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Thermal Oxidation of Silicon in a Home-Made Furnace System

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4900 Assessment Report
Thermal Oxidation of Silicon in a Home-Made Furnace System

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System setup

I approached Dr. Shen with a desire for a project in understanding how to manage and expand the capabilities of a laboratory. After some discussion, my senior project was to complete a gas and water chiller system to an existing furnace for chemical vapor deposition. It should be able to handle temperatures up to 1100 ºC, hold a vacuum to mTorr, be easy to move samples in and out of the furnace, and cost effective.

Previous students and Dr. Shen have designed a frame to support flanges to seal a 2-in diameter quartz processing tube. One flange allows access to four gas intakes and both flanges had a separately sealed internal reservoir for cooling water to protect the graphite gaskets from the heat of the furnace.

My first task was to complete the chiller plumbing system including a connection to a thermal evaporator that requires water cooling as well. We first completed a schematic flow chart. Taking that schematic I then proceeded to catalog each piece, starting from the chiller outlet followed by valves to allow/block flow to and from the two machines that would be connected to the chiller. Next with reducers and tees that branched out to each machines "in" connector, from the outflows returning back to the chiller using the same idea of reducers and tees (small to large to attempt to keep flow rates constant and equalized pressure) as well as a second valve on the return to isolate flow between machines. Knowing what each piece needed to be, I then combed through the Swagelok catalog creating a spreadsheet that narrated the schematics, identifying each part by name, how many we needed (narrating where), price per part and itemized totals as well as a direct link to the catalog. Once Dr. Shen confirmed my spreadsheet we proceeded to check inventory and place the order. When the parts arrived we assembled the system while reaffirming with our schematics and spreadsheet as an instructional guide. With the chiller system assembled we proceeded to test and check it for leaks.

With the chiller system completed we repeated the process for the gas system, the setup allowing four gas intakes, all needed to have the correct connections and leak proof. On the exhaust flange end we wanted a vacuum pump to obtain low pressure and a safe exhaust line into a hood. Again we considered what was on hand and needed to purchase. We ordered a new cylinder of nitrogen and a cylinder of oxygen connected with existing regulators in the laboratory. Ideally each gas line should be controlled by a digital mass flow controllers (MFC). However, at this point MFCs were out of our budget and so we decided to order a new rotameter and use that to calibrate an old rotameter to control these two gases. I poured through multiple scientific equipment catalogs and we settled on purchasing a rotameter from Matheson. Once the rotameter had arrived we then used it to give us a comparative flow rate table for the old Cole-Parmer rotameter. On the other end of the furnace, the gas outflow, we had arranged a tee, one end being connected with a pressure gauge and the other a second tee

with two valves. One valve is to allow exhaust gases to be disposed of into a hood and the second valve to a vacuum pump allowing us to evacuate the processing tube. Similar to the chiller system in checking for leaks and adjusted each bolt symmetrically and slowly, as well as both aluminum support plates to gain higher vacuum. The best vacuum we achieved was 8 mTorr. Dr. Shen reassured me that it was more than acceptable for what he wanted at this time.

With both the water chiller and gas systems complete, we proceed to test wet and dry thermal oxidation of silicon at atmospheric pressure to characterize the performance of the setup. The end objective of the system is to do both atmospheric and low-pressure thermal processes including annealing and chemical vapor deposition. The silicon oxidation experiments to characterize the system are as follows.

Temperature effect on dry oxidation

The reaction of Si dry oxidation is simply $Si + O_2 \rightarrow SiO_2$. [1] Due to the exponential dependence of temperature in both oxidation kinetics and diffusion coefficient of oxygen, it is well known that higher temperature increases oxide growth rate significantly. Initial oxidation growth is proportional to time, but further growth is limited to the oxygen diffusion through the existing oxide layer making the rate proportional to $\sqrt{t}$. Indeed, as shown in the figure below we observed that the growth rate increased significantly by 50 ºC at an O_2 flow rate of 1000 sccm (standard cubic centimeter). The oxide thickness was measured by Nanoscope 3000 reflectance spectrometer at NDL. In these experiments, the samples were in parallel to the gas flow. Only the oxygen molecules in the surface boundary layer will be able to react with Si. Therefore, the oxidation rate could be much slower than when the samples were in perpendicular to the gas flow. That would be the next experiments to do.
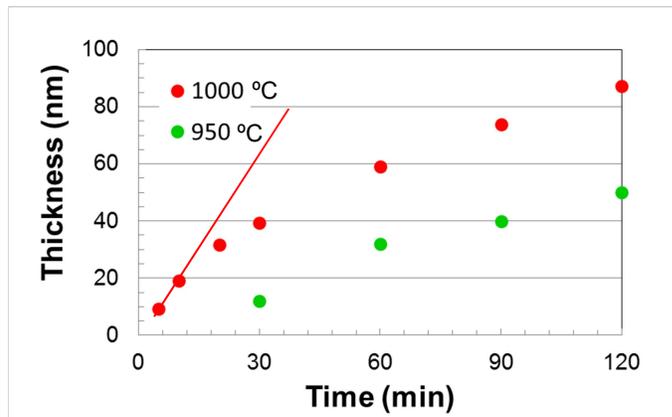

Oxidation suppressed by N_2 at 1000 °C

Since N_2 has little interaction with Si, it is interesting to test if adding N_2 will affect the oxidation rate. As shown in the figure below we find that oxide growth decreases substantially with more N_2 flow even with the same O_2 input flux at 1000 ºC for 2h. Apparently, the O_2-concentration in the surface boundary layer is reduced by the presence of N_2 molecules and results in lower oxidation rates.

