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Process control of reactive magnetron sputtering of thin films of Zirconium dioxides

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Abstract

Thin films of zirconium dioxides were deposited on room temperature glass substrates using emission from the dc magnetron sputtering plasma glow discharge as a process control for the reactive process inside the deposition chamber in low pumping speed vacuum system. An unbalanced magnetron source was used in an enclosed volume, within a vacuum chamber, into which oxygen gas was admitted. A systematic control of the reactive gas partial pressure allows injection of reactive gas into the deposition chamber, provided with a fast response time by observation of the spectral line emission of the sputtered zirconium target. This feedback loop control allowed the production of localized-optimized films of Zirconium dioxides. The optical quality and optimization process were assessed by ellipsometry and spectrophotometry.

Keywords: Plasma emission; Zirconium dioxide; Optical properties.
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1. Introduction

Reactive magnetron sputtering technique is the most used deposition process for depositing different compound films by ions bombarding metallic targets in the presence of reactive greases. It's currently the primary and promising deposition system for many applications of films technologies such as photo catalysts, surface acoustic wave gas sensor system, hard coatings, solar energy applications, IC technology, microelectronic device applications, and optical multilayer coatings [1-7]. It is versatile and has remarkable deposition flexibility compared with other techniques in terms of its ability to coat a wide range of areas, deposition of adhesive and homogeneous films, and automation. Consequently optimization and corresponding stoichiometry of compound films can be easily and accurately monitored and achieved when equipped especially with process control methods. The sputtered atoms possess a greater kinetic energy than those atoms deposited by other methods such as evaporation. The energy generated compensates the requirements of substrate heating during deposition on several types of substrate materials such as glass and plastic, allowing deposition to take place at room temperature, i.e. no deliberate heating of substrates.

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Deposition of high quality films of zirconium dioxide can be obtained with ease using reactive magnetron sputtering. Many deposition techniques have been attracted and performed to conduct intensive researches and investigation on zirconium dioxide due to its excellent dielectric properties and chemical composition. Zirconium dioxide has been deposited by metal organic chemical vapor deposition, bias sputtering, electron-beam gun evaporation, ion-assisted deposition, reactive pulsed-laser ablation , spray pyrolysis deposition, wet etching of heat treated atomic layer chemical vapor deposited (ALCVD), and reactive magnetron sputtering [8-15].

2. Deposition Techniques

Films of zirconium dioxides were deposited using a circular unbalanced magnetron with an affective diameter of zirconium target of 78 cm. The unbalanced magnetron source was mounted in an enclosed box, within a vacuum chamber, into which oxygen gas was admitted directly. The box was semi-sealed with a sliding lid allowing and maintaining sufficient argon flow into the box from the surrounding chamber, required for the sputtering process. Argon and oxygen of high purity were used as the sputtering and reactive gases respectively. Low speed vacuum pumping system was used consisting of a two stage rotary pump, a booster pump, and a Ploycold Meissner to remove water vapor from the vacuum chamber. The vacuum system was pumped down to $5x10^{-5}$ mbar before each stage of sputtering and substrate deposition. Glass of size 25x75x1 mm^3 was used as a substrate. Before deposition the target was sputtered-cleaned in argon atmosphere for a period of time to remove the oxide layer from the target surface and to provide stable operation of potential and output spectral signal of the zirconium target. The target-substrate distance was 6 cm. The deposition parameters were: argon pressure of 3 mtorr, magnetron current of 2 A, and magnetron potential of 290 volts.

