Process stabilization during reactive high power impulse magnetron sputtering of Ce/Gd target

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Abstract. In this study, a simple approach to stabilize reactive high power impulse magnetron sputtering process in the transition zone between the metallic and oxide modes was investigated. The method is based on the use of peak current value as feedback and control signal. It was shown that the change in the state of the target surface causes almost instantaneous change in the amplitude and shape of the current pulses. To stabilize the deposition process, the pulse frequency was regulated to maintain a constant maximum discharge current. The hysteresis behavior and the variations of the pulse current waveforms over a wide range of O$_2$ flow rates and pulse frequencies during a reactive HiPIMS deposition of gadolinia-doped ceria (GDC) thin films in an Ar-O$_2$ atmosphere were examined. Stable process conditions were maintained at the O$_2$ flow from 0.9 to 3.9 sccm by adjustment of the pulse frequency from 1.45 to 2.9 kHz. GDC films deposited using peak current regulation exhibited a stable stoichiometry and high deposition rate in comparison with films obtained without process stabilization.

1. Introduction
High power impulse magnetron sputtering (HiPIMS) is a modification of the cathode sputtering in the crossed electric and magnetic fields, realized at high density of power, transmitted to the sputtering target in the form of periodic short pulses to prevent system overheating [1]. Extremely high peak target power densities of several kW·cm$^{-2}$ leads to the generation of plasma, with increased concentration and a high degree of ionization of the sputtered material [2]. This inherent feature of HiPIMS offers new possibilities for deposition of coatings with improved characteristics.

Recently, the reactive high power impulse magnetron sputtering (R-HiPIMS) has received much attention as an alternative to conventional magnetron deposition of compound coatings (nitrides, oxides, carbides) in the reactive gases (oxygen, nitrogen, methane). In a number of research works the capabilities of R-HiPIMS for the deposition of nitride coatings with dense microstructure, high hardness, wear and corrosion resistance [3, 4], as well as oxide films with high refractive index, low residual stress and surface roughness [5, 6] were presented. It is shown that the variation of the HiPIMS parameters allows changing the composition of compound coatings and their properties [7].

One of the main problems of reactive magnetron sputtering is to stabilize the sputtering process in the transition mode between the ‘metal’ and ‘compound’ sputtering mode, where instability due to hysteresis is commonly observed [8]. Stoichiometric coatings with high deposition rates can be
deposited in the transition mode only [8, 9]. To stabilize the reactive process different approaches can be used, for example, increasing the pumping speed of vacuum system [10], reducing the target area [11], pulsed reactive gas flow control [12], reactive gas partial pressure control [13], optical control of emission from plasma [14], varying the discharge parameters [15]. Most commonly used methods for stabilization of reactive magnetron sputtering process are based on partial pressure control by adjusting reactive gas flow rate. They are relatively expensive and have a low response rate. For many reactive sputtering processes, the time required to obtain a feedback signal, should not exceed several tens of milliseconds. Long delays lead to oscillations between high and low partial pressures. Thus, high-speed and cost-effective methods to stabilize reactive magnetron sputtering process in the transition mode are necessary. Shimizu et al [16] shown that the discharge current can be used as an effective reference parameter to stabilize the reactive process at any given set point in the transition regime.

In this study, the possibility of stabilizing the process of high power impulse magnetron sputtering of Ce$_{0.9}$Gd$_{0.1}$ target based on the approach developed by Shimizu et al was investigated. Gadolinium-doped ceria (GDC) films are regarded as the promising electrolytes for intermediate temperature solid oxide fuel cells because they have high ionic conductivity at 500–700°C [17]. In order to improve the reproducibility and repeatability of properties of GDC films deposited by R-HiPIMS, the influence of the reactive gas flow on the electrical parameters of the magnetron discharge with Ce$_{0.9}$Gd$_{0.1}$ target was investigated.

2. Methodology and Materials
Experiments were performed in a vacuum stainless-steel chamber with a volume of 25 l and a base pressure 10$^{-4}$ Pa. A Ce$_{0.9}$Gd$_{0.1}$ disk with a diameter of 100 mm and a thickness of 6 mm was used as sputtering target. Unipolar pulses with a length of 50 μs and a frequency in the range from 400 to 3500 Hz were supplied by an APEL-M-HIPIMS power supply (Applied Electronics). The average sputtering power delivered to the target was varied in the range from 1 to 2 kW depending on the discharge current. The power supply allows to generate pulses of voltage and current with an amplitude of up to 1000 V and 1000 A, respectively. Magnetron discharge parameters were measured using the LeCroy WaveAce 1002 digital oscilloscope with a bandwidth of 60 MHz.

Ar and O$_2$ were introduced into the chamber through mass flow controllers. The Ar flow rate was fixed at 11 sccm and O$_2$ flow rate was varied from 1.5 to 6.0 sccm to grow films in the transition, and the oxide sputtering modes. GDC films were deposited onto 4 mm-thickness glass substrates with a size of 2.5×2.5 cm$^2$. Prior to the deposition, the substrates were cleaned by ion beam formed by multi-aperture ion source with anode layer APEL-IS-22CELL (Applied Electronics). The cleaning time was 5 minutes at a discharge voltage of 2 kV and a discharge current of 100 mA. Distance from target to substrate was about 80 mm. Deposition of GDC films was carried at room temperature. Film thickness was determined by the Linnik interference microscope MII-4. The stoichiometry of films was evaluated by measuring their integral transmittance in the visible wavelength range using an AvaSpec-2048 spectrometer (Avantes).

