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Structural and optical properties of zirconia thin films deposited by reactive high-power impulse magnetron sputtering

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ABSTRACT

Zirconia films are deposited by reactive high power impulse magnetron sputtering (HiPIMS) technology on glass and indium-tin-oxide (ITO)/glass substrates. Preparation, microstructure and optical characteristics of the films have been studied. During deposition, the influence of the target power and duty cycle on the peak current–voltage and power density has been observed in oxide mode. Transparent thin films under different oxygen proportions are obtained on the two substrates. Atomic force microscopy measurements showed that the surface roughness of the films was lower by reactive HiPIMS than DC sputtering for all oxygen contents. The transmission and reflectance properties of differently grown zirconia films were also investigated using an ultraviolet–visible spectrophotometer. The optical transmittance of films grown on glass substrates by HiPIMS reached maximum values above 90%, which exceeded that by DC sputtering. The band edge near 5.86 eV shifted to a lower wavelength for zirconia films prepared with oxygen flow rates lower than 4.5 sccm. For the films prepared on ITO/glass substrates, the transmittance and the band gap of zirconia films were limited by ITO films; a maximum average transmittance of 84% was obtained at 4.5 sccm O_2 and the energy band gap was in the range of 3.7–3.8 eV for oxygen flow rates ranging from 3.5 to 5.0 sccm. Finally, the electrical properties of zirconia films have also been discussed.

1. Introduction

Zirconia is an important structural and functional material characterized by wear resistance, good ionic conductivity, large band gap and wide spectral transparency range in both visible and near-infrared bands [1–3]. Because of its unique mechanical, optical and electrical properties, zirconia has received intensive interests in extensive relevant application areas [4–9] for the last decades.

Zirconia films have been widely synthesized by DC magnetron sputtering (DCMS) [10–12]. Magnetron sputtering is most frequently used among these methods, on account of the superiority in providing a uniform film on a large substrate. However, since DC power of conventional DCMS has always been open during deposition, the power-carrying capacity of targets is limited by target overheating [13], resulting from the bombardment of cations such as Ar+ from the plasma. A typical target power density is below 50 W cm^{-2} [14–16], yielding an ionization rate of targets of less than 10% [17,18]. The low target ionization is caused by electron-impact ionization [18], generating from a lower density plasma in an order of 10^{17} m^{-3} [14,19]. Consequently, the available sputtered species for deposition, in general, are neutral particles. These particle trajectories are determined by the distribution of velocity angular at the target and the scattering by gas atoms beforehand. This may result in an anisotropic flux towards the substrate and an inhomogeneous film structure, combined with a rapid deposition in DCMS [20]. In this case, high-power impulse magnetron sputtering (HiPIMS) emerges as a physical vapor deposition technology. HIPIMS and DCMS have the same average power level around a few hundred watts. By applying the power in a pulse DC mode, the average power of HiPIMS is kept at the same level as DCMS, but its peak power can reach a much higher value, as the target discharging and enough cooling realize at off-times. Hence, HiPIMS can provide a peak power density of more than 1000 W cm^{-2} [5,21–23] to the target, within an ultra-short on-time of several μs, and the ionization rate of the sputtered material can achieve a high level of 5–70% [15,20,24], sometimes even more than 90% for Ti [25]. Such high target ionization is generated by electron-impact ionization [14] with high-level plasma densities in an order of 10^{19} m^{-3} [24,26]. Compared with the behavior of sputtered neutral particles in DCMS, the high-density ion flux in HiPIMS is controllable, and can be collimated to the substrate in plasma by an electrical or

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magnetic field. The ions bombard and then transfer momentum to the film, which might increase the mobility of film atoms on the substrate. This is beneficial for improving the film quality [3,12,18,26–30] such as dense microstructure, and obtaining specific optical and electrical properties.

In previous studies, reactive HiPIMS has been employed for deposition of metal nitride thin films [12,20,27,29–32]. For instance, F. Magnus showed ultrathin TiN films by HiPIMS with excellent electrical characteristics [30]. Nanoindentation hardness of synthesized CrN_x films was a function of N_2/Ar flow ratio and superior film properties were observed [32]. Zirconium nitride coating with high adhesion was investigated by Y.P. Purandare [12]. Some efforts have been made on HiPIMS sputtered metal oxide films [33–36], but the development of which is relatively slower than nitride ones. Two dominant reasons may influence process characteristics in reactive HiPIMS with oxygen. First, many factors, including average power and pulse duty cycle can intensively affect the target current and voltage variation, and plasma density and deposition rate will change consequently [33]. Secondly, metal mode and oxide mode will present sequentially by increasing (O_2/Ar + O_2) mixing ratio (OMR). M. Aiempanakit [36] has shown the discharge behaviors of sputtering Ti and Al, which are determined by ionized oxygen in oxide mode. M. Hála [4] found that the discharge emission above a Cr target is dominated by oxygen species in pure oxygen. In addition, they pointed that no metal-dominated sputtering could be explored, unlike the discharges in N_2/Ar mixtures. K. Sarakinos [33] discussed the mechanisms on the plasma stabilization of the deposition process of ZrO_x and the exhibition of a hysteresis free zone. Therefore, it is possible to synthesize highly transparent metal oxide films by optimized deposition conditions. So far, however, few reports have been carried out on the microstructure and optical or electrical properties of the oxide films.