3. Results and discussion

3.1 Process Control of Zirconium Dioxide

Several models were presented to investigate targets coverage by reactive gases and mechanisms of providing solutions to control the pressure instability of reactive magnetron sputtering of oxides and nitrides in a region called transition zone [16-21]. Without a proper process control of either reactive gas flow or reactive gas pressure as the target surface is changed from a metallic mode to a compound mode, the sputtering rate is decreased drastically due to complete target coverage by the reactive gas, i.e., target poisoning. This eventually causes a profound effect on the deposition rate, stoichiometry, and chemical composition of deposited films. Possible solutions for pressure instability can be achieved by feedback control systems or high pumping speed. Partial pressure control of the reactive gas is more complex than flow control because it requires active feedback control, but it allows operation of the process in the transition region between the elemental and poisoned states of the target. Gas pulsing technique was also used as an attractive method of modifying films properties and minimizing instabilities of the reactive sputtering process [17].

In the present work, giving the limitation of the pumping speed of the vacuum system, a feed-back loop control of zirconium signal from the plasma glow discharge was used as a set point. Fig. 1 shows a diagram for the feed-back loop control.

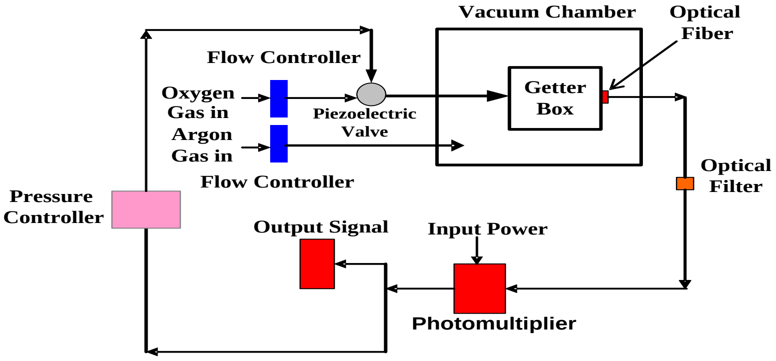

Fig. 1: A diagram of the feedback loop control.

Fig. 2 shows a systematic control of reactive magnetron sputtering of zirconium dioxide films using a feed-back loop control performed by the plasma emission monitor of the spectral signal of the sputtered zirconium. The oxygen consumption and absorption at 633 nm are plotted versus output spectral signal of Zr line set point. At low percentage of Zr line of 20% "low sputtering rate" and low oxygen consumption, an optimum ZrO_2 film was formed characterized by the lowest absorption of about 0.8%. As the percentage of Zr line increased between 20 and 40%, the reactive gas consumption increased between 18 and 27 sccm and absorption increased between 0.8 and 9.6% respectively. Beyond 40% of Zr line specifically at 70% and 80%, heavily absorbing films are deposited whereby both of the consumption and absorption reach a maximum of 41 sccm and 76% respectively. As the Zr line increased further up to 100%, the consumption of the reactive gas decreased reaching zero revealing the formation of pure zirconium film of 45% absorption.

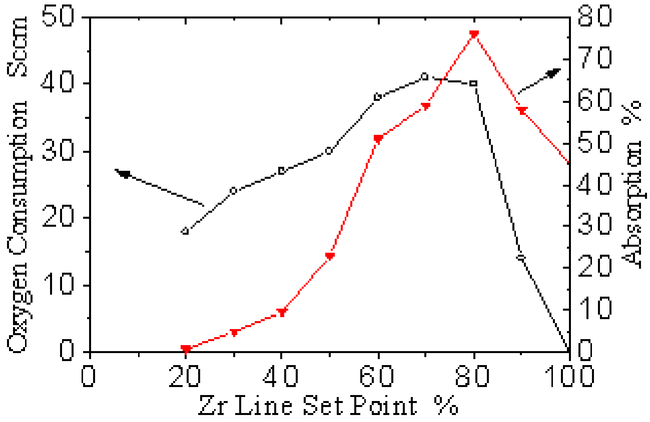

Fig. 2: The dependence of oxygen consumption and absorption on Zr line set point for reactively sputtered Zirconium dioxide films.

