Combining Plasma Enhanced Atomic Layer Deposition (PEALD) and Lithography for nanostructuring

Masoud Rastgou

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Center for Hybrid Nanostructures
University of Hamburg (UHH)
# Contents

1  **Internship**  
   1.1  Project information .......................... 1  
   1.2  Introduction .................................. 2  
   1.3  Deposition .................................... 3  
   1.4  Annealing ..................................... 5  
   1.5  Four-probe station (Van der Pauw method) .... 8  
   1.6  Transferring nanowires for SSPDs ............... 11  
   1.7  Conclusion .................................... 13  

**References** ................................. 14
1.1 Project information

Owing to their combination of outstanding properties, such as hardness, biocompatibility, high temperature stability, conductivity, and plasmonics, to name a few, metal nitrides are in the focus of various research and application fields for decades. Especially, titanium nitride is a well-established conductive material in the synthesis of micro-electrode arrays for electrically investigating neurons and muscle cells. Furthermore, superconducting TiNbN-based alloys are a promising candidate for implementation of next-generation radio-frequency superconducting cavities which might be used in the upgrade of the European XFEL (X-Ray Free-Electron Laser) which is running since fall 2017 and used to study and to investigate the structure and the dynamics of individual molecules, cells, and viruses. When this superconducting material is nanostructured, single photon detection based on superconducting nanowires is possible allowing for (bio-) medical imaging, such as single molecule fluorescence spectroscopy, optical coherence tomography, and flow cytometry, with ultra-high temporal resolution. Atomic layer deposition (ALD) based on its sequential, self-limiting gas-solid surface reactions allows for conformal coating of highly structured, three-dimensional substrates without shadowing effect and with sub-nm thickness resolution. ALD is already a state-of-the-art technique in semiconductor and solar cell industry for the deposition of high-k dielectric and passivation layers, respectively. The main objective of this project is to produce and characterize NbTiN-based micro- and nanostructures by a combination of plasma enhanced ALD and standard lithography processes. The aim is to develop proof-of-concepts
structures which can serve as starting point for future research on tailor-made superconducting nanowire single-photon detectors or microelectrode arrays. In detail, the fabrication of these structures will be carried out following two different approaches, (i) top-down and (ii) bottom-top. The top-down approach consists of ALD thin film deposition and subsequently performing lithography and etching, while the bottom-up approach starts with lithography and subsequent deposition and lift-off processing. Finally, the nano- and microstructured devices will be electrically characterized by magneto-transport measurements.

Tasks:

- Training at R&D semiconductor industry-compatible instruments
- Cleanroom ISO4 usage
- Fabrication of structures by combining ALD with lithography processing
- Magneto-transport characterization of the resulting structures
- Annealing process of superconductive thin films for post-deposition characterization

1.2 Introduction

Superconductive materials play an important role in recent technologies because of their specific properties like zero resistance in a range of temperature and their corresponding effect on electromagnetic fields. Nowadays, there are lots of researches and experiments around improving superconducting materials properties by using deposition of other materials and forming nanofilms. Niobium (Nb) and niobium nitride (NbN) are used as films for this purpose because they are resistant against frequent thermal cycling from higher to room temperature. Also, NbN films have better physical, electrical, and chemical characteristics which make it a proper material for hard surface coatings and superconducting ratio frequency cavities. One of the reasons behind the usage of Nb as a cover in superconductive materials films is that it has the highest superconducting transition temperature among other superconductors. For instance, NbN has a high transition temperature of about 17K. The deposition of NbN thin films can be implemented by different methods such
as physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD). For our project, we use combining plasma enhanced atomic layer deposition (PEALD) for making our nanostructures. After the deposition of NbN films, one can use the rapid thermal annealing process (RTP) to improve its superconducting properties. For instance, one can increase the critical temperature of NbN films up to 17K by this method. We are going to discuss the annealing process of niobium-titanium nitride (NbTiN) in this report. Another step is the resistivity measurement which normally depends on the geometry and boundary condition of the sample. Therefore, for measuring the resistivity of for instance a random shaped sample, one should consider specific correction factors. In this experiment, we use a four-probe station for measuring the resistivity of our random shaped samples. Calculation of the final resistivity from the values measured by probes will be done by Van der Pauw method. Also, we had experiments about transferring the ultrathin nanowires in order to make an array of coated nanowires with NbTiN for using them as a superconducting single-photon detector (SSPDs). SSPDs are one of the fastest devices to detect near-infrared photons and have many applications in fiber-based quantum communications, optical information processing, free-space satellite communications, and medical diagnostics. [1–7]

