Chapter 4. A radio-frequency plasma source of N atoms

4.1. Introduction

The use of fluxes of gases or chemical vapors as sources of film-forming elements was adopted in material science for production of many compounds. In chemical vapor deposition methods gases or chemically gasified solids are used at pressures from 1 atmosphere down to UHV conditions. In this case the background pressure results in a certain flux of gas at all parts of the sample. Physical vapor deposition requires low pressures (below $10^{-3}$ mbar) and line-of-sight geometry because of wall condensation. Each element needed for the production of the film can be delivered at the surface via a variety of routes. For example, oxygen can be supplied in the form of $O_2$, $O_3$, or $NO_2$ molecules or as atomic O as well. Atomic species of many non-metals are much more chemically reactive because they have a high affinity to drag in or to share electrons with another atom. The principle used to dissociate a molecule into atoms is always to add in one way or another some energy to the molecule so that it is excited and eventually dissociates. It can be done by irradiating the incoming flux of molecules with a laser beam [1]. Another way to dissociate a molecule is to lead the molecular flux through a hot nozzle made of special metal. For $H_2$ molecules a tungsten nozzle at 1800°C is often used [2], for $N_2$ we used an iron nozzle at $>900°C$ [3] (see the previous chapter). One can crack molecules in a plasma as well. For these purpose radio-frequency or micro-wave electromagnetic fields can be used.

Radio-frequency (RF) plasma sources are often used in accelerators for the generation of fluxes of ions for further acceleration and use in beam techniques. The principle of such a RF-source is based on the ionization of atoms and molecules by electrons accelerated in an alternating electro-magnetic field. The ionization process is accompanied by the production of more electrons, which again ionize neutrals. In this way, a steady state of partly ionized gas called plasma can be reached. Electrons move along spiral trajectories in a permanent magnetic field, which increases the efficiency of ionization. In accelerators ions are extracted from the plasma by a permanent electric field. We were interested in atoms of nitrogen, which are also produced in a plasma as a result of dissociation of $N_2$. The flux from the RF-source was obtained by maintaining a difference in pressure between the RF-source and the UHV chamber. The outgoing flux contained a certain fraction of atoms. This technique is used for the production of atomic fluxes already for two decades and commercial RF-sources of atomic nitrogen and oxygen are available (SVTA, TECTRA). At the same time, many reports on home-made sources of atoms were published in the nineties [4-7].
4.2. Design of the RF-source

We used a RF-source, which was designed and built in our laboratory. It was made as an independent system with its own turbo-pump and pressure gauge. It was mounted to the UHV system via a valve and could be easily removed without any effect on the vacuum. The base pressure in the source was \(<10^{-7}\) mbar. The plasma container was made of Pyrex, and normally it was etched with a dilute fluoric acid. Later, in order to obtain a boron coating at the walls of the plasma container, which reduces the recombination rate on N, we used the following recipe obtained from dr. N.J.C. Ingle [8]. After cleaning in 4% HF solution for 20 minutes, we boiled a saturated boric acid solution (~95 °C) in the Pyrex plasma container for 15-30 minutes. The resulting layer of the coating should appear to be homogeneous. Then, still wet, it is immediately placed in an oven and dried with a flow of nitrogen at 480-600 °C for 24 hours. The freshly produced coating can be easily damaged by water vapor from the atmosphere, so it is best to keep it under vacuum whenever possible. The plasma was ignited and maintained by a 70 MHz RF-coil coupled capacitively to the plasma. The electrodes attached to the RF-coil were clamped from the outside around the container (see figure 1). Two ring magnets confined the plasma in a magnetic field, which was also used to get spiraling trajectories of electrons. A retractable Teflon-coated tube, 46 cm long, 4 mm inside diameter was used to transfer and direct the gas flux from the plasma container to the sample during operation. It had two magnetic rings around it and could be slide in the UHV chamber and placed in the right position by an external magnet. The end part of the tube was brought at a distance of 4 cm from the sample. A gas system for the mixing of different gases was connected to the RF-source via a needle valve, so that the flux of the gaseous mixture could be controlled. The gas mixture was delivered to the surface of the sample by the gradient in pressure in the source (~1x10^{-2} mbar) and in the UHV chamber (~10^{-7} mbar during operation). We used nitrogen, ammonia and mixtures of nitrogen and hydrogen gases to produce a flux containing nitrogen atoms. The applied power was 60 W in all cases.

