Crystallization of Germanium using Nanosphere Lithography

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Objectives

1. Use nanosphere lithography to produce a hexagonally pattered nickel substrate via physical vapor deposition.
2. Determine if germanium crystallizing directly above a nickel substrate will induce the crystallization of surrounding germanium without an underlying nickel substrate.
3. Determine if the crystallization temperature for germanium with the nickel substrate is lower than a germanium layer without a nickel substrate.

Introduction

Developing an affordable yet efficient form of solar power has been the dream of many researchers and consumers for many decades. But having a power grid backed by fields of solar panels has not been an economic option, since most solar cells are expensive to produce and operate at low efficiencies. In hopes of developing low-cost efficient solar cells, thin-film germanium crystals can be grown, and may hold the key to establishing a strong solar based power supply. Germanium wafers have been used in solar cells before, but the cost per output ratio is too high for mass commercialization of these solar cells to be used in solar panels.

In order to create the germanium thin-films we are looking for, we have used a process known as nanosphere lithography. Nanosphere lithography is the process of using spherical nanoparticles to create a single layered uniform pattern on a TEM grid surface, and is used to create a hexagonally patterned substrate layer. It has been hypothesized that the crystallization of germanium atop a patterned nickel substrate would induce the crystallization of the surrounding germanium without a nickel substrate. This would produce large crystals of germanium at a lower temperature than what is usually needed to crystalize germanium.

Equipment

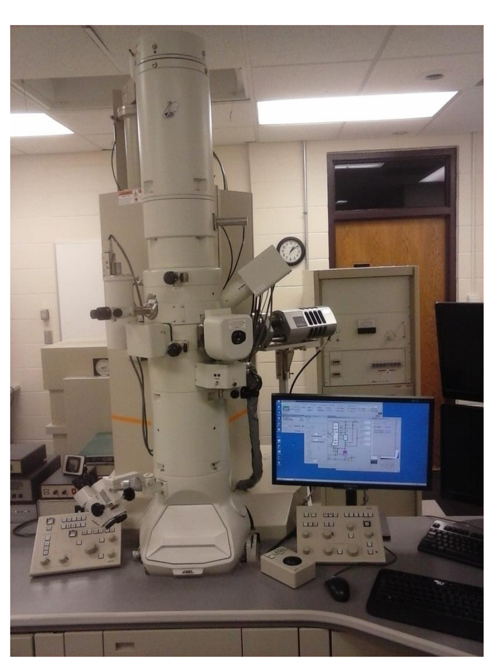

Figure 6: Transmission Electron Microscope

Figure 7: Vacuum Evaporator

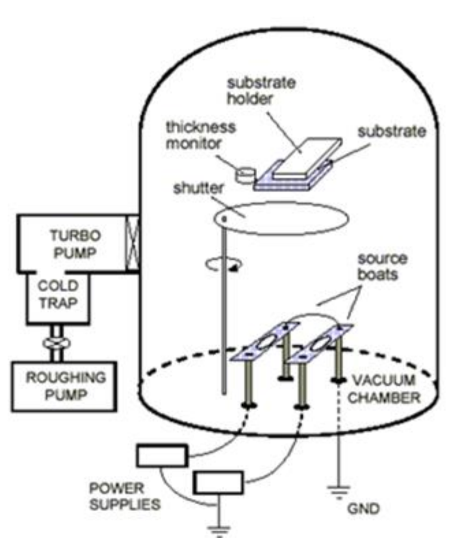

Figure 8: Schematic of Evaporator

Image taken from https://stuff.mit.edu/afs/athena.mit.edu/course/3/3.082/www/team2_f02/Pages/processing.html

Procedure

1) Arrangement of Nanospheres

We created a polystyrene nanosphere monolayer on the TEM grid by applying 3 microliters of a 456nm diameter nanosphere solution on the surface of the TEM grid. We then allowed the solution to evaporate for 2 hours to allow the nanospheres to self-assemble themselves into the wanted pattern.

