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In situ X-ray diffraction study of self-forming barriers from a Cu–Mn alloy in 100 nm Cu/low-*k* damascene interconnects using synchrotron radiation

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ABSTRACT

An in situ study of self-forming barriers from a Cu–Mn alloy was performed to investigate the barrier growth using X-ray diffraction on damascene lines. The associated evolution in interconnect texture and Cu stress was also observed. The shift in Cu diffraction peak position was used to determine the change in Mn concentration and hence, estimate the thickness of the $MnSi_xO_y$ barrier. The observed peak shift followed a log(t) behaviour and is described well by metal oxidation kinetics, following the field enhanced diffusion model. We used multiple anneal temperatures to study the activation of the formation process, demonstrating a faster barrier formation with higher ion excitation. A strong [1 1 1] Cu texture was shown to develop during the anneal in contrast to traditional PVD barrier systems. Finally, the stress in the 100 nm Cu lines was calculated, observing a large in-plane relaxation when using a self-forming barrier due to reduced confinement.

1. Introduction

As interconnect dimensions are scaled, conformal barrier/seed deposition using the conventional Physical Vapor Deposited (PVD) Ta based barriers is becoming more challenging [1]. Atomic layer deposition has received attention as a potential solution to scale barrier-seed for future technology generations [2]. However, poor adhesion [3] and precursor contamination [4] are a major concern. As an alternative to conventional barrier deposition, self-forming barriers (SFB) are being investigated as a potential solution [5–14]. The use of SFB as a sidewall Cu diffusion barrier allows the deposition of a Cu alloy seed layer directly onto the dielectric, negating the need for a barrier step and increasing the PVD step coverage window [5]. After plating the bulk Cu, barrier formation is induced by a thermal treatment. Strong oxide forming elements such as Mg [6], Al [7], and Ti [8] have been investigated as potential alloys. Koike and Wada identified Mn as the most favourable material [9], showing that after the formation of a stable barrier, the observed interconnect resistivity is close to that of pure Cu [10]. Previously Cu–Mn alloy based SFB have been applied to the Cu/SiO_2 dual damascene stack, showing significant improvements in electromigration and stress migration reliability [11]. Recently Watanabe et al. have also applied SFB to a porous dielectric stack [12].

Barrier formation has been investigated in the literature to control barrier thickness using blanket Cu/SiO_2 and transmission electron microscopy (TEM) with a sampling period of hours [13,14]. In the present work we utilise high intensity synchrotron radiation to investigate the early stage $MnSi_xO_y$ growth kinetics in situ, with a sampling rate in the order of minutes. We extend the study to more relevant patterned damascene lines, in a porous ultra-low-*k* material where the barrier formation is affected by the 3D architecture and reduced free oxygen species. We also observe the associated evolution in Cu texture during barrier formation and consider the stress in the patterned interconnects.

2. Experimental

All samples were fabricated on 300 mm ⟨1 0 0⟩ Si wafers. A 250 nm SiO_2 pre-metal dielectric was deposited followed by a

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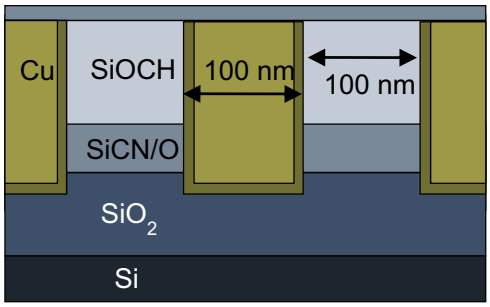

Fig. 1. Schematic cross-section of the XRD test structure.

25 nm SiCN/O etch-stop layer. Trenches 150 nm deep were prepared in a $k = 2.5$ porous organo-silicate-glass (OSG) material with an equal 100 nm line/space ratio and 150 nm line height. A Cu(8 at.% Mn) PVD seed was used, followed by electroplated Cu. An anneal of 1 hour at 430 °C in Ar was used to activate the barrier before chemical mechanical polishing (CMP). Finally, all samples were passivated with an 8 nm SiCN layer to prevent oxidation. On one sample, all thermal treatments were omitted to allow in situ barrier activation during the synchrotron measurements. A sample was also produced using a TaN/Ta barrier for comparison. This sample had an identical stack, receiving a 30 s post plating anneal of 180 °C. The sample stack of the two barrier systems is shown schematically in Fig. 1.

X-ray diffraction studies in this work were performed using a Bede MetrixL™ XRD metrology tool and beam line ID01 at the European Synchrotron Radiation Facility (ESRF). The Bede MetrixL™ was used to study the texture of the copper. The grazing incidence diffraction geometry (GIXRD) was used to measure the stress of the integrated structure and investigate the $MnSi_xO_y$ barrier formation [15]. The scattering vector (Q) was aligned perpendicular to the lines to measure the inter-planer spacing in the principle axis of Mn diffusion. The in-plane spacing and the out-of-plane spacing were also measured to calculate the tri-axial stress using the combined GIXRD and θ–2θ geometries respectively, as discussed elsewhere [15]. A large beam spot size of 0.1 mm by 0.1 mm was defined. This allows sampling of a large number of crystallites, increasing the available planes for diffraction and reducing the effect of point defects. Moreover, this set-up samples multiple lines giving greater averaging on the barrier formation. A Beryllium sample chamber equipped with a hot-plate was used to bring the patterned lines to elevated temperature in vacuum.

