

Towards understanding the superior properties of transition metal oxynitrides prepared by reactive DC magnetron sputtering

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Abstract

Thin films of several transition metal oxynitrides such as titanium, zirconium, hafnium, niobium and tantalum oxynitride have been produced at room temperature by direct current reactive magnetron sputtering. These films were characterized by a variety of methods including X-ray diffraction, X-ray reflectometry, Rutherford backscattering, optical spectroscopy, spectroscopic ellipsometry and wafer curvature measurements of the deposition stress in the thin films. The resulting film properties show a strong correlation with the deposition conditions. We frequently observed a substantial increase in growth rate and refractive index and a reduced roughness, but still maintained a sufficient transparency in the visible range compared with pure oxides. These attractive features are obtained even though the films contain only a small amount of nitrogen. A simulation package was developed that reproduces the variation of the deposition rate, target voltage and film stoichiometry with reactive gas flow. Based on the results, a scientific understanding is sought that explains both the film formation mechanism as well as the remarkable improvement in film properties.

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1. Introduction

Transition metal oxides have found numerous applications in many industrial applications [1,2]; for example, they serve as architectural, antireflection, solar control, protective and automotive coatings, etc., in the form of thin films, while nitrides (TiN, NbN, ZrN, etc.) are employed for chemically inert, hard and protective coatings. Several methods have been reported for the preparation of transition metal oxides including physical vapour deposition [3,4], chemical vapour deposition [5], arc deposition [6], etc. Among these methods, reactive DC magnetron sputtering is frequently employed for the deposition of these films, since this process can easily be scaled up from the small-sized substrates used in laboratory work to large-scale industrial applications. Nevertheless, the film deposition, especially for oxides, suffers from several drawbacks such as a low deposition rate and arcing. The possibility to tailor the material properties with employing

optimized growth conditions is one of the main driving forces for a large number of research in thin film studies.

During the last decade, metal oxynitride films have received considerable attention due to their unexpected and interesting properties. The presence of nitrogen in oxide films or the presence of oxygen in nitride films enables the preparation of a range of functional materials with technological importance. To date, silicon and tantalum oxynitride have found application in microelectronic devices and a considerable number of references are available on these materials [7–9]. So far, only very few groups have reported results on transition metal oxynitrides [10–12]. The transition metal oxynitrides possess superior properties of both the corresponding metallic nitride and the dielectric oxide compounds.

Often, very specific film properties are required for optimal performance. In optical multi-layers, for example, both types of films with particularly high and low refractive indices are of paramount importance. In an ideal case, the desired film properties can be obtained by selecting suitable process conditions. More specifically, this could be the addition of nitrogen to the argon–oxygen atmosphere

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typically used in sputter deposition, since a substitution of oxygen atoms in the anionic lattice by nitrogen should increase the index of refraction. Such an increase can be expected, since the polarizability of metal–nitrogen bonds tends to be lower than that of metal–oxygen bonds, leading to a higher polarizability of the metal–nitrides [13]. Apart from that, such oxynitrides normally show a variety of microstructural changes due to their tunable properties by varying the O/N flow during deposition. Our group has established in depth knowledge on transition metal oxides prepared by reactive DC magnetron sputtering [14–17]. Recently, the superior properties of the transition metal oxynitrides have motivated us to perform a systematic investigation of these materials. In this article, we discuss generic trends with the help of group IVa oxynitrides.