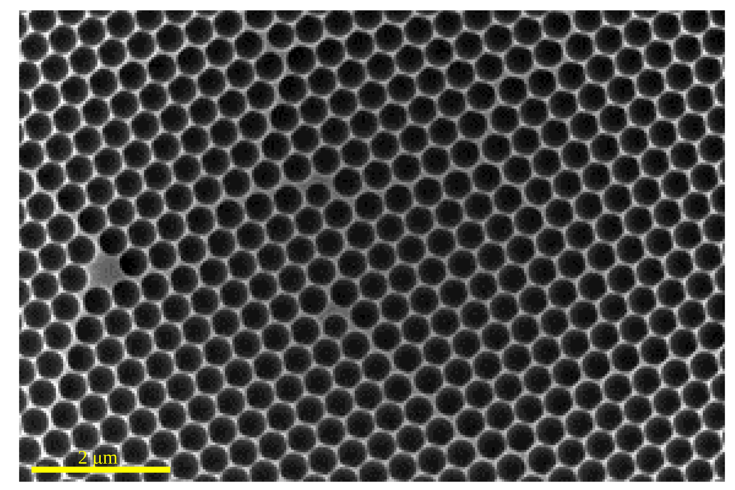

Figure 1 - Single Layer Polystyrene Pattern

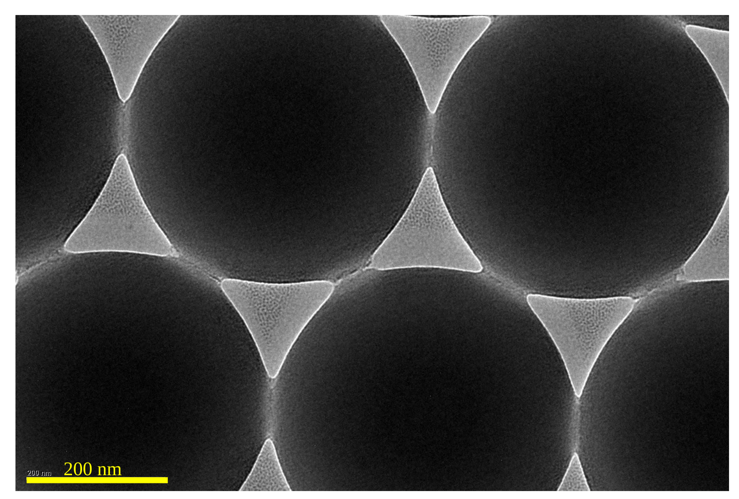

Figure 2 – Nickel Deposited onto Nanospheres

2) Nickel Application

To apply the nickel layer onto the TEM grid, we positioned the grid inside the vacuum evaporator, and placed a nickel pellet into a wire basket. This basket serves as the source boat seen in Figure 8. An electrical current is sent through the wire basket, thus heating and evaporating the nickel pellet. The evaporated nickel particles then condense onto the TEM grid.

3) Dissolution of Nanospheres

After the nickel layer has been deposited, the TEM grid must be submerged into chloroform to dissolve the nanospheres. This will allow the nickel on top of the nanospheres to separate from the gird, thus producing a hexagonal array of the nickel substrate, as seen in Figure 3.

