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Oxidation of ruthenium thin films using atomic oxygen

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ABSTRACT

In this study, the use of atomic oxygen to oxidise ruthenium thin films is assessed. Atomic layer deposited (ALD) ruthenium thin films (~3 nm) were exposed to varying amounts of atomic oxygen and the results were compared to the impact of exposures to molecular oxygen. X-ray photoelectron spectroscopy studies reveal substantial oxidation of metallic ruthenium films to RuO_2 at exposures as low as ~10^2 L at 575 K when atomic oxygen was used. Higher exposures of molecular oxygen resulted in no metal oxidation highlighting the benefits of using atomic oxygen to form RuO_2. Additionally, the partial oxidation of these ruthenium films occurred at temperatures as low as 293 K (room temperature) in an atomic oxygen environment.

1. Introduction

In recent years, ruthenium dioxide (RuO_2) has exhibited promising catalytic characteristics toward a range of important and industrially relevant chemical reactions [1–3]. The material has been in industrial use as dimensionally stable anodes (DSAs) in electrocatalysis for the past four decades [4,5], and has received significant attention for its ability to dehydrogenate small molecules such as ammonia [6], hydrochloric acid [2] and methanol [1] in heterogeneous catalysis. Metallic ruthenium is currently being investigated as a replacement liner layer for tantalum in order to promote copper wetting for interconnect fabrication in microelectronic devices [7], mainly due to its low electrical resistivity (~16 $\mu\Omega\cdot$cm) and compatibility with industrially relevant atomic layer deposition (ALD) processes. However, thin ruthenium films have displayed poor resistance to copper diffusion due to the formation of grain boundaries in the metallic layer [8]. As such, metallic ruthenium liner layers could only be used in conjunction with an additional copper diffusion barrier in a barrier/liner bi-layer configuration. Manganese silicate has been proposed as a potential barrier layer to accompany a ruthenium liner [9], however, the poor conduction properties of such a diffusion barrier could be improved using other materials which would promote superior overall line conductivity. Ruthenium dioxide belongs to the class of conducting transition metal oxides with an electrical resistivity of ~35 $\mu\Omega\cdot$cm, which is only a factor of 2 higher than that of the bulk metal and could be a suitable candidate as a copper diffusion barrier layer. RuO_2 films are in general polycrystalline, although amorphous layers have been reported to form at low substrate temperatures which could prevent the formation of grain boundaries and the subsequent diffusion of copper into the surrounding dielectric material [10]. Moreover, the conduction properties of ruthenium dioxide could be amenable to direct copper plating which would eliminate the need for a barrier/liner bi-layer system thereby reducing the real estate required for these functions, freeing up space for a larger cross section of highly conducting copper wire.

Many ruthenium dioxide preparation methods have been reported in the literature [10] such as metal organic chemical vapour deposition (MOCVD) [11], sol–gel spin coating [12], magnetron plasma sputtering [13] and pulsed laser deposition (PLD) [14]. However, the high temperatures and pressures required to form RuO_2 make such procedures incompatible with lower thermal budget processes such as back end of line (BEOL) interconnect fabrication. Ideally, oxygen is used as the transporting agent [15] in order to limit the impurity levels in the prepared metal oxide. However, large quantities of molecular oxygen (10^6 L, at 10^{-5} mbar) at temperatures in the range of 600 k to 750 k are required to produce 1–2 nm thick RuO_2 films with thicker films of 3–5 nm requiring even higher surface temperatures [10]. This study investigates the potential for neutral atomic oxygen to oxidise thin ruthenium metal films at lower partial oxygen pressures and temperatures than those reported in the literature to date.

2. Experimental details

The 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

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Mg Kα ($h\nu = 1253.6$ eV) X-ray source and an electron energy analyser operating at a 20 eV pass energy, yielding an overall resolution of 1.2 eV. The Ru thin films were deposited by ALD on a SiO_2 substrate with a targeted thickness of ~3 nm and were flat and continuous with a surface roughness of ~0.2 nm as determined by atomic force microscopy (AFM). All samples were degassed in ultra-high vacuum (UHV) by thermal annealing at 675 K for 1 h in order to remove the native oxide at the surface resulting in a pure metallic ruthenium thin film. The molecular oxygen exposures were performed at a total O_2 partial pressure of 5×10^{-6} mbar for time intervals of 500 s yielding an overall dosage of 1880 L per experimental cycle. The atomic oxygen exposures were performed at a partial pressure of 1×10^{-6} mbar (5×10^{-6} mbar total pressure — including 4×10^{-6} mbar O_2) for time intervals of 500 s yielding dosages of 376 L per cycle. It should be noted that during atomic oxygen exposure, a significant quantity of molecular oxygen was also present in the chamber due to the calculated cracking efficiency (~20%) of the thermal gas cracker (model TC-50 manufactured by Oxford Applied Research) at this pressure. The sample temperature was controlled during the gas exposures using resistive heating by passing a current through the sample holder. The Ru 3d core level spectra were curve fitted using an asymmetric line profile with a Shirly–Sherwood type background and Coster–Kronig broadening of the $3d_{3/2}$ peak [16] was allowed for by fixing the area ratio of the $3d_{5/2}$:$3d_{3/2}$ components to 0.67 rather than the peak intensities.

