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Investigations of titanium nitride as metal gate material, elaborated by metal organic atomic layer deposition using TDMAT and NH_3

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Abstract

This study reports for the first time, the evaluation of the work function and thermal stability of TiN gate material for deep sub-micron CMOS, elaborated by using metal organic atomic layer deposition, from TDMAT and NH_3 precursors. Composition, microstructure and electrical properties of atomic layer deposited TiN films are characterized by using combined analytical techniques. The TiN films exhibit suitable properties for nMOSFET requirement with an effective work function of 4.2 eV obtained on silicon oxide and a good stability up to 1050 °C. The effective work function measured on high-*k* dielectric (HfO_2) is found to be 4.3 eV and the stability upon high temperature annealing is less favorable.

Keywords: Metal gate; TiN; Work function; ALD; TDMAT

1. Introduction

As silicon devices are scaled below 45 nm, metal gate and advanced high-*k* materials are required to obtain less than 1 nm Equivalent Oxide Thickness (EOT) [1]. Metal gate electrodes appear more promising than doped polysilicon gates, which present many restricting factors, like high resistivity, poly depletion, boron penetration and instability on high-*k* materials. The selection of new metal gate materials is a challenge because it is necessary to account for several critical points: the gate key parameters are the electrical properties (work function, resistivity), the chemical compatibility

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of the gate material with the underlying dielectric, and the thermal stability of the MOS structure after standard CMOS process thermal step. Several metallic candidates exhibit attractive properties, like single metals [2], metal nitrides [3], conductive oxides [4] or more complex alloys [5]. Recently, Park et al. [6] have shown the benefits of a damage-free direct metal gate process using Atomic Layer Deposition (ALD) method for TiN deposition on SiO_2 gate oxide. If ALD is employed to obtain TiN metal gate, the interface state density (D_{it}) is lower than the one detected in PVD (Physical Vapor Deposition) films or standard CVD (Chemical Vapor Deposition) films. Furthermore, the leakage currents are also reduced with ALD. However, Westlinder et al. [7] report strong work function instability of ALD-TiN from $TiCl_4$/NH_3 with high thermal budget. Moreover, Moriwaki and Yamada [8] have shown that the amount of residual chlorine in TiN and the reliability degradation of the gate oxide are strongly correlated. For these reasons, others precursors than halide must be studied for TiN ALD.

Metal Organic Atomic Layer Deposition (MOALD) of TiN using TetrakisDiMethylAmido Titanium (TDMAT) and ammoniac (NH_3) has been already reported [9,10]. MOALD with these precursors has the advantage to be halide free. In this work, MOALD of TiN using TDMAT precursor is proposed to make a new possible metal gate material for deep sub-micron CMOS process technology. Studies of microstructure, chemical properties and work function of TiN films deposited on SiO_2 or HfO_2 are presented.

2. Experimental

2.1. Deposition

TiN films were deposited by using a MOALD deposition technique in a MOCVD chamber (TxZ: Applied Materials Technology Inc., ENDURA5500) using a commercial 8 in. single wafer deposition tool. TiN thin films were deposited on 7 nm oxidized (100) silicon wafer by using TDMAT as the titanium precursor and ammonia (NH_3, 500 sccm) as the reactant gas. Prior to deposition, the SiO_2 substrates were cleaned by rapid thermal cleaning at 350 °C for 25 s. The deposition process is made by applying a series of successive reactant pulses separated each other by purge. To achieve the TDMAT pulse, the titanium precursor was generated in an external bubbler. TDMAT is introduced into the chamber with a He carrier gas flow. NH_3 was introduced in the chamber as ammonia pulse. Nitrogen (N_2) and Helium (He) were introduced for the complete separation of the precursor and the reactant gas purging the deposition chamber. During deposition, substrate wafers were kept at 180 °C and the pressure was kept constant at 5 Torr. Previous experiments have shown that in these conditions, the film growth rate is close to 2 mono layers per cycle [11].

2.2. Characterization

The composition and density of the TiN films were determined from Rutherford Backscattering Spectrometry (RBS). RBS used a 1 MeV He^+ source with a backscattering angle of 135°. Impurities incorporation and compositional profiles in thin films were measured by secondary ion mass spectroscopy (SIMS, Cameca IMS 5F Ion spectrometer). A Cs^+ primary ion beam with an impact energy of 3 keV was used to analyze an area of 200 μm in diameter. For microstructure analysis, a Bruker diffractometer equipped with a Cu Kα source radiation was used. HRTEM images were obtained by using a JEOL 2010FX microscope.

2.3. Work function measurements

To assess the TiN work function, simple Metal Oxide Semiconductor (MOS) capacitors were fabricated by using a single damascene process on silicon p-type (100) oriented silicon and boron implanted silicon substrate. After cleaning, a 600 nm thick oxide was thermally grown. A conventional photolithography process was then used to define a 0.0072 mm^2 active region. Dry oxidation at 800 °C was performed to grow the gate oxide (≈3 nm thick). On some of the capacitors, a 4 nm thick layer of HfO_2 is deposited by