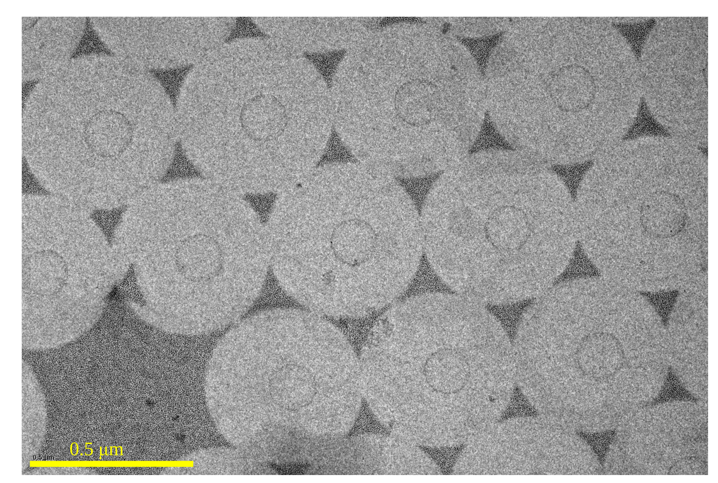

Figure 3 – Hexagonal Pattern of Nickel Substrate

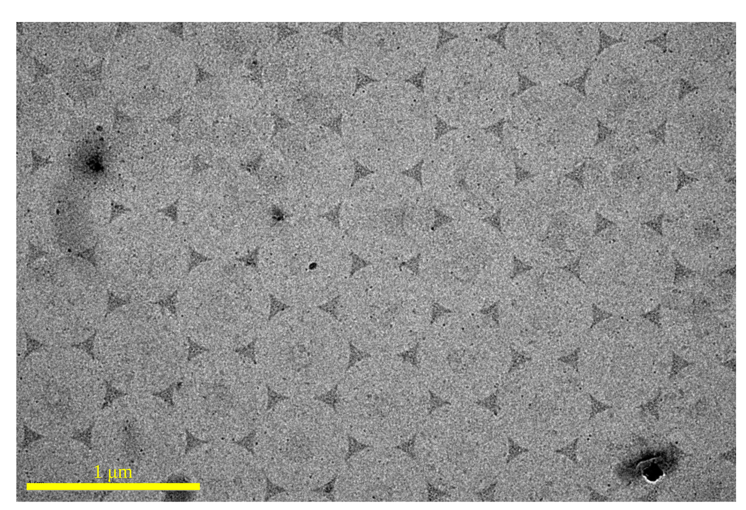

Figure 4 – Germanium Layer atop Nickel Substrate

4) Germanium Application

Once we have the hexagonal array of the nickel substrate, we then use the vacuum evaporator again to deposit a layer of germanium onto the TEM grid. This layer of deposited germanium will be amorphous until it is heat treated and becomes crystalline germanium.

5) Crystallization of Germanium

After the germanium has been deposited onto the TEM grid, the sample can then be annealed to instigate the crystallization of the amorphous germanium. A germanium layer atop a solid nickel substrate crystallizes at approximately 325°C, but germanium atop the patterned nickel substrate did not have noticeable patterning until approximately 375°C.

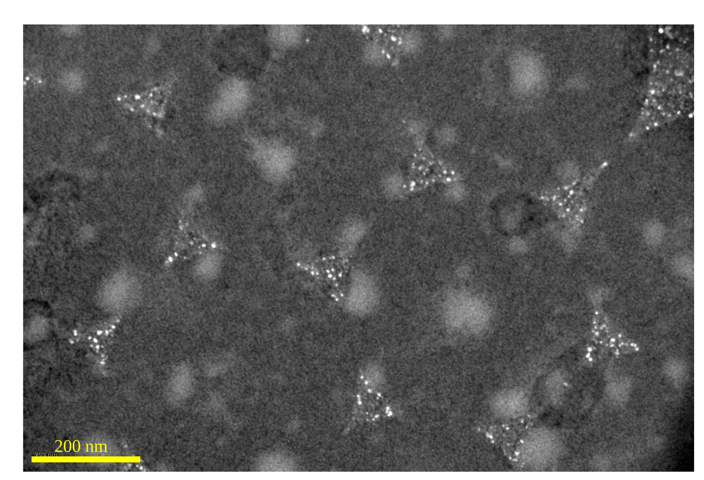

Figure 5 – Dark Field View of Crystallization

Data

Sample	Grid Type	Nickel Substrate Description	Germanium Crystallization
A1	Cu	Small trace of triangle pattern	None
A3	Cu	Many nickel triangles identified with minimal debris	5-10 nm crystal growth above nickel substrate
A5	Cu	Many triangles seen but covered by a nickel shell	None
A7	Cu	Small trace of triangle pattern	None
B1	Cu	Solid layer of nickel, as no nanospheres were used	100-200 nm crystal growth throughout grid
C1	Mo	Surface covered with nickel domes	None

Results

- A hexagonally patterned nickel substrate can be manufactured using nanosphere lithography using physical vapor deposition.
- Crystallization of germanium during heat treatment was only observed to happen to the germanium directly atop the nickel substrate, and did not instigate the crystallization of the germanium without an underlying nickel substrate.
- Germanium layer began to crystallize from 300°C – 350°C, with peak crystallization occurring around 325°C when paired with a solid nickel substrate layer. This was lower than an earlier report that found the crystallization of germanium without a substrate to be 590°C.
- The temperature at which the amorphous germanium began to crystallize atop the patterned nickel substrate is not precisely known, as the germanium crystalline grains were very small and difficult to notice. Despite this, small grains of crystalline germanium were noticed at approximately 375°C.
- Gained laboratory experience with experienced faculty and learned to operate laboratory equipment, such as a transmission electron microscope (TEM) and a vacuum evaporator used for physical vapor depositions.

Conclusion

The most difficult aspect of this research project was the nickel vapor deposition as we kept depositing a layer of nickel that tended to be too thick. But once a viable sample was produced and heat treated, it was found that the germanium only crystallized at the areas directly above the nickel substrates and didn't catalyze the crystallization of the surrounding germanium. This result contradicted the hypothesis that the crystallization of the germanium atop the patterned nickel substrate would induce the crystallization of the surrounding germanium.

Not only did the crystallization only stay atop the nickel substrate, but the germanium crystals found were considerably smaller than the crystals seen when produced on a solid nickel substrate. The crystals found on with the patterned nickel substrate were 5-10 nm in diameter, while the solid nickel substrate crystals were almost 100-200 nm in diameter.

Acknowledgments
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