![Figure 4.1. The layout of the RF-source.](image)

4.3. Gas flux calculations by Monte-Carlo simulations

In the introduction to this chapter it was mentioned that atomic N is very reactive. Because of this it is not stable and it tends to form a compound when it meets a metal atom or to recombine into N_2 molecules. In order to transport atomic N to the surface of the sample we used a Teflon tube. It is known from the experience of other groups that Teflon is inert to
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atomic N and does not promote the recombination process. Our early experiments described in chapter 3 showed that the output of the source is sufficiently high for the production of an iron nitride with a growth rate in the range of 20-60 s/Å. However, the lack of knowledge about the output of the source did not allow us to understand the results and to separate the influence of RF-source effects from the impact of surface processes. In order to control the output of the source, we need to know the efficiency of the source plus the transport system and the flux of N atoms and of other species at the surface of the sample.

It is well known [9] that the cosine law of distribution of the flux behind the exit of a narrow, long tube at low pressures is not valid. In this context, low pressure means a pressure at which the mean free path of a molecule exceeds the typical dimensions of the container, which is the case in our setup. In this case collisions of molecules with the walls must be described only, that is, the influence of intermolecular collisions can be neglected. The pressure regime where this applies is also known as the molecular flow regime. In order to estimate the flux at the sample surface, we performed a Monte-Carlo simulation of atom trajectories through the Teflon tube using our own code. The assumption we used was that a molecule hitting a wall has a uniform probability distribution to be desorbed in all directions. Results of this kind of simulations have been already published and we checked the outcome of our code with the published ones [9, 10]. We confirmed that the flux of particles from the Teflon tube is very much directed in a forward direction and it appeared to be very important to align the tube precisely with respect to the sample. We aligned the tube by observing the light spot created by a beam of light sent through the tube. The calculated flux at the surface of the sample was $2 \times 10^{14}$ at/s for a pressure of $5 \times 10^{-3}$ mbar in the source. This number includes all kind of species of the gas mixture in the plasma, assuming no change of the amount of particles because of absorption, dissociation and recombination. The content of nitrogen in the sample was determined by various techniques as described in chapter 3. The lowest limit of the efficiency of the source, $\kappa$, can be found assuming that the probability for N atoms arriving at the surface to stick and react with iron is equal to unity. In Chapter 5 we will argue that this is a realistic assumption when layers consisting of a mixture of Fe and Fe$_4$N are grown. Then we have the following expression for the efficiency $\kappa$:

$$\kappa = \frac{F_N}{2F_{N_2}},$$

where $F_N$ is the flux of N atoms at the surface, which is equal to the uptake rate of N in the growing Fe-N layer; $F_{N_2}$ is the total calculated $N_2$ flux in the gas mixture. The flux of $N_2$ is multiplied by 2 because two N atoms are obtained out of one $N_2$ molecule.

The highest efficiency of the source was observed when $H_2$ gas was admixed to the gas mixture. For a sample produced with a mixture of $N_2:H_2$ (20:80) the efficiency of the RF-source plus the transport system was estimated to be 2% assuming a sticking plus reaction coefficient of unity. When pure nitrogen was used, the efficiency of the source dropped to below 1%. There can be two principal reasons for this fact. One is that hydrogen has influence on the processes at the sample surface; the second one is that $H_2$ changes the efficiency of the source or/and of the transport tube. Concerning the first reason, it could be that the effective sticking coefficient is not unity but smaller than one and hydrogen increases this parameter. In this case, the actual flux of N atoms and the efficiency of the RF-source are higher than the one found on the basis of the nitrogen content in the produced samples using pure $N_2$ in the RF-source. In our later research, which will be described in chapter 5, we found out that the sticking probability of N atoms to Fe growing film is indeed unity under the described conditions, independent of the presence of hydrogen. This points to the important role of hydrogen in the RF-source itself or in the transport tube.

