PLASMA DIAGNOSTICS AND FILM CHARACTERIZATION OF TiN FILMS DEPOSITED IN A HOLLOW CATHODE ARC DISCHARGE

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Abstract

The influence of the palsma parameters on film deposition has been investigated for TiN_x films. In this paper we will focus on the dependence of the N / Ti ratio and the film structure on gas composition and substrate voltage. The films were deposited by hollow cathode arc evaporation (HCAE) on Si (100) wafers. Different N_2 gas flows and substrate voltages have been used. Electron temperature and electron density were determined by LANGMUIR-probe measurements. In addition the discharge was characterized by optical emission spectroscopy (OES) and energy resolved mass spectrometry (plasma monitoring). The composition of the deposited films was evaluated by means of x-ray photoelectron spectroscopy (XPS) and the structural properties were analysed by x-ray diffraction (XRD).

Both increasing N_2 gas flow and increasing negative substrate voltage at medium N_2 gas flow result in an increased N/Ti ratio. Correlated to the increase of N/Ti a decrease of the XRD peak-width and a changing texture has been observed. For high N_2 gas flow the x-ray pattern becomes similar to the pattern of polycrystallin bulk TiN. The results of energy resolved mass spectrometry demonstrate the dominant influence of the ions on the TiN formation.

1 Introduction

Plasma-deposition is one of the most common methods for deposition of thin films. In addition to substrate temperature and discharge power [1], gas composition and ion energy strongly influence composition and structure of the deposited film.

In earlier works the dominant influence of the ions on the formation and properties of Ti-films on Si (100) wafers has been demonstrated [3]. The present paper will give results of characterizing the discharge and the deposited TiN_x films. Mainly the results of the energy resolved mass spectrometry are correlated to the film properties determined by XPS and XRD. The experimental setup is described in section 2. The results for the different N_2 gas flows and substrate voltages are discussed in section 3, part A and part B respectively.

2 Experimental Setup

The films have been deposited in a Hollow Cathode Arc Evaporation Device (HCAED) on Si (100) wafers. The residual pressure of the preparation chamber was at about 10^{-3} Pa. The TiN_x films have been prepared in an $Ar+N_2$ gas mixture at constant Ar gas flow of 60 sccm. Without nitrogen the total pressure was 0.2 Pa. For all depositions the discharge current was 220 A and a voltage of 25 V between the hollow cathode anode and the crucible was chosen. Two different film series have been prepared. First, the substrate was put to ground and N_2 gas flow was increased from 0 sccm to 85 sccm. In a second series, the N_2 gas flow was kept constant (20 sccm) and the substrate voltage U_{sub} was varied from 0 V to -100 V. The plasma was characterized by LANGMUIR probe measurements next to the substrate. The second derivative of the probe current ($\frac{d^2 I_{pr}}{(dU_{pr})^2}$) was used to determine electron density n_e, mean electron energy $\bar{\epsilon}$ and plasma potential U_{pl} [4]. Also OES spectra of Ti I ($\lambda = 365.35$nm), Ti II ($\lambda = 368.52$nm) and Ar I ($\lambda = 763.51$ nm) were detected with a Jobin Yvon HR 640 spectrometer. Plasma characterization was completed by energy resolved mass spectrometry with a Hiden plasma monitor (HAL 301 S/EQP). The orifice of the plasma monitor was placed right at the position of the target. Reference potential of the plasma monitor and orifice were put to substrate potential. Neutrals and ions reaching the substrat were measured as well as the ion energy distribution function (IEDF). Preparation chamber and plasma dignostic are described in [2].

After depostion films have been analysed by XPS and XRD. The XPS-data presented in section 3 are from bulk TiN_x after sputter cleaning. The N / Ti ratio of the films have been evaluated using the peak areas of the N 1s and the Ti $2p_{3/2}$ peak and the well known sensitivity factors [5]. The peak areas have been calculated using a fit procedure [6]. The structural properties of the grown films have been analysed by XRD in Bragg Brentano and in grazing incidence geometry with a Siemens D5000 diffractometer equipped with a thin film attachement.