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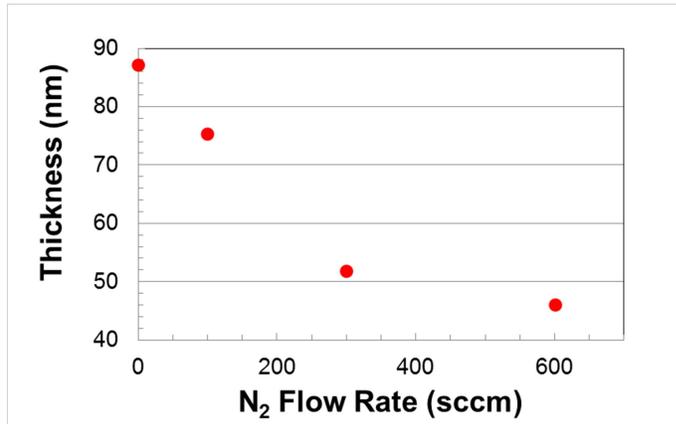
O₂ flow rate

It has been a lingering question for us; namely, will oxygen flow affect the oxidation rate? Information I found online indicates 1000 sccm were used. So we ran experiments from 1000 sccm to 100 sccm of O_2 flow for 2h at 1000 ℃. As depicted in the figure below, the oxidation rates are pretty much the same. Apparently, with an O_2 flow at 10 psi above atmosphere, N_2 diffusion from the ambient air is negligible to affect the oxidation rate for atmospheric pressure thermal oxidation. This result is consistent with the scenario that when the samples were parallel to the flow, only the O_2 in the boundary layer will be involved in the oxidation reaction. All other O_2 in the flow play a passive role of preventing other impurity molecules into the reactor. This result indicates a much smaller amount of O_2 flow is sufficient for Si oxidation, which could save a lot of ultrapure oxygen.
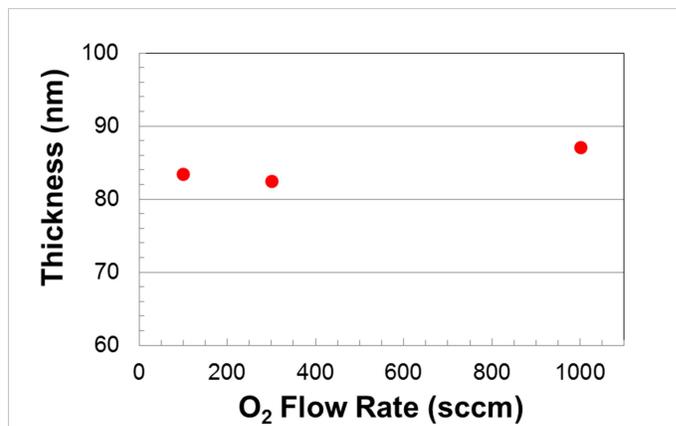
Water assisted dry oxidation at 1000 °C

It is known that Si oxidation rate is much faster by water vapor with the following reaction $Si + 2H_2O \rightarrow SiO_2 + 2H_2$, although the oxide quality is not as good as dry oxidation. [1] At this point, this furnace system cannot supply water vapor directly. However, we can add water vapor to the reactor by flowing O_2 at 1000 sccm through a water bubbler. [2] As shown in the

figure below, adding a small amount of water vapor indeed increases the oxidation rate significantly. At this point the concentration of water in the O_2 flow is unknown but it can be measured by a hygrometer in the future. We do know that after 2h operation, 4.1g of water was lost. Therefore, the water flow rate was 1.9×10^{-3} mole/min. If we use the O_2 density at room temperature, atmospheric pressure as 1.43 g/cm^3, 1000 sccm flow rate leads to 4.5×10^{-2} mole/min. Therefore, we can estimate the water concentration is 4.2%.
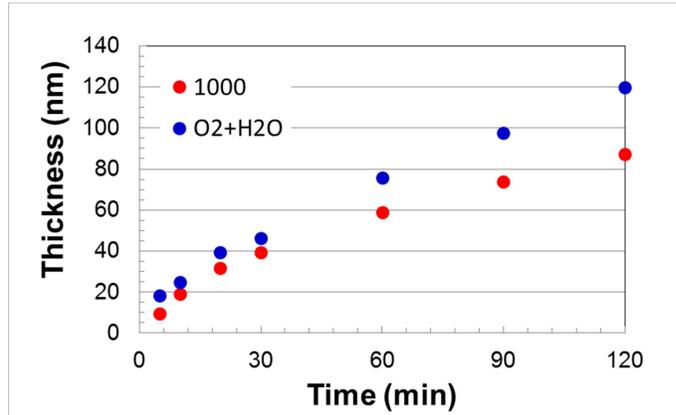
Future work

After conducting these experiments we looked over the system and considered aspects that could be improved upon.

- Steel support plates: Increasing thickness to improve vacuum seal with the quartz tube without deformation due to heat and tension.
- Flanges: improving their design for better water sealing.
- Acquiring a dry scroll pump and capacitance manometer to perform low-pressure chemical vapor deposition for processes such as graphene synthesis.
- Replacing the current rotameters with digital mass flow controller to achieve better gas control and reproducibility.
- Upgrading the current two inch process tube to six inch tube; allowing up to four inch wafer-scale thermal processes.

Final remark

My own experience on this project has been rewarding to see how a project manifests to meet the needs of a facility and the steps taken to accomplish this allowing further research and expansion. Learning the aspect laboratory management encompassing multiple tools and a vast inventory supply, and tin foil ...so much tin foil.

References

1. S. A. Campbell, *Fabrication engineering at the micro- and nanoscale,* 4th ed. (2012)

2. A. G. Revesz and R. J. Evens, Kinetics and Mechanism of Thermal Oxidation of Silicon with Special Emphasis on Impurity Effects, J. Phys. Chem. Solids **30, 551** (1969).