Thin Solid Films 519 (2011) 7779–7784

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Hysteresis and process stability in reactive high power impulse magnetron sputtering of metal oxides

Montri Aiempanakit [a,*], Tomáš Kubart [b,c], Petter Larsson [a], Kostas Sarakinos [a], Jens Jensen [d], Ulf Helmersson [a]

[a] Plasma & Coatings Physics Division, IFM-Materials Physics, Linköping University, SE-581 83 Linköping, Sweden
[b] The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden
[c] Department of Control Engineering, Faculty of Electrical Engineering, Czech Technical University in Prague, Technická 2, Prague 6, Czech Republic
[d] Thin film Physics Division, IFM-Materials Physics, Linköping University, SE-581 83 Linköping, Sweden

ARTICLE INFO

Article history:
Received 25 August 2010
Received in revised form 3 June 2011
Accepted 10 June 2011
Available online 16 June 2011

Keywords:
Reactive sputtering
High power impulse magnetron sputtering
Aluminum oxide
Cerium oxide
Hysteresis
Process stability

ABSTRACT

In the further development of reactive sputter deposition, strategies which allow for stabilization of the transition zone between the metallic and compound modes, elimination of the process hysteresis, and increase of the deposition rate, are of particular interest. In this study, the hysteresis behavior and the characteristics of the transition zone during reactive high power impulse magnetron sputtering (HiPIMS) of Al and Ce targets in an Ar–O_2 atmosphere as a function of the pulsing frequency and the pumping speed are investigated. Comparison with reactive direct current magnetron sputtering (DCMS) reveals that HiPIMS allows for elimination/suppression of the hysteresis and a smoother transition from the metallic to the compound sputtering mode. For the experimental conditions employed in the present study, optimum behavior with respect to the hysteresis width is obtained at frequency values between 2 and 4 kHz, while HiPIMS processes with values below or above this range resemble the DCMS behavior. Al–O films are deposited using both HiPIMS and DCMS. Analysis of the film properties shows that elimination/suppression of the hysteresis in HiPIMS facilitates the growth of stoichiometric and transparent Al_2O_3 at relatively high deposition rates over a wider range of experimental conditions as compared to DCMS.

1. Introduction

Reactive magnetron sputtering is a physical vapor deposition (PVD) technique which is widely employed for the growth of compound films allowing for good film uniformity, reliable control over the film properties, deposition on large area substrates, and cost efficiency [1]. Typical feature in reactive magnetron sputtering processes is that compound formation does not only take place on the substrate but also on the target surface (referred to as target poisoning). Deposition from a fully poisoned target (referred to as the compound sputtering mode) allows for growth of stoichiometric compound films, i.e. films with sufficient incorporation of the reactive gas atoms [2]. At these conditions deposition rates significantly lower than those obtained from an elemental (e.g. metallic) target are commonly observed, since the sputtering efficiency of the compound material is typically lower than the sputtering efficiency of the corresponding metal [2]. Growth of stoichiometric compound films with relatively high rates can be facilitated in the transition regime between the metallic and the compound mode [3]. However, the relationship between reactive gas flow and process parameters is complex leading to an unstable transition zone and a hysteresis in the process parameters, e.g. decrease and increase in the deposition rate does not occur at the same value of the reactive gas flow [2]. Therefore, operation in the transition zone using only the reactive gas mass flow as the control parameter is in most cases impossible [2,3]. The latter is particularly pronounced during reactive sputtering of metal oxides [2,3]. It has been shown that stabilization of the transition zone or elimination of the hysteresis can be achieved by feedback control systems [3], increase of the pumping speed [4,5], reduction of the target area [6], and for some metal oxide systems by the addition of nitrogen into the sputtering atmosphere [7].

