Hello, my name is Ian Emge. I'm an undergraduate research student at the University of Maryland, Baltimore County. This project was done in collaboration with Christopher Cooper, Sonali Saraf, Dan Kazal, Dr. Brian Cullum, Dr. Fow-Sen Choa, Dr. Bradley Arnold, Dr. Lisa Kelly, and Dr. N.B. Singh-- all of the University of Maryland, Baltimore County, along with Ching Hua Su from the NASA Marshall Flight Center in Huntsville. We would like to offer a special thank you to the NASA headquarters in Marshall Flight Center for their help with this project.

For this project, we focused on the optimization of sensor materials using Physical Vapor Transport growth method or known as the PVT growing method. For this presentation, we'll be going over our objectives, our background, our experimental design and methods, our results, and our conclusion. Shown in the right is a phase diagram. And at the bottom, you can see image of some crystals that were actually grown using the PVT method.

For a little background on our project, there's a great need for sensors that have potentials that are normally found in nature within animals, such as the potential ultraviolet light vision of birds, the IR sensing of snakes, the photoreceptors of scorpions sensing from deep UV to LWIR, and aquatic life can see through the UV into the red spectrum.

So when we observe nature, we can see all these different biosensors and such that animals have. And we want to replicate these for our own use, such as biosensors designs are based on the animals, which have great ability to sense incoming storms and earthquakes. How large fishes never get hit by boats. Imaging capabilities of animals. The changing skins as sensing for weather. And then, the contact sensors, such as potential thermal, mechanical, and chemical sensors. And the good thing about this is biosensors and bio-inspired sensors can be designed and based on novel materials.

For a little background on material growth methods that are used today. The first one is the Bridgman method, which can be done horizontally and vertically, which consists of a sealed glass chamber in which you have the material suspended. And then, as you move it through a heated zone, it melts. And then, as it comes out very slowly, it'll actually crystallize the material.

Next is the Czochralski method, which usually is a crucible, in which you have molten material. That you take a seed, which is a smaller piece of the crystal that's already been formed. You put it into the crystal and slowly move it outward, which allows the crystals to grow off of it.

Next is the vapor transport method in which vapors of material are brought into a chamber in which the crystal grows in. Then, there's a solution growth method. And the traveling solvent/heater method to grow these crystals.

In decomposition, materials with high incongruent systems and high vapor pressures, however, several methods can't be used, such as the melt growth methods cannot be used. As both the Bridgman and the Czochralski methods, actually, the melt will decompose the materials that you're trying to grow. The solution growth method can be used due to insolubility. And the traveling solvent and heater method cannot be used as there's issues with miscibility and solubility when trying to grow them.

So from all this, we can see that the method to grow the crystals depends greatly on the material that you're trying to actually use, and the size of the material which you are trying to get. The objectives of this project were to evaluate the feasibility of the physical labor transport method for the growth of the sensors and to determine the effect of the parameters on the quality of grown materials.

During the growth of nano-, micro-
, thin film and bulk crystals, in addition to growth parameters, fluid flow is one of the most important factors. This is as it can affect the morphology and hence the performance of the crystals themselves. An example of this can be seen on the skin pattern of salmon.

On the left here, we see an image of a salmon that grew up in a pond. And on the right is your typical normal salmon. As you can see, when they grow up in a pond, the scales grew to be very irregular and not very smooth whereas when one grow up typically, it's a very smooth and sleek-looking surface.

There has been some previous research on using PVT on infrared-
detector materials in our lab. These were growth studies on lead selenide both pure and doped tin. These studies were performed with physical vapor deposition on the silicon substrates. And during these studies, the effect of growth temperature, morphology, resistivity, effects of annealing, and transition of morphologies was all studied. There is some limited data for tin-doped materials on various substrates for MWIR detectors as well.

Shown here is the commercial PVT DENTON system that we used. The materials that we used-
- we used lead silicone and lead selenide at a 99.9999% purity. We also had a tantalum boat and resistively heated the material itself. For the substrate, however, we used silicon with dilute hydrofluoric acid to etch and remove any native oxides.

For our process, we had the base that was set in to a 10 to the negative 7 Torr range. It was stationary. It was resistively heated 2-inch substrate mount. And the temperature of the substrate did vary. We used a PVD process in which lead selenide was sublimated. And the deposition rate was done at 1 K per second. For characterization of the materials, we used an SEM, X-ray, and 4-point probe.

