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XAFS studies of Al/TiN$_x$ films on Si(100) at the Al *K*- and $L_{3,2}$-edge

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The effect of annealing on Al diffusion through a TiN$_x$ barrier on a Si(100) wafer has been studied with Al K-edge and $L_{3,2}$-edge absorption spectroscopy as a function of annealing temperature (400 °C - 600 °C). It is found that there is a noticeable change at high temperatures in the Al K- and $L_{3,2}$ -edge spectra as the temperature increases. This observation is attributed to the formation of a stable protective surface oxide. Fluorescence yield shows that most of the Al metal remains intact after annealing.

Keywords: Al K-edge, Al $L_{3,2}$-edge, XANES, diffusion barrier, high temperature processing

1. Introduction

TiN$_x$ thin films are commonly used in semiconductor industry as a diffusion barrier which prevents Al from diffusing into the Si substrate. It is important that the barrier remains effective during high temperature processing, an important step in manufacturing. The objective of this research is to investigate, from the Al perspective, what has taken place during high temperature processing. Using Al K- and $L_{3,2}$-edge XANES (X-ray Absorption Near Edge Structures), we have studied the effect of annealing on an Al film deposited on a TiN$_x$-barrier coated Si (100) wafer.

2. Experimental

All the samples were prepared at the Chartered Semiconductor Manufacturing (CSM) of Singapore. A Si(100) wafer was used as the substrate. A 300 Å TiN$_x$ layer was first deposited onto a clean Si(100) substrate by sputtering a Ti target in a nitrogen environment (4 mtorr). A 400 Å Al film was subsequently deposited on the TiN$_x$ coated Si(100) in UHV using a Al (5% Cu) target. The alloy target has superior properties over pure Al and is commonly used in manufacturing. The samples were annealed to a desired temperature (400 °C, 450 °C, 500 °C, 560 °C and 600 °C) for one hour under nitrogen atmosphere. After annealing, samples were stored in ambient atmosphere.

XANES experiments were carried out at the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison (Aladdin). Al K-edge data were obtained using the Double Crystal Monochromator beamline (quartz crystals) while the Al $L_{3,2}$-edge data were recorded at the grasshopper beamline. Both total electron yield, TEY (specimen current) and fluorescence yield, FLY (channel plate detector) were used to record the XANES spectra (Rosenberg et al. 1992; Hiraya et al. 1995; Kasrai et al. 1996). While TEY is sensitive to the surface and near surface regions of the film, FLY is generally sensitive to the bulk. Thus this double-detection channel technique permits the probing of different regions of the film preferentially. All photon energies are referenced to the edge jump of the as-deposited film at 1560 eV and 72 eV for the K- and L_3-edge, respectively.

3. Results and Discussion

Fig.1 shows the Al K-edge XANES for a series of samples. All spectra are normalized to the incident flux (TEY = I_{yield}/I_o) with the overall edge jump (a flat region at ~30 eV above threshold) normalized to unity. TEY probes the surface and near surface of the film due to the short escape depth of electrons (10 -30 Å) (Kasrai et al. 1996) despite that the one-absorption length just above the Al K-edge is ~ 0.9 μm (Henke et al. 1982).

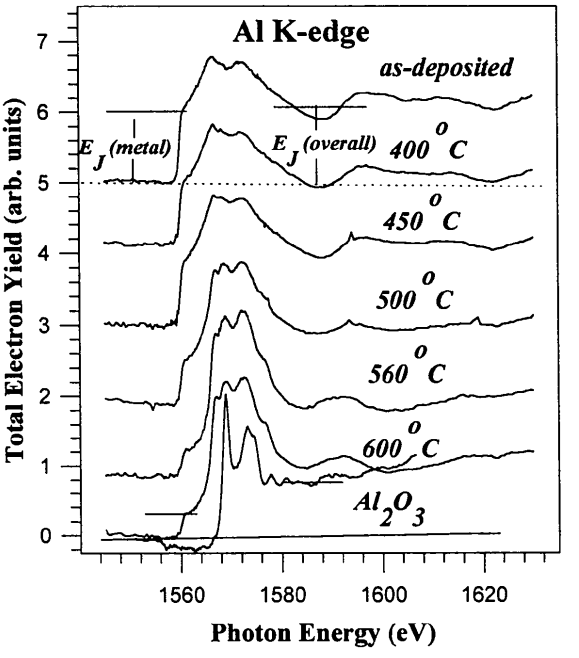

Fig.1
Al K-edge XANES (TEY) for a series of Al/TiNx/Si(100) samples annealed for an hour at various temperatures. Spectra are normalised to the edge jump and shifted vertically for clarity.

From Fig.1, we see that the as-deposited film exhibits an edge jump at ~ 1560 eV immediately followed by a doublet. These features are characteristic of the K-edge XANES of Al metal (Tamura et al. 1995). The magnitude of the jump at the threshold is incidentally ~ unity. The relative intensity of this jump to unity will be used below to monitor the relative amount of metal in the film. Upon heating, several features are noted. First, at low temperatures (< 450 °C), the XANES changes very little: a small decrease in the metal edge jump (sharp rise at 1560 eV) and a small increase in the intensity of the doublet due to oxide contribution. Second, at higher temperatures (> 500 °C) several new sharp features appear and they are accompanied by a significant drop in the intensity of the metal edge jump at ~ 1560 eV. These new features are characteristic of thermal oxide films containing equilibrated oxide and suboxide phases on the Al surface (Hu 1997). Third, the oxide film appears to stabilize above 560 °C and no further change is seen at 600 °C. Finally, the metal edge-jump at 1560 eV for the high temperature samples (560

and 600 °C) is ~ 1/3 of the overall edge jump (unity). Assuming that there is no countervailing transition matrix element arguments, this ratio represents a lower bound of the relative amount of Al metal in the film.