3. Results and discussion

Fig. 1(a) and (b) shows the Ru 3d spectra of two metallic 3 nm ruthenium thin films before and after exposures to molecular and atomic oxygen (AO) respectively. The sample temperature was maintained at 675 K during the exposures. There is a very limited change in the peak profile of the Ru 3d spectra after molecular oxygen exposures of 1880 L and 3760 L indicting the metallic film has remained largely unchanged. There is the emergence of a small peak (~5% of overall Ru signal) on the higher binding energy side (HBE) of the Ru 3d metal which is attributed to chemisorbed oxygen at the surface of the film. The very limited oxidation of the ruthenium film is in agreement with reports in the literature where much larger exposures to O_2 (~10^6 L) were required in order to oxidise ruthenium thin films [17,18]. In contrast, ruthenium films that were treated in an atomic oxygen (AO) environment at reduced exposures displayed significant changes in both the peak shape and the BE position of the Ru 3d peak profile, as shown in Fig. 1(b). The first exposure of 376 L AO resulted in the growth of an additional HBE peak separated from the metal Ru $3d_{5/2}$ component by ~0.6 eV, and constituted ~36% of the overall ruthenium signal which is attributed to the formation of RuO_2 in agreement with Over et al. [17]. After the 752 L AO exposure the metal Ru 3d peak at 280.1 eV was no longer detected, replaced entirely by the RuO_2 component. The complete transition from metal ruthenium to RuO_2 is supported by both

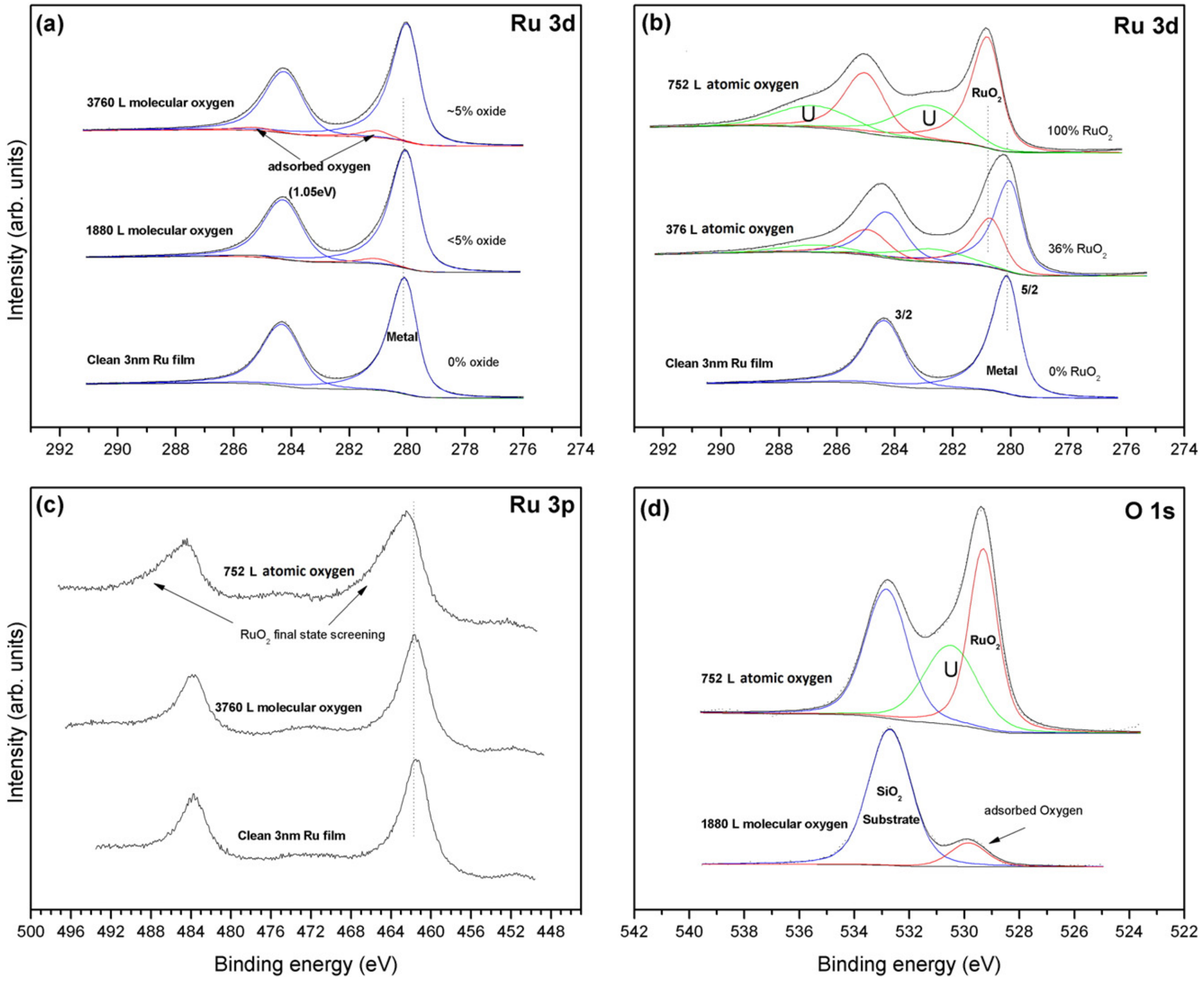

Fig. 1. (a) Ru 3d XPS spectra of a 3 nm ruthenium thin film exposed to 1880 L and 3760 L to molecular oxygen. (b) Ru 3d XPS spectra of a 3 nm ruthenium thin film exposed to 376 L and 752 L of atomic oxygen. (c) Ru 3p spectra of 3 nm Ru metal film, 3 nm Ru film exposed to 3760 L of molecular oxygen and 3 nm Ru film exposed to 753 L of atomic oxygen. (d) O 1 s spectra of 2 Ru samples exposed to 752 L of atomic oxygen and 1880 L of molecular. The sample temperature was maintained at 675 K during all exposures.