresist, and photolithography or electron beam lithography (EBL) is used to define micro- or nanoscale patterns in the resist. In EBL, selected areas on the wafer are exposed to a highly-focused, high-energy electron beam to expose the resist from those areas. The resist is then developed to remove the exposed regions. Next, the wafer is coated in MHA, and the solution is allowed to dry. The patterned photoresist acts as a mask, allowing the MHA to reach only those exposed areas that have been patterned by EBL, while the areas covered in photoresist remain protected from the MHA. Finally, the photoresist is removed using acetone, leaving a wafer patterned with MHA.[6]

The carbon nanotubes are then dispersed across the surface, where they adhere only to the MHA patterns.

Results and Discussion

After the above methods were completed, scanning electron microscopy was used to confirm that the CNTs adhered directly to the dried MHA on a nitride surface. The procedure allowed MHA solution to dry on a nitride substrate, although it should in theory work for any hydrophilic substrate. This opens up possibilities for the directed self-assembly of CNTs on a range of substrates using MHA.

Another encouraging result is that the technique works for both single-walled (SWNT) and multiwalled (MWNT) carbon nanotubes. In Figure 1 SWNTs are shown, and in Figure 2 atomic force microscopy was used with MWNTs. Virtually all related studies to this point have used only SWNTs because of difficulty in manipulating MWNTs on Au.

The next crucial step was to determine if the CNTs attached selectively only to the MHA as opposed to the entire nitride surface. Figure 3 shows that the boundary between the MHA-coated and bare substrate appears as a slightly darker shaded line, and it is clear that the CNTs adhere only to the MHA side. This selective assembly is critical in order to ensure that the CNTs stick only to the desired patterns.

Based on these initials trials, there are a few issues that should be addressed in the future. One major issue is that clumps sometimes formed as the saturated MHA-ethanol solution dried. As the ethanol evaporates from the solution, MHA precipitates due to the increased concentration. In Figure 4, the large clumps of MHA can clearly be seen at the edges of the dried MHA. These clumps interfere with the assembly of the CNTs and result in excess debris on the substrate. A method needs to be found to either remove the MHM or prevent it from clumping as it dries. Future studies should also be conducted to gain a better understanding of how the MHA physically binds to the nitride substrate at a molecular level.

Conclusions

In summary, the major finding of this study is that nitride can in fact be used as an effective substrate on which to pattern carbon nanotubes. Additionally, this method of dried MHA should in theory work on a variety of surfaces, so CNTs have the potential to assemble on many substrates. The implications are far-reaching in that this method allows for the complete removal of the Au layer that has traditionally been required to pattern CNTs by DPN and microcontact printing. By eliminating the gold layer, the design process of circuits might be greatly simplified because the conductive layer that would otherwise short any device is no longer necessary.

This ability to pattern on a range of substrates shows promise for future work in many directions. The photolithographic liftoff method could potentially be used to pattern MHA for the selective assembly of carbon nanotubes. The alternative "dry" liftoff method could also be tested as another prospective direction in patterning. By exploring the potential to pattern on alternative substrates, such as nitride, the previously required conductive gold layer can be removed, simplifying the circuit design process.

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