Fig. 3 shows a relation between absorption versus oxygen consumption for films indicated in the Fig. 2. It interprets how the feed-back loop control can be performed as an excellent tool in predicting the stoichiometry and controlling the reactive gas partial pressure and the corresponding oxygen consumption. The optimized film in this work had a high refractive index of 2.134 and a thickness of 96 nm. The absorption at 500 nm was 1.1 %. ZrO_2 is a hard material with a high refractive index that is highly sensitive to the deposition conditions [22]. The refractive index of the initial evaporated layer was 1.76 and that for ion assisted deposition of evaporated ZrO_2 films was 2.08 at wavelength of 633 nm [23]. For biased and annealed sputtered ZrO_2 films, the refractive index increased to 2.17 (at 550 nm)

[9]. The refractive index for films deposited by reactive magnetron sputtering was found to be 1.93 at 600 nm for the as deposited films and it changed to 1.71 on annealing at 850 ºC. The optical constants were found to be constant in the wavelength region beyond 400 nm, below which dispersion was observed [24]. It can be concluded that the improved quality of present films is attributed to the effect of the unbalanced magnetron causing energetic ions to bombard the substrate during deposition. The activation energy imparted by impinging positive ions enhances the mobility of deposited atoms resulting of denser films with good optical properties.

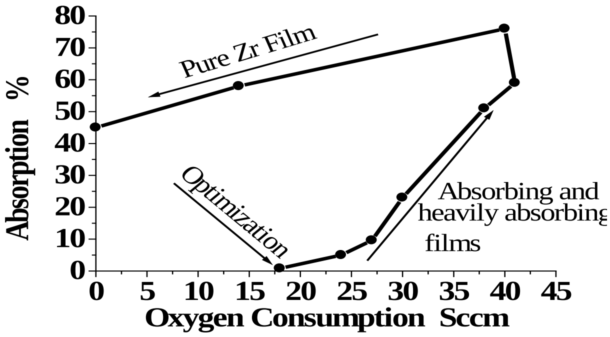

Fig. 3: The dependence of film absorption on oxygen consumption at each metal line set point for zirconium dioxide films.

The search for alternative dielectric materials with high dielectric constant, thermodynamic stable on silicon substrate and low direct tunneling current leads to oxide based materials like zirconia [15]. Understanding of the factors leading to the deposition of high-quality ZrO_2 dielectric thin films is crucial for films applications that meet the requirements for capacitors in next-generation memory devices [25].

Fig. 4 shows a transmission and reflection spectra in the visible region for the optimized film indicated in Fig. 3. A transmission beak of 89% and a minima reflection of about 8.2% can be clearly seen at 440 nm. Such a high transmittance can be very useful in anti-reflecting coating if thinner films can retain a comparable transmission. Consequently, the embedded thin metal film can reflect the infrared solar radiation while the highly transparent film suppresses the reflection from the metal film increasing the transmission in the visible; this is the performance of heat mirrors.

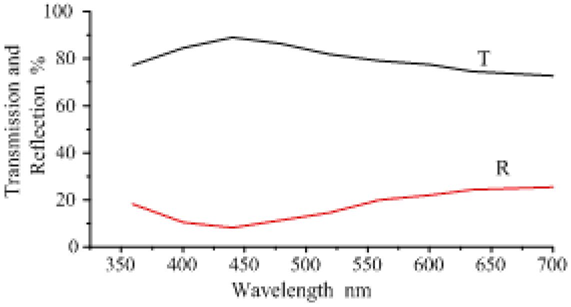

Fig. 4: Transmission and Reflection spectra in the visible region for an optimum Zirconium dioxide film of thickness 96 nm.

4. Conclusion

It was demonstrated that zirconium dioxide films can be optimized in low pumping speed vacuum system using plasma emission monitor for the spectral signal of the sputtered zirconium target. The instability of reactive gas partial pressure can therefore be systematically controlled allowing the injection of reactive gas as required by reaction kinetics of the deposition process. The unbalance magnetron added an advantage by bombarding the films during deposition by energetic ions leaking from the plasma thus enhancing the activation energy and mobility of deposited atoms. Consequently, improvement in optical properties can be easily achieved.

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