Characterization of a Magnetron Plasma for Deposition of Titanium Oxide and Titanium Nitride Films

R. Hippler 1, S. Wrehde 1, V. Straňák 2, O. Zhigalov 1, H. Steffen 1, M. Tichý 3, M. Quaas 4, and H. Wulff 4

1 Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Domstr. 10 a, 17489 Greifswald, Germany
2 University of South Bohemia, Department of Physics, Jeronýmová 10, 371 15 České Budějovice, Czech Republic
3 Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 180 00 Praha 8, Czech Republic
4 Institut für Biochemie und Chemie, Ernst-Moritz-Arndt-Universität Greifswald, Soldmannstraße 16, 17489 Greifswald, Germany

Received 09 May 2005, accepted 13 June 2005
Published online 29 July 2005

Key words Film deposition, magnetron sputtering, titanium oxide and nitride.

PACS 52.70.-m, 52.77 Dq, 52.80 Sm, 81.15.-z

Experimental results for the energy distribution of electrons and plasma ions in a magnetron discharge with a titanium target and with pure argon, argon/nitrogen and argon/oxygen mixtures as working gas are reported. Typical electron temperatures measured 6.5...9.5 cm above the magnetron target range between 2–3.5 eV. Typical values for the plasma potential are in the 0.4–2 V range, as are mean ion energies measured with the help of energy-resolved mass spectrometry. Deposited titanium films show some dependencies on oxygen flow and on substrate bias.

1 Introduction

Plasma based techniques have wide-spread applications in fundamental research and in industry [1]. Rather common are their use in etching and deposition processes. Deposition of thin solid films is frequently achieved by means of magnetron discharges [2] [3]. Here we report an investigation of plasma properties of a planar magnetron operated in so-called balanced as well as in unbalanced mode and its use during deposition of titanium and titanium oxide films. The employed plasma diagnostics rests on two rather common approaches, Langmuir probe diagnostics [4] and energy-resolved mass spectroscopy.

The measurements with electric probes belong to the oldest as well as to the most often used procedures of low-temperature plasma diagnostics. Originally developed in the twenties of the last century by Langmuir and his co-workers [4], the method has been the subject of many extensions and further developments in order to extend its applicability to more general conditions [5].

Energy-resolved mass spectroscopy is a versatile tool to investigate particular properties of a plasma, i.e., the density of plasma ions and their energy distributions after travelling through the plasma sheath in front of the analyzer.

2 Experimental set-up

The experimental set-up essentially consists of a vacuum chamber housing a magnetron plasma source, a substrate holder for deposition of thin solid films, and a Langmuir probe. Details of the apparatus have been described previously [2]. The employed 3” magnetron (GENCOA Vtech75) was operated in both so-called balanced and unbalanced mode. A titanium target was used. Typical operation voltages were 320–400 V and 430–590 V

* Corresponding author: e-mail: hippler@physik.uni-greifswald.de
in balanced and unbalanced mode, respectively. Discharge power was varied between 10–110 W at total gas pressures of 0.3–1.2 Pa, with pure argon, argon/nitrogen and argon/oxygen mixtures as working gas. The residual gas pressure was below $10^{-6}$ Pa. For the present investigation, the substrate holder was replaced by an energy-dispersive mass spectrometer or plasma process monitor (Balzers PPM 421) suitable for an investigation of the energy spectra of selected plasma ions. Its entrance orifice is located about 9.5 cm above the magnetron. Langmuir probe measurements were performed with an electrical probe placed 6.5 cm (Ar/O$_2$) and 8.8 cm (Ar, Ar/N$_2$) above the magnetron. Details of the Langmuir probe measurements have been described previously [6].