High power impulse magnetron sputtering (HiPIMS) is a PVD technique in which the power is applied to the target in short unipolar pulses of low duty cycle (<10%) and frequency (<10 kHz) [8]. This mode of operation allows for maximum target power density values during the pulse on-time (referred to as peak target power density) in the order of several $kWcm^{-2}$, while the average target power density is maintained in the order of several tens of Wcm^{-2} comparable to conventional magnetron sputtering processes [9]. The high peak target power densities in turn facilitate the generation of dense plasmas (electron densities up to 10^{19} m^{-3}) resulting in high degree

* Corresponding author at: Department of Physics, Chemistry & Biology, Linköping University, SE-581 83, Linköping, Sweden. Tel.: +46 13 286616 (Office); fax: +46 13 137568.
E-mail address: monai@ifm.liu.se (M. Aiempanakit).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.06.021

of ionization for both gas and sputtered species [8–12]. These plasma conditions have been shown to allow for the deposition of films with superior properties as compared to those obtained by conventional magnetron sputtering techniques. HiPIMS in reactive mode has been extensively employed for the deposition of metal nitrides and oxides [12]. In the particular case of metal oxides, investigations of the process characteristics by Wallin and Helmersson [13] and Sarakinos et al. [14] during reactive sputtering of Al–O and Zr–O, respectively, have shown that, in contrast to direct current magnetron sputtering (DCMS), HiPIMS allows for elimination of the hysteresis and stabilization of the transition zone without the use of a feedback control systems. The observed behavior has been attributed to several mechanisms, i.e. depletion of reactive gas in front of the target during the pulse on-time [13,15,16] (referred to as gas rarefaction [17–21]), limited target oxidation during the pulse off-time [13], and higher target erosion rate due to the higher target voltage used in HiPIMS as compared to DCMS [14]. However, the question regarding the origin of the process stabilization in reactive HiPIMS still remains. Moreover, the process stabilization has only been reported for a narrow range of experimental parameters [13,14]. At the same time, Sproul et al. [3] have reported the need for a feedback control of the reactive gas partial pressure using HiPIMS, while Audronis et al. [22] have claimed that there is no evidence to support the hysteresis elimination/suppression using HiPIMS.

The goal of the present study is to explore the feasibility of HiPIMS to stabilize transition zone and eliminate the hysteresis during reactive deposition over a wide range of experimental parameters. In addition, we seek to contribute to the understanding of the fundamental mechanisms that determine the process characteristics in reactive HiPIMS processes. To this purpose we study the process characteristics during reactive HiPIMS and DCMS of Al and Ce in an Ar–O_2 ambient using a variety of experimental parameters with respect the pulsing frequency and the pumping speed. The results obtained are discussed in light of the mechanisms suggested in the literature. Finally Al–O films were grown and their optical properties were compared for the two deposition techniques.