1.3 Deposition

In this experiment, we were using the ALD device in form of PEALD to fabricate NbTiN films on silicon substrates. ALD is working based on the atomic layer by layer growth with influencing the surface of the material to make a high aspect ratio structure with almost low temperatures. In the case of NbTiN, the growth of layers should be in a way that Nb layers do not lose their superconducting ratio frequency. In order to satisfy this condition, we prevent combining materials to make a layer of NbTiN. Instead, we coat the internal surfaces in the form of superconductor-insulator-superconductor. It means that we use different precursors with specific timing to make a layer of Ti and the layer of Nb on its top and so on. That will also lead to a controlled thickness of aimed NbTiN layers. Theoretically, in the PEALD process, plasma pulses are performed on niobium chloride (NCl₂), and ammoniac NH₃ to produce NbN. NH₃ is used as a reducing agent to dominate Nb in the formation of NbN from NCl₃. There are some problematic effects
during this process that will affect the quality and density of films. For instance, experiments showed that the composition process of niobium superconductive films can be influenced by oxygen diffusion which will decrease it’s the critical transition temperature. It is based on the oxygen effect on their crystal structures and makes it inhomogeneous in case of grain sizes. Also, precursors such as halide precursors have been shown that might cause corrosion and environmental issues. Therefore, these will affect the superconductive properties of the deposited films such as critical temperatures and resistivity. In order to fix this problem, we use another precursor to produce aluminum nitride (AlN) to avoid oxygen diffusion. For the plasma source, we use nitrogen (N$_2$) or hydrogen (H$_2$) pulses with the power of 300 watts. Figure 1.1, demonstrates the ALD device that we are using for our process.

![Figure 1.1: Plasma atomic layer deposition device](image)

The precursor for depositing is a metalorganic precursor named (tert-butylimido)-tris (diethylamino)-niobium (V) (TBTDEN), which will be exposed by H$_2$ plasma pulses. During this process also N$_2$ originated from the precursor will cause carbon contamination. In that case, NH$_3$ is used to limit the oxygen and nitrogen agents. Also, we use tetrakis (dimethylamino) titan (TDMAT) and trimethylaluminium (TMA) precursors to produce TiN and AlN respectively. Then, we perform our plasma pulses in a specific timing to produce layer by layer our aimed film with
the best possible prevention of corruption and contamination of gases on the silicon substrates.

The deposition temperature fixed at 250°C and the chamber purged at every 40-second intervals. For TDMAT precursor, plasma pulses were implemented by 500 milliseconds duration for initiating Ti and TiN and plasma dose time has been changed from 60 to 120 seconds. For TBTDEN precursor, producing Nb has been done by 500 milliseconds to 40 seconds with three different plasma dose time of 120, 60-60-60, and 120-120 for sample labeled as S20, S22, and S24 respectively. Also, it should be mentioned that in order to facilitate transportation of the precursor into the chamber, we use a boost system (which is adding Ar gas by 20 milliseconds intervals). TDMAT and TBTDEN were kept in 70 and 90°C during the process. Therefore, the process will result in a coat of NbTiN on the silicon substrate. For improving the properties of the process, we also use aluminum nitride (AlN) which has a precursor named TMA with 21 milliseconds to 30 seconds pulse duration and 10 to 100 seconds plasma dose time. [1–3]

1.4 Annealing

As I mentioned in the introduction section, one of the main goals of this experiment was to improve the superconductive properties of our nanofilms by annealing them under certain parameters. For performing the implementing process we would use two different ovens which one of them would perform the rapid term annealing and the other one would be used for longer time annealing.

In the long term annealing process, we use our deposited films produced by PEALD method and anneal them in a tubular furnace with controlled argon (Ar) gas atmosphere in an interval of 400 to 800°C inside an alumina tube with a heating rate of 20°C per minutes and the gas flow rate was fixed at 50 Pa. Figure 1.2, illustrates the device which we were using for long term annealing.
For the Short term annealing or rapid annealing process we will consider one main annealing process argon-hydrogen (ArH$_2$) and one extra annealing process nitrogen (N$_2$) on certain ArH$_2$ annealed samples to see the improvement in superconducting properties. Short term annealing process is relatively similar to the previous process but we have a faster annealing process with 300 Pa Ar flow rate. In our laboratory, we use Ar flow with a negligible amount of H$_2$. That is the reason we name it ArH$_2$ annealing. The temperature intervals would be from 800 to 1000°C with a grain temperature rate of 0.3 and 1°C per second. The aim of this annealing process is to achieve a set of conditions which we can use to improve the level of functionality. Theoretically, after TiNbN crystallizes in the deposition process, there will be produced oxygen (O$_2$) and carbon (C) inside the crystals and nanolayers. Therefore, by ArH$_2$ annealing process, we can be able to remove these impurities and fortify our structure to oxidize. Figure 1.3, shows the device which we were using for rapid term annealing.
The second process is annealing the already ArH\textsubscript{2} annealed samples with N\textsubscript{2} gas. Back to the theory part, after removing O\textsubscript{2} and C from our structure, due to the changes in the crystal structure, we would have free Ti\textsuperscript{+3} and Ti\textsuperscript{+4} (basically, they can also exist before the first annealing process and after deposition). Therefore, the nitrogen (N\textsubscript{2}) annealing with cause producing titanium-nitride (TiN) and due to the structure of layers of the deposition will form TiNbN again in our samples. Then, we also will be able to reduce the effect of these free Ti\textsuperscript{+3} and Ti\textsuperscript{+4}. In order to characterize our deposit and annealed samples, we are going to describe the measurement process with the help of four-probe station and Van der Pauw method. [1–3]
1.5 Four-probe station (Van der Pauw method)