Fig.2 shows the corresponding FLY XANES of Fig.1. FLY is more bulk sensitive than TEY because the K shell fluorescence photons have large escape depth compared to the electrons and the thickness of the film (Henke et al. 1982). We see that the difference in the XANES, especially the metal edge jump, is less dramatic. The oxide contribution is much smaller. The overall edge jump does not change significantly either indicating no significant loss of Al to diffusion. The ratio of the metal edge-jump for the 600 °C sample to unity is ~ 80 % indicating that ~ 320 Å (upper bound) of the Al layer underneath the oxide layer remain metallic. The actual thickness should be quite close to the upper bound value.

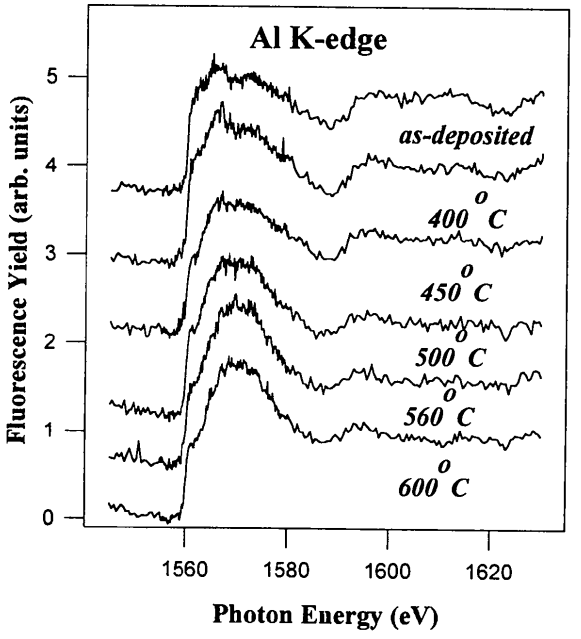

Fig. 2
Corresponding Al K-edge XANES (FLY) for the same series described in Fig.1

Fig. 3 shows the $L_{3,2}$-edge XANES for the two extreme cases (as-deposited and 600 °C). It should be noted that TEY at the L-edge is more surface sensitive than at the K-edge because of its shorter one-absorption length (~ 400 Å above the edge) and short electron escape depth while FLY is less bulk sensitive relative to the K-edge because of the Al oxide overlayer and self-absorption (L-shell fluorescence photons are at very low energy, < 70 eV, they have a escape depth comparable to the thickness of the film).We see that the TEY spectra are dominated by oxide absorption with the Al metal edge barely visible even for the as-deposited sample while the FLY exhibits a noticeable spin-orbit resolved metal edge even for the 600 °C sample despite distortion (a skew shape compared to TEY) due to self-absorption and a significant oxide signal. Self-absorption is primarily responsible for the distortion of the Al $L_{3,2}$-edge FLY XANES (Brown 1974). Recently, It was shown that a ~ 70 Å film of surface Si oxide will totally suppress the Si $L_{3,2}$-edge TEY signal from the Si underneath (Kasrai 1996). For Al oxide on Al, an oxide film with comparable thickness will also be sufficient to suppress the metal TEY signal totally. Thus the TEY indicates that the Al oxide film is comparable to this thickness. This value, albeit with large uncertainty, implies that most Al metal remains in tact after annealing, in good accord with the K-edge results. Finally, it is interesting to note that the as-deposited sample exhibits different surface and bulk oxide phases within the oxide layer. More details of the phase transition and corresponding spectroscopy for other elements will be discussed elsewhere.

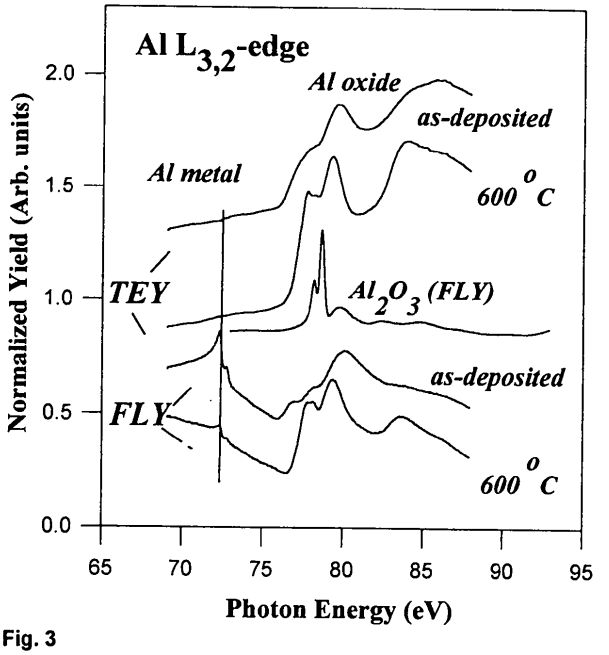

Fig. 3
Al $L_{3,2}$-edge XANES recorded in TEY and FLY for the as-deposited and the 600 °C sample. The threshold position for the metal is marked with a vertical line. The $L_{3,2}$-edge XANES (FLY) for crystalline Al_2O_3 is also shown for comparison.

4. Conclusion

Using Al K- and $L_{3,2}$-edge XANES, we have shown that while the Al film oxidizes in the ambient, a majority of the Al in the Al/TiNx/Si(100) system remains metallic after high temperature annealing. We have also shown that the multi-core, multi-detection channel scheme enhances the probing capability of XAFS in thin films.

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