2. Experimental procedure

Experiments were performed both in DCMS and HiPIMS modes in an ultra high vacuum stainless-steel chamber with a base pressure below 10^{-6} Pa. Disks 50 mm in diameter and 3 mm in thickness made of Al (99.9995% purity) and Ce (99.9% purity) were used as sputtering targets. Ar gas with a purity of 99.9997% was introduced into the chamber through a mass flow controller and the Ar flow was adjusted to maintain a constant partial pressure ranging from 0.65 to 0.9 Pa depending on the experimental conditions. O_2 gas (99.9995% in purity) at various flows was introduced into the chamber through a fast solenoid valve connected to a partial pressure feedback system. An O_2 lambda probe (Zirox XS22.3H) was used as an O_2 partial pressure sensor. This experimental arrangement enabled one to maintain control over the O_2 partial pressure at all values of O_2 flow employed and therefore operate within the transition sputtering zone. In order to monitor the O_2 partial pressure, a Spectra vision 1000-P differentially pumped mass spectrometer was used. In this experiment, the O_2 partial pressure values were calculated by measuring mass 32 and mass 40 of O_2 and Ar, respectively and using a relative sensitivity factor of $Ar/O_2 = 1.2$ [23]. For the experiments carried out in DCMS mode power was applied to the target by an MDX 1 K Pinnacle dc generator operated at constant power mode. In the HiPIMS case, unipolar pulses with a length (t_{ON}) of 35 μs and a frequency between 1 kHz and 10 kHz were used supplied by a SPIK 1000 A pulsing unit fed by the MDX generator. These relatively short pulse lengths were employed to minimize the probability for the occurrence of arcing during the process [18]. The discharge voltage was adjusted as the reactive gas flow was varied in order to keep the average power delivered to the target constant. For experiments performed in DCMS mode, the target voltage, current and power were directly obtained from the readout of the dc generator. In the case of HiPIMS process both target current and voltage are time dependent quantities which were measured using a Chauvin Arnoux C 160 current clamp and 1:100 voltage divider, respectively, and monitored in a Tektronix TDS 520 C digital oscilloscope. The power was subsequently obtained by the product of the voltage and the current signals. The measurements of the time dependent target voltage revealed nearly rectangular waveforms. To determine the width of the hysteresis and thus evaluate the process stability at the various deposition conditions the target (discharge) voltage, the O_2 partial pressure, and the mass deposition rate (monitored by a quartz crystal microbalance) were recorded as functions of the O_2 flow. It is known that the hysteresis effect and the process stability are also influenced by the pumping speed of the system and the hysteresis may be eliminated if the pumping speed is higher than a critical value [4]. Therefore, the process characteristics during reactive DCMS and HiPIMS of the Al target were studied by varying the pumping speed from 20 to 50 l/s employing a throttle valve at the entrance of the turbomolecular pump. In this particular case the average power in the HiPIMS mode was adjusted so that the same mass deposition rate from pure metallic target (i.e. without the presence of a reactive gas) as for DCMS was obtained.

To unravel the effect of the process characteristics on the films properties, Al–O films were deposited onto Si (100) substrates located at a distance of 11 cm from the target employing both reactive DCMS and HiPIMS. Prior to the deposition the Si substrates were cleaned ultrasonically in acetone and isopropanol. Film uniformity was assured by substrate rotation. The Ar partial pressure was maintained at a fixed value of 0.9 Pa while the O_2 partial pressure was varied to grow films in the metallic, the transition, and the compound sputtering zones. Based on the deposition rate data the deposition time was adjusted to grow films with thickness of 200 nm. The effect of the deposition conditions on the atomic composition of the films was determined by means of time-of-flight elastic recoil detection analysis (ToF-ERDA) using a 40 MeV $^{127}I^{9+}$ ion beam. A detailed description of the ToF-ERDA experimental set-up has been presented elsewhere [24]. Film thickness and as a consequence the deposition rate was determined by scanning electron microscopy (SEM) using a LEO 1550 Gemini. The effect of the deposition conditions on the crystal structure was investigated by means of grazing incidence X-ray diffractometry (GIXRD). The GIXRD measurement was performed with Philips PW1830 diffractometer operated at 40 kV and 40 mA with a Cu anode (Cu Kα, $\lambda = 1.540597$ Å). The incident beam angle, ω, was 1° while the scanning range in 2θ was 15–85°. In order to investigate the optical properties of the films, spectroscopic ellipsometry measurements were performed [25] using a dual rotating compensator ellipsometer (RC2) from J. A. Woollam Co., Inc. The ellipsometric data were recorded at angle of incidence of 45, 55, and 65° in the spectral range of 300 to 1700 nm with an increment of 1 nm. The optical properties and thickness of thin film may be derived by fitting of the relative amplitude change (Ψ) and the relative phase change (Δ) using the CompleteEASE software from J. A. Woollam Co., Inc. The optical response of the Al–O layer (refractive index, n, and extinction coefficient, k) was described using the Cauchy dispersion formula [26]. The thickness of the Al–O layer was obtained by the iteration process and compared to the value measured by SEM.

3. Results and discussion

3.1. Process characteristics

The discharge voltage, mass deposition rate, and O_2 partial pressure curves as functions of the O_2 flow during reactive DCMS of the Al target are shown in Fig. 1. An Ar partial pressure of 0.8 Pa, a