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Effect of Ta incorporation on the microstructure, electrical and optical properties of $Hf_{1-x}Ta_xO$ high-*k* film prepared by dual ion beam sputtering deposition

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ABSTRACT

The microstructure, electrical and optical properties of $Hf_{1-x}Ta_xO$ ($x = 0$, 0.18, 0.28, 0.36 and 0.43) high-*k* thin films deposited by a novel deposition technique—dual ion beam sputtering deposition (DIBSD) have been investigated. From the O1s and Si 2p spectra of X-ray photoelectron spectroscopy (XPS), it is worth noting that the thickness of the interfacial layer significantly decreases after doping appropriate content Ta, and the formation of metal silicate components (M–O–Si) can be effectively suppressed by doping 43% Ta concentration into $Hf_{1-x}Ta_xO$ system. Compared to the pure HfO_2 sample, $Hf_{1-x}Ta_xO$ with 43% Ta after post-deposition annealing (PDA) exhibits the highest *k*-value ($\sim$21.0 $\pm$ 0.2) and crystallization temperature (950 °C), the smallest root mean square (RMS) surface roughness of $R_a \sim 0.12$ nm, Max height–depth $R_{p-v} \sim 1.5$ nm and *C*–*V* hysteresis of 50 mV, the lowest leakage current density of 1.13×10^{-8} A/cm^2 at $V_g=(V_{fb}-1)$ and an acceptable value of $E_g \sim 4.68 \pm 0.1$ eV.

1. Introduction

The continuous downsizing in the feature dimensions of ultra large integrated circuits (ULSIs) has necessitated ever thinner dielectric oxide layers [1]. One of the consequences is an order-of-magnitude increase in tunneling leakage current through the ultra-thin gate dielectrics. Consequently, high dielectric constant (high-*k*) materials have been introduced as gate dielectrics alternative to the conventional SiO_2 because of their potential for reducing gate leakage current while keeping the identical equivalent oxide thickness (EOT). Among various candidates of high-*k* materials, Hf-based gate dielectrics and their stacking structure are considered to be potential competitor for applications in further device because of excellent dielectric properties [2–7].

Studies have shown that the crystallization temperature, thermal stability and electrical properties can be greatly promoted by means of the appropriate doping of silicon, aluminum, tantalum and nitrogen into HfO_2. In the past few years, $Hf_{1-x}Ta_xO$ as a novel gate dielectric has been gained considerable attention because the incorporation of tantalum effectively avoids the *k* value degradation due to the high dielectric constant of Ta_2O_5 ($k \sim 25$) [2]. The influence of doping amount of Ta on electrical properties of $Hf_{1-x}Ta_xO$ prepared by the radio frequency (RF) magnetron sputtering, direct current (DC) reactive co-sputtering and physical vapor deposition (PVD) or a combination of various techniques has been studied [8–11]. However, no systematic investigation on the $Hf_{1-x}Ta_xO$ with varying Ta composition grown by dual ion beam sputtering deposition (DIBSD) technique has been carried out. As compared with the RF and DC sputtering, the DIBSD has more available sputtering and deposition parameters owing to the adjustable location of ion sources, substrate and target. The films

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fabricated by DIBSD have an excellent adhesion to the substrate since a wide atomic intermixed zone could be set up at the film/substrate interface by ion-assisted dynamic mixing [12], which plays a very important role for improving the interface quality. Besides, the moderate energy power of ion-assisted source can significantly improve the flatness and compact density of film.

In this letter, the influence of Ta doping concentration on microstructure, electrical and optical properties of $Hf_{1-x}Ta_xO$ ($x = 0$, 0.18, 0.28, 0.36 and 0.43) high-k films synthesized by DIBSD have been investigated deeply by means of a variety of measurements, such as X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), capacitance–voltage (C–V), leakage current density–voltage (J–V), ultraviolet–visible spectrophotometry (UVS) absorption spectra. A special focus of the study is to reveal the relationship between Ta-doped content and the surface roughness, interfacial layer formation mechanism, electrical and optical properties.

2. Experimental section

$Hf_{1-x}Ta_xO$ thin films were deposited at room temperature by employing DIBSD at base pressure of 5×10^{-4} Pa and work pressure of 3.2×10^{-2} Pa. A Ta_2O_5 (99.99%) disk (100 mm in diameter) with a small HfO_2 (99.999%) disk (50 mm in diameter) placed on it was used as the sputtering composite target. The different Ta concentration samples were obtained by changing the Ta/[Hf + Ta] ratio to 0%, 18%, 28%, 36%, and 43% in the composite target, which were denoted as HfO_2, HTO-1, HTO-2, HTO-3 and HTO-4, respectively. Before deposition, to remove organic and metallic impurities on the wafers, the p-type Si (100) substrates with a resistivity of 3–8 Ωcm were pre-cleaned by a standard Radio Corporation of American (RCA) processing [13]. All substrates then were bombarded using an assisted ion source, which was pumped in N_2 and Ar mixed gas for 5 min to remove native oxides (SiO_x), polish and passive the surface layer. The more detailed information regarding to preparation parameters and process are described elsewhere [14,15]. To investigate the crystallization temperature of HfO_2 and $Hf_{1-x}Ta_xO$ thin films, the post-deposition annealing were performed step-by-step from 400 °C to 1000 °C for 60 s in N_2 ambient. Among them, five samples (HfO_2, HTO-1, HTO-2, HTO-3 and HTO-4) that received a PDA in N_2 ambient at 800 °C for 60 s were used to perform the AFM, XPS, C–V, J–V and UVS measurements, in order to study the properties of interface structure, electrical and optical properties for low Ta doping system (HfO_2, HTO-1, -2 and -3) with polycrystallization structure and high Ta doping system (HTO-4) with amorphous structure after 800 °C PDA. For "gate-last" and "gate-first" integration strategies, high-k materials must be exposed to the high temperature source-drain dopant activation process, commonly above 800 °C for 5 s in N_2. Pt metal (100 nm-thick) was deposited using DC sputtering and patterned to form a gate electrode with an area of 0.2694×10^{-2} cm^2. Aluminum (Al) was used as the backside contacts for the MOS capacitors, and they were received post-metallization rapid thermal annealing at 400 °C in N_2 gas for 30 s. The thickness of the $Hf_{1-x}Ta_xO$ films was approximately 20 nm, measured by a spectroscopic ellipsometer.