3 Results and Discussion

Part A: Variation of the N_2 gas flow

The N_2 gas flow was varied from 0 sccm to 80 sccm with the substrate put to ground. N_2 and Ar neutrals were found with the plasma monitor where as Ti neutrals could not be detected for any preparation condition. The plasma monitor was not mounted perpendicular above the Ti crucible so that the Ti neutrals entering the plasma monitor hit its wall. In contrary to argon and nitrogen, titanium has a high sticking coefficient and can not be detected. This problem demonstrates that plasma monitoring can only deliver qualitative results. With increasing N_2 gas flow the Ar concentration remains constant and the content of nitrogen neutrals increases. The OES peak of Ti I decreases with increasing N_2 gas flow. As the OES peak hight only represents the density of the excited Ti species, the decreas might be caused from a change in the EEDF reducing the amount of excited Ti. From the OES spectra it can not be distinguished wether only the amount of excited Ti decreases or wether there is a decrease of the total amount of Ti. Further investigations will be done to decide this question.

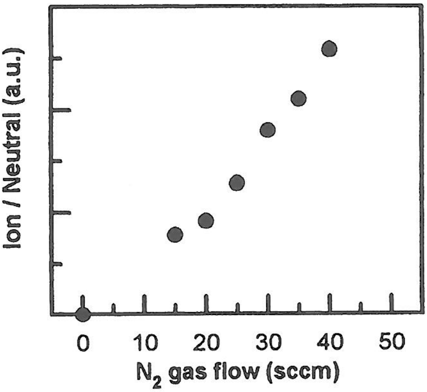

Fig. 1: Ion to neutral ratio for nitrogen

In addition to the neutrals, Ar^+, Ar^{++}, Ti^+, Ti^{++}, ${N_2}^+$ and ${N_2}^{++}$ or N^+ have been detected in the SIMS mode of the plasma monitor. The IEDF is very broad and remains constant for all N_2 gas flows. It is almost symmetric around the plasma potential what might be due to instabilities of the discharge current. While the area of the Ar and Ti ion peaks remain constant, the number of ${N_2}^+$ and ${N_2}^{++}$ ions increases with increasing N_2 gas flow. Comparing the nitrogen ions with the neutrals an increase of the ion to neutral ratio can be observed (Fig. 1). So an increase of the total amount of nitrogen can be found as well as an increase of the ion to neutral ratio for the reactive gas.

The common influence of these two effects on the properties of the TiN_x films is shown in Fig. 2 and 3. For N_2 gas flow lower than 40 sccm the XPS measurements show an increase of x from 0 to approximately 1. The binding energy of the Ti $2p_{3/2}$ electron increases from 453.8 eV (pure Ti) to 454.6 eV (TiN). For higher N_2 gas flows N / Ti and the peak position remain constant. The excess N_2 can not be built in but is pumped.

In Fig. 3 the interplanar spacings of the (002) planes in the hexagonal α-Ti (hcp) and the (111) planes of the cubic δ-TiN (fcc) are given. A transition from the hcp to to the fcc phase is observed at a N_2 gas flow of 20 sccm. Lattice parameters higher than the literature values indicate overstoichiometry or lattice distortion.

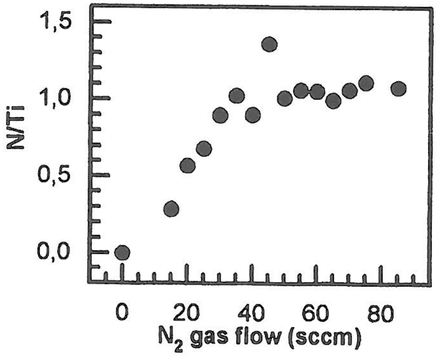

Fig. 2: Film composition vs. N_2 gas flow

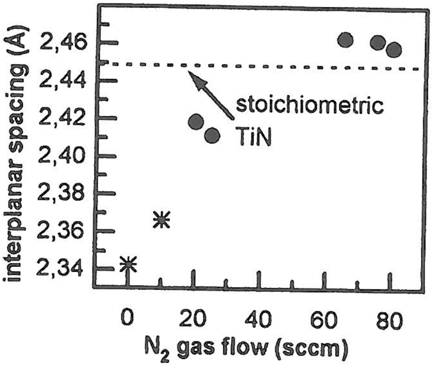

Fig. 3: Interplanar spacings of (002) α Ti (∗) and (111) δ TiN planes (•)

The composition x can be calculated from the comparison of integral intensities of even and odd type reflections [7]. The composition calculated from (111) and (222) reflections correlate well with x determined from XPS.

The understoichiometric films show strong preffered orientation with the close packed lattice planes parallel to the substrate surface. With increasing N_2 gas flow the XRD patterns become comparable with polycristalline TiN. This suggest different growth mechanisms depending on the N_2 gas flow. At low N_2 gas flow nitrogen can be incorporated on the octahedral sites of both the hcp lattice and fcc sublattice and thus form TiN_x (canon ball rule). TiN_x is formed with (111) orientation. A further increase of the N_2 gas flow results in an increase of the ion to neutral ratio (Fig. 1). The increased bombardement with ions forms TiN_x without preffered orientation. The same effect has been described for reactive sputtered TiN films by Petrov et al. [8].

