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PREPARATION AND CHARACTERIZATION

KINETICS AND MECHANISM OF REACTION AT ROOM TEMPERATURE IN THIN Au/METAL COUPLES

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The reaction kinetics of compound formation at room temperature in thin film Au/Me (Me = Al, Cd, Ga, In, Pb, Sb, Sn, Zn) couples have been investigated by X-ray diffraction. The decrease in the (111) diffraction peak of gold or of the metal, or the increase in the diffraction peak of the corresponding compound, has been followed as a function of time. These reactions were found to be diffusion controlled. The interdiffusion coefficients have been calculated for the investigated couples and the relation

$$D = 3.66 \times 10^{-11} \exp(-0.015 T_t)$$

has been found to exist between the diffusion coefficient D (cm^2 s^{-1}) and the melting temperature T_t (K) of the metal.

1. INTRODUCTION

The conditions for the formation of intermetallic compounds at room temperature in thin film couples consisting of gold and another metal (aluminium, cadmium, gallium, indium, lead, antimony, tin or zinc) have been described in our previous work[1]. It has been shown that 23 compounds can be formed in this manner: four compounds with each of gallium, indium and tin, three compounds with each of lead and zinc, two compounds with each of cadmium and aluminium and one compound with antimony. All the compounds known from the phase diagrams are formed in the case of gallium, lead and antimony, but not all the compounds known have been found with aluminium, cadmium, indium, tin and zinc. The present paper shows the results of a study of the reaction kinetics and mechanism of compound formation at room temperature for these couples.

It is known that the rate of reaction of compound formation in metal couples can be measured by following either the concentration (or thickness) increase of the compound formed or the concentration decrease of one of the starting components. The measurements can be performed either directly[2] or by following some physical property which is proportional to the starting metal concentration (thickness)[3–5].

Hugsted *et al.*[2] have measured at different time intervals the thickness of the

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AuSn compound formed in the Au/Sn thin film couples at room temperature using Rutherford backscattering. The reaction rate constant $k = 3.8 \times 10^{-15}$ cm^2 s^{-1} has been calculated using the relationship $w^2 = kt$, where w is the thickness of the compound formed and t is the time.

Weaver and Brown[3] have studied the rate of compound formation in thin film Au/Pb couples. They used an indirect method, consisting in the measurement of the time t during which the mirror reflection of gold decreases to the value of the reflection of lead, which occurs when gold has reacted completely with lead to form the $AuPb_2$ compound. Considering the thickness of the reacted gold layer to be the diffusion path, they calculated a diffusion coefficient value $D = 1.45 \times 10^{-15}$ cm^2 s^{-1}. The same researchers have studied[4] compound formation in thin film Au/Al couples at temperatures ranging from 70 to 164 °C. From the time elapsed until the reflection of the gold side drops to a minimum and the starting gold layer thickness (considered to represent the diffusion path), they calculated the diffusion coefficient D to be 1.01×10^{-14} cm^2 s^{-1} for Au_2Al compound formation at 84 °C.

Kolesnikov *et al.*[5] have also investigated Au/Al thin film couples at temperatures ranging from 100 to 300 °C using the indirect method of following the electrical resistance change during the determined annealing time. Taking the initial gold layer thickness to be the diffusion path, they obtained $D = 5 \times 10^{-13}$ cm^2 s^{-1} for Au_2Al formation at 150 °C.

2. EXPERIMENTAL DETAILS

Thin films of both gold and the other metal were prepared by vacuum evaporating them onto unheated glass plates. The gold layer was always first evaporated[6-11]. The total thickness of the two layers amounted typically to 150–170 nm.

The reaction kinetics were investigated by X-ray diffraction. The decrease in the diffraction maxima of Au(111) and of the other element in the couple as well as the increase in those of the formed compound were followed. This method is based on the fact that the intensities of the diffraction maxima of thin films are proportional to the film thickness when other conditions are the same[12]. Lau and Sun[13] investigated the reaction kinetics in thin film Au/Pd couples at elevated temperatures by this method.

