Reaction of thin metal films with crystalline and amorphous Al_2O_3

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We have investigated the thermal reaction between thin transition metal films and sapphire, alumina or amorphous Al_2O_3 using backscattering spectrometry and x-ray diffraction. Thin films of Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and Pt were deposited on the substrates by rf sputtering in an Ar gas ambient. The samples were subsequently annealed in vacuum at 800–900 °C for 20 min to 4 h duration. We found that only films of Y, Ti, and Hf react, regardless of the type of substrate, by forming aluminides near the substrate and oxides on the surface. The other metal films do not react with the Al_2O_3 substrates. Our results agree with thermodynamic consideration based on the heats of reactions between metals and Al_2O_3.

I. INTRODUCTION

Al_2O_3, like SiO_2, is a common and useful insulator material for oxide ceramics and the electronics industry. Reactions between metal films and these insulator substrates are of importance, for example, for bonding and hermetic sealing purposes, and for creating durable electrically conducting layers on these substrates. In addition, sapphire is a commonly used substrate for preparation of superconducting alloy and compound films.[1] The chemical reactions of transition metals with Al_2O_3 substrates at 800–900 °C we report here are also important in connection with the behavior of metal films on Al_2O_3 during annealing and ion mixing.[2] These results can be helpful in understanding the influence of native oxide layers on the reaction between Al and transition metals.[3]

In this work, we have investigated the chemical reactivity of a series of transition metals (Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and Pt) with Al_2O_3 substrates. We have also compared our results with thermodynamic predictions based on heats of reaction between metals and Al_2O_3 to test if this method, which was successfully applied to explain the reactions of metals with SiO_2,[4] operates also in the case of metal/Al_2O_3 systems.

II. EXPERIMENTAL PROCEDURE

The substrates used in this study were commercially prepared and polished sapphire, alumina, and amorphous Al_2O_3 films ($\sim$2000 Å) on Si wafers which were sputter-deposited from a hot pressed Al_2O_3 target. These Al_2O_3 layers were characterized by backscattering spectrometry. Prior to the deposition of the metal layers, the substrates were cleaned with trichloroethylene, acetone, and methanol in an ultrasonic bath. The films were deposited by rf sputtering in Ar gas with a planar magnetron cathode. The base pressure in the sputtering chamber was $3–8\times10^{-7}$ Torr. The thicknesses of the various films were about 2000 Å. After sputtering, the samples were annealed in a vacuum of 3×10^{-7} Torr at 800–900 °C for a duration of 20 min to 4 h. Annealing at 900 °C for 4 h was performed for nonreactive systems including Zr/Al_2O_3. Samples with films of reactive metals, such as Ti, Y, and Hf, were wrapped in Ti foils to prevent oxidation from the ambient. Without this precaution, these metal films rapidly reacted predominantly with the residual gas, but only somewhat with the substrate. Both as-deposited and annealed samples were analyzed by x-ray diffraction using a Read camera and by backscattering spectrometry using a $^4He^+$ perpendicular beam incident on the sample and particles scattered by 170°.

III. RESULTS

All the metal films deposited on sapphire behaved the same as those deposited on alumina and on an amorphous substrate. The backscattering spectra and the diffraction data both indicate that Y, Ti, and Hf reacted with Al_2O_3 substrates. In contrast, Zr, V, Nb, Ta, Cr, Mo, W, and Pt showed no signs of reaction with Al_2O_3.

Typical backscattering spectra of a Hf film on sapphire before (dots) and after (solid line) annealing of the sample at 800 °C for 2 h are shown in Fig. 1. From the spectrum of the annealed sample, it is clear that signals from a portion of oxygen and aluminum originally located in the Al_2O_3 substrate, appeared after annealing in the Hf film, near the surface and near the substrate, respectively. Also, the width of the Hf signal widened and its height decreased. From the measured ratios of the signal heights of Hf, Al, and O, the composition was calculated[5] to be $Hf_{0.32}Al_{0.01}O_{0.67}$ near the surface and $Hf_{0.47}Al_{0.52}O_{0.0}$ near the substrate, which indicated that the compound HfAl formed at the substrate inter-

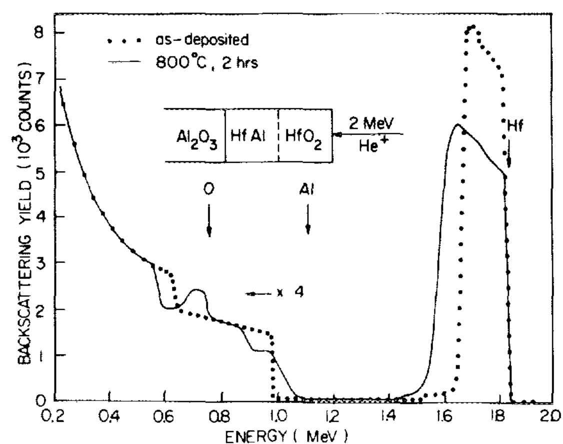

FIG. 1. 2 MeV ^4He backscattering spectra of a film of 180 nm Hf on a sapphire substrate, before annealing (dots), after vacuum annealing (solid line) at 800 °C for 2 h. Reaction between Hf and Al_2O_3 was observed. The Hf contains about 7 at. % Zr. The dots indicate the average trace of the spectrum.