3. Results and discussion

3.1. Barrier formation

The patterned samples with no thermal processing during fabrication were used to study the barrier formation. Initially Mn atoms are in substitution on the Cu f.c.c. lattice, which causes modification of the lattice parameter as compared to pure copper [16]. A linear relationship between the fraction of the solute (Mn) and the atomic spacing of the alloy can be assumed following Vegard' Law [17]. This relationship has been demonstrated for Cu–Mn for low solute concentrations [18]. As Cu at the sub-micron scale has a pure elastic behaviour below 300–400° [19], one can neglect plastic lattice parameter modification. Therefore, only chemical modification of the lattice parameter due to Mn substitution is assumed in this study. Upon annealing the Mn atoms leave the copper lattice and the atomic spacing parameter of the metal is restored to that of pure copper. Such lattice parameter modifications can be investigated by X-ray diffraction techniques.

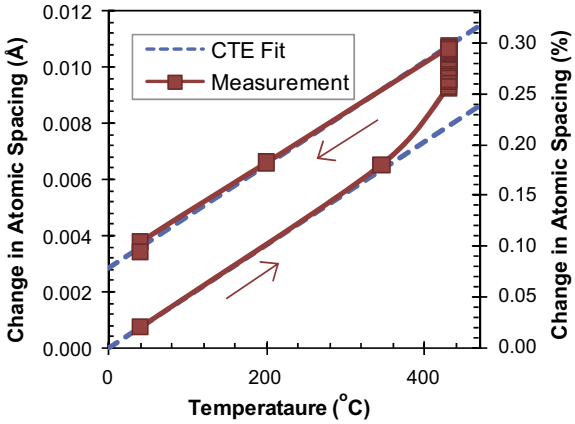

Fig. 2. Change in atomic spacing during temperature cycle.

The high angle Cu [2 2 0] peak was used to give a greater measurement resolution. Fig. 2 shows measurements of the ramp-up to 430 °C, hold and ramp-down sequence. As the Mn moves from the Cu–Mn seed layer the measured Cu peak is shifted. The measured Cu peak is an average of the strained Cu lattice (due to intrinsic or thermal stress) and strained Cu–Mn lattice (due to Mn substitution). The actual peak shift must be decomposed into the two separate contributions. This is performed using a fraction based on a line area cross-section area estimated from TEM images of seed layer deposition on similar samples. In the present work, a 15 nm seed layer was measured on the side walls and 43 nm on bottom of the trench. This results in approximately equal fractions of Cu and Cu–Mn prior to annealing. Hence, the formula for the time resolved atomic spacing follows:

$$a(t) = \beta(t)a_{Cu} + \theta(t)a_{Cu-Mn} \quad (1)$$

where, a is the measured atomic spacing at time t; a_{Cu} and a_{Cu-Mn} are the intrinsic atomic spacing of the Cu and Cu–Mn layers; and β and θ are the time evolved the fractions of Cu and Cu–Mn making up the line cross-section respectively (where $\beta + \theta = 1$). Eq. (1) can be solved using, $a_{CuMn} = a_{Cu} + \gamma$, based on Vegard's Law [17], where $\gamma = 0.03$ Å was derived from a blanket study and consistent with the literature [18]. Therefore, the portion of the Cu–Mn seed area which has been depleted of Mn can be calculated using $\theta(0)$–$\theta(t)$, and related to the $MnSi_xO_y$ thickness. The effect of Cu shrinkage from the Mn depletion is neglected as the samples were prepared in a compliant dielectric.

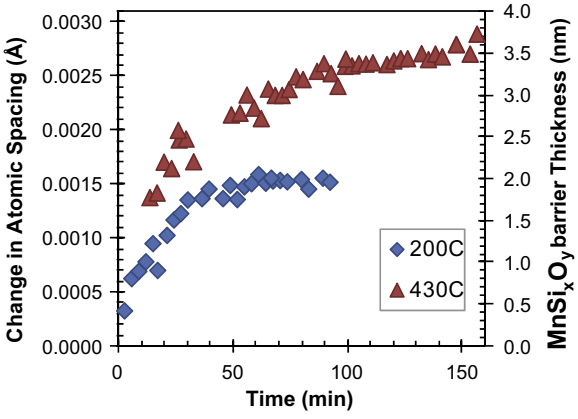

Fig. 3. Comparison of the $MnSi_xO_y$ barrier formation annealed at 200 and 430 °C, showing a both change in atomic spacing and estimated $MnSi_xO_y$ barrier thickness.