Immediately after evaporation of the layers, the sample was placed into the X-ray diffractometer, the angle θ being set to a corresponding value, and the impulses were counted during a period of 1 min. The procedure was repeated every 5–10 min until the intensity of the maximum of gold or of the other metal decreased to the background level. In the case of slower reactions the X-ray diffraction patterns of the sample were taken at time intervals depending on the rate of the reaction, and then the diffraction maxima were measured. By plotting the intensity of the diffraction maxima against the square root of time straight lines were obtained using the least-squares method. From the gold thickness, assumed to be the diffusion path X, and time elapsed until the gold has completely reacted t, the interdiffusion coefficients D have been calculated for all the investigated couples using the relation

$$X^2 = Dt \tag{1}$$

3. RESULTS

3.1. *Au/In*

In the thin film Au/In couples four compounds can be formed: $AuIn_2$, AuIn, Au_7In_3 and Au_4In, depending on the ratio of the elements' concentrations and time of reaction at room temperature[6].

The reaction kinetics were determined for the sample having thicknesses of 67 nm and 180 nm for gold and indium respectively (Fig. 1). A graphical representation of the results give straight lines (Fig. 2), indicating that diffusion is the rate-determining process. The time required for the 67 nm thick gold layer to react completely is 200 min. The diffusion coefficient D_1 determining the rate of $AuIn_2$ compound formation was thus calculated to be $3.7\times10^{-15}\,cm^2\,s^{-1}$. In another sample having gold and indium layer thicknesses of 100 nm and 50 nm respectively, indium reacts with part of the gold in 180 min, producing again $AuIn_2$. From these data follows $D_1 = 2.3\times10^{-15}\,cm^2\,s^{-1}$, calculated in this case from the time of indium disappearance. It can be seen that the two D_1 values are very close to each other. In the latter sample, the excess gold reacts with $AuIn_2$ to form the AuIn compound within 5 days. If the entire indium layer has reacted to form $AuIn_2$ which was then transformed into AuIn, it can be considered that the $AuIn_2$ thickness was at least equal to the initial indium thickness, *i.e.* 50 nm. From these data follows $D_2 = 5\times10^{-17}\,cm^2\,s^{-1}$, which approximately determines the rate of AuIn formation (the errors made on calculation of the diffusion coefficient extend up to one order of magnitude). In the sample having gold and indium thicknesses of 80 nm and 16 nm respectively, reaction proceeds in the same manner as in the previous case; however, since the sample contains more gold, the reaction continues by the transformation of AuIn through Au_7In_3 into Au_4In. This transformation is completed within 4 months, giving the final Au_4In product. From these data follows $D_3 = 2.4\times10^{-19}\,cm^2\,s^{-1}$, which approximately determines the rate of Au_4In formation.

3.2. *Au/Pb*

Three compounds can be formed from the thin film Au/Pb samples: $AuPb_3$, $AuPb_2$ and Au_2Pb, depending on the thickness ratio of the elemental films and on the time of reaction at room temperature[7].

The reaction kinetics were investigated for a sample having gold and lead thicknesses of 60 nm and 430 nm respectively. The obtained straight lines of Fig. 3 indicate that the rate of $AuPb_3$ formation is diffusion controlled. Gold has reacted completely within 225 min. From these data follows $D_1 = 2.6\times10^{-15}\,cm^2\,s^{-1}$ determining the rate of $AuPb_3$ formation.

In another sample consisting of two gold and lead layers with thicknesses of 74 nm and 67 nm respectively, lead has reacted completely with part of the gold within 4 h, producing $AuPb_2$. From these data follows $D_1 = 3.1\times10^{-15}\,cm^2\,s^{-1}$, determining the rate of $AuPb_2$ formation. The obtained diffusion coefficient corresponds to that calculated by Weaver and Brown[3] from the rate of decrease in the mirror reflection of gold. In the above-mentioned sample the reaction continues by the reaction of the excess gold with $AuPb_2$ to form Au_2Pb within 27 days. If the

