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Investigation of nitrogen incorporation into manganese based copper diffusion barrier layers for future interconnect applications

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ABSTRACT

Manganese silicate has been shown to be an effective copper diffusion barrier layer for potential complimentary metal-oxide-semiconductor integration, but issues arise with regard to subsequent thin film metal adhesion. In this work, X-ray photoelectron spectroscopy has been used to systematically investigate the effect of incorporating nitrogen within manganese-based films in terms of both surface chemistry and adhesion of subsequently deposited copper. Results show that while all manganese films are heavily oxidised, and the deposition of single phase Mn nitride thin films appears to be very difficult, manganese oxide films containing small amounts nitrogen are shown to improve the adhesion of the copper to the underlying dielectric. Furthermore, it is shown that the incorporation of nitrogen into the manganese films does not inhibit the formation of manganese silicate at the dielectric interface.

Introduction

Continued miniaturization of electronic devices within the microelectronics industry has resulted in improved performance. However, as transistor gate length is scaled down, the RC time delay brought about by the interconnect layers becomes the limiting factor over gate time delay, and the intrinsic speed of the integrated circuit is now limited by this factor [1]. The continued need to improve the switching performance of future circuits has resulted in changes in back-end-of-the-line (BEOL) processing, from the well-established Al/TiN/Ti/SiO_2 interconnect technology to the use of Cu interconnects, Ta/TaN barrier layers [2], and low-k dielectric insulating layers. However, the currently used Ta/TaN barrier layers have poor electrical conductivity and there is an ever-increasing need to reduce the thickness to the minimum required for future technology nodes where increasingly porous dielectric materials will be utilized [3].

The ideal barrier layer for complementary metal-oxide-semiconductor (CMOS) interconnects should have resistance as low as possible to improve the overall interconnect resistance, provide good adhesion to both the dielectric and the copper interconnects, be chemically stable at the ambient pressures used in advanced manufacturing processes, and offer excellent control over the thickness of the barrier. Among the materials currently under investigation, are manganese based barrier layer systems [4–6]. Approaches involving manganese have shown that, upon thermal annealing the manganese forms manganese silicate at the dielectric interface which has been shown to be a good copper diffusion barrier [7,8]. However, one of the main challenges preventing the integration of the copper-manganese system into large scale manufacturing is the adhesion of the copper to the barrier layer/ dielectric stack. In previous technology nodes, metal/metal nitride bi-layers (Ti/TiN and Ta/TaN) were used as the barrier layer with the nitride layer acting as an adhesion promoter [9,10]. Following this trend of metal-nitrides as the buffer layer for adhesion of the metal, manganese nitride has gained some interest as a potential adhesion promoting layer within manganese based barriers.

Early work on the formation of manganese nitride films involved the use of bulk powders prepared by treating pure manganese in an ammonia atmosphere at high temperatures (>1000 °C) [11]. This approach to forming manganese nitride was aimed at forming thick films, and the temperatures involved are beyond the thermal budget for BEOL processing. Some efforts to form and characterise manganese nitride thin films involve ion implantation using an ion gun [12]. In a separate study, Liu et al. introduced nitrogen ions to a Cu lattice and deposited manganese which then forms manganese nitride on further treatment [13]. X-ray diffraction (XRD) studies confirm the various phases on thermal treatments but the amount of nitrogen that can be incorporated into the metal lattice is not studied in detail. However, the use of ion implantation as a means to form nitride films is highly incompatible with CMOS processing, and the formation of ultra-thin single phase Mn nitride films continues to be a challenge for researchers working within

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BEOL processing. It is for these reasons that for incorporation into Ultra Large Scale Integration (ULSI) processes, the deposition of Mn nitride by methods such as Chemical Vapour Deposition (CVD) or Atomic Layer Deposition (ALD) would be desirable.

Herein, we present a detailed spectroscopic study of thin films deposited from a nitrogen containing metal organic Mn precursor by CVD in order to understand the chemical composition of metal and nitrogen in the film, and the chemical nature of the nitrogen containing manganese films (oxidation state, single or multi-phase, etc.). Previous studies on the electrical characteristics of nitrogen containing manganese films showed promising results [14]. As a control, CVD manganese films from a separate metal organic precursor, which did not contain nitrogen were deposited on the same dielectric substrate in order to better understand the impact of nitrogen on the chemical interactions within the material system. The surface morphology of the films is studied using atomic force microscopy (AFM) to gauge surface roughness and in particular the impact of nitrogen incorporation on the surface. Finally, as adhesion is the key driver for nitrogen incorporation into the barrier layer stack, qualitative tape testing was carried out on both nitrogen containing and non-nitrogen containing samples to ascertain whether the incorporation of nitrogen improves the adhesion of copper to the barrier layer stack.