In this work, zirconia thin films have been deposited onto glass and indium-tin-oxide (ITO)/glass substrates from a zirconium (Zr) target by reactive HiPIMS. The current–voltage characteristics as well as the plasma densities have been determined with the target powers, duty cycles and OMRs under consideration. The microstructures of zirconia thin films on the two substrates have been investigated using an atomic force microscope (AFM) analysis. The optical band gap energies of zirconia thin films under different substrates and OMRs have been calculated in a high-absorbance region. The band gap of zirconia on ITO/glass (3.7–3.8 eV) is less than that on glass (around 5.9 eV). The results are supported by measuring optical properties, including transmittance and reflectance with UV–VIS spectrophotometer. The leakage current densities of 20 nm zirconia thin films on ITO glass are less than 10^{-7} A/cm^2.

2. Experiments and measurements

2.1. Experimental details

Zirconia thin films have been prepared by reactive HiPIMS system from a metallic Zr target with a diameter of 7.6 cm and a purity of 99.95%. The experiment was performed in a cylindrical ultra-high vacuum chamber with 60 cm in diameter, equipped with a turbo-molecular vacuum pump (Leybold TMP 600C). The vacuum chamber was computer controlled and loaded with three different target cathodes. The target was fixed using a circular, balanced, planar magnetron. A rotatable substrate holder facing the target cathode surface was located at the center of the chamber bottom. The distance between the substrate holder and the target was 8 cm. The power was supplied to the target by a pulse power generator (Melec SPIK 2000A) operating in the negative unipolar voltage mode. An insulated-gate bipolar transistor (IGBT) was used to determine the pulse duration of the glow plasma. The turning on of IGBT was initiated by the pulse generator, and the off time was in turn controlled by a DC power supply. The discharge current and voltage of the target were measured with a combined current and voltage transducer and an Agilent digital storage oscilloscope.

Initially, the vacuum chamber was evacuated to a base pressure lower than 0.7 mPa and monitored with a vacuum gauge controller (Granville Phillips 307). The substrate temperature was kept at room temperature. Pure argon (99.995%) was used to pre-sputter the target for cleaning about 15 min, while the substrate was shielded by a baffle. The target power was 300 W, and the pulse on time and off time were 50 μs and 1500 μs, respectively. Films were deposited on both pure glass and indium tin oxide (ITO)/glass substrates.

The pulsed target power had a great impact on a reactive process. Appropriate sputtering power was then necessary to achieve high-power density and sustain a much stabler process condition without excessive arcs. In our study, the power supply was run in the target power mode varying from 200 to 700 W, in order to assess the relationship between the deposition power and peak discharge current, and between the voltage and the plasma density in the target. The power was applied to the target cathode with a low duty cycle, which is a signal feature of HiPIMS. The duty cycle refers to the ratio of the pulse on time to the whole pulse length. Low duty cycle operation in the form of short pulses can provide enough time for cooling the targets and magnets. It can also determine lower average power density of targets and the peak power in the order of kW cm^{-2}. The pulse frequency and duty cycle were changed by setting the turn-off time from 500 μs to 3500 μs. The on time was 50 μs in all duty cycle experiments.

Metal mode and oxide mode influence the target power density and the film constitution in both conventional and reactive HiPIMS sputtering processes [36]. K. Sarakinos [33] illustrated that transparent zirconia films were much easier to obtain in oxide mode when the oxygen content was improved in argon and oxygen mixed gases. The aims of this paper were to investigate the effect of the OMR ratio on composition, microstructure and optical characteristics of zirconia thin films, thus oxide mode was essential. In this case, the reactive oxygen (99.995% purity) was introduced into the chambers at a flow rate reaching up to 5 sccm (standard cubic centimeters per minute at standard temperature and pressure) and monitored by a mass flow controller. The argon was adjusted to maintain the total gas at a constant mass flow rate of 40 sccm, and the deposition pressure was controlled to be 0.67 Pa.

2.2. Measurements and analytical methods

Thin film surface topography was characterized by an AFM system (DI Dimension 3100 with a Nanoscope III system controller). The AFM system can automatically provide surface characteristics of thin films within a diameter of 200 mm, using scanning probe microscope techniques. The effect of the OMR ratio on crystallization and microstructure has been discussed based on the surface graphs and root-mean-square (RMS) of different zirconia films.

The optical transmittance and reflectance spectroscopy of thin films in the visible region has been employed with an ultraviolet–visible spectrophotometer (UV/VIS, Jasco-V650) in the wavelength range of 190–900 nm. The transmittance normally expressed as a percentage T% can be obtained by the ratio of the intensity of the light through zirconia films to the intensity of the light through the air for comparing. For measuring reflectance, which was expressed as a percentage R%, the UV/VIS spectrophotometer was configured with a diffuse reflection plate of barium carbonate as a reference. The absorbance, based on the transmittance and reflectance, was used to calculate and illustrate the relationship between the optical band gap and the oxygen content.

In addition, metal–insulator–metal (MIM) structures were fabricated on ITO-coated glass with aluminum electrodes to investigate electric properties of zirconia films. All the thickness of zirconia films was 20 nm while the thickness of aluminum films was 100 nm. Current–voltage measurements were made while the voltage was ranging from −2 V to +2 V at room temperature.