Time-resolved measurement of film growth during reactive high power pulsed magnetron sputtering (HIPIMS) of titanium nitride

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Abstract

The growth rate during reactive high power pulsed magnetron sputtering (HIPIMS) of titanium nitride is an inherent time-dependent process. By using a rotating shutter setup it is possible to gain an insight into its variation with a temporal resolution of up to 25 µs. In this apparatus a 200 µm slit is rotated in front of the substrate synchronous with the HIPIMS pulses. This ensures that the incoming growth flux is laterally distributed over the substrate. By measuring the resulting deposition profile with profilometry and x-ray photoelectron spectroscopy, the temporal variation of the titanium and nitrogen growth flux per pulse is deduced. The analysis reveals that film growth occurs mainly during an HIPIMS pulse, with the growth rate following the HIPIMS phases ignition, current rise, gas rarefaction, plateau and afterglow. The growth fluxes of titanium and nitrogen follow slightly different behaviours with titanium dominating at the beginning of the HIPIMS pulse and nitrogen at the end of the pulse. This is explained by the gas rarefaction effect resulting in a dense initial metal plasma and metal films which are subsequently nitrified.

(Some figures may appear in colour only in the online journal)

1. Introduction

Reactive magnetron sputtering is a well-established technology used for depositing materials such as metals or oxides, carbides and nitrides. Applications span from hard coatings to bio compatible layers and are used in many industrial sectors, such as the automobile and medical industries. It is known that the properties of the resulting film structure are governed by the dissipated energy per atom during the growth process. Furthermore, ion fluxes are able to collisionally enhance the surface mobility of absorbed species [1, 2]. The energy of the incoming ions can be controlled by additional substrate biasing or by varying from a balanced to an unbalanced magnetron configuration. Therefore a high ionization degree is desirable for achieving a good control over film properties. The inevitable high power loads on the target due to the necessary high powers are a limiting factor for this approach. This limitation can be circumvented by the use of high power pulse magnetron sputtering (HIPIMS). Here, short high power pulses generate an almost fully ionized plasma followed by a long off time to limit the thermal stress of the targets [3]. The beauty of this method is that, with exception of the power supply, no changes on the magnetron or setup are required.

HIPIMS plasma have also been employed to deposit compounds such as oxides, nitrides or carbides. These are produced by the addition of reactive components such as oxygen, nitrogen or methane to the argon sputter gas. The additional reactive gas molecules are dissociated in the plasma and a compound is formed on the substrate together with the sputtered metal from the target. These reactive neutrals, however, may also react with the metal target. This has drastic consequences for the process, because the sputter yield at the target depends sensitively on the surface composition usually having a much smaller sputter yield for the poisoned
target surface. As a consequence, the growth rate decreases drastically and the system turns into its poisoned state \[4\]. This can be adjusted by using proper feedback control of the plasma process. The need for feedback control is apparently very much reduced for HIPIMS processes compared to dcMS processes. This has been attributed either to the sputter wind emerging from the target, which results in gas rarefaction and a corresponding lower flux of reactive neutrals towards the target \[4, 5\] or to the intense sputtering of any compound at the emerging from the target, which results in gas rarefaction and processes. This has been attributed either to the sputter wind due to the high voltages of the HIPIMS process \[6\].

These effects and the interplay between working gas, reactive gas and target surface might better be understood when the growth processes during a single HIPIMS pulse can be temporally resolved. Typical pulse lengths are between 50 and 200 $\mu$s. During an HIPIMS pulse, current and voltages constantly change and reach peak powers from 0.5 to 10.0 kW cm$^{-2}$. The $IV$ characteristics give an insight into the state of the plasma, allowing the discrimination of five distinct phases \[7\]. Particle fluxes per pulse are in the order of 10$^{15}$ cm$^{-2}$ s$^{-1}$. This means that only 10$^{-7}$ monolayers are deposited per discharge. Furthermore, the growth rate is not constant during a pulse but changes with the titanium content of the plasma. It is therefore almost impossible to measure the varying growth rate directly during a single pulse by using methods like ellipsometry or quartz microbalances in the environment of an HIPIMS plasma reactor. A useful way to measure film growth is by using a rotating shutter in front of the substrate, which was introduced recently \[8\]. It is used to distribute the temporal changing incoming particles on a lateral scale on a substrate. By using that method, the individual growth processes during titanium sputtering have been resolved \[9\]. The individual phases as described by Gudmundsson et al \[7\] could be clearly identified from ignition, current rise, gas rarefaction, plateau and afterglow. In this paper we develop this method further by combining it with x-ray photoelectron spectroscopy (XPS) analysis of the deposition profiles. Thereby, the growth rate can be temporally separated into a metal part and a compound part.