In order to measure the resistivity of our deposit and annealed samples, we use a device called four-probe station which is shown in figure 1.4.

![Four-probe station](image_url)

**Figure 1.4:** Four-probe station

It contains four arms which lay on specific or random places of the sample. In principle, there are many methods for measuring resistivity (with the help of Hall Effect) of the nanofilms with this device. We use a method which allows us to measure the resistivity and Hall mobility of a random shaped sample called Van der Pauw method. It should be noticed that the sample should have a uniform thickness. The arms can be placed in the boundaries of a random shaped sample as shown in figure 1.5.
Figure 1.5: Random shaped sample with four contacts at arbitrary places along the circumference

We consider the sheet resistivity to be $R_s$ and then we would have:

$$R_s = \frac{\pi R' + R''}{2} f \left( \frac{R'}{R''} \right)$$  \hspace{1cm} (1.1)

Where $f(R'/R'')$ is Van der Pauw’s function of the ratio $R'/R''$, $R' = V_{CD}/I_{AB}$, and $R'' = V_{DA}/I_{BC}$. There is a relation that Van der Pauw proposed for the function $f$:

$$\frac{R' - R''}{R' + R''} = f_{arccosh} \frac{\exp(ln2/f)}{2}$$  \hspace{1cm} (1.2)

where $f = f(R'/R'')$.

This equation was numerically assessed by researchers and has been verified. The final equation proposed by Van der Pauw is:

$$\frac{R' - R''}{R' + R''} = f_{\ln2} \frac{\exp(ln2/f)}{2}$$  \hspace{1cm} (1.3)

where the factor $\ln2$ appeared.

Evaluating numerically the equation 1.3, there is shown a set of values which refer to the ratio between the resistivity measured by the four-probe station (see reference [5] for the whole numeric). The correction function is now available in a tabulated form and can be used to calculate the sheet resistivity of samples ($R_s$).
Considering the mentioned theory, we did the measurement for deposit and annealed samples with 120, 60-60-60, and 120-120 plasma time respectively. Resistivity values from annealing processes illustrated in the tables below has been implemented by the short-term annealing device. Also, samples mentioned in tables have been chosen between several other measurements and they show the most stable and optimized cases in our annealing process. Every sample has been separated into many pieces which we named them in terms of test samples.

**Table 1.1**

<table>
<thead>
<tr>
<th>ArH₂ annealing condition</th>
<th>Sample</th>
<th>Deposit</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C,10min,1°C/s ramp</td>
<td>Sample 20</td>
<td>830.89126</td>
<td>601.59212</td>
</tr>
<tr>
<td>800°C,30min,1°C/s ramp</td>
<td>Sample 22:T4</td>
<td>934.7647</td>
<td>560.93826</td>
</tr>
<tr>
<td>900°C,5min,1°C/s ramp</td>
<td>Sample 22:T14</td>
<td>1050.10331</td>
<td>387.02559</td>
</tr>
<tr>
<td>900°C,30min,1°C/s ramp</td>
<td>Sample 22:T5</td>
<td>976.9062</td>
<td>668.2515</td>
</tr>
<tr>
<td>1000°C,5min,1°C/s ramp</td>
<td>Sample 22:T15</td>
<td>1204.98503</td>
<td>324.96231</td>
</tr>
<tr>
<td>1000°C,30min,1°C/s ramp</td>
<td>Sample 22:T9</td>
<td>1077.61043</td>
<td>456.69057</td>
</tr>
<tr>
<td>1000°C,50min,1°C/s ramp</td>
<td>Sample 22:T11</td>
<td>1037.31127</td>
<td>159.01111</td>
</tr>
<tr>
<td>1000°C,3min,1°C/s ramp</td>
<td>Sample 22:T26</td>
<td>1472.77269</td>
<td>262.98264</td>
</tr>
<tr>
<td>1000°C,3min,15°C/s ramp</td>
<td>Sample 22:T24</td>
<td>1253.8412</td>
<td>174.49361</td>
</tr>
</tbody>
</table>

