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Abstract

Titanium Nitride (TiN) can be sputtered into a thin film, and is a promising component for battery and supercapacitor electrodes. This research explored the relationship between Nitride partial pressure and film characteristics. We sputtered TiN into thin films in a low vacuum environment at temperatures of approximately 70^o C. Most films were deposited over the course of one hour including a five minute presputtering period where the substrate was covered. We found that film thickness, system voltage, and film resistivity to be a function of N₂ partial pressure.

Keywords

TiN, Magnetron Sputtering, Titanium Nitride

Cover Page Footnote

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Deposition of TiN for Battery and Supercapacitor Electrodes for Energy Storage

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Abstract

Titanium Nitride (TiN) can be sputtered into a thin film, and is a promising component for battery and supercapacitor electrodes. This research explored the relationship between Nitride partial pressure and film characteristics. We sputtered TiN into thin films in a low vacuum environment at temperatures of approximately 70° C. Most films were deposited over the course of one hour including a five minute presputtering period where the substrate was covered. We found that film thickness, system voltage, and film resistivity to be a function of N_2 partial pressure.

I. INTRODUCTION

As reliance on renewable energy sources become more necessary and popular, energy infrastructure must adapt to accommodate the transition from fossil fuel and coal power plants. Popularity of wind and solar energy alternatives have increased recently. These are both promising sources of renewable energy, but due to the cyclical nature of solar power and the unpredictability of wind, the current power storage systems would be ill equipped to store the adequate volume of energy to meet consumer demand.

For Implementation of wide scale wind and solar energy, more efficient energy storage is required. Current storage strategies primarily focus on batteries and capacitors, because materials for storage must be low cost, earth abundant, and easily scalable. Many compounds have proven to be especially efficient in various components of batteries and capacitors in lab scenarios. However, in order to fundamentally change macro-scale energy storage, it is crucial that the compound is easy to synthesize in large quantities. Titanium Nitride (TiN) is a promising candidate in this regard. Additionally, TiN has previously demonstrated desirable traits to be used as components for battery and supercapacitor electrodes^{1,2}. TiN demonstrates superconductive properties at sufficiently low temperatures^{3,4}, and the sputtering process used in this experiment is easier to scale up than many other methods of synthesizing superconductive materials.

This experiment sought to both synthesize TiN thin films for future applications in battery and supercapacitors and to understand the effect various initial sputtering conditions had on the film's characteristics.

This experiment utilized DC magnetron sputtering of a Titanium target in a nitrogen rich atmosphere. This resulted in a deposition of TiN on our substrate after a sputtering period of one hour.

II. EXPERIMENT AND PROCEDURE

We used DC magnetron sputtering with Argon Plasma to deposit TiN films onto glass substrates over the course of one hour with a titanium target and a varying nitrogen atmosphere. A representation of the system we used is included in Figure 6. After depositing the films, we measured various characteristics of the film. We measured the thickness of

the films as well as their resistivity using a four-point resistivity probe. Using this data we could calculate the system voltage of each film. Additionally, we performed X-ray diffraction (XRD) analyses of each film to determine intensity peaks and what material we were working with. We compared the XRD results of our films with known XRD results of both Ti and TiN to determine if we had successfully deposited Ti, TiN, or TiN_n.

Our first goal was to successfully sputter a thin film of TiN. To sputter, we used a DC magnetron operating at 150 W and a Ti target. Our first operation ran at a N_2 partial pressure of 0, in hopes of testing the magnetron and the stability of the vacuum we set up. Fortunately, we were successful in creating a Ti thin film and created a reference for other tests. Subsequent testing involved raising the N_2 partial pressure and repeating the sputtering process. We did this successfully completed process for a total of ten films.