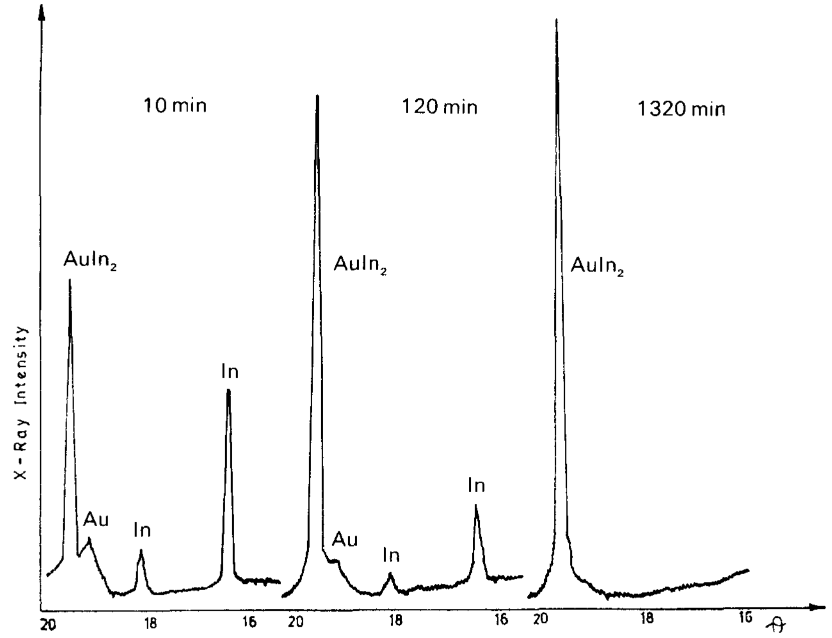

Fig. 1. Part of the X-ray diffraction patterns of an Au/In sample with original structure Au(67 nm)/In(180 nm) taken at different times after evaporation.

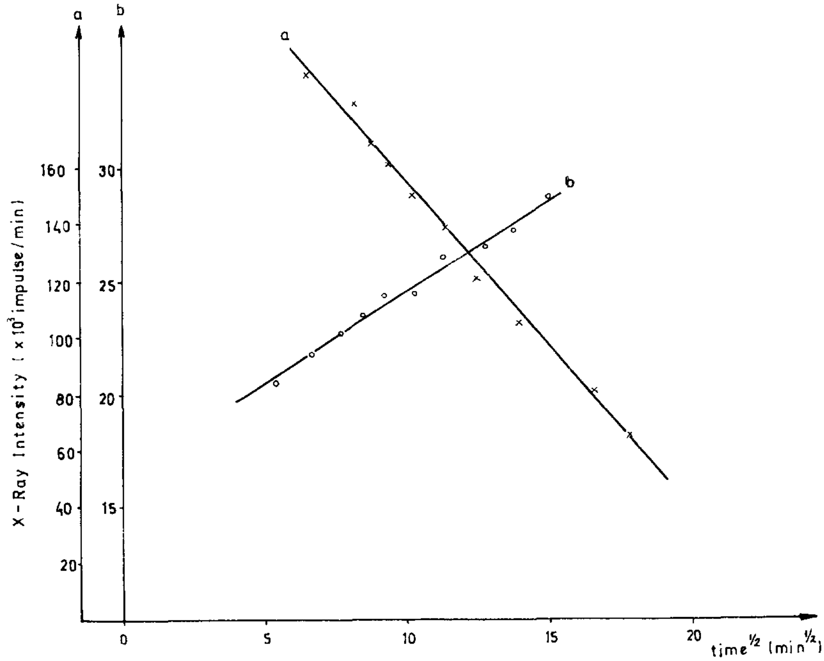

Fig. 2. Diffraction intensities of Au(111) (curve a) and AuIn$_2$ (curve b) for a sample with original structure Au(67 nm)/In(180 nm) *vs.* square root of time. Aging takes place and measurements are made at room temperature.