Deposited films were characterized by means of x-ray photoelectron spectroscopy (XPS), by x-ray reflectometry and grazing incidence x-ray diffractometry (GIXD). X-ray photoelectron spectroscopy (XPS) measurements were performed with a conventional surface analysis system (VG MT 500) to investigate the composition of the deposited TiO$_x$ films. Samples were transferred under vacuum from the deposition chamber to the surface analysis chamber. X-ray reflectometry investigations were performed on a $\Theta - 2\Theta$ diffractometer (Siemens D 5000) with a special thin film attachment. The films were scanned in the range 0.4–3$^\circ$/2$\Theta$ (step width 0.01$^\circ$/2$\Theta$, scanning time 30s per step.) Film thickness and density were determined by fitting the resulting reflectometry curves using the REFSIM1.1 software (Siemens). The deposited films were investigated by grazing incidence x-ray diffractometry (GIXD) to investigate the phase composition, domain sizes and the preferred orientation. The angle of the incident x-ray beam was fixed at 1$^\circ$/2$\Theta$. The scanning region was 25–45$^\circ$/2$\Theta$ (step width 0.02$^\circ$, scanning time 5 s per step).

3 Results

Measurements were performed with pure argon and with argon/nitrogen and argon/oxygen gas mixtures as working gas.

3.1 Argon

The measured mean electron energy or electron temperature, as function of discharge power, is displayed in Fig. 1. It features a maximum that shifts to higher power values with decreasing pressure; typical values range between 2 eV and 3.5 eV, depending on the conditions of operation [6]. The decreasing electron temperature at large discharge powers is attributed to an increasing cooling effect due to sputtered titanium atoms. The measured plasma potential also shows pronounced variations which, to some extent, resemble those for the electron temperature. Measured values for the plasma potential of a pure argon plasma range between 0.4 and 1.4 V (Fig. 2).

The electron density measured 8.8 cm above the magnetron with a Langmuir probe is of the order of $10^{16}$/m$^3$; it displays a pronounced increase with discharge power (Fig. 1). The electron density in unbalanced compared to balanced mode is about 50–100% larger.

![Fig 1](#)
Typical energy distributions of $^{36}$Ar$^+$ and Ti$^+$ ions as function of magnetron power are displayed in Figs. 3 and 4. The observed ion energy distribution functions of Ar$^+$ ions are rather narrowly peaked at about 0.6–1.8 eV. With increasing magnetron power the peak position moves to higher energies, indicating a shift of the plasma potential. The peak positions are about 1 eV larger in unbalanced compared to balanced mode. This observation is in qualitative agreement with results for the plasma potential obtained from Langmuir probe measurements [6].

The deduced mean ion energies and the Ti$^+$/Ar$^+$ ion ratios are displayed in Fig. 5 and Fig. 6, respectively. The significant increase of the mean ion energy with magnetron power, reflecting the increase of the plasma potential, is clearly noticeable. There are some further points to be mentioned: (i) As for the plasma potential, the mean ion energy is larger in unbalanced compared to balanced mode. (ii) The mean ion energy for Ti$^+$ ions exceeds that of Ar$^+$ ions under the same conditions. This observation indicates that titanium ions being produced by cathode sputtering, thereby receiving kinetic energies in the order of a few eV, do not fully thermalize in the plasma under the here considered conditions. In the absence of thermalizing collisions the ion energy distribution of Ti atoms should resemble the energy distribution of atoms sputtered from the cathode. Fig. 7 displays measured energy distributions of Ti atoms at different gas pressures. It is noted that the energy distributions display a high-energy tail extending up to about 10 eV and being more pronounced at low gas pressures. For example, at a gas
Fig. 4  Energy distribution of Ti$^+$ ions in pure argon plasma in balanced (left) and unbalanced (right) mode. Magnetron power was varied between 10–110 W; argon gas pressure 0.7 Pa.

Fig. 5  Mean ion energy versus magnetron power in balanced (○ Ar$^+$, △ Ti$^+$) and unbalanced (● Ar$^+$, ▲ Ti$^+$) mode. Argon gas flow 20 sccm, total gas pressure 0.7 Pa.