III. RESULTS AND DISCUSSION

PN2 mTorr	Thickness nm	Type	Voltage Calculation (V)	Resistivity (Ohm Meter)	Name
0	160	Ti	3.194	2.32E-05	TINA3
0.05	355	int	14.842	0.000239	TINA10
0.1	340	TiN	25.94	0.0004	TINA4
0.13	455	TiN	60.5	0.001248	TINA9
0.15	540	TiN	63.75	0.00156	TINA6
0.17	220	TiN	164.36	0.001639	TINA7
0.2	200	TiN	240.9	0.002184	TINA5
0.25	135	TiN	208.2	0.001274	TiNA11
0.5	25	TiN	791.9	0.000897	TINA2
1	10	TiN	660	0.000299	TINA1

TABLE I. Table of Film results

Figure 1 is the XRD analysis of film TINA3. This was a sputtering of a the titanium target with no nitrogen atmosphere. This resulted in a thin film of titanium and the XRD analysis performed is consistent with XRD peaks of Titanium.

Figure 2 is the XRD analysis of TINA 6, which was the trial with magnetron sputtering of

the titanium target and an N_2 partial pressure of .15 mTorr. The XRD clearly shows different peaks from TINA3, the titanium only sputtering, confirming that we have successfully made a film chemically different from Ti. The peaks in this sample correspond with known TiN peaks.

TINA6 successfully demonstrates that using our methods, it is capable of making TiN thin films. From this point we began altering initial conditions to see their effects on the characteristics of the films.

Figure 3 demonstrates the relationship we found with resistivity and Nitride Partial Pressure. There are several interesting features in this graph. First, it is important to note that the thickness for the films TINA1 and TINA2 created at partial pressure .5 and 1 mTorr respectively, were very thin which could compromise the measurement of the four-point resistivity probe, and thus the calculation for system voltage. However, we see a general increase in resistivity until around the partial pressure of .2 mTorr. This indicates that changing the Nitride partial pressure can result in characteristic differences in the films. This also is some evidence that the films created at lower Nitride partial pressures could be TiN_n films where we have not successfully synthesized pure TiN onto the substrate. We hypothesize this because Ti has very low resistivity, and the jump seen in resistivity from TINA4 at Nitride partial pressure of .1 mTorr to TINA9 at Nitride partial pressure of .13 might be indicative of a change in the film's composition.

Figure 4 demonstrates the relationship between film thickness and Nitride partial pressure. There are several components at play in this graph. First, TiN should deposit a thicker film than Ti alone in the same amount of time. This has to do with the molecular size of Ti versus TiN. Secondly, there are various dampening effects in terms of deposition speed as Nitride partial pressure increases. As we increase Nitride partial pressure, the likelihood of target poisoning increases. Target Poisoning in this case refers to the scenario when a small layer of TiN forms on the target itself, so rather than the magnetron sputtering pure Ti, it sputters TiN instead. This likely has a different sputtering rate than pure Ti, therefore we see a decrease in sputtering efficiency. Another reason we may see the decrease in efficiency displayed in Figure 4, has to do with the Argon plasma we used to sputter the target. If the presence of Nitride is high enough in the chamber, it is possible that the Magnetron could ionize Nitride rather than Argon. Due to the mass difference in Nitride and Argon, ionized Nitride would be less efficient at sputtering Ti than Argon.

This leads us to finding a potential "sweet spot" for sputtering. We need the partial pressure of Nitride to be high enough in the chamber to ensure that we are depositing TiN, but not high enough that we see significant target poisoning or Nitride ionization. This leads us to look at the Nitride partial pressure range of .13 to about .2 mTorr. In Figure 5, we see system voltage as a function of Nitride partial pressure. Higher system voltage could indicate a target poisoning effect. While, having target poisoning will result in a decrease in sputtering efficiency, this data seems to indicate that the window to sputter TiN without significant target poisoning is relatively small. We found that the precision of our instruments for controlling the flow rate of Nitride were potentially insufficient for accurately maintaining this small window.