3. Results and Discussion
Waveforms of target current at various O$_2$ flow rates during the reactive HiPIMS process are presented in figure 1. A voltage waveform at O$_2$ flow of 3 sccm is also shown as a reference. The Ar flow rate was kept constant in all experiments while the O$_2$ flow was increased from 0.9 to 3.9 sccm. A constant pulse voltage with amplitude of 380 V and a frequency of 2 kHz was applied to the target. As can be seen from the waveforms variation, the slope at the initial rise of the waveforms gradually becomes less steep with increasing O$_2$ flow from 0 to 3 sccm. The peak current value $I_p$ at first slightly decreases from 55 to 45 A, but then begins to grow from 60 to 175 A with increasing O$_2$ flow from 3 to 3.9 sccm. The observed increase in $I_p$ with increasing O$_2$ flows in the later stage of the HiPIMS discharge pulse is a consequence of a higher O$^{1+}$ fraction near the target that is taking part in the sputtering process. Aiempanakit et al. [18] has been reported that the ionized oxygen determines the
discharge behavior in reactive HiPIMS, and its contribution to the increased discharge currents in oxide mode is significant. Furthermore, the secondary electron emission increases in the oxide sputtering mode resulting in an increased discharge current. It is known that the Ce oxide has a much higher secondary electron emission yield than the originating metal [19].

Figure 1. Variations of current waveform as a function of O\(_2\) flow rate. The data were obtained during a pulse with duration of 50 μs and a frequency of 2 kHz. A voltage waveform at O\(_2\) flow of 3 sccm was plotted as reference.

Figure 2 shows the variation of the target voltage and current amplitudes as a function of the O\(_2\) flow rate measured at constant frequency of 2 kHz and average power of 1.4 kW. At an O\(_2\) flow rate below 4.5 sccm, the increase of O\(_2\) flow results in a more or less constant target voltage and current amplitudes, indicating that amount of sputtered metal is sufficient to getter the majority of the oxygen. As the O\(_2\) flow rate is increased to 5.1 sccm, the target current amplitude increases from 100 to 170 A, but the target voltage amplitude remains almost unchanged. However, as the O\(_2\) flow rate increases slightly to 5.3 sccm, the target voltage amplitude decreases sharply from 353 to 238 V and the target current amplitude increases drastically to 270 A, indicating the change of the discharge from metallic to oxide mode. Furthermore increase of O\(_2\) flow rate results in no significant change in the target voltage and current amplitudes. As the O\(_2\) flow rate is decreased from 5.3 to 0.9 sccm, there is no noticeable change in the target current and voltage amplitudes, indicating that the target surface was completely covered by an oxide layer. A decrease of the O\(_2\) flow rate less than 0.9 sccm leads to a sharp increase the target voltage and decrease in the target current amplitudes, demonstrating the transition from oxide to metallic mode of sputtering. It can be seen that both the target current and voltage variations have a hysteresis behavior between the increasing and decreasing O\(_2\) flow.

To study the dependence of the \(I_p\) versus the pulse frequency, current waveforms at several pulse frequencies ranging from 1.45 to 2.9 kHz were obtained as shown in figure 3. A discharge voltage of 380 V, pulse duration of 50 μs and an O\(_2\) flow of 2.3 sccm were used during the experiment. As it observed in the experiment with O\(_2\) flow variation, the start of the current rise becomes slower with decreasing pulse frequencies. The \(I_p\) value begins to increase at frequency of 1.7 kHz and the lowest frequency corresponds to the highest peak current.
Figure 2. Variations of voltage and current amplitude as a function of O$_2$ gas flow rate. The data were obtained during a pulse with duration of 50 $\mu$s, a frequency of 2 kHz and average power of 1.4 kW.

Figure 4 shows the variations of peak target current depending on the pulse frequency at several O$_2$ flow rates. It can be seen that the O$_2$ flow in the range 1.5–4.5 sccm does not affect the dependence of the peak current on the frequency. As can be expected, $I_p$ decreases with increasing pulse frequency since the oxide layer of the target surface is reduced due to the increased sputtering. Therefore it is possible to control the state of the target surface by changing the pulse frequency.

Figure 3. Variations of current waveform as a function of frequency. The data were obtained during a pulse with duration of 50 $\mu$s and at an O$_2$ flow of 3 sccm.

Figure 4. Variations of $I_p$ as a function of pulse frequency. The data were recorded during a pulse with duration of 50 $\mu$s, average power of 1.4 kW and at several O$_2$ flow rates.