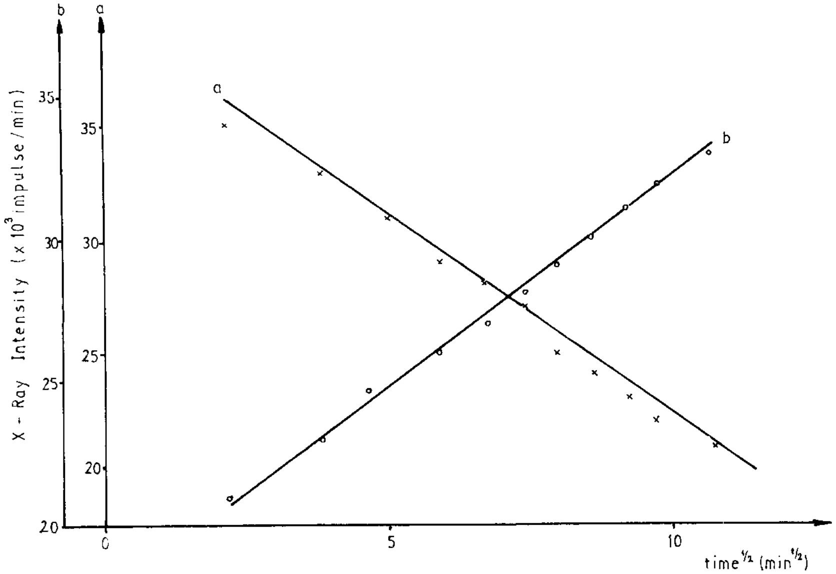

Fig. 3. Diffraction intensities of Au(111) (curve a) and $AuPb_3(222)$ (curve b) for a sample with original structure Au(60 nm)/Pb(430 nm) *vs.* square root of time. Aging takes place and measurements are made at room temperature.

thickness of $AuPb_2$ is at least equal to the initial lead layer thickness, from these data can be obtained $D_2 = 1.9 \times 10^{-17}\,cm^2\,s^{-1}$, which determines the approximate rate of Au_2Pb compound formation.

3.3. *Au/Sn*

Four compounds can be formed from the Au/Sn samples: $AuSn_4$, $AuSn_2$, AuSn and Au_5Sn, depending on the thickness ratio of the elemental films and on the time of reaction at room temperature.

The reaction kinetics were investigated for the sample in which only $AuSn_2$ is formed (53 wt.% Sn; Fig. 4). The experimental results shows that the diffraction maximum of gold (gold thickness, 67 nm) drops to the background level within 100 min. This yields a diffusion coefficient $D_1 = 7.4 \times 10^{-15}\,cm^2\,s^{-1}$, which determines the rate of $AuSn_2$ formation.

In the sample containing 37 wt.% Sn, in which only AuSn is formed, the rate of formation and, consequently, diffusion coefficient are close to those obtained by Hugsted *et al.*[2]

3.4. *Au/Sb*

The only compound formed in the film-film Au/Sb couple is $AuSb_2$[9].

The reaction kinetics were investigated for a sample having thicknesses of the gold and antimony layers of 60 nm and 210 nm respectively. The straight lines obtained in Fig. 5 indicate a diffusion-controlled reaction. From the diagram it follows that the rate of decrease in the Sb(102) diffraction peak (curve b) is higher