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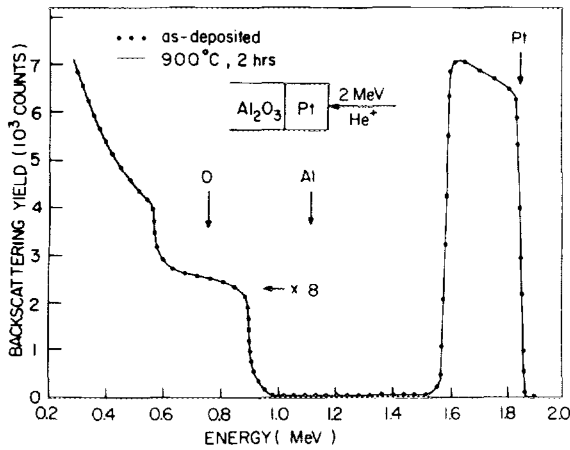

FIG. 2. 2 MeV ^4He backscattering spectra of a film of 180 nm W on a sapphire substrate before (dots), and after vacuum annealing (solid line) at 900 °C for 2 h. No reaction between Pt and Al_2O_3 is observed (compare with Fig. 1). The dots indicate the average trace of the spectrum.

face, while HfO_2 formed at the surface. The presence of these compounds was confirmed by x-ray diffraction data. Spectra similar to those of Fig. 1 for Hf/Al_2O_3 were obtained also for Ti/Al_2O_3 and Y/Al_2O_3. Although the annealing conditions were the same for Hf/Al_2O_3, the amount of oxygen in the reacted layers was much higher for Ti and Y than for Hf. According to x-ray data taken for both as-deposited and annealed samples, possible compounds which could have formed in the case of the Ti/Al_2O_3 were AlTi, TiO, and Ti_2O, and Y_3Al_2, Y_2O_3, and a ternary compound $Y_4Al_2O_9$ in the Y/Al_2O_3 system. When the annealing was carried out at 900 °C for a long time, the oxygen tended towards a uniform distribution in the reacted layer for all three systems.

Backscattering spectra as well as x-ray diffraction patterns obtained from Zr, V, Nb, Ta, Cr, Mo, W, and Pt samples showed no difference between the samples before and after heat treatment at 900 °C for 2–4 h, indicating that there were no detectable reactions between these metals and Al_2O_3. Figure 2 shows, as an example, the backscattering spectra of the as-deposited and the annealed Pt/Al_2O_3 sample.

In contrast to the results reported by Pretorius *et al.*[4] for metal/SiO_2 systems, we have not observed any "balling up" effects in our metal/Al_2O_3 systems after annealing, except for Cr.

IV. DISCUSSION

Thermodynamically, a chemical reaction is favorable when the difference between the heats of formation of the reaction products and the reactants is negative. We calculated the heats of reaction between metals and Al_2O_3 at 25 °C, assuming that the products of the reaction are aluminide and oxide. The heats of formation of oxides were taken from Ref. 4. The Miedema model[6] was used to estimate the heats of formation of the aluminides because experimental data were scarce. The results of these calculations for all possible combinations of aluminides and oxides are plotted in Fig. 3 for most transition metals. In this figure, the data reported in Ref. 4 for M/SiO_2 systems are also included. According to this plot, one expects that Y, La, Ti, Zr, and Hf will react with Al_2O_3. All other metals from V to Pt clearly should not react. Our experimental results agreed with those thermodynamic predictions except for Zr. Hence, investigations reported here confirm that the chemical reactions between metals and Al_2O_3 can generally be predicted by thermodynamic considerations.

The Zr/Al_2O_3 system, in which reaction should be thermodynamically favored, showed no reaction. The backscattering spectra show no detectable reaction after annealing, except for a slight and uniform lowering of the Zr yield.

