A Novel Use for Gold Diffusion Barriers in Studies of Oxygen Absorption in Titanium Films

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The use of an intervening gold layer between a copper substrate and a titanium film is shown to be a novel method to determine the effect of oxygen absorption on the surface oxidation of titanium.

Thin films of metals and/or alloys are of great technological importance. Titanium and titanium alloys are of great commercial importance and the interaction of oxygen with these systems has received much attention. However, relatively few studies have focused on the importance of the absorption of oxygen into the bulk of the metal or alloy. In recent years it has become increasingly apparent that coupled surface–bulk reactions are important in the reaction of titanium with oxygen.[1,2] However, it is difficult to isolate the bulk material from the near surface region in order to determine which are truly surface phenomena and which effects can be attributed to the bulk. In previous work by Cocke and co-workers,[3–5] the importance of oxygen absorption on surface reactions, such as zirconium carbide formation, has been established.

In order to delineate further the role of the bulk material *vs.* that of the near-surface region, the reactivity of 70 nm films of titanium prepared by vapour deposition in an ultra-high vacuum (UHV) system, has been examined by X-ray photoelectron spectroscopy (XPS). The metal films are examined as deposited (AD) and after treatments from room temperature to 600 °C in either (*a*) vacuum of 1×10^{-6} Torr or (*b*) 5×10^{-3} Torr O_2. The films were deposited on either copper or gold-coated (200 nm) copper substrates at room temperature. Details on the experimental equipment used in the deposition of the films have been published previously.[6]

The relative amounts of each of the oxidation states of titanium present after each of the vacuum anneal treatments, as calculated from the Ti2p XPS results, are shown in Fig. 1. As can be seen readily from a comparison of Fig. 1a (copper

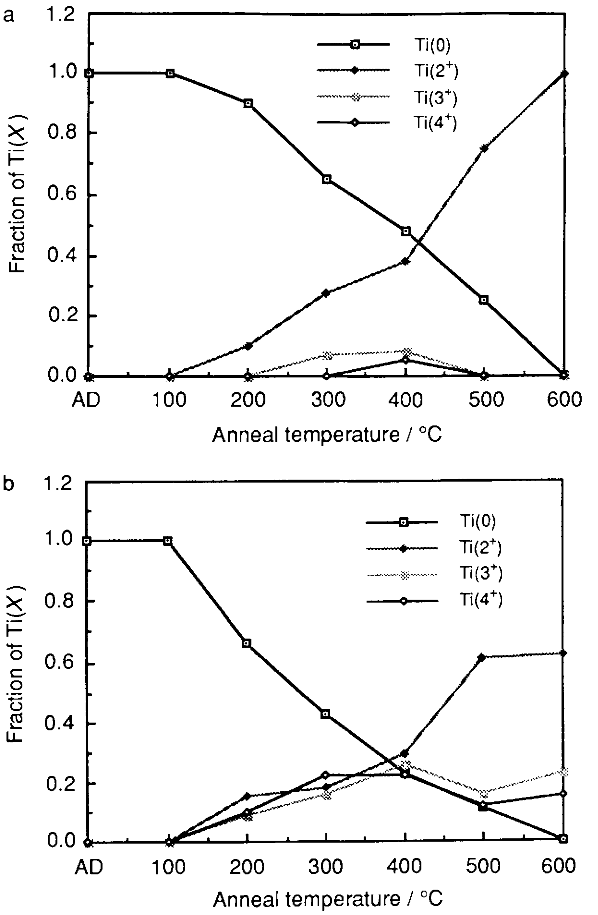

Fig. 1 Fraction of Ti present in its various oxidation states as deposited (AD) and after annealing in vacuum (10^{-6} Torr) for 15 min at temperatures between 25 and 600 °C for: (*a*) 70 nm Ti film on a copper substrate and (*b*) 70 nm Ti film on a gold-coated copper substrate