Fig. 6  Ti$^+/Ar^+$ ratio versus magnetron power in balanced (open symbols) and unbalanced (closed symbols) mode. Ar-
gon gas flow 20 sccm, total gas pressure 0.7 Pa. ○●, Ar; △▲, Ar + 1 sccm N$_2$; ▽▼, Ar + 1 sccm O$_2$.

pressure of 0.3 Pa the integrated intensity of the high-energy tail amounts to about 10% of the total intensity. With increasing gas pressure, the low-energy peak becomes more pronounced and shifts to lower energies. At a pressure of 1.2 Pa, the intensity of the high energy part compared to main peak is in the range of 0.1% only. Similar arguments should also hold for neutral titanium atoms. The measured Ti$^+/Ar^+$ ion ratio increases with magnetron power, indicating that Ti$^+$ ions are produced in two steps: a sputtering event being linearly depending on magnetron power, followed by an ionization event taking place in the gas phase that again depends linearly on magnetron power. Somewhat surprising, the Ti$^+/Ar^+$ ratio is larger in balanced compared to the unbalanced mode (see below).

It should be emphasized that the velocity distribution of plasma ions to some extent is determined by inelastic processes in the plasma sheath that forms in front of the orifice. For a collision-free sheath and pre-sheath the Bohm-criterion is valid. Accordingly, ions are accelerated to ion sonic speed in the pre-sheath and their energy at the transition from pre-sheath to sheath becomes equal to $kT_e/2$, where $T_e$ is the electron temperature. In the absence of collision processes, plasma ions becoming further accelerated by the sheath potential gain energy that is determined by the plasma potential. For such a collision-free sheath we may, hence, expect an ion energy distribution with a maximum corresponding to the plasma potential and a small thermal broadening. In reality the occurrence of collisions has to be taken into account. The dominant reaction for argon ions is resonant charge

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transfer whereby a fast ion is destroyed and a slow ion is created. Under the present experimental conditions, and taking into account a charge transfer cross section of \( \sim 100 \, \text{Å}^2 \) [7], the mean free path for charge changing collisions amounts to \( \approx 2–3 \, \text{cm} \). The pre-sheath dimensions are of the same order of several cm while the Debye length that determines the sheath dimensions amounts to \( \approx 0.01 \, \text{cm} \) only. This implies that argon ions may undergo at most a few inelastic collisions in the pre-sheath leading to the formation of slower ions while the chance for charge-changing collisions in the sheath is much smaller and thus negligible.

**Fig. 7** Energy distribution of Ti\(^+\) ions in pure argon plasma in balanced mode at different gas pressures (● 0.3 Pa; ○ 0.7 Pa; ▼ 1.2 Pa). Magnetron power 50 W.

**Fig. 8** Mean electron energy versus magnetron power (left: balanced mode; right: unbalanced mode). Argon gas flow 20 sccm, total gas pressure 0.7 Pa (○ Ar; ▽ Ar + 0.75 sccm O\(_2\); □ Ar + 0.75 sccm N\(_2\)).

### 3.2 Argon/nitrogen mixture

The mean electron energy or electron temperature in argon/nitrogen mixture measured 8.8 cm above the magnetron is displayed in Fig. 8. The electron temperature as function of discharge power is relatively constant at \( kT \approx 2 \, \text{eV} \) in balanced mode and with \( kT \approx 2.2 \, \text{eV} \) about 0.2 eV larger in unbalanced mode. The electron temperature for the argon/nitrogen gas mixture thus turns out to be somewhat larger than compared to the pure argon gas case.

The total ion flux of selected ions (Ar\(^+\), N\(^+\), N\(_2^+\), Ti\(^+\)) measured with the plasma process monitor is displayed in Fig. 9. The largest ion flux is due to Ar\(^+\) ions, followed by N\(_2^+\) molecular and N\(^+\) atomic ions. The intensity
of Ti$^+$ ions is 2–3 orders of magnitude smaller than Ar$^+$. As expected, the ion flux increases approximately linearly with magnetron power. An exception is again the Ti$^+$ ion flux which is close to a quadratic increase. The Ti$^+$/Ar$^+$ ratio in Ar/N$_2$ mixture is smaller compared to pure Ar gas (Fig. 6) reflecting to some extent a decrease of the sputtering yield of the cathode with increasing N$_2$ admixture.