Experimental details

Thin metallic manganese and nitrogen containing manganese films were deposited on 300 mm wafers of Tetra Ethyl Ortho Silicate (TEOS) sol-gel SiO_2 using CVD. As the films are targeted for industrial applications, they were deposited under conditions relevant to industrial manufacturing processes. Metallic manganese was deposited from Bis (tetramethylcyclopentadienyl)manganese(II) = $C_{18}H_{26}Mn$, while nitrogen containing manganese films were deposited using bis(2,2,6,6-tetramethylpiperidido)manganese(II), $Mn(tmp)_2 = Mn(NC_9H_{18})_2$, with ammonia as a co-reactant. In order to study the effect of nitrogen incorporation, a similar deposition process was carried out for both films. Both samples were heated to 150 °C at moderate pressure (1 mbar) and 5 nm thick films were targeted. It is worth noting that while both manganese metal and the nitrogen containing manganese films were deposited within the same 300 mm industrial CVD deposition tool, a vacuum break was required in order to load individual 1 cm^2 coupons into the surface analysis chamber.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Microtech electron spectrometer at a base pressure of 1×10^{-9} mbar. The photoelectrons were excited with a conventional Mg Kα (hν = 1253.6 eV) x-ray source and an electron energy analyser operating at 20 eV pass energy, yielding an overall resolution of 1.2 eV. All XPS curve fitting analysis presented in this study was performed using AAnalyzer curve fitting software program version 1.20. Si *2p* spectra were fitted with Voigt doublet profiles with a Lorentzian value of 0.39 eV. O 1s and N 1 s spectra were fitted with Voigt profiles with Lorentzian values of 0.55 eV, and 0.5 eV, respectively. Mn *2p* spectra are fitted with Voigt – asymmetric profiles. A Lorentzian value of 0.87 eV was used to fit all Mn *2p* spectra.

In agreement with previous work the Mn *2p* peaks shown in this study are primarily used to identify the presence of oxidised Mn species on the sample surface, with the O 1s and Si *2p* spectra used to conclusively identify the presence of differing oxidised Mn species such as Mn silicate and Mn oxide [15]. A Shirley-Sherwood type background was used for all core level spectra. The full width at half maximum (FWHM) of the Si *2p* components, stayed constant throughout the study with bulk silicon component peak of 0.6 eV. Following initial analysis, the films were thermally annealed at 200 °C and 400 °C in UHV at a pressure of 1×10^{-9} mbar, with samples maintained at the target temperature for 60 min, in order promote the formation of $MnSiO_3$.

All AFM images and the root mean square (RMS) surface roughness values were obtained from tapping mode measurements taken by a Veeco Dimension 3100 atomic force microscope. The AFM silicon cantilever probes used were supplied by Budget Sensors with dimensions of: L x W x T = 125 × 30 × 4 μm^3, resonant frequency = 300 kHz, force constant = 40 N/m, tip radius of < 10 nm, with an Al reflective coating. All images were analysed using Gwyddion software version 2.39.

In order to test the adhesion of copper, approximately 80 nm of copper was simultaneously deposited on a TEOS substrate, a Mn metal film and a nitrogen containing manganese film using hot-filament thermal evaporation in a Leybold Univex chamber at a vacuum pressure of 2×10^{-6} mbar. A laser diced Si shadow mask with square structures of side dimensions 500 μm was used to deposit several small copper structures with a single deposition. The samples were then analysed using a Bruker Dektak XT stylus profiler to test for uniformity and thickness of the deposited copper structures. Following the Dektak measurements, the samples were subjected to a tape test as an initial test of adhesion. The tape test was carried out by securing the samples to a glass slide using double sided tape and then placing the scotch tape 5912 over the samples, fully covering the surface. The tape is then peeled off in a single motion and the sample is viewed under an optical microscope for signs of delamination. A Keyence VHX 2000E 3D digital microscope was used to image the Cu structures before and after the tape test to ascertain whether the deposition of Mn-metal and Mn-nitride impacts on the adhesion of copper.

Results and discussion

XPS survey spectra of the deposited manganese metal and nitrogen containing manganese films are shown in Fig. 1. Similar peak profiles are acquired in both cases, however, the presence of a N 1s peak in the case of the nitrogen containing manganese films, indicates that nitrogen was successfully incorporated during the CVD process. A Si 2p signal is detected during scanning of the nitrogen containing manganese film, indicating that the film is sufficiently thin such that the Si substrate is within the sampling depth of XPS.

The manganese metal and the nitride films show a significant amount of oxygen is present. This indicates that both the Mn metal and Nitrogen containing manganese films are heavily oxidised. Enthalpy studies on bulk manganese oxide and nitride have shown that manganese oxide has a lower enthalpy of formation than that of manganese nitride [16] and so manganese oxide forms more readily than manganese nitride.

The presence of a silicon signal in the nitrogen containing manganese films and not in the manganese metal films suggests that volume

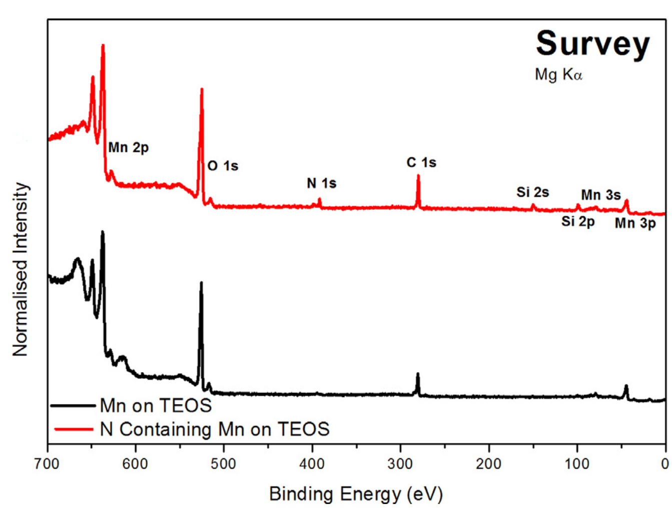

Fig. 1. XPS survey spectra of Mn metal and Nitrogen containing manganese films on TEOS SiO_2.