Investigation of the role of sputtered particles on the plasma properties during rf-magnetron sputtering of Zn and ZnO targets

Lanoir Maaloul[1], Luc. Stafford[1 (*)], and Andranik Sarkissian[2]

[1] *Département de Physique, Université de Montréal, Montréal, Québec, Canada H3C 3J7.*
[2] *Plasmionique Inc, Varennes, Québec, Canada J3X 1S2.*

(*) luc.stafford@umontreal.ca

Abstract: A combination of Langmuir probe and optical absorption spectroscopy measurements were used to determine the electron density, electron temperature, and number density of Ar atoms in metastable $^3P_2$ and $^3P_0$ states in rf magnetron sputtering plasmas used for the deposition of ZnO-based thin films. While the electron temperature and density of Ar $^3P_2$ and $^3P_0$ were fairly independent of self bias voltage, the Ar ($^3P_2$)-to-electron number density ratio decreased by approximatively a factor of five when going from -115V to -300 V. This decrease was correlated to an increase by about one order of magntitude of the number density of sputtered Zn atoms measured by actinometry. These results were found to be in excellent agreement with the predictions of a simple collisional-radiative model accounting for Penning ionization processes.

1. Introduction

ZnO-based thin films deposited by magnetron sputtering show promises for a wide variety of electronic and optoelectronic devices, including flexible and inexpensive thin film transistors, solar cells, etc. In magnetron sputtering, ions accelerated in the plasma sheath surrounding the Zn or ZnO target release atoms from the surface provided the ion energy is above the threshold energy required for sputtering. The particles ejected from the surface are then transported and eventually thermalized in the gas phase before reaching the substrate where film deposition occurs. In this work, we investigate the role of sputtered particules on the evolution of the plasma properties using Langmuir probes, optical absorption spectroscopy, and actinometry.

2. Experimental details

The rf magnetron sputtering plasma reactor was described in details elsewhere [1]. In the present work, the discharge was sustained in pure Ar at a pressure of 5 mTorr. The self-bias voltage was varied by adjusting the rf power. The positive ion number density (and thus the electron density assuming quasi-neutrality) and the electron temperature were obtained from the current-voltage characteristics of a rf-compensated, cylindrical Langmuir probe. The number density of Ar atoms in metastable $^3P_2$ and $^3P_0$ states were measured by optical absorption spectroscopy using the emission lines from an Ar spectral lamps. Finally, the absolute number density of sputtered Zn atoms was determined by actinometry on Zn atoms using Ar as the actinometer gas. More precisely, we used the Zn emission at 481.1 nm and the Ar emission at 750.4 nm and we assumed that both emitting levels were populated by electron-impact excitation from the ground state. The actinometry constant was determined using the set of cross sections reported in refs. [2,3].

3. Results and discussion

Figure 1 shows the influence of the self-bias voltage on the number density of Ar atoms in the $^3P_2$ and $^3P_0$ states near the vicinity of the target (Z=4cm) and far from the target (Z=13cm). Over the -115 to -300V range of self-bias voltages investigated, the number densities of metastable Ar atoms was fairly constant. For example, at Z=4cm, it was about 4×10^9 and 6×10^8 cm^{-3} for Ar $^3P_2$ and Ar $^3P_0$ respectively. These values are comparable to those reported by other authors in magnetron sputtering apparatus. The influence of the self-bias voltage on the radially-integrated electron temperature, $<T_e>$, at Z=4cm is illustrated in Fig. 2 for Zn and ZnO targets. $<T_e>$ was about 4eV and again remained fairly constant. This result is in sharp contrast to the well-known cooling of electrons in the presence of sputtered metallic particles in the gas phase (see, for example, ref. [4]). In the experimental conditions investigated, it seems that the release of Zn and O atoms following the sputtering of the Zn and ZnO targets has only a minor role on the plasma properties.

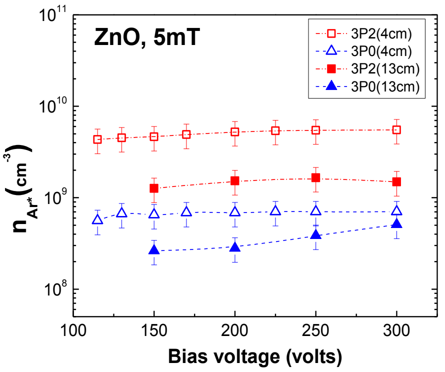

Fig. 1: Influence of the self-bias voltage on the number densities of Ar atoms in metastable $^3P_2$ and $^3P_0$ states at 4 and 13 cm from the ZnO target.

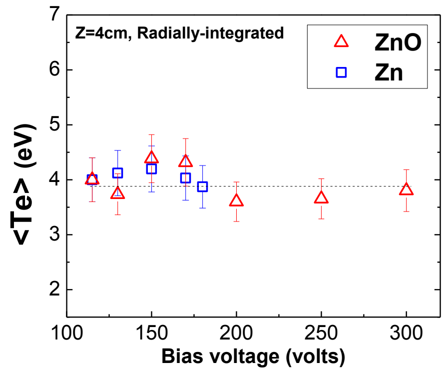

Fig. 2: Influence of the self-bias voltage on the radially-integrated electron temperature at 4cm from Zn and ZnO targets.

We have examined the possible role of sputtered particles by correlating the variation of the Ar $^3P_2$-to-electron number density ratio with the number density of Zn atoms obtained by actinometry. The results are presented in Fig. 3. This ratio decreased by approximately a factor of 5 when when going from -115V to -300 V, i.e. as the zinc number density increased by about one order of magnitude. These results were correlated to the predictions of a simple collisional-radiative model based on the resolution of the particule balance equation of Ar $^3P_2$ atoms. In this model, the Ar $^3P_2$-to-electron number density ratio becomes [1]

$$\frac{n_{Ar\,^3P_2}}{n_e} = \frac{k_{exc}(T_e)n_{Ar}}{\left(D_{eff}/\Lambda^2\right) + \sum_i k_{e,i}n_e + \sum_j k_{q,j}n_j} \qquad (1)$$

where k_{exc} is the electron-impact excitation rate, (D_{eff}/Λ^2) represents the diffusion losses, the sum over i accounts for losses by collisions with electrons, and the sum over j accounts for losses by quenching on neutral species, including the Penning reaction $Ar\,^3P_2 + Zn \rightarrow Ar + Zn^+ + e$.

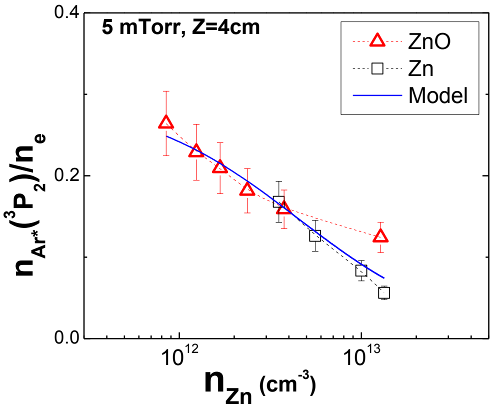

Fig. 3: Influence of the Zn number density on the Ar $^3P_2$-to-electron number density ratio at 4cm from the Zn and ZnO targets.

For all experiments, since the pressure was kept constant and $<T_e>$ was also constant (see Fig. 2), the only parameter that varies in Eq. (1) is the number density of Zn in the sum over j. The set of data presented in Fig. 3 was fitted with a function $a/(b+c\,n_{Zn})$, where a, b, and c are fitting parameters. An excellent fit was obtained indicating that Penning ionization of sputtered particles are indeed playing an important role in the range of conditions investigated. In addition, the reaction rate for the Penning ionization of Zn atoms (related to c) was 4.5×10^{-8} cm^3/s. As for $k_{exc}n_{Ar}$ (related to a), it was 6×10^4 s^{-1}, which is consistent with the value expected for $<T_e>$=4eV [2].

4. Conclusion

We have investigated the role of sputtered particules on the properties of rf magnetron sputtering discharges used for the deposition of ZnO-based materials. The Ar $^3P_2$-to-electron number density ratio decreased with increasing number density of sputtered Zn atoms; a feature that was consistent with the predictions of a collisional-radiative model accounting for Penning ionization processes.

References

[1] L. Maaloul, S. Morel, and L. Stafford, J. Vac. Sci. Technol. A **30**, 021301 (2012).
[2] M. V. Malyshev and V. M. Donnelly, phys. Rev. E **60**, 6016 (1999).
[3] O. Zatsarinny and K. Bartschat, Phys. Rev. A **71**, 022716 (2005).
[4] J. Hopwood and F. Qian, J. Appl. Phys. Vol. **78** No. 2 (1995).