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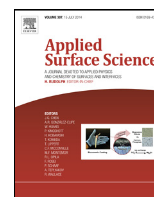

The addition of aluminium to ruthenium liner layers for use as copper diffusion barriers

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ABSTRACT

The chemical interaction of Al on a SiO_2 dielectric layer and the addition of Al into Ru thin films on SiO_2 for use as copper diffusion barrier layers are assessed in situ using X-ray photoelectron spectroscopy. Thin (~1–2 nm) Al films were deposited on a SiO_2 substrate and in a separate experiment on a 3 nm Ru liner layer on SiO_2, and both Al/SiO_2 and Al/Ru/SiO_2 structures were subsequently thermally annealed. Results indicate the reduction of SiO_2 and the subsequent formation of Al_2O_3 with the release of Si from the dielectric. The Al/Ru/SiO_2 structure showed evidence for the diffusion of Al through the Ru layer and the subsequent interaction of the Al with the underlying SiO_2 dielectric to form Al_2O_3. In this case, the reduction of SiO_2 leads to the release of Si from the dielectric and the subsequent chemical interaction of Ru with Si.

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1. Introduction

The continued reduction in the critical dimensions of integrated circuits (ICs) poses challenges to the current copper diffusion barrier layer arrangement of Ta/TaN. The ratio of the cross-sectional area of the barrier to the total width of the conducting wire in integrated circuits will increase significantly if the current barrier thickness remains constant. As a result, both the structure height-to-width (aspect) ratio and the overall wire resistance will increase. This deterioration in aspect ratio and line resistance can be improved by reducing the width of the copper barrier and seed layer between the dielectric and the conducting wire, particularly as the wire dimensions breach the 32 nm technology node [1].

Ruthenium thin films have been demonstrated to be an excellent substrate for conformal Cu electroplating [2,3], and as such have attracted interest as a replacement liner material. Ru also displays favourable bulk resistivity characteristics (ρ ~7 $\mu\Omega$ cm) compared to that of α-Ta (ρ ~15–30 $\mu\Omega$ cm), and is compatible with conformal deposition techniques such as atomic layer deposition (ALD). Although Ru is an excellent scalable liner candidate its barrier properties to Cu diffusion are poor, as Cu readily diffuses through the polycrystalline columnar grain structure of Ru thin films [4,5]. Improving the barrier layer properties of Ru films would enable a single barrier/liner layer and minimise the cross-sectional area of the barrier layer arrangement. It has been shown that introducing elements such as nitrogen and phosphorus into Ru thin films enhanced copper diffusion barrier properties [6,7]. Manganese has also been shown to form effective barriers to Cu diffusion on dielectric substrates [8–10], and as such has been added to Ru films to improve the films barrier properties [11,12]. McCoy et al. [12,13] reported that the deposition of manganese on Ru thin films resulted in the diffusion of the metal through the film and the subsequent reaction with the underlying SiO_2 substrate to form manganese–silicate at the Ru/SiO_2 interface. Ruthenium has also been reported to be involved in catalytic activity in a barrier layer context [14], potentially impacting upon the choice of elements added to improve the diffusion barrier properties of the liner layer.

Aluminium has been investigated as a potential self-forming barrier layer material, mainly because it has been used for IC metallization in the past. Perng et al. [15] showed that adding small amounts of Al to bulk Cu is an effective way to produce a self-forming AlO_x copper diffusion layer on porous low-*k* films. Given that aluminium segregates to the interfaces of copper films [16], a focus of this study is to determine if the same effect is observed in ruthenium liner layers. The addition and segregation of Al in ruthenium layers is of interest as it may improve the diffusion barrier properties of the Ru film by forming an AlO_x layer upon its interaction with the underlying dielectric. A small concentration of Al in Ru films is unlikely to impact upon the excellent copper plating attributes of the Ru liner as Al itself is conuducting, and so the

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Al–Ru system may be a viable option to act as a liner and provide diffusion barrier characteristics to Cu.

2. Experimental

High quality thermally grown SiO_2 layers on Si (1 1 1), with a measured thickness of 5.4 nm, as determined by tranmission electron microscopy (TEM), were grown using the Semitool dry oxidation process in a Thermoco 9002 series furnace at 850 °C. The SiO_2 surfaces were prepared using a standard degreasing procedure of successive dips in acetone, methanol and isopropyl alcohol (IPA) before being loaded into a UHV deposition and analysis system. SiO_2 samples were then degassed at ~200 °C for 4 h, with the UHV chamber reaching a maximum pressure of 5×10^{-9} mbar during degassing. The ALD Ru films were degassed in UHV at 300 °C for 3 h, resulting in the removal of surface oxide as determined by X-ray photoelectron spectroscopy (XPS) [12]. The 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 ($h\nu$ = 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. A high temperature annealing study up to 500 °C as measured at the sample stage was carried out in ultra-high-vacuum (UHV) at a pressure of 5×10^{-9} mbar, with samples kept at the target temperature for 60 min. Ultra-thin aluminium layers were deposited in situ using thermal evaporation from a tungsten filament, at a base pressure of 5.0×10^{-8} mbar. The sample was at room temerature during the deposition. The XPS core level spectra were curve fitted using Voigt profiles composed of Gaussian and Lorentzian line shapes in a 3:1 ratio with a Shirley-type background as previously reported [8]. The Al metal peak was curve fitted using an asymmetric Voigt line shape. The FWHM and asymmetry parameters were obtained from an Al reference sample which showed no evidence of oxygen or carbon contamination to within the detection limit of XPS.

