

A study of titanium nitride diffusion barriers between aluminium and silicon by X-ray absorption spectroscopy: the Si, Ti and N results

Y.F. Hu,^{ab*} T.K. Sham,^b Z. Zou,^{cd} G.Q. Xu,^c L. Chan,^d B.W. Yates,^a G.M. Bancroft^b

^aCanadian Synchrotron Radiation Facility, University of Wisconsin-Madison, 3731 Schneider Dr. Stoughton WI 53589, USA, ^bDepartment of Chemistry, The University of Western Ontario London Ontario N6A 5B7, Canada, ^cDepartment of Chemistry Faculty of Science National University of Singapore 10 Kent Ridge 119260, Singapore, ^dChartered Semiconductor Manufacturing Pte. Ltd., 60 Woodlands Industrial Park D, Street 2, 738406, Singapore. Email: yhu@julian.uwo.ca

We report a multi-element, multi-edge and multi-detection mode X-ray photoabsorption study of a series of Al/TiN_x/Si(100) thin films as a function of the TiN_x film thickness (100Å–500Å) and of the annealing temperature (400 °C–600 °C). The Si K- and L-edge results show that Si does not diffuse to the surface for all the films. The high resolution Ti L-edge and N K-edge spectra show that the TiN_x layer undergoes a dramatic chemical reaction with the gradual increase in the annealing temperature. This chemical reaction stabilizes at 560 °C at which the TiN_x film is known to fail to act as an effective diffusion barrier between Al and Si.

Keywords: XANES, diffusion barrier, titanium nitride, oxidation reaction

1. Introduction

Titanium nitride (TiN_x) thin films have long been used as an effective diffusion barrier between Al and Si in semiconductor technology because of their high thermal and chemical stability and low electrical resistivity (Wittmer, 1980). These properties allow TiN_x to withstand the repeated thermal cycles in multi-step processes of integrated circuit devices. It is generally known that TiN barrier thin films are vulnerable to breakdown when annealed to temperatures above 550 °C due to the Al and Si interdiffusion.

Many techniques, such as X-ray photoelectron spectroscopy (XPS) (Prieto & Kirby, 1995), Auger electron spectroscopy (AES) (Tompkins, 1991; Kottke *et al.*, 1991), electron energy-loss spectroscopy (EELS) (Walker *et al.*, 1997), transmission electron microscopy (TEM) and electron dispersive spectroscopy (EDS) (Lee *et al.*, 1999), and X-ray absorption spectroscopy (XAS) (Soriano, *et al.*, 1993), have been used to study the thermal properties of TiN_x films and to understand the failure mechanism of the TiN_x barrier. In this work, we study a series of Al/TiN_x/Si(100) thin films as a function of the TiN_x film thickness (100Å–500Å) and of the annealing temperature (400 °C–600 °C), using multi-element, multi-edge and multi-detection mode X-ray photoabsorption spectroscopy. Major advantages of this technique for studying these sandwich samples are three folds: (1) By measuring XANES (X-ray Absorption Near Edge Structures) in both the surface sensitive total electron yield and the interface and bulk sensitive fluorescence yield, it provides

depth information of a multi-layer material. (2) By studying XANES at different edges of different elements containing in a multi-layer material, it provides chemical composition information. (3) It is a non-destructive technique so there is little sample modification during the measurement, which is a common problem for the other conventional tools, such as AES. A review of this technique can be found elsewhere (Sham, *et al.*, 2000). We have recently reported the XANES studies of these samples from the Al perspective (Zou, *et al.*, 1999), we will focus on the Si, Ti, and N results in the present work.

2. Experimental

All the samples were prepared at the Chartered Semiconductor Manufacturing of Singapore. A Si(100) wafer was used as the substrate. Two sets of samples were studied. In the temperature series, a 300Å TiN_x film was deposited onto the clean Si(100) substrate by sputtering a Ti target under nitrogen atmosphere. This TiN_x layer was then capped by a 400Å Al film in an UHV chamber (using a Al target containing 5% Cu). Samples were then annealed for one hour under nitrogen atmosphere to a desired temperature (400 °C, 450 °C, 500 °C, 560 °C and 600 °C). In the thickness series, all the samples were prepared in the same routine except that the thickness of the TiN_x film varied from 100Å, 200Å, 300Å, 400Å to 500Å and all the samples were annealed to 560 °C for one hour.