There are indications that surface reactions also contribute to the formation of plasma ions. For reactive gases like nitrogen or oxygen a contamination of the magnetron cathode by reactive molecules and/or atoms occurs, eventually causing unwanted side-effects like poisoning of the cathode followed by arcing [8] [9]. Sputtering of reactive gas atoms and molecules from the contaminated cathode also occurs and thus contributes to the formation of energetic plasma ions. Fig. 10 displays ion energy distributions of N$^+$ and N$_2^+$ ions for different gas pressures. As for the Ti$^+$ ions, a high-energy tail is clearly visible in the ion spectra, particularly at low gas pressure while it seems that at high pressures thermalization occurs. At this pressure, the peak position is close to 1 eV and thus in fair agreement with results for the plasma potential (Fig. 2). It should be emphasized that positively charged ions in general have insufficient energy to escape from the negatively charged cathode. Rather, the before-mentioned
ions with energies in the 3–10 eV range must be created as neutral atoms at the cathode but become ionized on their way through the plasma.

3.3 Argon/oxygen mixture

The mean electron energy or electron temperature in argon/oxygen mixture measured 6.5 cm above the magnetron is displayed in Fig. 8. The electron temperature is about 3 eV in both balanced and unbalanced mode and thus somewhat larger than compared to the pure argon and the argon/nitrogen cases.

![Diagram](image)

**Fig. 11** Ion flux versus magnetron power (left: balanced mode, ○ Ar⁺; ▽ O₂⁺, □ O⁺, △ Ti⁺; right: unbalanced mode, ● Ar⁺; ▼ O₂⁺, ■ O⁺, ▲ Ti⁺). Argon gas flow 20 sccm, oxygen gas flow 1 sccm, total gas pressure 0.7 Pa.

The total ion flux of selected ions (Ar⁺, O⁺, O₂⁺, Ti⁺) measured with the plasma monitor is displayed in Fig. 11. The largest ion flux is due to Ar⁺ ions, followed by O₂⁺ molecular and O⁺ atomic ions. The intensity of Ti⁺ ions is almost 4 orders of magnitude smaller than compared to Ar⁺. As expected, the ion flux increases approximately linearly with magnetron power. This also holds for the Ti⁺/Ar⁺ ratio in Ar/O₂ mixture is much smaller compared to both the pure Ar gas and the Ar/N₂ gas mixture (Fig. 6). This not only reflects a decreasing sputtering yield but already a "poisoning" of the cathode with increasing O₂ admixture.

![Diagram](image)

**Fig. 12** Energy distribution of O⁺ (left) and O₂⁺ (right) ions in pure argon plasma in balanced mode. Magnetron power 50 W. Note the different vertical scales.
Similarly as in the case of nitrogen, fast oxygen atoms and molecules are to some extent formed at the contaminated cathode and afterwards ionized in the plasma. The measured ion energy distributions for $O^+$ and $O_2^+$ ions again display high-energy tails that are more pronounced at low gas pressures (Fig. 12). Not yet understood is the shift of the peak position to rather small ($\approx 0$ eV) kinetic energies. This observation also contrasts with the behavior of the plasma potential which with $\approx 1.5$ eV in balanced mode for the Ar/O$_2$ mixture is the largest of the three investigated gases (Fig. 2). A particular feature of oxygen-containing plasmas is the appearance of negative ions. Fig. 13 displays the energy spectrum of negative $O^-$ ions. It is noted that a large fraction of these ions have small energies but also ions with large kinetic energies being produced by sputtering off the negatively charged cathode are clearly observed.

Fig. 14 Deposition rates of Ti films versus magnetron power in balanced (•) and unbalanced (○) mode. Argon gas flow 20 sccm, total gas pressure 0.7 Pa.

4 Deposition of titanium and titanium oxide films

Fig. 14 displays the measured deposition rate of titanium films versus magnetron power in balanced and unbalanced mode. The deposition rate increases almost linearly with magnetron power, as follows from sputtering
theory [9]. The deposition rate in unbalanced mode is 10–20 % larger than in balanced mode, indicating an enhanced sputtering yield presumably due to the higher bias voltage. This observation is in some contrast to the larger Ti\(^+\)/Ar\(^+\) ion ratio in balanced compared to unbalanced mode, however, (see Fig. 6).