The chemical composition of the thin films was analyzed by the energy dispersive spectroscopy (EDS) of Hitachi S-4700. The crystallization temperature of the $Hf_{1-x}Ta_xO$ films was investigated by a Rigaku D/Max-3C X-ray diffraction (XRD) using Cu $K\alpha$ radiation at 40 kV. X-ray photoelectron spectroscope (XPS) spectra were obtained using a Kratos Axis Ultra DLD XPS instrument equipped with a monochromatic Al $K\alpha$ ($h\nu = 1486.6$ eV) X-ray source. Prior to the XPS measurement, about 15 nm-thick top layer was etched by 1 keV Ar ion bombardment to remove surface contaminants and to investigate the interface chemistry due to the detecting depth of XPS less than 10 nm. The intensities for all the XPS spectra recorded here have been normalized for comparison and the adventitious hydrocarbon C 1s binding energy at 284.5 eV was used as reference to calibrate the energy shift of the Hf 4f, Ta 4f, O 1s and Si 2p shallow core levels [16–18]. The surface roughness of $Hf_{1-x}Ta_xO$ films were investigated by AFM (NT-MDT Solver P47-PRO). The optical transmission spectra were recorded by an ultraviolet–visible spectrophotometer (JASCO V-570) in the range of 190–800 nm. The capacitance–voltage (C–V) and leakage current–voltage (J–V) curves were measured using an Agilent B1500 semiconductor parameter analyzer and operated at 1 MHz. All electrical measurements were performed under a light-tight, electrically shielded and room temperature condition.

3. Results and discussion

3.1. Crystallization of $Hf_{1-x}Ta_xO$ films

Fig. 1 shows the typical XRD spectra of HfO_2, HTO-1, -2, -3 and -4 samples prepared by DIBSD after different temperature annealing in N ambient for 60 s. It is noted that the crystallization temperature of HTO-1, -2, -3 and -4 samples are 750 °C, 800 °C, 800 °C and 950 °C, respectively, which far exceeds that of pure HfO_2 (400 °C–500 °C) [19]. The incorporation of Ta into HfO_2 film enhances the crystallization temperature significantly. This fact is partially due to the disordering of the periodic arrangement in lattice or the inhibition of continuous crystal growth in gate dielectric layer by increasing the doped Ta content (into HfO_2 film) [20]. Fig. 2 displays the XRD crystallization patterns of HfO_2, HTO-1, -2, -3 and -4 as a function of annealing temperatures. The major peaks have been identified according to the Joint Committee on Powder Diffraction Standards (JCPDS) card, and corresponding lattice structures are labeled against the peaks. It can be seen that the crystalline peak of HfO_2 starts to show up clearly after 500 °C annealing, which originates from the monoclinic and tetragonal structure of HfO_2. The round hump around 33° results from the signal disturbance of Si substrate (2 2 0) in HfO_2 sample. With the increase of Ta concentration, the diffraction peak ($2\theta = 36.9°$) in HTO-3 and -4 samples are found corresponding to the high temperature orthorhombic Ta_2O_5 (1 11 1) after PDA in N_2 ambient at 800 °C and 950 °C, respectively. It is interesting to find that the HTO-4 sample exhibits the highest crystallization temperature ~950 °C. This indicates that the appropriate amount of Ta acts as a network modifier and stabilizes the amorphous phase of the metal oxides [19].

3.2. Surface roughness of $Hf_{1-x}Ta_xO$ films

Research on the surface roughness of both as-deposited and annealed films, especially high-k materials, appears very important because it induces shifts in electronic energy levels and degrades electrical characteristics [21,22]. To reveal the correlation between the surface morphology and the doping content of Ta, AFM images were taken for $Hf_{1-x}Ta_xO$ ($x = 0.18$, 0.28, 0.36 and 0.43) films after PDA in N_2 ambient at 800 °C for 60 s and are shown in Fig. 3. Scan size is 2×2 μm^2. It is clear that the surface roughness of $Hf_{1-x}Ta_xO$ films is improved slightly by increasing the Ta concentration. The RMS surface roughness calculated from the AFM images for HTO-1, -2, -3 and -4 samples are approximately $R_a \sim 0.47$, 0.38, 0.20, 0.12 nm and $R_{p-v} \sim 4.2$, 3.5, 2.8, 1.5 nm, respectively. It is interesting to find that the surface of HTO-1 sample consists of dense narrow spikes in shape, while that of the HTO-3 and HTO-4 are more mountainlike, smooth and void free. This sharp increase in roughness for HTO-1 and -2 is likely attributed to a structure phase transformation after annealing, which is apparently corroborated by XRD results. It is considered that the increase of the grain size