2. Experiment

A two inch magnetron with a titanium target is used as sputter source. The magnetron is powered by a Melec HIPIMS power supply. The power supply is operated in voltage mode. In the used power range it is capable of maintaining the voltage level during the whole pulse.

The thin films are deposited on a silicon wafer, which can be introduced in the substrate holder behind the rotating shutter via a load lock system. The working pressure in the chamber is 0.25 Pa with argon as the background gas. The pumping speed was constant during all experiments. Gas flows in the range of 15–28 sccm were used but also kept constant for a single experiment. The base pressure in the chamber is 4 × 10$^{-3}$ Pa. A constant HIPIMS pulse length of 200 $\mu$s and a duty cycle of 6% is applied to the target. The average power is adjusted to $(P) \simeq 40$ W, while the peak power goes up to 0.75 kW. The utilized $Vf$ probe consists of an LEM LA305-S current transducer with a response time $t_r < 1$ $\mu$s and a $dI/dt > 100$ A $\mu$s$^{-1}$ and an LEM CV3-1500 voltage transducer with $t_v = 0.4$ $\mu$s and $dV/dt = 900$ V $\mu$s$^{-1}$. Voltages and currents are measured at the output of the Melec power supply.

Nitrogen is used as the reactive gas for all experiments. Control of the hysteresis effect is achieved by using an active control system for the nitrogen flux. This system monitors the intensity of the titanium line at 307 nm (3d$^2$2p $\rightarrow$ 3d$^2$4s). The intensity of this line is damped with increasing nitrogen concentration. It is therefore used as an actuating variable to regulate the reactive gas influx. The optical emission of the HIPIMS plasma is monitored by a Hamamatsu RCA 78-09 IP28 photomultiplier. The photomultiplier is directed between the magnetron and the substrate. An optical filter with a centre wavelength of 307 ± 2 nm and an FWHM of 10 ± 2 nm is placed in front of the photomultiplier in order to isolate the titanium line of interest. The signal of the photomultiplier is processed by an analogue integrator and an amplifier followed by an analogue-to-digital converter. This signal is the input parameter for a software PID-controller which then regulates the reactive gas influx via a fast-acting Pfeiffer RME 005 A valve. In all experiments, the emission intensity was kept at 15% of the maximum emission intensity for the whole deposition time.

In this study the deposition time was six hours, which is necessary because of the rotating shutter. Details of the diagnostic method are presented elsewhere \[9\]. After deposition, the substrates are extracted and the film deposition profiles on the wafers are measured using profilometry. In order to improve the accuracy of the profilometry it is helpful to create a step edge between substrate and film. Such a step edge is produced first by placing a vacuum tape on the substrate. After deposition, this vacuum tape is removed leaving a sharp edge behind. The accuracy of the method is then ±10 nm.

The minimum spread of the deposition profile can be used to estimate the temporal resolution of the shutter concept. It can be deduced if deposition with a stopped shutter takes place. The minimum temporal resolution in this study is 25 $\mu$s for the shutter rotating at 30 Hz. Details of this calibration can be found elsewhere \[9\].

The composition of the deposition profiles is ex-situ measured by XPS. These measurements are performed by using a Versaprobe Spectrometer from Physical Electronics, using monochromatic Al $K\alpha$ radiation at 1486.6 eV and a pass energy of 23.5 eV, which results in a FWHM of 0.58 eV for the Ag3d$_{5/2}$ core level of a clean silver sample. The measurement spot has a diameter of 200 $\mu$m. The TiN samples are introduced to the measurement chamber without any prior cleaning. Due to the ex-situ measurement, the samples may react with ambient air. We assume that any Ti atom not saturated by N may react with O$_2$ to form TiO groups. The surface of the sample is not neutralized. It is expected that the samples show good conductivity. Further, the relative position of the photoelectron lines is independent of the sample composition. The take-off angle between the sample surface and the analyser level is 45°.

Measurements are done parallel to the deposition profile, where in a first step a survey spectrum is taken every 1 mm.
Markings on the silicon wafer serve as a reference position for XPS and profilometry. The N1s photoelectron line is used to define the measurement spots for a more detailed investigation. In regions where N1s is observed, the distance between two measurement spots is chosen as 200 μm, while it is 1000 μm for the outer parts where no nitrogen is found. By using MultiPak™ software, the ratios of N1s, O1s and Ti2p are determined by weighting the data with their individual sensitivity factors. These composition profiles can be used to deconvolute the deposition profile, obtained by profilometry, into its individual components.

3. Results and discussion

3.1. Deposition profile for titanium and nitrogen

The deposition profile has been measured for a 200 μs pulse with 6% duty cycle at a pressure of 0.25 Pa and \( \langle P \rangle \approx 40 \text{ W} \), as shown in figure 1(a). The start and the end of the pulse are indicated with dashed lines. The profiles are synchronized in time by regarding the end of the current pulse. Some deposition might be indicated before plasma ignition, although it is only caused by the finite width of the deposition profile [9].

The evolution of the smoothed current is presented in figure 1(b) with the individual HIPIMS phases indicated as 1 (ignition), 2 (current rise) [10], 3 (gas rarefaction) [5, 11], 4 (plateau) [12], and 5 (afterglow) [13]. The deposition rate follows these phases in a characteristic manner. At first, the plasma starts (phase 1), the current rises steeply (phase 2) and finally goes through a maximum and declines again (phase 3). At the same time, the growth rate increases only slowly in phase 2. A strong increase of the growth rate is observed in phase 3 followed by saturation at a constant value (phase 4). After the end of the pulse, the growth rate decreases sharply with a time constant to the order of 100 μs followed by a tail with a slower decay constant (phase 5). For details see [9].

This temporal evolution of the growth rate can now be separated into the contribution of titanium and nitrogen in the film by measuring along the deposition profile with XPS. Figure 1(a) shows the corresponding concentrations in at% of titanium, nitrogen, and oxygen.

The XPS analysis reveals that all titanium in the deposition profiles is either nitrided or oxidized. This is attributed to the fact that the film growth during the experiment is spread by the rotating shutter along the silicon wafer, rendering the absolute film thickness and thus the local growth rate very small. If we deposit 100 nm titanium in 6 h, as shown in figure 1, we can deduce an average titanium flux of \( 1.3 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \). The titanium flux during the pulse for a duty cycle of 6% is 2.2 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1}. At these small growth rates, the flux of residual gas species such as O2 and H2O from the base pressure becomes important. If we take a typical base pressure of 10^{-8} mbar, a typical flux density of these residual species of the order of 10^{13} \text{ cm}^{-2} \text{s}^{-1} is obtained. Consequently, we interpret the composition of the deposition profiles as follows: during the plasma pulse, the fluxes of titanium and nitrogen are higher than the fluxes from the background pressure and the stoichiometry of titanium versus nitrogen in the deposited material depends on the incident fluxes of both species times their corresponding sticking coefficients. If titanium atoms remain metallic, they are readily oxidized by incident O2 and H2O from the base pressure during the off phase of the plasma pulse or by post oxidation after extraction of the samples from the system. Based on this assessment, we regard only the ratio of titanium versus nitrogen in the deposition profile as a real fingerprint of the reactive HiPIMS process. Therefore, only the ratio between titanium and nitrogen is discussed in the following.

One observation is that the titanium and the nitrogen profile do not exhibit the same shape. At the beginning and at the end of the deposition profile, the surface is titanium rich with a very low concentration of nitrogen. Such behaviour may be consistent with the gas dynamics in an HIPIMS pulse:

- **Start of the HIPIMS pulse.** At the beginning of the plasma in phases 1 and 2, a strong gas rarefaction sets in, because the sputtering wind expels the neutral reactive gas in front of the target [5]. The dominant contribution of titanium in comparison to nitrogen to the growth flux in the beginning of the pulse is explained by the intense sputtering of titanium during the current maximum, which causes a much higher metal flux to the surface in comparison to the nitrogen flux. Apparently, the dissociation of nitrogen in the plasma is not efficient enough to generate stoichiometric Ti:N. This might be due to gas rarefaction or simply due to the fact that titanium sputtering and nitrogen dissociation scale differently with plasma current. Later in the pulse, the fluxes of titanium and nitrogen come to an equilibrium after the initial current peak goes into the plateau phase 4 and the nitrogen uptake of the surface can take place.
end of the HIPIMS pulse. At the end of the pulse, the nitrogen concentration drops much more sharply than the titanium concentration. One may speculate that the incorporation of nitrogen into the layers is dominated by incident nitrogen ions rather than neutrals, because only ions disappear on a short time scale of the order of 100 µs. A low sticking coefficient for incident nitrogen atoms is a reasonable assumption.

It is important to note that the deposited atoms before and after the HIPIMS pulse constitute only a small fraction of the total amount of deposited material. Nevertheless, it indicates that the HIPIMS process is a sequential process where a titanium rich layer is followed by a TiN layer. If one regards the temporal evolution of the growth rate, the profiles are titanium rich for all three pressures. The biggest difference is in the pressure dependence of the growth rate. With a pressure increase from 0.25 to 1.00 Pa, the growth rate diminishes almost by a factor of three. This indicates the transition from ballistic to diffusive transport of the species from target to substrate [9].

3.2. Dependence on pressure

The deposition profiles are further analysed for pressures of 0.25, 0.5 and 1 Pa, as shown in figure 2. All experiments are performed at an average power of ∼ 40 W, a pulse width of 200 µs and a duty cycle of 6%. This results in different target voltages for different pressures. Consequently, all experiments correspond to different HIPIMS plasma pulses. The deposition time for each sample is six hours.

With the knowledge of the concentrations of the different species (figure 2), it is possible to deconvolute the total deposition profile in a titanium and nitrogen profile (figure 3). All three measurements are consistent with the characteristics described in section 3.1. At the beginning and the end of the growth pulse, the profiles are titanium rich for all three pressures. The biggest difference is in the pressure dependence of the growth rate. With a pressure increase from 0.25 to 1.00 Pa, the growth rate diminishes almost by a factor of three. This indicates the transition from ballistic to diffusive transport of the species from target to substrate [9].

4. Conclusion

The dynamics of the growth rate and the composition of the resulting films are consistent with the current understanding of the physics of an HIPIMS pulse as being expressed by the five phases from ignition to afterglow. It is observed that the deposition profile is titanium rich with a low nitrogen content at the beginning and the end of the pulse. This behaviour seems to be coherent with the gas dynamics of an HIPIMS pulse. The temporal evolution of the growth rate is dominated by the dynamic change of the transport properties between collisional to ballistic transport whereas the composition depends on the gas depletion and the metalicity of the plasma.

Summarizing, one can state that the rotating shutter method is an excellent tool to resolve the time dependence of growth processes in pulsed plasmas. This will help to elucidate the nature of the HIPIMS growth process in the future.

Figure 2. Deposition profile (solid symbols), concentration of titanium, oxygen, and nitrogen (open symbols) at pressures of $p = 0.25$ Pa (a), $p = 0.5$ Pa (b) and $p = 1$ Pa (c) and a constant power of $\langle P \rangle \approx 40$ W. The vertical dashed lines indicate the start and the end of the HIPIMS pulse.

Figure 3. Deposition profile (solid symbols) and deconvoluted deposition profiles for titanium (open circles) and nitrogen (open diamonds) at pressures of $p = 0.25$ Pa (a), $p = 0.5$ Pa (b) and $p = 1$ Pa (c) and a constant power of $\langle P \rangle \approx 40$ W. The vertical dashed lines indicate the start and the end of the HIPIMS pulse.
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