Fig. 15 displays the density of deposited titanium oxide films as function of oxygen flow. With increasing oxygen flow the density displays a maximum indicating a transition from pure Ti via TiO to TiO\(_2\) films.

5 Discussion

In order to understand the elementary processes taking place in a magnetron plasma we have to recall that plasma ions are accelerated towards the cathode where they liberate atoms, positively and negatively charged ions and secondary electrons. Subsequently, secondary electrons become accelerated towards the plasma by the electric field caused by cathode potential. Magnetic field lines are parallel to the magnetron surface in the region of the magnetron etch track and, hence, perpendicular to the electric field direction. The joint action of both, electric and magnetic, fields confines sufficiently energetic electrons to a region just above the cathode. In order to escape from that region, electrons have to loose kinetic energy by inelastic collisions with gas atoms, whereby a significant fraction of these atoms become singly or even doubly ionized. Electrons detected outside the trap region hence have already lost most of their energy and, if measured with standard Langmuir probe techniques sufficiently far from the cathode, the significant but small high-energy part of the electron distribution present only in the trap region is not detected. In fact, Sheridan et al. [10], for the case of a magnetron discharge in helium, have observed a “hot” electron component with kinetic energies of about 7.5 eV that is confined to the trap region close to the magnetron cathode. On the other hand, since the mean free path of plasma ions is sufficiently large, ions even when produced inside the trap region can spread all over the plasma and may become detected far away from their place of origin. The argument even holds for resonant charge exchange in Ar\(^+\)–Ar collisions (mean free path \(\sim 1\) cm under the conditions of interest here, estimated from published cross section data [7]), since every neutralized Ar\(^+\) will produce a new Ar\(^+\) ion, and no loss of plasma ions occurs. Thus, while Langmuir probe measurements in general and in the here considered magnetron discharge in particular investigate the local electron temperature, ion ratios resemble an average over many plasma regions. It thus appears reasonable to assume that most ions originate from the plasma region where the ionization rate is largest, i.e., from the electron trap region close to the cathode. The idea is corroborated by a comparison of the measured Ti\(^+\)/Ar\(^+\) ratios (Fig. 6). A pronounced increase with magnetron power is noted, largely caused by the with increasing magnetron power increasing density of sputtered titanium atoms. At first glance surprising is the large difference of about a factor of 6 in that ratio between balanced and unbalanced mode. The large difference is due to both a smaller Ar\(^+\) density and a larger Ti\(^+\) density in balanced compared to the unbalanced mode, as can be noted from a comparison of the measured energy distributions (Figs. 3 and 4). In unbalanced mode the magnetic field lines open up towards the substrate region with the electron trap region becoming less defined. As a consequence, we observe an increase of the electron density in unbalanced compared to the balanced mode as electrons are directed away from the cathode region towards the substrate region. Apparently, a significant fraction of Ar\(^+\) is produced outside the trap region, whereas Ti\(^+\) ions are largely produced inside the trap region where, due to the presence of high energy electrons, ionization is most likely. As seen before (Fig. 14) the deposition rate increases by \(\approx 10–20\%\) in unbalanced mode indicating an enhancement of the titanium density. The smaller Ti\(^+\) density thus reflects a reduced ionization probability in unbalanced mode due to the less confined trap region which Ti atoms have to pass to reach the substrate region.

6 Conclusions

Experimental results for the energy distribution of electrons and in a magnetron discharge with a titanium target and with pure argon, argon/nitrogen and argon/oxygen mixtures as working gas are reported. It is observed that 6.5–8.8 cm in front of the magnetron cathode electrons have small kinetic energies corresponding to electron temperatures of typically \(kT = 2–3.5\) eV. It is thus believed that plasma properties are to a large extent determined by a minority of electrons originating from the negatively biased cathode possessing kinetic energies in excess of several 100 eV and being trapped close to the magnetron cathode by the joint action of electric and magnetic fields.
Acknowledgements  The work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungs- 
bereich 198 “Kinetik partiell ionisierter Plasmen”.

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