2. Experimental

The transition metal oxynitride films were prepared on Si (100) and microscopic slides by reactive DC magnetron sputtering of an elemental target (metallic Ti, Zr, Hf, etc. of 99.9% purity) in an Ar/O₂/N₂ atmosphere. The typical target thickness is 6 mm and the diameter is 76 mm. Initially, the sputter chamber was evacuated down to 10^{−3} Pa by a turbo pump with an effective pumping speed of 345 l/s. Deposition took place at room temperature conditions with a constant cathode current of 900 mA and a total pressure of 0.8 Pa regulated by the Ar flow measured by an ion gauge. The target-to-substrate distance was kept constant at 70 mm. All targets were sputter cleaned in pure argon atmosphere before oxygen and nitrogen were introduced. Starting from oxidic mode sputtering of the targets [15, 17], nitrogen was added to the reactive gas inside the chamber, while simultaneously the oxygen flow was decreased to keep the total supply of reactive gases constant. The details of our deposition system were described in previous reports [14–19].

The structural properties of the films were studied by X-ray diffraction employing a Philips X'pert MRD diffractometer. To determine the crystalline structure of the films, grazing angle diffraction measurements have been performed for an angle of incidence of 0.75°. The grazing angle geometry is more sensitive to the surface structure of thin films. Typical penetration depths in the film for the chosen incidence angle 0.75° are a few hundred nanometers. The same instrument was used to carry out X-ray reflectivity (XRR) measurements. From these XRR measurements, thickness, density and surface roughness of the films were derived by performing theoretical simulations using the simulation software package WINGIXA supplied by Philips. In this software, the thickness of the films is determined from the period of the intensity oscillations and the density is determined from the total reflection edge [20]. The decay of the oscillation amplitude and overall intensity is related to the roughness of the films. Optical measurements were

performed in the range from 1.1 eV to 6.2 eV employing a Perkin-Elmer Lambda-25 spectrometer, while a Woollam M2000UI variable angle spectroscopic ellipsometer was used for the determination of the ellipsometric angle ψ and Δ from 0.7 eV to 5.1 eV. The experimental curves were modeled by a optical simulation program (SCOUT) [21]. From the theoretical modeling, both the thickness and the dielectric function (DF) of the films were calculated by the use of different oscillator models. Since we were mainly interested in the Visible–UV region, electronic transitions had to be adequately described. We used a model proposed by O'Leary et al. [22], which was adapted for computer simulations [21]. Details about the model and this adaptation can be found in the literature [14–19,23]. Rutherford backscattering spectroscopy (RBS) has been used to determine the stoichiometry of the films by means of a tandetron accelerator with 1.4 MeV alpha particles and a current of 14 mA. The backscattered particles were detected at an angle of 170° with respect to the incident beam direction by a semiconductor detector. To derive the appropriate stoichiometry of the films, the experimental spectra were simulated by using the Rutherford backscattering universal manipulation program (RUMP). The induced stress in the films (deposition stress) was determined by wafer curvature measurements of the substrate curvature (k) before and after the deposition on glass substrates of approximately 150 μm thickness. The Stoney [24] equation was used to calculate the film stress, according to

$$\sigma = \frac{1}{6} \frac{E_s}{1 - \nu_s} \frac{d_s^2}{d_f} k \quad (1)$$

where E_s and ν_s are elastic modulus and the Poisson ratio of the substrate, while d_s and d_f are the thickness of the substrate and the film, respectively.

3. Results and discussion

3.1. X-ray diffraction

The crystallinity of the samples was investigated by grazing incidence X-ray diffraction analysis. Figs. 1 and 2 show the typical measurements performed on Si (100) substrates for TiO_xN_y and HfO_xN_y films, respectively. We observed that these films remain in a single phase, either amorphous or crystalline, from pure oxidic deposition up to a certain nitrogen flow, at which the films became crystalline. For example, in the case of TiO_xN_y, the XRD measurements reveal that pure titanium oxide films are amorphous (Fig. 1). With increasing nitrogen fraction in the reactive gas mixture, there is no change in the amorphous structure of the films prepared below 94% of nitrogen flow in the reactive gas, but above 94% of N₂ flow, crystalline TiO_xN_y peaks (JCPDS No. 049-1325) were observed [25]. A similar trend has also been observed for TaO_xN_y [26]. In contrast, for HfO_xN_y, both the pure oxide and nitride films

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