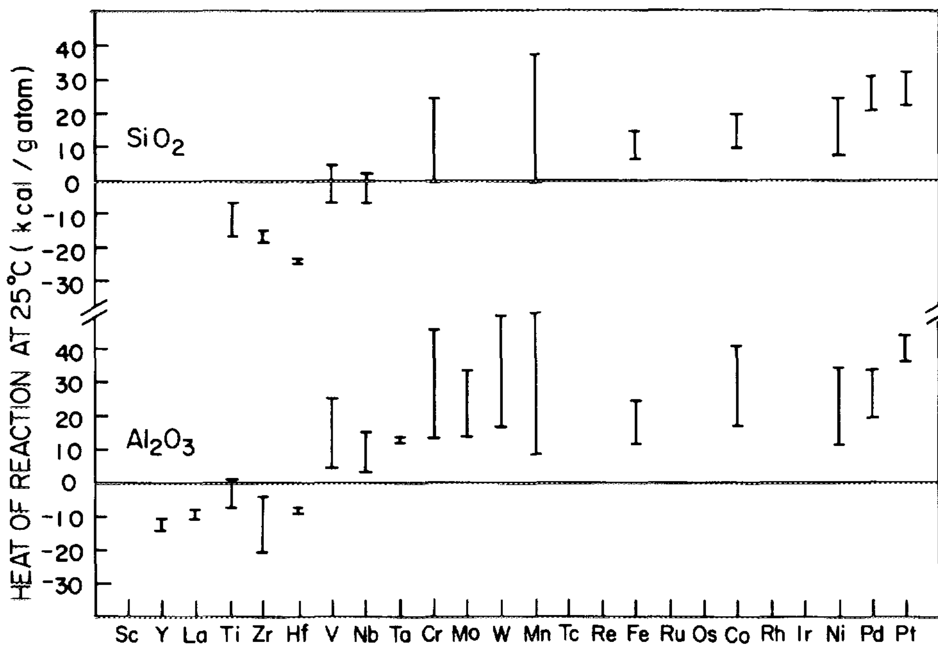

FIG. 3. Calculated heats of reaction (ΔH_f° at 25 °C) for various metals wth Al_2O_3, for combinations of metal oxides and aluminides which exist in phase diagrams, vs reacting metal. For the SiO_2 substrate, ΔH_f° was taken from Ref. 4.

This reduction was probably caused by an incorporation of oxygen from the annealing ambient, as was established by oxygen profiling.[3] A reaction might perhaps be observed in a much improved vacuum. It is expected that the thermodynamical data at 25 °C deviate significantly from the actual ones at 900 °C. It is not clear at present why these arguments should apply only to Zr. In an ion mixing study of metal/Al_2O_3 systems, Farlow *et al.*[2] found that W is clearly not mixed with Al_2O_3 and Cr exhibits only collisional mixing with Al_2O_3. These results are consistent with thermodynamic considerations. Zr and Ti behave like Cr, however, and do not react with Al_2O_3 to form a compound or stoichiometric mixture. In contrast, Nb and V, unlike W, show intermixing even though the thermodynamics are unfavorable. These results demonstrate that the correlation between ion mixing and thermal annealing is only partial. We believe that ion mixing depends on the details of the collision cascade and that the kinetic constraints are very different from those of thermal annealing.[7]

It is of interest to compare the surface morphology of the films on both SiO_2 and Al_2O_3 substrates after heat treatment. According to our experimental results for Al_2O_3 substrates, as well as the results for SiO_2 substrates of Pretorious' *et al.* the reacting layers were rather uniform. In the case of nonreacting metals on SiO_2, like Mn, Fe, Co, Ni, Pd, and Pt, Pretorious *et al.* found that these metals tend to coalesce or to ball up into islands upon annealing. In that study, Cr was a special case of a nonreacting metal which did not ball up. According to Ref. 8, however, Cr is not an exception because Cr in fact reacts with SiO_2. In contrast, we did not observe a balling up of nonreacting metals (Zr, V, Nb, Ta, Cr, Mo, W, and Pt) on Al_2O_3, except for Cr. This behavior of coalescence may be explained by differences in the thermal expansion coefficients[9] between the metal and the substrate for SiO_2 and Al_2O_3, or by the melting point of metals. The melting point argument would predict that metals with low melting points should coalesce, and that the others should not. The thermal expansion argument would predict that only metals with high differential expansion against the substrate should coalesce. The experimental data favor the latter interpretation, based primarily on the behavior of Pt and Cr. We therefore believe that balling up is principally caused by thermal stresses due to the difference between the thermal expansion coefficients of the metal and the substrate.

V. CONCLUSION

This study showed that the reactivity of thin metal films with a substrate can be properly predicted by thermodynamic consideration. The main significance of this observation is twofold: (i) the accuracy of the thermodynamic database is, in general, accurate enough to predict the outcome correctly; and (ii) the outcome can be modified strongly by impurities from the annealing ambient when the metal reacts easily with them. These conclusions although clearly quite general, should apply to any film–substrate combination.

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