As we can see from table 1.1, the ArH₂ annealing process improved the superconductivity of our NbTiN samples by decreasing their resistivity. Considering the table 1.1, we can find the best possible parameters for our annealing process to gain better results. In this case, we observed that higher temperature values with lower processing time give us better superconductivity. Although, the measurement depends also on many other factors like the accuracy of the four-probe device, condition of our samples, and ramping rate of the annealing process. Considering two last rows of the table 1.1, one can see that if we fix the time and the temperature, the annealing process with a higher ramping rate would result in better superconductivity. Better superconductivity means we would increase the critical temperature of our samples. In the case of our samples, in the ArH₂ annealing process, the average rate of improvement in critical temperature values was 0.08. For example, sample
22:T15 had deposit critical temperature of 12.777K and it has increased to 12.79K and the critical temperature of sample 22:T11 increased from 12.1417K to 12.16K. Every sample has been separated into many pieces which we named them in terms of test samples.

Next, we evaluated the superconductivity of some of our samples in the N\textsubscript{2} annealing process. The results of the two of them have been shown in the table 1.2.

<table>
<thead>
<tr>
<th>N\textsubscript{2} annealing condition</th>
<th>Sample</th>
<th>ArH\textsubscript{2} annealed</th>
<th>N\textsubscript{2} annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C,5min,1°C/s ramp</td>
<td>Sample 22:T15</td>
<td>324,96231</td>
<td>132,7056</td>
</tr>
<tr>
<td>1000°C,60min,1°C/s ramp</td>
<td>Sample 22:T9</td>
<td>456,69057</td>
<td>189,42366</td>
</tr>
</tbody>
</table>

We observe an improvement in the resistivity of our samples as well as the best possible parameters for our annealing process. The difference is not considerable but higher value for both time and temperature leads to a lower value for resistivity. Also, the experiment showed that a higher value of ramping rate would improve the superconductivity. In terms of critical temperature, we observe considerable improvement. Giving the same examples, we were able to increase the critical temperature of sample 22:T15 to 13.93K and sample 22:T11 to 12.7K. [1–5]

1.6 Transferring nanowires for SSPDs

In this section, I will report the process of transferring NbTiN nanowires to a host silicon substrate for forming a superconducting single-photon detector (SSPD). Nanowires are produced by plasma-enhanced atomic layer deposition on top of a silicon substrate. The aimed length of the average nanowire has been chosen to be around 5 to 6 micrometers and a diameter of around 50 nanometers. There is used the cover of chromium on the top of nanowires. Theoretically, the process of producing nanowires with specific thickness is based on the cycle of the plasma pulses (cycle) and growth per cycle rate (GPC) of the atomic deposition. The thickness would be the result of the multiplication of these two:
$Cycle \times GPC = Thickness$ (1.4)

We set the parameters of the microscope in the best possible condition. For instance, we used a magnification rate of 50 times with 20 micrometers and the green color filter for better observation. In order to pick nanowires, there is a station with the capability of movement in three dimensions of x, y, and z. We use a metallic bar with a rotatory grip on the tip to hold the micro- and nano-stripe. The main part of this stick is the size and the properties of its tip which uses the electro-static feature to absorb the aimed nanowire on the sample. During the process, focusing on the both stick and the sample substrate is important. The best possible technique is to focus first on the nano-part of the stick and then move it out of the focal point in the y-direction. Then, we can focus on the sample and bring the stick back to the focal point, and then we can observe both nanowires on the sample and the nano-part of our stick. The by rubbing, we activate the electro-static property to attached the aimed nanowire to the stick. The same process can be done on the substrate that we want to move our nanowires to. By contacting the nano-part of the stick (which now contains the nanowire) we lay the nanowire on the substrate. The process of transferring nanowires is implemented by an objective microscope (figure 1.6).
In designing the SSPDs, we consider an area of $10 \times 10 \, mm^2$. The detector performance is less than around 4.2 kelvin (which is below NbN critical temperature). There is also a subcritical electrical current connected to the detector. The process is that the detector will absorb a photon and it causes a change in the superconductivity of the detector (basically the resistivity) and then the detector tends to come back to the initial resistivity condition satisfied by the nanowires. Therefore, this process will produce a voltage signal which can be detected. Normally, SSPDs are known from their parameters such as their high critical temperature and also their critical current density which defines the operating bias current. [6,7]

1.7 Conclusion

In this internship, I worked on characterizing the superconductivity of NbTiN thin films coated on silicon substrates produced by plasma-enhanced atomic layer deposition. We experimented with the samples in the annealing process and tried to find the best possible parameters in order to have the maximum improvement in the superconductivity of our samples. The results have been discussed and shown in
this report. Another experiment was measuring the resistivity of the samples with
the four-probe station which has been discussed theoretically and experimentally in
this report. And the last task was about transferring nanowires for their usage in
SSPDs. The setup was in a cleanroom lab therefore working discipline was needed
to avoid possible contamination.


