# APPLICATION OF PLASMA MASS SPECTROMETRY TO REACTIVE PLASMA PROCESSES

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Keywords: Plasma Mass Spectrometry, High Rate Sputtering

Compounds: Tin doped $In_2O_3$

## ABSTRACT

Plasma mass spectrometry and other analytical methods have been used to observe conventional sputtering and plasma etching processes (1, 2, 3).
The arrangement used for the ion analysis directly from the plasma, the plasma mass spectrometer and some of its application have been described elsewhere (4, 5, 6).
The applicability of this system to the high rate sputtering process (7, 8) is given by its small entrance part. This allows the extraction of ions within the space between the electrodes configuration of the sputtering system. The application of the ion analysis during reactive sputtering of indium with 5 % tin in an argon/oxygen plasma to form $In_2O_3$ is described.

## 1. INTRODUCTION

During the last years high rate sputtering has been introduced to industrial thin film production (9, 10). The high deposition rates observed for this technique are originated by the application of a magnetic field at the cathode. By the influence of this magnetic field combined with the electric field at the cathode the electrons are concentrated at a sharp defined region in front of the cathode. In the low pressure range most of the ions are formed in the volume containing the plasma of high density. For the analysis of ions in this region the plasma mass spectrometer has been used. Most of the reactive species are generated by electron impact in the plasma of high density. It has to be expected that the basic conditions for the controlled deposition of target material and to form compounds with the reactive gas are present in the plasma.

## 2. EXPERIMENTAL

Semiconducting tin doped $In_2O_3$ thin films have been prepared on soft glas substrates. The 5 x 5 cm² substrates have been fixed on a rotating substrate holder of 50 cm diameter. The potential at the substrate holder was floating. Excentrically from the center of rotation a high rate sputtering cathode has been installed, to allow the coating of substrates during rotation takes place.
The cathode was provided with a permanent magnet consisting of Co/Sm - material. At the target surface of the metallic Tin-Indium-target a maximum magnetic field strengh of 250 Oerstedt has been found. The target diameter was 75 mm, the thickness 6 mm and the distance to the substrate holder was 25 mm. A schematic of the arrangement is shown in fig. 1.

The cylindrically entrance part of the plasma mass spectrometer has been positioned to be with the entrance whole 7 mm below the eroded zone.

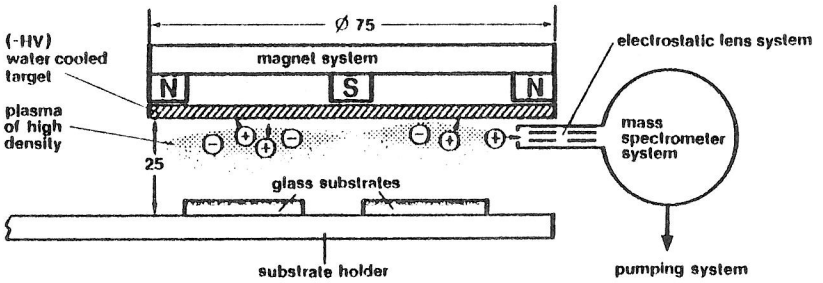


fig. 1 Schematic of the high rate sputtering system combined with the plasma mass spectrometer

The inlet of the sputtering gas composition has been controlled by mass flowmeters. Three gases, Ar, $O_2$ and $H_2$ have been introduced into the vacuum chamber. The total gas pressure has been in the $10^{-2}$ mbar range.

The quadrupole mass spectrometer used in the PMS-system works optimally at a pressure below $10^{-5}$ mbar. Then the analyzed particles have a low probability to interact with neutrals on the path to the ion detector.

For the detection of ions a secondary electron multiplier with adjustable current gain has been used.

To reduce the pressure the mass spectrometer chamber is pumped differentially by a grease lubricated turbomolecular pump-system.
Using a 300 µm-diameter whole to form the entrance aperture of the analytical system during sputtering the pressure in this system is lower than $10^{-5}$ mbar.

The mass filter system has to be electrically adjusted with respect to the potential where most of the analyzed ions are originated.

The production of 400 - 700 nm thick $In_2O_3Sn$ doped n-type semiconducting infrared reflecting and in the visible range of the spectrum high transparent films has been controlled using the plasma mass spectrometer.

During the film preparation selected elements have been observed. In the visible range of the spectrum the light transmission of the film-glass system has been recorded. After annealing the films in an argon atmosphere at 300 °C the sheat resistance and the light transmission have been measured.

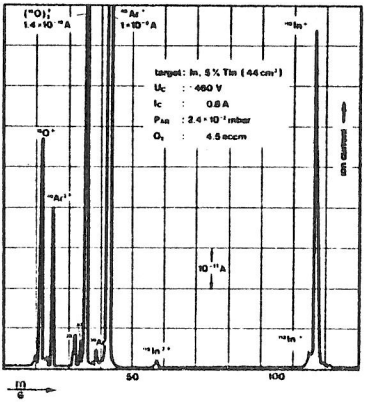


fig. 2

mass spectrum of ions recorded during the reactive deposition of indium/tin

In Fig. 2 a typical mass spectrum recorded during the coating process is shown. The 115 $In^{2+}$-signal obtained in this spectrum is in the order of some percent of the 115 $In^{+}$-signal. A comparable ratio is given for $40Ar^{2+}$ and 40 $Ar^{+}$. For the $In^{2+}$ the ionization level is at 18.86 eV, this means that a penning ionization by argon metastables (E*-11.49 and 11.66eV) is not possible.

Combined with the fact that no $In^{+}Ar$ ion molecules have been observed it is indicated that electron impact ionization is the dominant ionization process for the neutrals sputtered from the target.

The signal for $Ar_2^{+}$-ion molecules given by interaction of argon atoms with highly exited argon atoms was not found in the spectra. At a pressure of 2.4 x $10^{-3}$ mbar Ar in an conventional RF or DC disharge the In ($E_I$ = 5,8 eV) is mainly ionized by the penning ionization process. In this case $Ar_2^{+}$ ion molecules have been observed. For the process analysis a peak processor has been used.

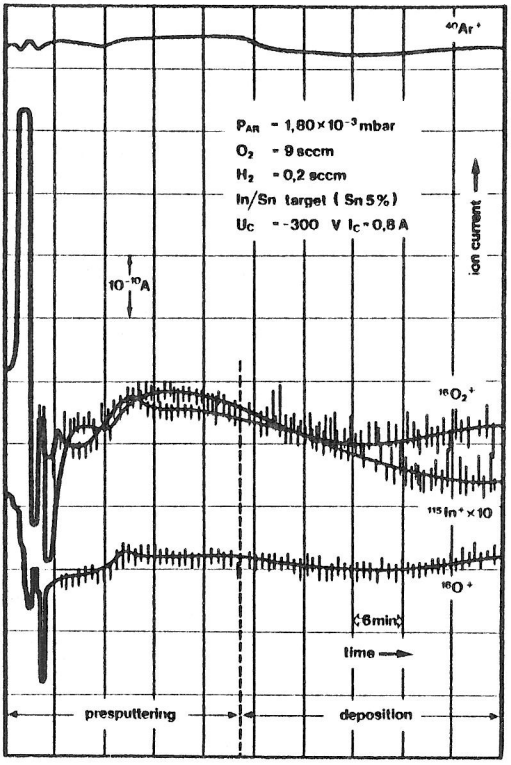


fig. 3

ITO process control by plasma ion analysis

The $^{16}O^+$. $(^{16}O)_2^+$, $^{115}In^+$ and $^{40}Ar^+$ signals and the background signal compared with the current amplification factor are repeatedly controlled over the process time. This is shown in fig. 3.
Beginning with the presputtering of the target the amplitudes of the ion signals change rapidly.
After a presputtering time of 40 minutes a process stability over some minutes process time is reached.
Then the ion signals for $^{40}Ar^+$ and $^{16}O^+$ are nearly constant.

The flux of indium atoms going from the target to the substrates is proportional to the measured $^{115}In^+$-signal height if the plasma parameters are constant.

The deposion rate and the $In^+$ amplitude are decreasing in the order of 20 % within the total coating time of 30 minutes. This indicates that the target is oxidized under the conditions giving a proper fully oxidized and transparent indium oxiden film.

To prevent the oxidation process at the target a small percentage of hydrogen has been used in the discharge. The hydrogen content can be optimized increasing the hydrogen flow until the long term oxidation of the target stops.

After heating the films one hour at 300 °C in nitrogen atmosphere the electrical conductivity increases. Free electrons are given from the oxide structure being formed during heating.

Controlling the $O^+$ to $In^+$ ratio all films being prepared in these experiments are in a range of specific electrical resistance between $2.4 \times 10^{-4}$ Ω cm and $3.9 \times 10^{-4}$ Ω cm.

The deposition rates depending from the power density of the target and the content of oxygen in the discharge have been found between 20 and 60 Å $s^{-1}$. The optical transmission in the visible range between 380 and 800 nm wavelength observed for 250 nm thick film is typically better than 75 %.

The infra red reflection at 8 µm wavelength is higher than 86 %.

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