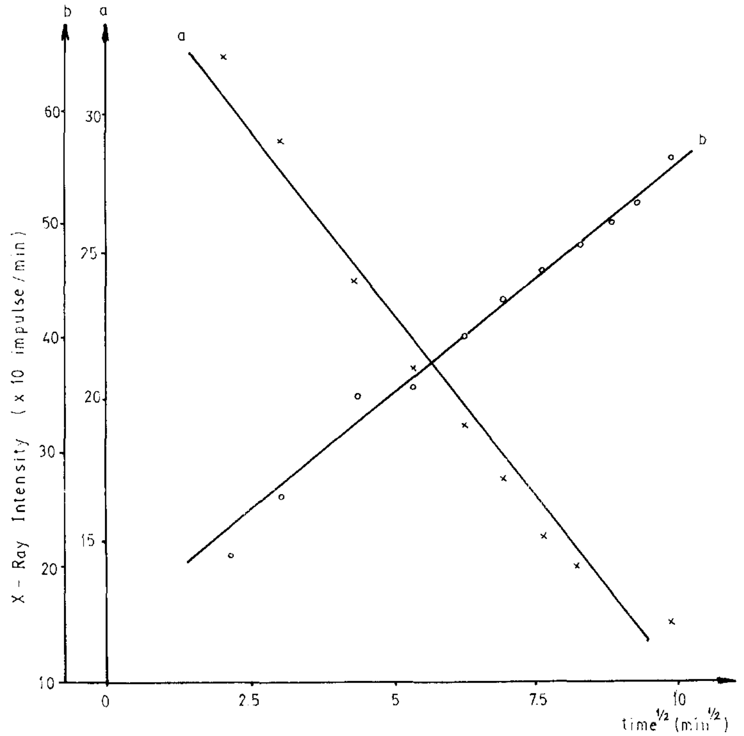

Fig. 4. Diffraction intensities of Au(111) (curve a) and $AuSn_2(204)$ (curve b) for a sample with original structure Au(67nm)/Sn(183 nm) *vs.* square root of time. Aging takes place and measurements are made at room temperature.

than that of the Au(111) peak (curve a). This happens because the $AuSb_2(200)$ and Au(111) peaks appear at the same angle ($\theta = 19.15°$) so that the increase in the former masks the decrease in the latter. The reaction rate was determined from the decrease in the Sb(102) peak. The straight line obtained by plotting the Sb(102) peak intensity *vs.* $t^{1/2}$ intersects the abscissa at 97 days. This is the time necessary for the reaction to be completed. From these data we obtain the diffusion coefficient value $D = 5 \times 10^{-17}\,cm^2\,s^{-1}$, which determines the rate of $AuSb_2$ formation.

3.5. *Au/Zn*

Depending on the thickness ratios and time of reaction at room temperature, some of the three compounds $AuZn_3$, AuZn and Au_3Zn can be formed[1, 10].

The rate of formation of $AuZn_3$ was investigated for a sample having gold and zinc thicknesses of 60 nm and 300 nm respectively. The results, graphically represented in Fig. 6, indicate a diffusion-controlled reaction. By extending the straight line representing the decrease in the diffraction maximum intensity of Au(111) to its intersection with the abscissa, the time necessary for the intensity to fall to the background level is obtained and is equal to 169 min. From these data the diffusion coefficient value $D_1 = 3.5 \times 10^{-15}\,cm^2\,s^{-1}$, determining the rate of formation of $AuZn_3$, has been obtained. The approximate rates of formation for the other

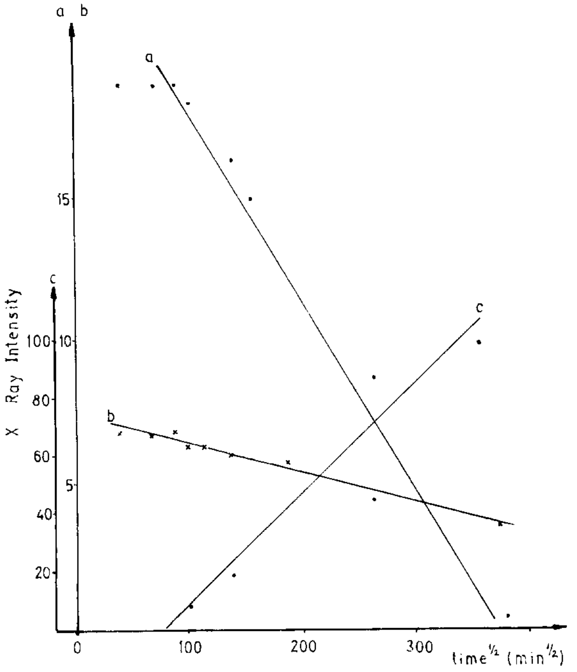

Fig. 5. Diffraction intensities of Au(111) (curve a), Sb(102) (curve b) and $AuSb_2(200)$ (curve c), for a sample with original structure of Au(60 nm)/Sb(210 nm) *vs.* square root of time. Aging takes place and measurements are made at room temperature.