Part B: Variation of the Substrate Potential

The substrate potential was varied from 0 V to -90 V at constant N_2 gas flow of 20 sccm.

The plasma parameters determined by LANGMUIR probe measurement were indepedent on the substrate voltage ($n_e \approx 4.5 \times 10^{16}$ m^{-3}, $\bar{\epsilon} \approx 6$ eV, $U_{pl} \approx 12$ V). Also the emission spectra of Ti I, Ti II and Ar I did not change with increasing substrate voltage. The results of plasma monitoring for $U_{sub} = 0$ V and $U_{sub} = -70$ V are shown in Fig. 4. Integration of the peaks and correction with the transmission of the plasma monitor for different ion energies result in a constant value for all substrate voltages. The constant ion current to the substrate is determined from the ion density in the presheath of the discharge.

Only the mean ion energy and the IEDF varied with U_{sub}. The ion energy is shifted for all ions by the amount of the substrate voltage. Additionaly the IEDF of the single and double charged Ar and N_2 ions show low energy tails for negative U_{sub}. As the mean free path is large in relation to the thickness of the plasma sheath these low energy tails can not be due to collisions. Probabely argon and nitrogen ions are backscattered from the substrate surface. Titanium has a high sticking coefficient (≈ 1) and no backscattered ions can be observed.

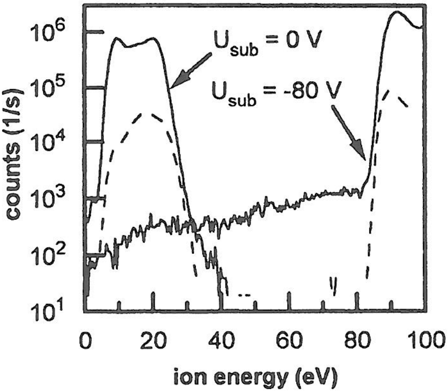

Fig. 4: Ar^+ (solid) and Ti^+ (dashed) IEDF

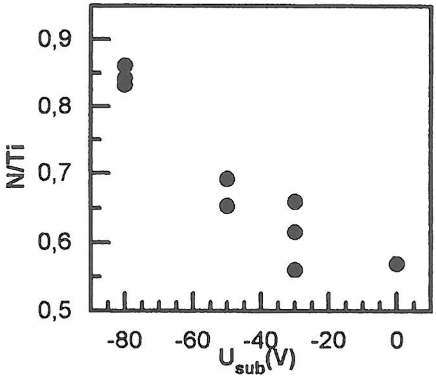

Fig. 5: Film composition vs. U_{sub}

As the amount of the low energy ions is small mainly the increase of the ion energy is responsible for the changes of the film properties. The XPS spectra show an increase of the N / Ti ratio for U_{sub} varied from 0 V to -80 V (Fig. 5). As the ion energy is less than 100 eV ion implantation can not be the reason for this increase. Probabely the ions deliver some energy which increases the probability for the formation of Ti-N bondings. The results demonstrate that the ion bombardement increases the efficency for the incorporation of nitrogen.

The influence of U_{sub} on the microstructural properties is appreciable. The preffered orientation observed for low N_2 gas flows at $U_{sub} = 0V$ disappears with negative substrate voltage. This is similar to part A where crystallites become more statistically oriented with increasing ion bombardement. The interplanar spacings are comparable with stoichiometric TiN. The line profiles are considerably broadened. Domain sites and microstrains were calculated by single line fourier method (WARREN-AVERBACH-plot [9]). The domain sizes decrease from 25 nm ($U_{sub} = 0V$) to 6 nm ($U_{sub} = -30V$) and increase to 12 nm ($U_{sub} = -80V$). The mean microstrain rise up about one order of magnitude.

4 Summary

The influence of N_2 gas flow and substrate voltage on the formation of TiN_x films was investigated. Plasma monitoring delivered information about the neutral- and ion composition as well as the IEDF. Correlating these measurements with the film properties demonstrated the influence of the ions on the film growth.

The composition and microstructure of TiN_x depends on two parameters: first the total supply of nitrogen, correlated with the amount of reactive gas ions (part A) and second the ion energy (part B).

For both, varying the N_2 gas flow and U_{sub} the preffered orientation is influenced from the ion flux to the substrate. Increasing ion energy enhances the efficiency of nitrogen incorporation and causes increasing lattice distortion.

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