3. Results and discussion

3.1. Investigation of the interaction of Al on SiO_2

Approximately 2 nm of Al was deposited onto a 5.4 nm thermally grown SiO_2 layer in the absence of Ru and the Al/SiO_2 system was subsequently thermally annealed up to 600 °C for 1 h. The focus of this experiment was to develop an understanding of the inherent chemical interactions at the Al/SiO_2 interface in the absence of Ru, so that the impact of the Ru liner may be accurately determined in a separate study. Fig. 1 shows the progression of the O 1s and Al 2p core level peaks through the experimental cycle. It is evident from the relative integrated areas of the metal and oxide component peaks within the Al 2p spectrum that the Al was in a primarily metallic state (~80%) upon deposition. The metal Al component peak is at a bingeing energy position of ~72.7 eV in agreement with Kim et al. [17]. An additional component peak at a binding energy position of ~75 eV is also present which has been identified as Al_2O_3 in agreement with previous studies [18], attributed to oxidation of the Al film due to the presence of residual oxygen within the UHV chamber during deposition. In agreement with this, there is also evidence for a small component peak on the lower binding energy side of the SiO_2 O 1s peak attributed to the presence of this limited amount of Al_2O_3. It is clear from the Al 2p peak in Fig. 1 that the area of the Al_2O_3 component grows with thermal anneal, suggesting the conversion of Al metal to Al_2O_3. Also, in agreement with this, the area of the Al_2O_3 component in the O 1s peak profile grows with respect to that of SiO_2. While it is possible that the conversion of Al metal to Al_2O_3 is partially due to the presence of

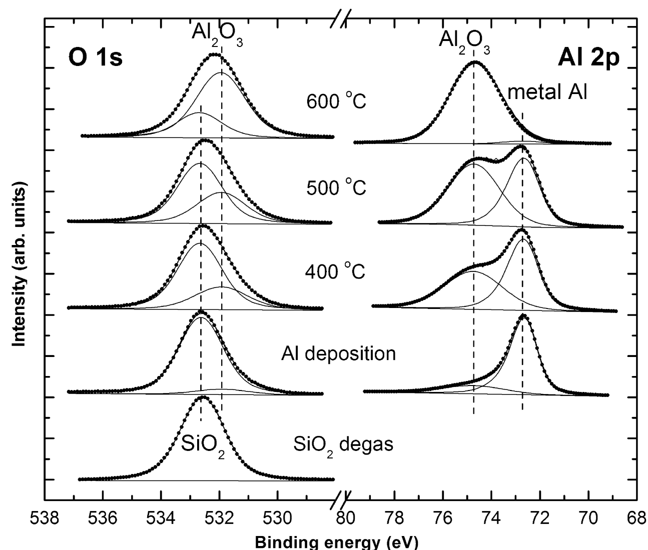

Fig. 1. O 1s and Al 2p spectra taken from the Al/SiO_2 surface following Al deposition and subsequent UHV thermal annealing treatments.

residual chamber oxygen during thermal anneal, the reduction in the intensity of the SiO_2 signal shown in Fig. 2 strongly indicates that the Al layer was converted to Al_2O_3 mainly due to the reduction of the SiO_2 following thermal annealing. This is in agreement with Bauer et al. [19] who reported the self-limiting conversion of SiO_2 to Al_2O_3 under similar experimental conditions. Al_2O_3 is thermodynamically more stable than SiO_2 with Gibbs free energies of −1582.3 kJ/mol and −856.4 kJ/mol, respectively [20], supporting the results outlined. The Si 2p spectra in Fig. 2 also show the growth of the Si component peak at a binding energy position of ~99 eV with respect to the SiO_2 bulk, concurrent with the growth of Al_2O_3. This is as a result of the reduction of SiO_2 during the formation of Al_2O_3, leaving Si at the interface at a binding energy indistinguishable from the silicon substrate signal. The presence of a Si peak at ~99 eV prior to Al deposition is due to the fact that the sampling depth of the XPS exceeds the thickness of the 5.4 nm SiO_2 film. At this point it is important to note that the release of Si during

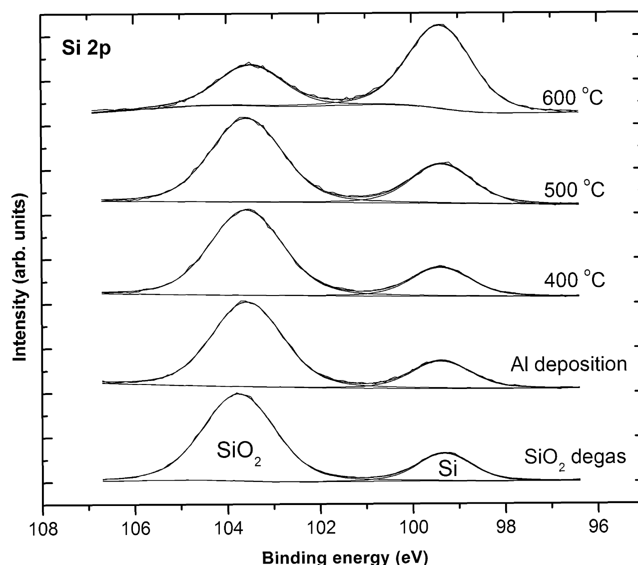

Fig. 2. Si 2p spectra taken from the SiO_2 surface following Al deposition and subsequent UHV thermal annealing treatments showing the reduction of the oxide and the presence of unbonded silicon.

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