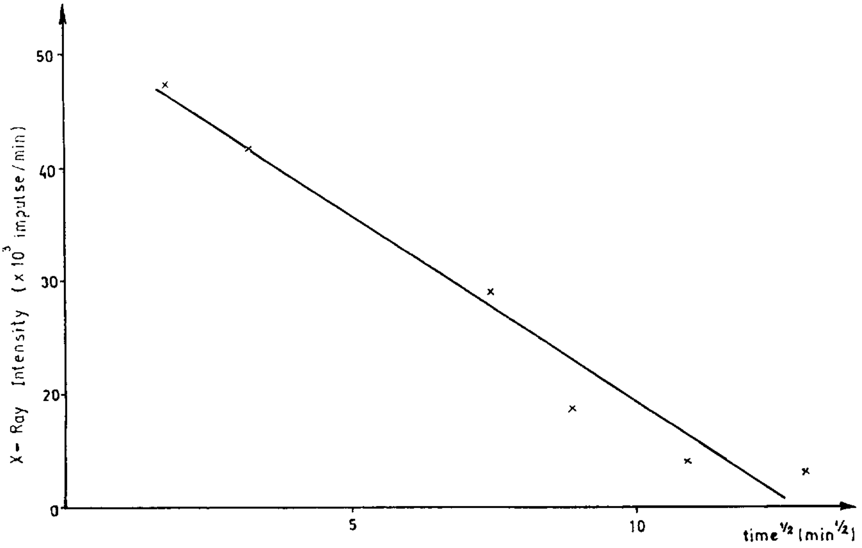

Fig. 6. Diffraction intensity of Au(111) for a sample with original structure Au(60 nm)/Zn(300 nm) *vs.* square root of time. Aging takes place and measurements are made at room temperature.

compounds have been determined by analysing the X-ray diffraction patterns of the sample containing 10% Zn (gold and zinc thicknesses of 80 nm and 24 nm respectively). The reaction leading to $AuZn_3$ formation is completed within a few hours. It can be supposed that the compound thickness is at least equal to the initial thickness of the zinc layer, *i.e.* 24 nm. This compound then reacts with the excess gold, the reaction being completed in 4 days, to produce AuZn. The diffusion coefficient D_2 determining the rate of AuZn formation obtained from these data is equal to 1.6×10^{-17} cm^2 s^{-1}.

It takes 8 years for the AuZn contained in the sample to react completely with the excess gold to form Au_3Zn. From the AuZn layer thickness, taken to be at least 24 nm, and the time of 8 years, the diffusion coefficient determining the rate of Au_3Zn formation is obtained: $D_3 = 2 \times 10^{-20}$ cm^2 s^{-1}. The D_2 and D_3 values should, however, only be treated as indications of the order of magnitude.

3.6. Au/Ga

Four compounds, *i.e.* $AuGa_2$, AuGa, Au_2Ga and Au_7Ga_2 can be formed in the Au/Ga thin film samples, depending on the thickness ratios and time of room temperature reaction[11].

In the sample containing 70% Ga, gold reacts with gallium during the layer preparation to form only one compound, $AuGa_2$. Therefore the reaction could not be followed by the X-ray method, only visually. The 100 nm thick gold layer reacts with gallium within 1 min, leading to disappearance of the gold colour. The diffusion coefficient $D_1 = 1.6 \times 10^{-12}$ cm^2 s^{-1}, determining the rate of formation of $AuGa_2$, has been obtained from these data.

Diffusion coefficients for the remaining three compounds could not be determined because in the samples containing 10%–50% Ga more than one compound was formed and the individual compounds could not be separated.

3.7. Au/Cd

In the thin film Au/Cd samples two compounds, $AuCd_3$ and AuCd, can be formed, depending on the thickness ratios and reaction time[10].

All the diffraction peaks from gold, cadmium and $AuCd_3$ have the same angular position, $\theta = 19.15°$. Therefore it was not possible to follow the reaction rate through the decrease in the diffraction maxima, but visually by following the disappearance of the gold colour. The sample containing 71% Cd with a gold layer 31 nm thick loses its colour within 1.5 h, giving rise to $AuCd_3$ only. From these data the diffusion coefficient $D_1 = 1.7 \times 10^{-15}$ cm^2 s^{-1} was estimated. In another sample containing 30% Cd, the cadmium layer 77 nm thick reacts completely within several hours with part of the gold to form $AuCd_3$ and then the excess gold reacts with the first compound formed, which is thereby transformed into AuCd within 8 days. The diffusion coefficient $D_2 = 8.5 \times 10^{-17}$ cm^2 s^{-1} which determines approximately the rate of AuCd formation has been estimated from these data.