XANES measurements were performed at the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. Si K-edge results were obtained using the Double Crystal Monochromator beamline, Si L-edge results were obtained using the grasshopper beamline, and the Ti L-edge and N K-edge results were obtained using the Canadian Spherical Grating Monochromator beamline. The photon energy was calibrated using a standard TiO₂ (rutile), clean Si/SiO₂ samples and N₂ gas. XANES spectra were recorded in both the total electron yield (TEY) and the fluorescence yield (FY) modes. The TEY mode was measured by directly monitoring the sample current, it is surface and near surface sensitive with an estimated sampling depth of eg, 50Å at the Si L-edge (Kasrai, *et al.*, 1996). The FY mode was measured using a detector comprised of two channel plates, it is generally sensitive to the bulk with an estimated sampling depth of eg, a few thousand angstrom at the Si K-edge (Kasrai, *et al.*, 1996). All measurements were normalized to the incident flux. All reported spectra were recorded at the normal incidence angle.

3. Results and Discussion

3.1 Si results.

It has been known that Si has some solid solubility in Al (Hanson & Anderko, 1958), and the Si content has been determined in the Al layer when annealed to high temperatures (Ting & Wittmer, 1983). Our Al results showed that while the Al film oxidizes in the ambient, about 80% of the Al in the Al/TiN_x/Si(100) system remains metallic after high temperature annealing, and there was no Si contribution (eg, formation of the Al silicide) observed in the Al K and L-edge XANES spectra (Zou, *et al.*, 1999). Fig. 1 shows the Si K-edge XANES for a series of Al/TiN_x/Si(100) samples, with the thickness of the TiN_x film varied from 100Å to 500Å. Also shown in Fig. 1 are reference spectra of a clean Si(100) and of a TiSi₂ sample. FY spectra of all these samples

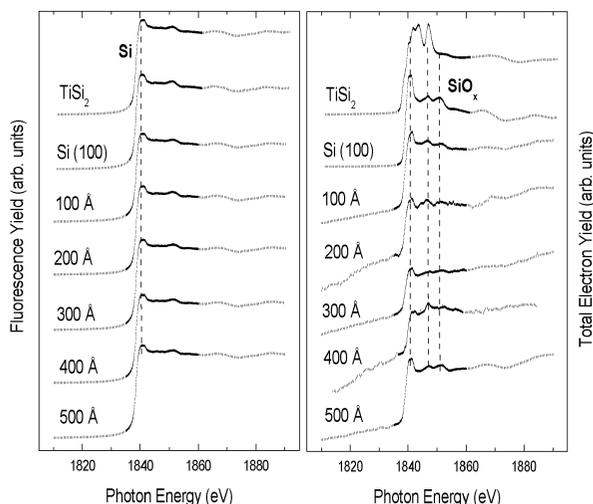


Figure 1
Si K-edge XANES of a series of Al/TiN_x/Si(100) samples, as a function of the thickness of TiN_x layer. The thickness of the Al layer was 400 Å for all the samples and all the samples were annealed to 560 °C for one hour. Spectra of a clean Si(100) wafer and a TiSi₂ are also shown.

shown on the left side of Fig. 1 are all characteristic of a clean Si(100) substrate (Kasrai, *et al.*, 1996). This is not surprising since the K shell fluorescence photons have a much larger escape depth than electrons (Henke *et al.*, 1982) and the sampling depth of the Si K-edge in the FY mode is expected to be much larger than the thickness of the sample. Therefore, the contribution from the bulk Si, i.e., the Si(100) wafer, dominates in the FY mode at the Si K-edge of all the samples.

On the other hand, the TEY mode at the Si K-edge was reported to have an estimated sampling depth of 700 Å in a SiO₂/Si(100) system (Kasrai, *et al.*, 1996). The TEY mode allows us to probe the surface and interface Si content in these sandwich samples. TEY spectra of these Al/TiN_x/Si(100) samples shown on the right side of Fig. 1 are all similar to that of the spectrum of a clean Si(100) but certainly different from that of the TiSi₂. The resonance at ~1840 eV photon energy of the Si(100) wafer is due to the transition from the Si and the signal at ~1846 eV is originated from transitions from the surface SiO₂. Thus, these results indicate that there are interface states between Si and metal layer and these interface states are most likely Si oxides, but not of silicide origin.