Ultimately, the goal of this research, and future endeavors is to find initial conditions which produce the film in which charge carriers most freely flow through; we are looking for low resistivity for a given thickness. Therefore, if it happens to be the case that these initial conditions exist in a N_2 partial pressure where target poisoning or Nitride ionization, then value of sputtering efficiency will have to be weighed against film characteristics.

IV. CONCLUSION AND FUTURE WORK

This experiment was successful at using DC Magnetron sputtering to synthesize thin films of TiN. In this regard, the experiment was a success. However, there is still much research that can be done on this topic. First, we only studied the growth of film under a relatively narrow assortment of initial conditions. It would be easy to study the affects of temperature on the formation of films, for example. Additionally, adding components to enhance our precision of Nitride partial pressure would make the results found in this experiment more conclusive.

Furthermore, an area of research we were hoping to look at but ran into technical limitations was analyzing the surface morphology of the films versus deposition conditions using the scanning electron microscope. This could help shed some insight on the composition of the films as well as the film structure. Depending on the structure of the films, some may serve as better electrical components than others. Knowing if we can vary surface morphology just by changing Nitride partial pressure would be valuable information as well, as it would affect how the deposition process could be scaled up.

ACKNOWLEDGMENTS

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V. FIGURES

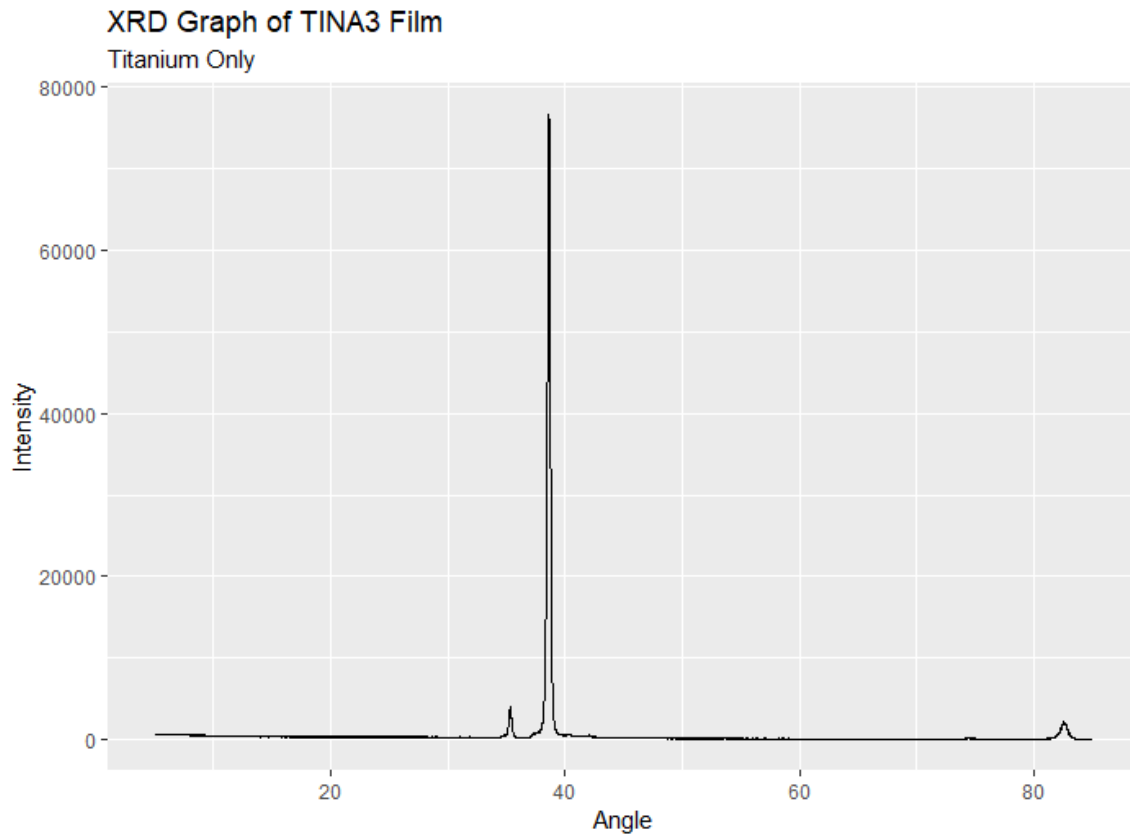


FIG. 1. XRD of a TiN thin film

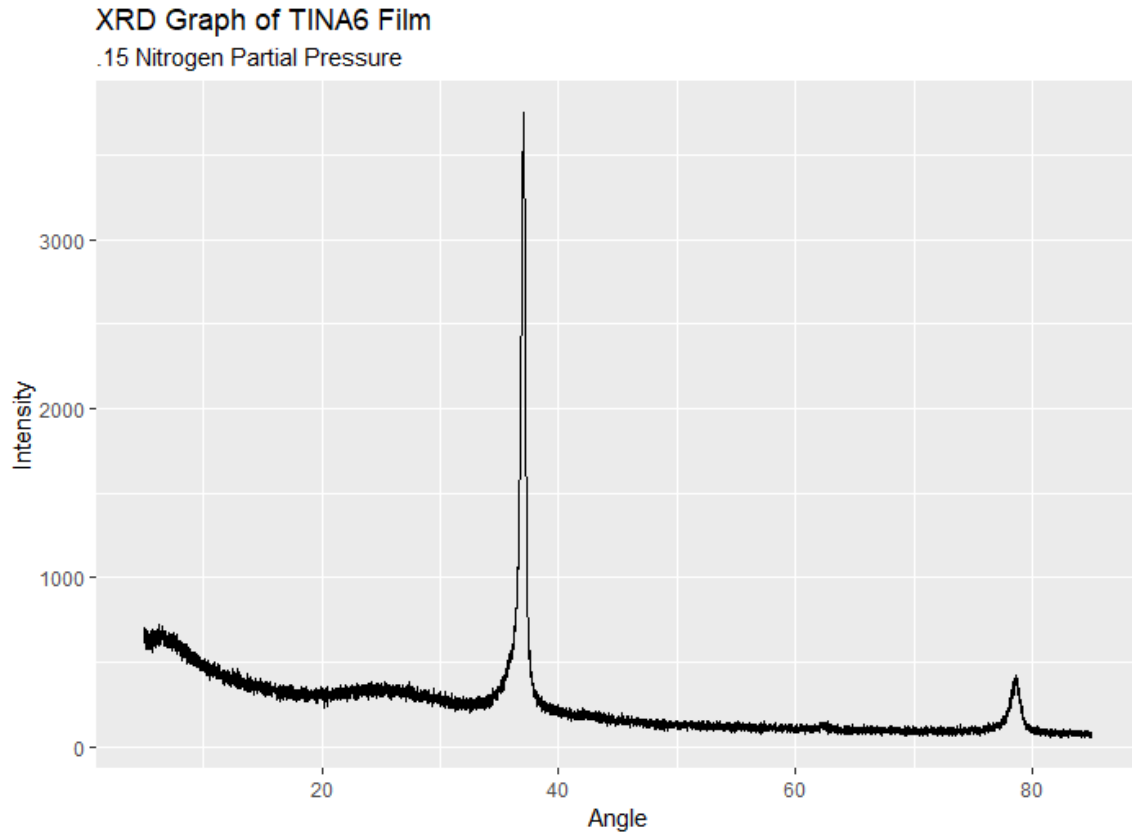


FIG. 2. XRD of a TiN thin Film

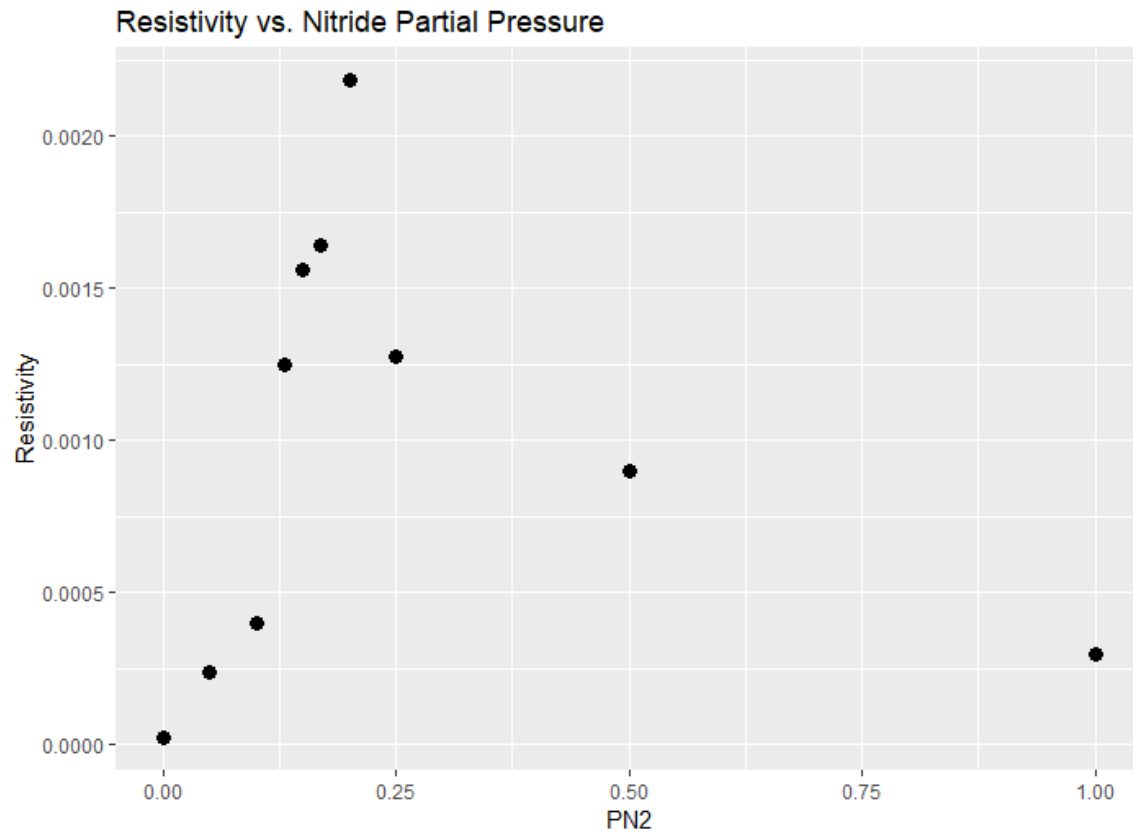


FIG. 3. Plot of Resistivity (Ohm meter) of film versus sputtering nitride partial pressure (mTorr)