According to our calculations, a particle, which passes through the long narrow tube, hits the wall of the tube on average 5000 times. Assuming that recombination may occur at the walls when a N atom has hit the wall and has attached to it, we can estimate the upper
limit of the recombination probability at the walls. It will be highest if the efficiency of the source itself is 100% and all the reduction of the flux of N atoms occurs in the Teflon tube. Then the probability for recombination at the Teflon walls for the case when the efficiency of the RF-source plus the transport tube was 2% would be ~0.0008. We have to mention here that we also used a Teflon tube with 6 mm inner diameter. According to calculations, in this case a particle passing through the tube would hit the walls on average only ~3000 times. This should decrease the probability for a N atom to recombine by ~8 times and would result in a much higher flux of N atoms from the source. This effect was not observed and samples with a similar content of nitrogen were obtained. This implies that the probability for N atoms to recombine at Teflon walls is below $10^{-4}$. Then, the only possible explanation of the higher content of N in the samples produced in the presence of hydrogen would be the higher efficiency of the RF-source itself, which should be determined by the recombination at the walls of the source. In our later work, we used a special treatment of the Pyrex plasma container, namely the coating by boiling in boric acid, in order to reduce the recombination rate at the walls. We noticed that in such a source the presence of hydrogen did not have such a big effect on the efficiency of the source and on the uptake of N any more. The role of hydrogen will be described in more detail in Chapter 5.

4.4. Optical spectroscopy

In order to gain a better insight into the processes in the RF-source and to have some control over the efficiency of the RF-source, we have undertaken an investigation of the optical emission from the plasma of the source. We used an Ocean Optics PC1000 spectrometer to probe the light in the wavelength range of 350 – 860 nm with a resolution of 2.5 nm. The composition of the working gas, the pressure and the geometry of the electrodes were varied.

The resolution of the spectrometer was insufficient to resolve the emission lines of atomic N out of the sea of molecular lines. We observed the first and the second positive series of molecular lines as well as transitions of N$_2^+$ ions (see figure 4.2). The atomic transitions corresponding to the $^4P-^4S^0$ multiplet of nitrogen were expected at wavelengths of 742, 744 and 747 nm [11]. They overlap with a broad molecular peak at 750 nm.

In order to overcome this difficulty and to identify atomic transitions, we compared an optical emission spectrum from the N$_2$ plasma at relatively high pressure with the one at working conditions. It is known that in the plasma the percentage of atomic nitrogen decreases with increasing pressure [6]. This is due the shorter mean free path length at higher pressures whereby the recombination rate by collisions increases. So the optical emission at a somewhat higher pressure is mainly due to molecular transitions. We took emission spectra at the working (5x10$^{-3}$ mbar) pressure and at a higher (10$^{-1}$ mbar) pressure in the source (see figure 4.2). The presence of atomic peaks could be observed as an increase of intensity near the wavelength of a molecular peak (figure 4.2). In addition, a peak at 822 nm corresponding to the $^4P-^4P^0$ multiplet of atoms could be observed directly.
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![Graph](image1.png)

**Figure 4.2.** Optical emission spectra of the plasma in the RF-source at a pressure of 10⁻¹ mbar and at a pressure of 5x10⁻³ mbar.

![Graph](image2.png)

**Figure 4.3.** Optical emission spectra from the RF-plasma containing different gas mixtures.

The intensity of these peaks was used as a measure of the efficiency of the source. This allowed us to optimize the geometry of the set-up and to compare the efficiency of the source with different working gases (figure 4.3). The efficiencies of the source with N₂, N₂:H₂(20:80) and NH₃ working gases were comparable as we obtained iron nitrides at a growth speed of 20-60 s/Å with any of these combinations. Pure N₂ seemed to be the worst working gas for the production of nitrogen atoms.

### 4.5. Conclusions

Concluding, a home-made radio-frequency plasma source has been successfully tested and used in MBE assisted by a flow of N atoms for the growth of iron nitrides. The efficiency of the source plus the transport tube with the working gas mixture of N₂:H₂ (20:80) was estimated to be 2%. This mixture of gases seemed to be the best with regard to the efficiency of the source. Monte-Carlo simulations of atomic trajectories allowed us to conclude that the
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Teflon transport tube cannot be the cause for the difference in the output of the source when hydrogen is admixed to the working gas. Probably hydrogen contributes to the passivation of the Pyrex walls of the RF source. When these walls are passivated by a boron-containing layer, the influence of hydrogen is diminished. The probability for N atoms to recombine at the walls of the Teflon tube is below $10^{-4}$. The geometrical parameters of the source were optimized by using optical emission spectroscopy. Different mixtures of nitrogen and hydrogen as well as ammonia were used. The efficiency of the source was sufficient in all cases for the successful growth of nitrides at a speed of ~20-60 s/Å.

4.6. References

8. N.J.C. Ingle, private communication.