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Structure dependent resistivity and dielectric characteristics of tantalum oxynitride thin films produced by magnetron sputtering

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ABSTRACT

The main purpose of this work is to present and to interpret the change of electrical properties of $Ta_xN_yO_z$ thin films, produced by DC reactive magnetron sputtering. Some parameters were varied during deposition: the flow of the reactive gases mixture (N_2 and O_2, with a constant concentration ratio of 17:3); the substrate voltage bias (grounded, −50 V or −100 V) and the substrate (glass, (1 0 0) Si or high speed steel). The obtained films exhibit significant differences. The variation of the deposition parameters induces variations of the composition, microstructure and morphology. These differences cause variation of the electrical resistivity essentially correlated with the composition and structural changes. The gradual decrease of the Ta concentration in the films induces amorphization and causes a raise of the resistivity. The dielectric characteristics of some of the high resistance $Ta_xN_yO_z$ films were obtained in the samples with a capacitor-like design (deposited onto high speed steel, with gold pads deposited on the dielectric $Ta_xN_yO_z$ films). Some of these films exhibited dielectric constant values higher than those reported for other tantalum based dielectric films.

1. Introduction

Tantalum based thin films have been a mainstay in the microelectronics industry for several decades and have been studied for the fabrication of long-term stability resistors, for diffusion barriers, and as an adhesion promoter layer for platinum films used for high temperature applications, among others [1].

A new class of tantalum based thin films, with potential applications in the microelectronics industry, is the tantalum oxynitride $Ta_xO_yN_z$ family. The main advantage of this type of compounds is the possibility to tune both the metallic/non-metallic atomic ratio (Ta/(O + N)) and the non-metallic elemental atomic ratio (N/O) by changing the deposition parameters. This leads to a large spectrum of compositions and microstructures thus opening the range of potentially attractive properties. The main idea behind the development of these types of thin films is that the final product can potentially benefit from properties exhibited by the oxide, the nitride, the tantalum phases, or a combination of the above. Considering that the properties exhibited by the film are highly dependent on the type and characteristics of the constituent phases, some key details regarding the tantalum, tantalum oxide, and tantalum nitride phases will be presented hereinafter.

Tantalum thin films can be obtained in two crystalline configurations, the stable α-Ta bcc phase, with a resistivity close to that of bulk tantalum, with values between 1.5×10^{-2} and 6.0×10^{-2} Ω cm, and the metastable tetragonal β-Ta phase, which has a one order of magnitude higher resistivity domain, between

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17×10^{-2} and 21×10^{-2} Ω cm [2]. The transformation temperature between the α-Ta and β-Ta phases, in the region of 700 °C, has to be considered if the particular applications necessitate the stability of the properties. Besides the substrate temperature, which can promote the preferred crystalline structure (bcc α-Ta or tetragonal β-Ta), the substrate material has also an influence on the type of structure. The deposition on silicon and copper substrates was reported to promote the growth of the tetragonal β-Ta structure [3], while the deposition on aluminum seems to promote the growth of the bcc α-Ta phase [4].

Out of the multitude of tantalum oxide phases reported in the literature, (TaO_x, TaO_y, TaO_z, TaO_u, $\alpha_1Ta_{16}0$, $Ta_{12}O$, α'_1Ta_4O, α_2Ta_4O, α'_2Ta_2O, TaO, Ta_2O_3, TaO_2, Ta_2O_5, Ta_3O_9, among others [5]), tantalum pentoxide Ta_2O_5 is one of the few well-established equilibrium phases and one of the most used compounds in microelectronics devices. Other tantalum oxide phases are encountered mainly in thin films, and seem to be stabilized usually by impurities present in the films [5]. Ta_2O_5 has been studied due to several potential applications: as an antireflective layer for optical or photovoltaic applications, as a dielectric material meant to replace other dielectric films (silicon dioxide or silicon nitride) [6]. Depending on the processing parameters, Ta_2O_5 is characterized by a dielectric constant of 25 or above, (27 at 100 kHz [7]). It also presents stable thermal and chemical properties, making it suitable for applications such as: component of dynamic random access memories [8], as gate insulator in metal–oxide semiconductor field effect transistors (MOSFET) and as an insulating layer in thin film electroluminescent devices [9]. The properties of the Ta_2O_5 film as a dielectric material in these types of applications are very important. The dielectric constant, leakage current density, breakdown field strength and the effects of frequency or temperature on the dielectric constant are the key parameters [10].

The variation of the electrical properties in tantalum nitride thin films is directly related to the type of structure and to the atomic ratio between the metallic and non-metallic elements. As a barrier layer in semiconductors, TaN-type films with low resistivity are preferred to reduce the contact resistance, while TaN phases with high resistivity are preferred as a seed layer for GMR (giant magneto-resistance) sensors [11]. Kim et al. observed in tantalum nitride thin films resistivity values in a seven orders of magnitude domain, from 1×10^{-3} to 2×10^{3} Ω cm [12]. A similar trend, from a conductive to insulator character, dependent on the nitrogen content, was reported elsewhere [13,14].

