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DETERMINATION OF THE GROWTH RATES OF Au$_2$Al DIFFUSIONALLY FORMED IN THIN STEP-SHAPED Au-Al COUPLES

I.M. Reda, A. Wagendristel, H. Bangert and P. Schattschneider

Institute of Applied and Technical Physics, Technical University, Vienna, Austria

Abstract - Gold and its compounds Au$_2$Al, Au$_5$Al$_2$ show marked differences in their spectral reflectivity in the visible range. These differences, observable with the naked eye, have been used to detect the approach of the phase front of diffusionally grown compounds against the gold surface of a Au-Al thin film couple. From a continuous sequence of such couples evaporated in different thicknesses onto the same substrate, i.e. a step-shaped diffusion couple, of a total atomic ratio 2Au/Al, the growth rate constants were obtained. The temperature for the diffusion anneal ranged from 333 to 373 K. Excellent agreement with recent literature data for the rate constants was found only in the thicker part of the couple: $D = 2.1 \exp(-1/kT) \text{cm}^2/\text{s}$ whereas the thinner part showed slightly higher rates.

I - INTRODUCTION

Contacts between Au and Al metallisation are often found in micro-electronic circuitry. Unfortunately this bimetallic system forms already well below 100°C compounds revealing undesired properties such as high electrical resistance and brittleness. For this important practical reason the thin film diffusion system Au-Al was the subject of extensive research in the past /1-4/ as well as up to recent times, where more elaborate methods could successfully clarify the kinetics of phase formation in this system under different conditions /5-11/. Mainly the papers of Vandenberg /11/, Campisano /5/, Majni /9,10/ and their coworkers showed that in
couples with a composition according to \( 2\text{Au}/\text{Al} \) and annealed somewhat below 100° C the phase \( \text{Au}_5\text{Al}_2 \) always appears first as a layer parallel to the original interface. On the aluminium interface of this compound very soon \( \text{Au}_5\text{Al}_2 \) appears as a second intermediate layer, growing with a comparable rate. If the couple is set up such that the atomic ratio is \( 2\text{Au}/\text{Al} \), the \( \text{Au}_5\text{Al}_2 \) phase front reaches its limit at the Au surface, then this phase reacts with the remaining Al to form also \( \text{Au}_5\text{Al}_2 \) until all \( \text{Au}_5\text{Al}_2 \) and Al is used up. The final state is given by a homogeneous film of Au Al. A scheme of this process is shown in fig.1. The growth rate constants have been found to be rather high (in the temperature range from 60 to 100° C between \( 3 \times 10^{-15} \) and \( 1 \times 10^{-13} \text{cm}^2\text{s}^{-1} \)) and depending on the film structure. Polycrystalline reaction partners showed higher rate constants. In a previous paper /7/ we reported growth rates in very thin couples (60 nm) which exceeded those for thicker films. For this reason we reexamined this diffusion system in a wide range of couple thicknesses by means of a rather simple method making use of the discolouring of the gold part of the couple when it is replaced by the newly formed alloy.

II. METHOD

The characteristic yellow colour of gold is caused by a low reflectivity below 500 nm wavelength, whereas the colour of \( \text{Au}_2\text{Al} \) is typically neutral-gray, showing no significantly structured reflection spectrum in the visible range but rather generally low reflectivity around 55%. \( \text{Au}_5\text{Al}_2 \), however, appears dark gray with a slight purple shade corresponding to a continuous decrease in reflectivity with decreasing wave length. In fig. 2 the

![Fig.2: Reflectance at normal incidence of Au, Al and their intermetallic compounds \( \text{Au}_5\text{Al}_2 \), \( \text{Au}_2\text{Al} \) as a function of photon wavelength.](image-url)
reflectivities of Au, Al, \( \text{Au}_2\text{Al} \) and \( \text{Au}_5\text{Al}_2 \) are plotted for comparison. The different colours of Au and \( \text{Au}_2\text{Al} \) or \( \text{Au}_5\text{Al}_2 \) can clearly be distinguished with the naked eye and offer a simple possibility to observe the approach of the phase front of the reacted layers towards the surface of the gold film during the anneal of a Au-Al thin film couple. Of course one must expect quite a large lack of definition of the end of the growth process as the remaining part of the gold film becomes successively more transparent and hence its colour is changing continuously. But since the human eye is quite sensitive to difference in colour and brightness, when it can compare neighbouring areas, this lack of definition can be drastically reduced if there is a \( \text{Au}_2\text{Al} \) standard next to the couple. For this reason we have used films where this possibility exists automatically. Our films consisted of individual couples all with an atomic ratio of \( 2\text{Au}/\text{Al} \) but of increasing thickness and each is deposited spacelessly next to the other. In such a stair like bimetallic couple (fig.3) the phase boundary of the reaction products successively reaches one step after the other, thus making each previous one a standard \( \text{Au}_2\text{Al} \) for comparing it with the next.