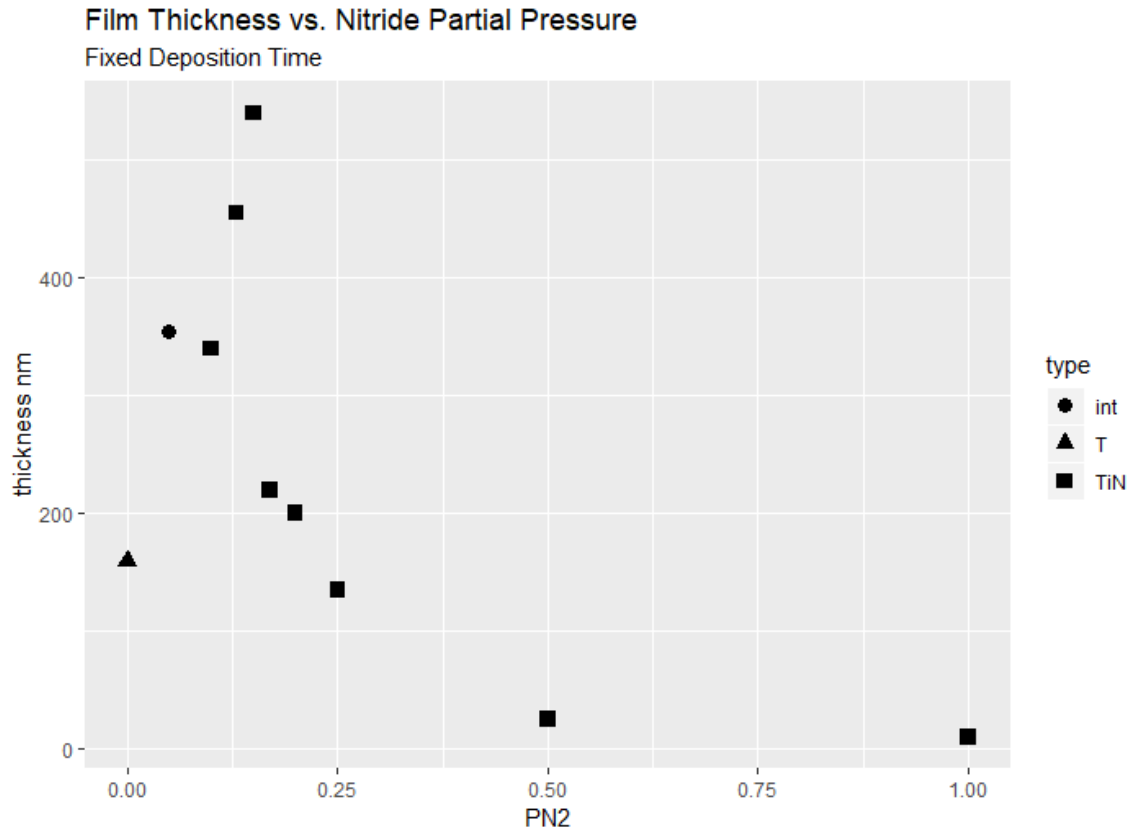


FIG. 4. Plot of Thickness of film versus sputtering nitride partial pressure (mTorr)

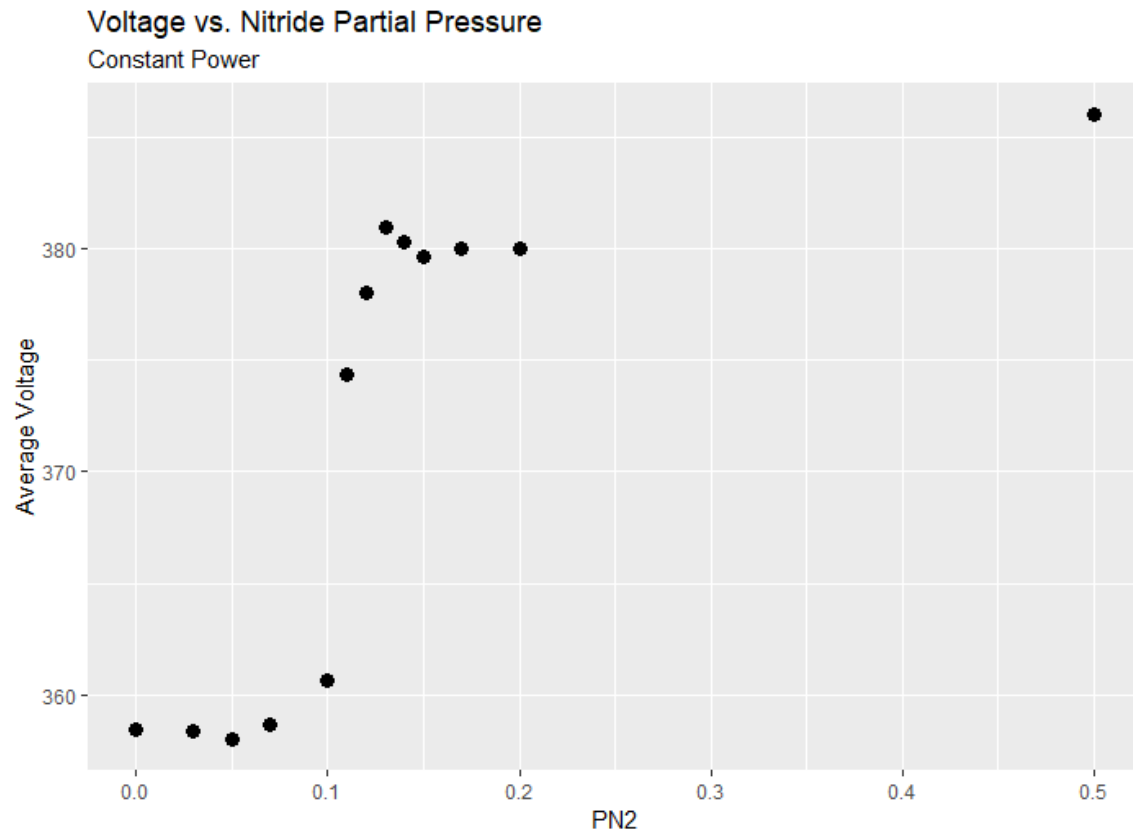


FIG. 5. Plot of voltage (volts) versus sputtering nitride partial pressure (mTorr)

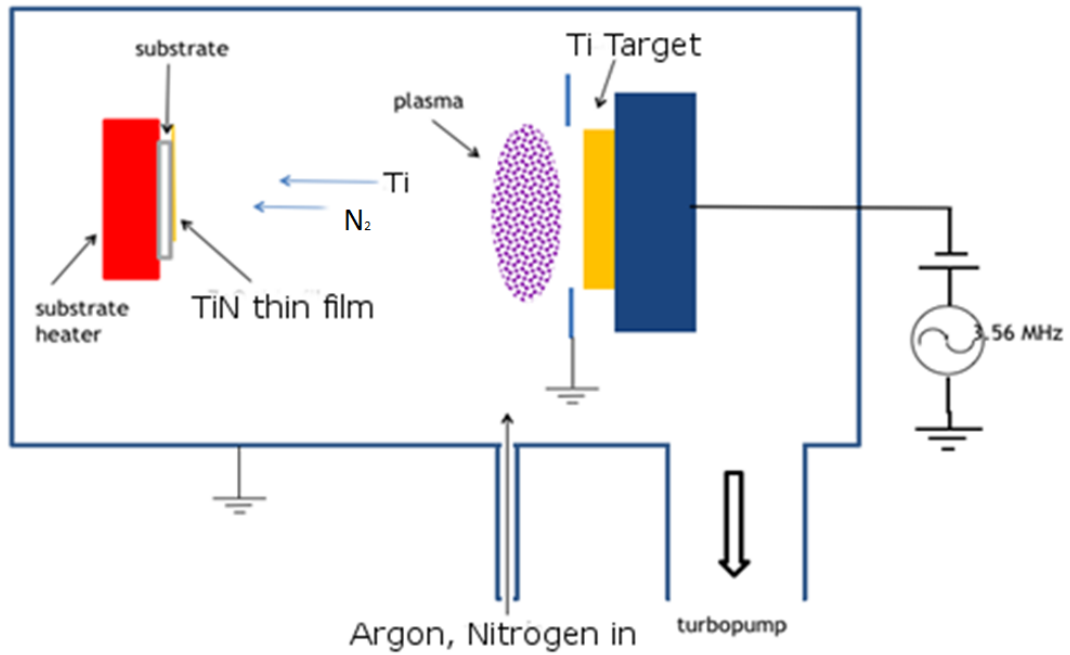


FIG. 6. Representation of the system used in deposition experiment.