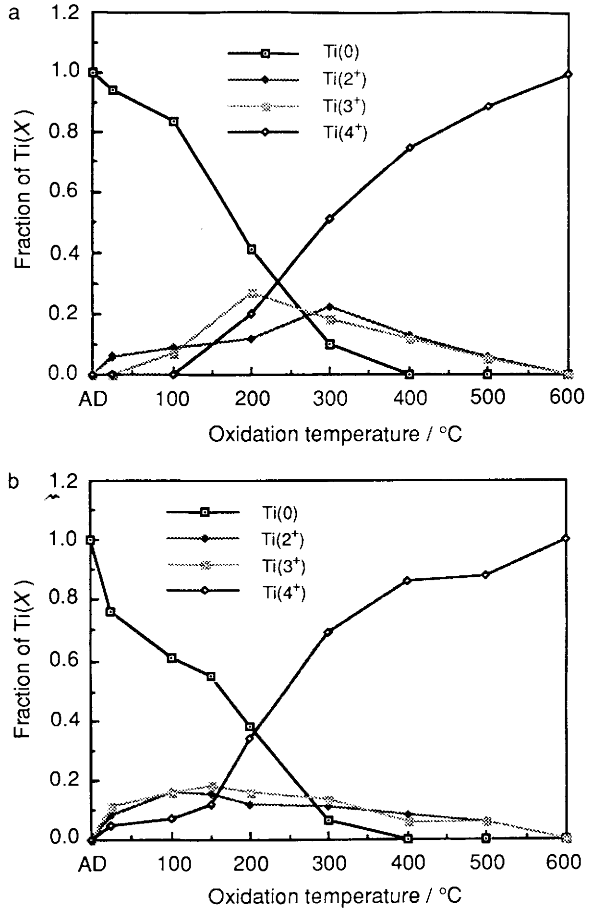

Fig. 2 Fraction of Ti present in its various oxidation states as deposited (AD) and after oxidation (5×10^{-3} Torr oxygen) for 15 min at temperatures between 25 and 600 °C for: (*a*) 70 nm Ti film on a copper substrate and (*b*) 70 nm Ti film on a gold-coated copper substrate

substrate) with Fig. 1b (gold-coated copper substrate), the titanium film deposited on the gold-coated substrate shows an increased amount of the higher oxidation states of titanium after nearly every treatment. In particular, the formation of TiO_2 occurs 200 °C earlier on the gold-coated copper substrate. At 500 °C, Ti_2O_3 and TiO_2 completely decomposed on the copper substrate such that at 600 °C the Ti oxide overlayer is solely composed of TiO and titanium carbide. The formation of carbides along with oxide decomposition has been observed previously for thin oxide overlayers on metals.[3–7] Similarly, at 500 °C on the gold-coated substrate, some of the Ti_2O_3 and TiO_2 decomposed; however, the decomposition was not complete and at 600 °C the fraction of Ti_2O_3 and TiO_2 increased, so that the oxide overlayer was composed of TiO, Ti_2O_3, TiO_2 and titanium carbide. The oxidation and decomposition reactions for titanium are as in eqns. (1)–(3). The continued presence of the higher oxidation states of titanium on the titanium film deposited on the gold-coated copper substrate is a result of the intervening gold layer. The gold layer acts as an oxygen diffusion barrier, suppressing the decomposition reactions of titanium oxides which are driven by the absorption of oxygen into the bulk.

Oxidations Decompositions

$$\mathrm{Ti} + \mathrm{O} \rightarrow \mathrm{Ti}^{2+} + \mathrm{O}^{2-} \qquad (1)$$

$$\mathrm{Ti}^{2+} + \mathrm{O}^{2-} + \tfrac{1}{2}\mathrm{O} \rightarrow \mathrm{Ti}^{3+} + \tfrac{3}{2}\mathrm{O}^{2-} \rightarrow \mathrm{Ti}^{2+} + \mathrm{O}^{2-} + \tfrac{1}{2}\mathrm{O(abs)} \qquad (2)$$

$$\mathrm{Ti}^{3+} + \tfrac{3}{2}\mathrm{O}^{2-} + \tfrac{1}{2}\mathrm{O} \rightarrow \mathrm{Ti}^{4+} + 2\mathrm{O}^{2-} \rightarrow \mathrm{Ti}^{2+} + \mathrm{O}^{2-} + \mathrm{O(abs)} \qquad (3)$$

As further evidence for the role played by the gold layer, data for the oxidation experiments, at 5×10^{-3} Torr oxygen, are presented in Fig. 2. In this case, with an abundant oxygen supply, the differences between the titanium on pure copper substrate (Fig. 2a) and the titanium on the gold-coated copper substrate (Fig. 2b) are not as apparent as in the vacuum anneals discussed above. The major differences are: (*a*) a decreased amount of metal present at 25–150 °C, (*b*) earlier formation of Ti^{3+} and Ti^{4+} and (*c*) an increased amount of Ti^{4+} from 200 to 400 °C on the gold-coated sample. An additional difference in the reactivity of the samples was noted after the 600 °C oxidation. In the case of the titanium film on the gold-coated copper substrate, the copper migrates through the titanium film where it is found as Cu^{1+} (no gold was detected by XPS). As detected by visual inspection of the substrate, copper is observed to alloy with gold on both the vacuum-annealed and oxidized samples; however, the higher oxygen activity is required to drive the oxidation and subsequent migration of copper to the surface. The diffusion of copper through titanium oxide overlayers has been observed previously for Ti–Cu alloys under similar experimental conditions.[7] The diffusion of copper through the titanium film on the gold-coated copper substrate may be attributed to differences in extent of oxidation of the titanium and/or structural or morphological variations in the oxide overlayer which have occurred during the course of the oxidation experiments.

It appears from the above results that gold subsurface layers can be used to differentiate the reactivity of the surface from the contribution of the underlying bulk; however, more controlled studies on highly characterized systems are needed to demonstrate the full potential of this approach.

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