The literature concerning the electrical properties of tantalum oxynitride thin films is, to this day, relatively limited; however some promising results and key information can be found. Kato et al. [15] have studied the electrical properties of tantalum oxynitride films by measuring a metal–insulator–metal (MIM) structure of Al/TaON/Ru/Si (Si used as support) and a metal–insulator–semiconductor (MIS) structure of Al/TaON/Si. The authors obtained $Ta_xN_yO_z$ films with dielectric constants greater than 30, sensibly higher than the values reported for tantalum pentoxide or other tantalum based films, with viability for capacitor dielectrics and gate oxides applications.

Chung et al. [16] reported the deposition and characterization of $Ta_xN_yO_z$ thin films, where the ratio of reactive gases to total flow gases was controlled from 6% to 30%. The resistivity of the films increased with increasing O/(O + N) content, from 2.88×10^{-8} Ω cm (conducting) to resistivity values higher than 1.92×10^{2} Ω cm, in the semiconducting–insulator domain. In this particular case, the oxygen content seems to dominate the microstructure formation and resistivity of the $Ta_xN_yO_z$ system compared to nitrogen. The diffusion barrier stability as a function of the temperature, for DC reactively sputtered $Ta_xN_yO_z$ thin films has been studied by Misra et al. [17], reporting that the $Ta_xN_yO_z$ barriers were stable up to 500 °C.

One observation that is of great importance is the fact that most if not all the reports found in the literature present rather different deposition parameters, hence the discrepancy in the reported electrical property results. For example, Le Dreo et al. [18] have studied tantalum oxynitride thin films, prepared by reactive magnetron sputtering using a Ta target and N_2 and O_2 as reactive gases, obtaining permittivity values between 14 and 23, depending on the nitrogen content. In this case, the nitrogen flow was kept constant while the oxygen flow was pulsed periodically. On the other hand, Kato et al. [15] reported permittivity values over 30, but the deposition parameters and equipment differ greatly compared to the former case.

Other possible microelectronics related applications have been proposed by several authors. Tantalum oxynitrides have also been investigated as new cathodes for polymer electrolyte fuel cells without platinum [19]. In this case, the films were prepared using a radio frequency magnetron sputtering under $Ar + O_2 + N_2$ atmosphere at substrate temperatures from 50 to 800 °C. In another study [20], the bipolar resistive switching characteristics of the resistive random access memory (RRAM) device based on $Ta_xN_yO_z$ thin films were investigated. In this particular case the RF sputtering was done using a TaN target in a gas mixture of argon and oxygen ($Ar:O_2 = 1:1$) at room temperature.

As can be seen, considering the multitude of possible deposition parameters and hence, the large spectrum of possible microstructures and properties, tantalum oxynitride thin films have great potential in microelectronics applications, amongst other fields of interest.

This work intends to present our findings concerning some of the electrical properties of tantalum oxynitride thin films, deposited by reactive magnetron sputtering. Considering that the chemical composition (atomic ratios) and the microstructural features (type of structure, crystallization orientation, and others) are amongst the important characteristics that affect significantly the electrical properties of the films, some correlations will be established.

2. Experimental details

$Ta_xN_yO_z$ thin films were deposited onto glass, silicon (1 0 0) wafers and AISI M2 high-speed steel (HSS) substrates, by DC reactive magnetron sputtering, using a laboratory-size deposition chamber. Rectangular glass substrates have been obtained from microscope glass slides. Each slide (75 mm × 26 mm) has been cut in 8 equal pieces (~9.4 mm × 26 mm). Silicon wafers have been cut to rectangular shapes, with an area of ~3 cm^2. The steel substrates have been cut from a cylindrical bar, with 3 cm diameter. A detailed description of the deposition equipment can be found elsewhere [21]. A tantalum target (200 mm × 100 mm × 6 mm) and 99.6% purity has been used for all depositions. The axial component of the magnetic field, caused by the magnetron, was measured in the substrate holder and had a value of 3.3 mT. The base pressure of the chamber before plasma etching was 10^{-3} Pa, or lower. Before each deposition, the substrates were plasma etched during 500 s, using a pulsed current of approximately 0.6 A in a pure argon atmosphere with a partial pressure around 0.3 Pa. The deposition parameters that were kept constant for all the sets were: the deposition time (3600 s); the argon flow rate (70 sccm); the ratio of the reactive gases (N_2 and O_2 = (17:3)), injected from the same source; the substrate holder temperature (100 °C) and the DC current density (50 A/m^2). The variable deposition parameters, along with the thickness, and the chemical composition in atomic percentages for the produced thin films are registered in Table 1.

The atomic composition was measured on the samples deposited on Si wafers by Rutherford backscattering spectrometry (RBS). The measurements conditions were: