Thermodynamic stability of \( \text{Al}_2\text{O}_3 \) films in contact with Ti and Mo thin films

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Introduction

Aluminium oxide (Al\(_2\text{O}_3\)) is one of the most promising candidates being considered as a possible gate oxide to replace SiO\(_2\) in microelectronic circuits.\(^1\)–\(^3\) Other materials of interest are ZrO\(_2\) and HfO\(_2\). The interest in these oxides is due to their high dielectric constants (\(K \sim 10\) for Al\(_2\text{O}_3\) and \(\sim 20–30\) for ZrO\(_2\) and HfO\(_2\)). Reducing the overall size of electronic devices requires that all parts of the chip be made smaller as well as the thickness of gate oxides. This must be accompanied by the maintenance of low leakage currents, hence the desire for high-\(K\) oxides. In this article we report on the thermal stability of the Al\(_2\text{O}_3\) interface when in contact with either Ti or Mo thin films at high temperatures (400–900°C) for anneals in vacuum lasting up to 2 hours.

Experimental

Silicon \(<100>\) wafers were cut into 9 mm × 9 mm squares, cleaned chemically and then dipped into de-ionized water. Films of Al\(_2\text{O}_3\) were evaporated by electron gun onto the wafers in a vacuum of better than \(6 \times 10^{-7}\) torr. Either Ti or Mo thin films were then deposited by electron beam on top of the Al\(_2\text{O}_3\) film. In all cases the Al\(_2\text{O}_3\) film between the silicon and metal was made thicker than 3000 Å to prevent Si coming into contact with the metal during annealing. In some cases a layer of Al\(_2\text{O}_3\) was deposited on top of the metal film, so as to reduce oxidation of the metal. Al\(_2\text{O}_3\) films, evaporated by electron gun, had unequal thicknesses as the plume evaporated from the source was strongly directional. This could clearly be seen from the colour of the sample films, which varied in concentric circles from the centre outwards. Rutherford backscattering spectrometry (RBS) confirmed that the samples had thicker centres than the edges.

All samples were analysed by RBS. The RUMP software code\(^4\) was used for phase identification and to determine the thickness of deposited layers as well as of these compounds. To identify the composition of the compound phases formed, the samples were analysed by X-ray diffraction (XRD). Customized computer programs were used to analyse the complex XRD spectra.

Results

Samples made up of Al\(_2\text{O}_3\)-(bulk)/Mo(2500 Å) layers were annealed in vacuum at various temperatures for two hours. Figure 1 shows representative RBS spectra. The one sample (whose spectrum is a dotted line) was annealed at 800°C, whereas the other (whose spectrum is a continuous line) was a virgin sample. Clearly, the two spectra resemble each other. Within the detection limits of RBS, the Al\(_2\text{O}_3\) film appeared to remain intact during the anneal even at temperatures as high as 800°C.

RBS results for the Si\(<100>/\text{Al}_2\text{O}_3(6500 \text{ Å})/\text{Ti}(2000 \text{ Å})/\text{Al}_2\text{O}_3(750 \text{ Å})\) composite are shown in Fig. 2. The spectrum for the virgin sample shows that there was no interaction between the two films of Al\(_2\text{O}_3\) and Ti. There was also no visible oxidation of the metal. Si has a greater atomic mass than Al, which is why there is a peak due to an overlap between signals from these two
elements. No reaction between Al₂O₃ and Ti was observed for samples annealed at temperatures lower than 620°C (results not shown). The RBS spectrum of the sample annealed at 620°C for 1 hour shows that Al had diffused into the Ti layer. The peak heights of Ti also fell. This was due, in part, to the oxidation of Ti and also to the formation of other phases between O, Ti and Al. We can also see that, compared to the virgin sample, the peak height of the sample annealed at 620°C rose between the two oxygen peaks. This indicates the presence of O in the Ti film of this sample. The RBS spectrum of the sample annealed at 820°C for 1 hour looks almost similar to that of the 620°C sample. No clear shoulder (or step) developed on the Ti signal to allow us to estimate stoichiometric ratios closest to known equilibrium phases. RUMP simulation revealed that Al was present throughout the reacted region in varying ratios (and so were Ti and O).

Figure 3 shows an X-ray diffraction spectrum of the Si<100>$/\text{Al}_2\text{O}_3$(6500 Å)/Ti(2000 Å)/$\text{Al}_2\text{O}_3$(750 Å) samples. The spectrum of the virgin sample shows that Ti crystallized on deposition. No oxidation peaks were found on the spectrum of the virgin sample, confirming the RBS results that the sample was not oxidized. The peak corresponding to Ti for the sample annealed at 620°C has fallen, showing that some of the free (original metallic) Ti had been converted to some other phase. There are peaks in this spectrum which we identified as belonging to TiO₂ (anatase). Small peaks corresponding to $\text{Al}_2\text{TiO}_5$ indicated that this phase had begun to form. The XRD spectrum of the sample annealed at 820°C for 1 hour has no peaks belonging to Ti, implying that the metal had been completely consumed by this stage. Peaks belonging to TiO₂ have become more prominent as did those identified as corresponding to $\text{Al}_2\text{TiO}_5$.

### Discussion
RBS showed that $\text{Al}_2\text{O}_3$ did not react with Mo. A heat of reaction calculation indicates whether a particular phase is possible from a reaction between $\text{Al}_2\text{O}_3$ and Mo or not, as follows:

$$2\text{Al}_2\text{O}_3 + 15\text{Mo} \rightarrow 4\text{AlMo}_3 + 3\text{MoO}_2$$

$$10(–335.2) + 15(0.0) \rightarrow 16(–15.8) + 9(–196.0)$$

$$\Delta H = (1335.2)/25 = + 53.4 \text{ kJ/mol.at.}$$

Since the heat of reaction, $\Delta H$, is positive, it is unlikely that $\text{Al}_2\text{O}_3$ will react with Mo to form $\text{AlMo}_3$ and $\text{MoO}_2$. Heats of formation for possible phases between the elements investigated are given in Table 1 and the heat of formation of $\text{Al}_2\text{O}_3$ is from ref. 6. Table 2 shows calculated heats of reaction.

Both RBS and XRD indicated that thin films of $\text{Al}_2\text{O}_3$ decomposed when annealed in the presence of Ti, to form TiO₂ (anatase) and $\text{Al}_2\text{TiO}_5$. This reaction started at about 620°C. The heats of reaction for possible phases that may result from a reaction between $\text{Al}_2\text{O}_3$ and Ti were calculated as follows.

$$3\text{Al}_2\text{O}_3 + 8\text{Ti} \rightarrow 2\text{TiAl}_2 + 3\text{TiO}_2$$

$$15(–335.2) + 8(0.0) \rightarrow 8(–39.3) + 15(–304.2)$$

$$\Delta H = (150.6)/23 = + 6.5 \text{ kJ/mol.at.}$$

The heat of reaction is positive, so it is unlikely that $\text{Al}_2\text{O}_3$ will react with Ti to form TiAl₂ and TiO₂. On the other hand, a reaction between $\text{Al}_2\text{O}_3$ and Ti may give rise to TiAl.

$$2\text{Al}_2\text{O}_3 + 13\text{Ti} \rightarrow 4\text{TiAl} + 3\text{TiO}_2$$

$$10(–335.2) + 13(0.0) \rightarrow 8(–60.7) + 15(–307.4)$$

$$\Delta H = (1744.6)/23 = –75.9 \text{ kJ/mol.at.}$$

We could not obtain values for the heat of formation of $\text{Al}_2\text{TiO}_5$, the observed compound phase.

### Conclusion
RBS and XRD are convenient, complementary techniques to investigate thermal stability and possible reaction between thin
films. RBS may be used to find stoichiometric ratios of atoms of different elements as well as thicknesses of formed layers. XRD can confirm the presence of a compound phase. In this study we found that thin films of Al$_2$O$_3$ deposited by electron gun were stable when in contact with Mo, even when annealed to temperatures as high as 900°C. No reaction was observed between these films and the metal. The films also tended to peel at the interface between the Al$_2$O$_3$ and Mo. We also found that thin films of Al$_2$O$_3$ were unstable on annealing when in contact with Ti. We began to see inter-diffusion and reaction at about 620°C. The reaction produced compound phases of TiO$_2$ and Al$_2$TiO$_5$. Some of the calculated heats of reaction between Al$_2$O$_3$ and Ti to give various products had negative values. This suggests a possible reaction between Al$_2$O$_3$ and Ti. No peeling (or delamination) was observed at the interface between Al$_2$O$_3$ and Ti. Titanium films may therefore be used in microelectronic fabrication as a ‘glue’ between Al$_2$O$_3$, and any other material that does not adhere well to Al$_2$O$_3$, but does adhere to Ti.

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