In order to grow the materials for the PVT process, we used several different growth chambers that are actually available to us at UMBC. Shown here on the left is the DENTON furnace that was used during the deposition of lead selenide, zinc selenide, and several other materials, In the center, you can see an image of the crucible and the holder itself. And on the right is an example of lead tin selenide that was grown by the PVD process onto a glass substrate. It should be noted that during this, the temperature and transfer path can be controlled during the deposition.

For this project, we used high resistivity silicon and glass as substrates. We would cut the silicon wafers into four pieces when we used it however. We did several deposition runs, where we performed them using both lead selenide and tine-doped lead selenide as our source materials. This says the present attempt was to study the effects of tin on the lead selenide.

So shown here in A is a film that was grown on a silicon substrate. B shows us the morphology at a low temperature showing uniform morphology. However, when we go to C, we can see a large DT showing the different shaped grains and nonuniformity within the actual structure. This says, morphology is different and varies greatly with the growth condition.

Shown here is an example of the nanomorphology of a pure lead selenide material that was grown on a silicon substrate. It should be noted that purity has a significant effect on the morphology as elongated morphology on the nanocubes was observed. Morphology of the lead selenide materials on silicon substrates with slight variations in the growth conditions are pictured here. It should be noted that shiny tin-rich phases were observed when tin was introduced. However, from this, we can also see that changes in the growth parameters did not change the morphology itself.

Pictured here is a doping of the lead selenide which changes nanomorphology of the lead selenide itself. It should also be noted that annealing could change the morphology as well. Shown here is the nanomorphology of pure and doped lead selenide. On the left is pure. And on the right is doped.

In the case of cadmium selenide doped grains grew on the top of the thin film grains but morphology did not change. Therefore, from all of this, we can see the morphology was d ifferent but did not change. Shown here is the tin-
doped lead selenide. And as we can see, when we dope the actual lead selenide with tin, it created an octahedral morphology to the material itself.

Shown here are several material spots that we selected to evaluate their composition. Th e composition of each components for the selected spots of 1 and 4 are shown in the figu res on the right. We do not find any cadmium selenide-rich phases in the actual matrix.

We have several furnaces in our laboratory that we can use for actual PVT growth. On the left here is image one of them. On the left, we can also see an up-
close image of them and a typical thermal profile of the actual process itself. On the right , we have an image of the crystal that was actually growing using the PVT method. Vertic al PVT is commonly used for the growth of bio, organic, and inorganic materials.

In the optimization of PVT, fluid flow is a very important parameter in the process. This is a s the hot to cold convection flow causes multiple cells to be created. This can be seen wit h both a "fire" and a "pond." As in the "fire," you can see multiple cells of smoke cloud crea ted.

And in the "ponds," you can see areas of white which impurities are found in the water. An d they're actually formed cells due to the convection of itself. From this, we can see the in stabilities that can be controlled by modeling fluid flow during a PVT growth process.

The PVT method in controlled conditions has shown to produce some very good quality materials. Pictured here on this slide are two of the main equations that were used durin g this project. The model shows that pressure, temperature, path, and diameter affect th e number of molecules that travel from the hot to cold ends of a chamber. Shown here is the velocity equation that we used during our project. This was using the PVT growth opti mization, as we can actually predict the growth velocity from all the parameters that we set up.

From the X-
rays that we took of our materials, we were able to determine that the material quality de creases as the flow increases. And the material quality increases as the flow decreases. T herefore, in order to grow a very good material, you want a very low flow. As gravity contr ols the diffusion rates, it should be noted that for achieving good quality pure diffuse gro wth, you need around 10 to the negative fourth g in order to achieve this.

In summary, the controlled PVT method is an excellent method for the growth of biosensor materials. This is as bulk, thin films, and nanocrystals can all be grown by this PVT method. Fluid flow has one of the most significant effects on the materials, and therefore, the performance of the sensors that the materials are used in. Also, using this method, a variety of materials can actually be made, including oxides, selenides, sulfurs-- all of this can be grown by the PVT method. Further study to the optimization is based on the materials for their growth. From all this, we can see that morphology of materials controls the performance of the sensors that are actually made using them.

I would like to thank you all very much for your time spent listening to this presentation. And I hope you have a wonderful day.