III. EXPERIMENT

Films have been prepared by evaporation of a stair film Al, 5, 10, 15...nm on a glass substrate-which was overlayed by Au 10, 20, 30...nm. The thickness ratio \( 1\text{Al}:2\text{Au} \) of the individual couples corresponds directly to the atomic ratio since structure and lattice constant are almost the same for Au and Al. The pressure during evaporation was \( 10^{-5} \) torr. These samples were annealed by pressing them with the substrate side onto a heated copper block. The temperature was measured at the film side and kept constant within a range of \( 1\degree C \). The gold film at the outer surface protects the couples automatically against oxidation of samples which was checked by comparing the results of samples annealed under atmosphere and in situ. Annealing temperatures were 60, 74, 78, 80, 88 and 98\degree C. During the anneal the successive discolouring of the gold layer from step to step in the film was observed. The end of the reaction (\( t^* \)) in the original films was found from the disappearance of the boundary between the step just reacted and the one reacted before. The uncertainty to define this moment is about 20\% and arises mainly from the similarity in colour of \( \text{Au}_5\text{Al}_2 \) and that of \( \text{Au}_2\text{Al} \).

The distance to be crossed by the diffusing atoms is the thickness of the formed compounds (fig.3). Hence the growth rates constant is given by \( x/t \). For the entire reaction this relation yields the mean rate constant according to \( d^2/t^* \).
IV. RESULTS

From each sample six values according to the step heights were obtained (fig.4). In all cases we found higher rate constants (given by the slope of $d^2$ vs $t$) for thinner films.

![Graph showing $d^2$ vs time for a step-shaped ZAu/Al thin film annealed in situ at 353K.]

Growth rate constants between 333 and 371 K are displayed in fig.5 together with literature data in form of an Arrhenius plot. The length of the bars is given by the initial and the final growth rate. The lower values (corresponding to the thicker couples) compare very well with those found by other authors whereas the higher limit tends towards rate constants which we have reported for very thin films/7/. The final rate obeys $D = 2.1 \exp\left(-\frac{1}{kT}\right) \text{cm}^2/\text{s}$.

![Graph showing temperature dependence of growth rate constants in Al-Au thin film couples.]

To envisage the reaction speed e.g. at room temperature one finds by extrapolation a thickness of the reacted layer of 10 nms and 1 μm after a time of 5.4 h and 3.15 h respectively.
Majni et al. /10/ reported growth rates for Au$_2$Al grown into a thin film and a single crystal of gold which differ by about one order of magnitude. This makes clear that the speed of the reaction is strongly dependent on the supply of the diffusing atoms via grain boundaries. The transport of the atoms across the reacted layer can hardly be understood by lattice diffusion since in this case the stoichiometry of Au$_2$Al and Au$_5$Al$_2$ would have to be broken. Fast grain boundary diffusion, however, explains the high growth rates as well as their decrease with time: The density of grain boundaries in the just grown layer is higher in the initial state and is gradually reduced by recrystallisation during the extended anneal. Especially in the Au$_2$Al layer significant changes from a highly disordered or a very fine grained structure to the crystalline state are taking place during the reaction /8/. (Diffusion coefficients reduced by defect annihilation during the heat treatment is very often found in freshly deposited thin film couples). To recognize grain boundary diffusion as the driving mechanism of the reaction one may also consider the activation energy of 1 eV typical for grain boundary diffusion in metals. In our previous paper we had also to assume "grain boundary spikes" in the reaction fronts to explain the x-ray-optical reflection curves. So, in conclusion, we may consider the growth process of the reacted intermediate layers as limited by the diffusion of Au and Al via the grain boundary network in the reacted layers. This fast transport supplies these elements to the phase-front where they react with their residual counterpart Au$_5$Al$_2$ at the Au side and Au Al at the Al side. Finally, when all Au is used up the little remainder of Al has to be brought to the Au$_5$Al$_2$/Au$_2$Al interface which moves towards the other surface. The possibility for the easy transport of atoms to the actual reaction front is decreased as the structure of the reacted layer is improved during the heat treatment.

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