To demonstrate the stabilization of the reactive HiPIMS process in the transition regime, the peak target currents with the values of 100 and 150 A were kept constant by manual adjustment of the pulse frequency while varying the O$_2$ gas flow from 0.3 to 3.4 sccm. Variations of the controlled pulse frequencies with increasing O$_2$ gas flow are summarized in figure 5. The data were obtained at constant target voltage of 360 V. As the flow rate of oxygen increases, the oxidation of the target surface increases. This leads to an increase in the peak current. In order to maintain the peak current at the same value, it is necessary to increase the sputtering rate of the target by increasing the frequency. This increases the average discharge current and average power. When certain values of O$_2$ flow rate were exceeded, the frequency increased almost linearly with increasing O$_2$ flow. At a peak current of
150 A, the frequency starts to increase at a higher oxygen flow rate because the amount of sputtered material in this case is greater than at $I_p = 100$ A.

The usability of the $I_p$ regulation by the above described frequency control on the actual GDC film growth was evaluated by comparing the properties of films deposited at an $O_2$ flow rate of 3 sccm with and without $I_p$ regulation. Both processes were operated at constant target voltage of 360 V. Time variations of the $I_p$ during deposition with and without $I_p$ regulation are shown in figure 6.

**Figure 5.** Dependences of pulse frequency on $O_2$ flow rate during stabilization of discharge current on the values of 100 and 150 A.

**Figure 6.** Time variations of the $I_p$ and frequency during deposition process at an $O_2$ flow rate of 3 sccm. Comparison between with and without using $I_p$ regulation.

Without $I_p$ regulation peak current was 120 A in the beginning of the process and the frequency of 1.8 kHz did not change during the sputtering process. Over time, the $I_p$ begins to grow due to the oxidation of the target surface, until it reaches a value limited by the power supply. Simultaneously, the film deposition rate is significantly reduced due to target poisoning. The deposited film had a thickness about 20 nm (deposition rate of 1 nm/min) and transmittance of glass sample with film was 79%.

When a peak current of 120 A was kept constant, the frequency was regulated in the range from 1.7 to 1.95 kHz. In this case the film deposition rate practically did not change with time and was 40 nm/min. The transmittance of 800 nm thick film with glass substrate was 74%. The smaller transmittance value of the sample in this case is associated with a larger film thickness but, despite this, it corresponds to a stoichiometric oxide film.

It is known that in magnetrons the discharge parameters change with time due to erosion of the target. The target voltage decreases and the current increases in time as the target erode, because the magnetic field at the target surface increases. The deepening of erosion groove modifies the deposition conditions, and hence the hysteresis behavior [20]. To understand the time-evolution of the reactive HiPIMS process, the variations of peak voltage and peak current depending on the pulse frequency were measured for new Ce-Gd target and target with erosion groove depth of 3 mm (figure 7). It is clearly seen from the figure that with the target erosion, the voltage decreases by approximately 70 V, and the current increases by 20–25 A, but the character of the frequency dependencies of peak voltage and current does not change. This means that the applicability of the $I_p$ regulation by the frequency control does not depend on the depth of erosion of the target.

Approximate stoichiometries of deposited films were estimated by transmittance measurement. Stoichiometric GDC films had yellowish color and high optical transmittance. Films with oxygen deficiency had visually black color and low transmittance in visible range of spectrum. Variations of the deposition rate and film transmittance at altering the $O_2$ flow and peak current were clearly observed from the films deposited with $I_p$ regulation (figure 8).
Figure 7. Variations of peak voltage and current as a function of pulse frequency. The data were recorded at average power of 1.4 kW and O$_2$ flow rate of 3 sccm. The open symbols – new target, the closed symbols – eroded target.

Figure 8. Comparison of the deposition rates and transmittance of GDC films deposited with $I_p$ regulation at different peak currents and O$_2$ flow rate of 1.5 and 3 sccm.

It is seen that at a constant O$_2$ flow, the deposition rate decreases with increasing peak current. At low current of about 50 A, the target is sputtered in a metal mode, where the deposition rate is relatively high and deposited film has low transmittance. As the peak current increases, the frequency decreases, which results in a decrease in the sputtered material and in the oxidation of the target. At high current of about 170 A, the films become stoichiometric, but their deposition rate is reduced twice. An increase in O$_2$ flow rate from 1.5 to 3 sccm at a constant peak current leads to increase of the deposition rate of the GDC films by 15–25 nm/min. This result is due to the relatively higher applied average discharge power by increasing the pulse frequency for the higher O$_2$ flow conditions.

4. Conclusion
In this work, the variation of the pulse current waveforms as a function of reactive gas flows and pulse frequencies during a reactive HiPIMS process of GDC films deposition in an Ar–O$_2$ atmosphere has been investigated. It was shown that the reactive HiPIMS process in Ar/O$_2$ mixtures can be stabilized by maintaining a constant peak value of the current. This is because the peak current value is connected to the state of the target surface (metallic, poisoned or intermediate) and begins to increase as the target is covered with an oxide film. Therefore, it can be a reference parameter to stabilize the reactive process at any given set point in the transition regime. It should be taken into account that the working peak current will require correction as the target is eroded. GDC films were deposited using the $I_p$ regulation regime. A deposition process with relatively high deposition rate compared to the conventional HiPIMS process without $I_p$ regulation was demonstrated with maintained stoichiometric composition of the film.

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