There are two other points worth noting about the TEY XANES of these samples. First, there is no obvious difference in the TEY spectra of these samples as the TiN_x film thickness increases. This implies that there would be Si diffusion to the surface if the TEY sampling depth at Si K-edge were assumed to be ~700 Å (Kasrai, *et al.*, 1996). However, we could not detect any Si signal in the more surface sensitive Si L-edge XANES of these samples in both TEY and FY modes (spectra not shown), and there is no indication of the formation of the titanium silicide at the interface between the TiN_x layer and the Si substrate. This titanium silicidation was commonly observed when the TiN_x/Si system was annealed to high temperature (Kottke, *et al.*, 1991). Furthermore, we did not observe the formation of Al and Si alloys in the surface and the bulk of these samples from the Al perspective (Zou *et al.*, 1999). We think the effective sampling depth in the TEY mode at Si K-edge for these samples (with Al and TiN_x on top of the Si) is probably greater than 700 Å (estimated for a SiO₂/Si system). Therefore, only the substrate Si (with less or no bulk Si contribution) was detected in the TEY

mode of these samples and as a result, there is no significant spectral difference when the total thickness of the layer on top of Si is 500 Å or 900 Å. Second, there is a noticeable difference between Al/TiN_x/Si(100) XANES and that of the Si(100) in the silicon oxide region (around 1850 eV). We attribute this difference to the formation of interface states (SiO_x, other than SiO₂) when Al/TiN_x/Si(100) samples were annealed to 560 °C.

3.2 Ti L-edge results

Fig. 2 presents the Ti L-edge TEY and FY spectra of three 400 Å Al/300 Å TiN_x/Si(100) samples (as deposited and annealed to 450 °C and 560 °C, respectively) and of TiO₂ (rutile) and of a standard TiN_x sample. For the as-deposited sample, both TEY and FY spectra show two peaks (around 458.5 and 464 eV photon energies) corresponding to transitions from the Ti 2p_{3/2} and 2p_{1/2} initial states to vacant d orbitals. In previous XAS studies of TiN_x, only TEY mode was used and the oxide contribution at the surface was always present (see the TEY spectrum of the TiN_x in Fig. 2, and see eg., Soriano *et al.*, 1993, Esaka, *et al.*, 1997). This is the first time that a clean TiN_x spectrum is reported in both TEY and FY modes. This also confirms that the TiN_x layer in our as-deposited sample was protected by the Al layer from oxidation before annealing.

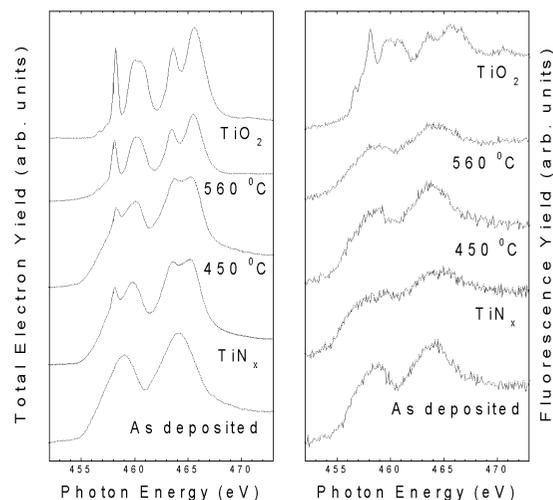


Figure 2
Ti L-edge XANES of a series of Al/TiN_x/Si(100) samples, as a function of the annealing temperature. The thickness of the Al and the TiN_x layer is 400 Å and 300 Å, respectively. Reference spectra of TiO₂ (rutile) and a TiN_x sample are also shown. Please note that the fluorescence yield spectrum of TiO₂ single crystal is distorted due to self-absorption.

Upon annealing, the TiN_x layer in the Al/TiN_x/Si(100) sample is slowly oxidized. The TEY spectrum of the 450 °C annealed sample is almost identical to that of the ambient TiN_x sample. At 560 °C annealing, TiO₂ feature dominates the TEY spectrum, showing the spin-orbit and crystal field resolved fine structures, just like that of a true TiO₂ spectrum (Fig. 2 and van der Lann, 1990). In contrast to spectra measured in the TEY mode, FY spectra of Al/TiN_x/Si(100) samples exhibit no TiO₂ feature, even when the sample was annealed to 600 °C (spectrum not shown). It is concluded that, based on the Ti L-edge results, the surface TiN_x is oxidized to produce TiO₂ during the annealing process, but the bulk TiN_x layer remains intact.

3.3 N K-edge results

Fig. 3 illustrates the N K-edge TEY and FY spectra of the 400Å Al/300Å TiN/Si(100) samples as a function of annealing temperatures. FY spectra of all the samples are dominated by features due to the unreacted bulk TiN_x (Pfluger, *et al.*, 1982), with the gradual increase in the relative intensity of the 401 eV peak with the increase of the annealing temperature. This indicates that the bulk TiN_x in these samples remains intact, from the N perspective, in agreement with findings based on the Ti L-edge results. The increase in the relative intensity of 401 eV peak is due to the oxidation reaction of the TiN_x layer after the high temperature annealing (see below). We also note that FY spectra of 560 °C and of 600 °C annealed samples are virtually identical, implying the saturation of the oxidation reaction at 560 °C.

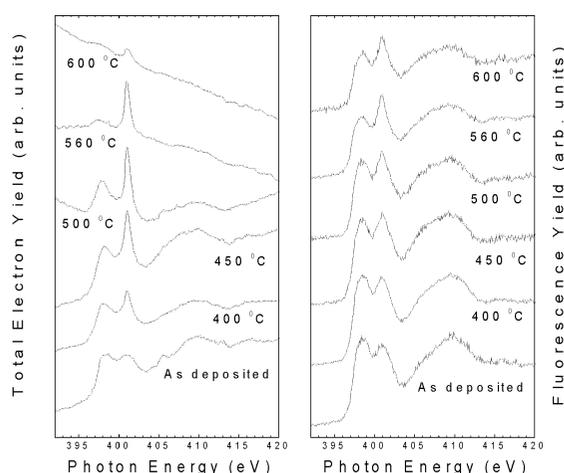


Figure 3
N K-edge XANES of a series of 400Å Al/300Å TiN_x/Si(100) samples, as a function of the annealing temperatures.

When the 400Å Al/300Å TiN_x/Si(100) sample was annealed to high temperatures, there is a more dramatic spectral change in the TEY spectra of this series of samples. There is a gradual decrease of the TiN_x feature as the temperature increases. Oxidation of TiN_x at 560 °C and 600 °C causes the TiN_x feature to disappear almost completely from the TEY spectra. These spectra are dominated by a sharp peak at 401 eV photon energy which has been observed previously in TiN_x films after similar thermal treatment (Soriano, *et al.*, 1993, Prieto & Kirby, 1995, Esaka *et al.*, 1997). This peak can be assigned to the contribution from the molecular N₂, as a result of the TiN_x oxidation. This oxidation reaction ($2TiN_x + 2O_2 \rightarrow 2TiO_2 + xN_2$) is thermodynamically favorable (Wittmer, *et al.*, 1981). The N₂ molecule generated by this reaction was then trapped in the TiN_x layer by physical and/or chemical absorption. The vibrational fine structure due to the interstitial N₂ molecules, similar to that due to the N₂ gas, has recently been resolved in the high resolution XAS spectrum of the thermally oxidized TiAlN film (Esaka, *et al.*, 1998).

4. Conclusion

We demonstrated that the multi-element, multi-edge and multi-detection mode X-ray photoabsorption spectroscopy is a powerful, non-destructive technique in providing chemical and

structural information for surface, interface and bulk of complicated films. For the Al/TiN_x/Si(100) films, our results showed that there is no inter-diffusion for Al and Si, even with high temperature annealing. When annealed to temperatures higher than 560 °C, the TiN_x layer is not an as effective diffusion barrier due to oxidation reactions.

We thank staff at CSRF and SRC, especially Dr. K.H. Tan, for their technical assistance. Research performed at CSRF and UWO is supported by NSERC (Canada). SRC is supported by the US National Science Foundation Grant No. DMR-9531009.

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