3.8. Au/Al

Two compounds, Au_2Al and $AuAl_2$, are formed at room temperature, the first within several days and the second after 3 years[7].

The diffraction peaks of Au(111), Al(111) and Au_2Al(510) all occur at $\theta = 19.15°$. Therefore the disappearance of the gold colour was again used to follow the reaction rate.

For the sample with gold and aluminium layer thicknesses of 62 and 30 nm respectively, the gold colour disappeared within 20 days. From these data the diffusion coefficient $D_1 = 2.2 \times 10^{-17}\,\mathrm{cm^2\,s^{-1}}$, determining the rate of Au_2Al formation, has been calculated. In another sample with gold and aluminium layer thicknesses of 39 nm and 33 nm respectively, the gold colour disappeared after 3 years, by which time $AuAl_2$ had been formed. A rough estimation gives a diffusion coefficient $D_1 = 1.6 \times 10^{-19}\,\mathrm{cm^2\,s^{-1}}$.

4. DISCUSSION

From the results presented it follows that the rate of compound formation in the thin film Au/metal couples is diffusion controlled. Table I contains diffusion coefficient values which determine rates of formation of compounds in the Au/metal

TABLE I

INTERDIFFUSION COEFFICIENTS IN Au/Me FILM COUPLES AT ROOM TEMPERATURE

Metal	*Melting point of metal* (°C)	*Compound formed*	*Melting point of compound formed* (°C)	*Interdiffusion coefficient* ($\mathrm{cm^2\,s^{-1}}$)
Ga	29.7	$AuGa_2$	492	$D_1 = 1.6 \times 10^{-12}$
		AuGa	470	—
		Au_2Ga	350	—
		Au_7Ga_2	455	—
In	156	$AuIn_2$	542	$D_1 = 3.7 \times 10^{-15}$
		AuIn	510	$D_2 = 5 \times 10^{-17}$
		Au_7In_3	482	—
		Au_4In	674	$D_3 = 2.4 \times 10^{-19}$
Sn	231	$AuSn_4$	252	—
		$AuSn_2$	309	$D_1 = 7.4 \times 10^{-15}$
		AuSn	418	—
		Au_5Sn	195	—
Cd	320	$AuCd_3$	500	$D_1 = 1.7 \times 10^{-15}$
		AuCd	627	$D_2 = 8.5 \times 10^{-17}$
Pb	327	$AuPb_3$	250	$D_1 = 2.6 \times 10^{-15}$
		$AuPb_2$	390	$D_1 = 3.1 \times 10^{-15}$
		Au_2Pb	418	$D_3 = 1.9 \times 10^{-17}$
Zn	419	$AuZn_3$	225	$D_1 = 3.5 \times 10^{-15}$
		AuZn	725	$D_2 = 1.6 \times 10^{-17}$
		Au_3Zn	418	$D_3 = 2.0 \times 10^{-20}$
Sb	630	$AuSb_2$	460	$D_1 = 5.0 \times 10^{-17}$
Al	660	Au_2Al	625	$D_1 = 2.2 \times 10^{-17}$
		$AuAl_2$	1060	$D_2 = 1.6 \times 10^{-19}$

couples. It is seen that for a given couple the value of D_1 is two orders of magnitude greater than that of D_2 which, in turn, is two orders of magnitude greater than that of D_3. The first-formed compounds are produced directly from the elements, but the second compound is produced by the reaction of the first compound with excess gold or, in the case of the Au/Al couple, with excess aluminium.

From Fig. 7, representing the natural logarithms of the diffusion coefficients for the first-formed compounds *vs.* the melting points of the metals reacting with gold, it follows that the diffusion coefficients D increase with decreasing melting point. A linear least-squares fit gives the relation

$$D(\mathrm{cm^2\,s^{-1}}) = 3.66\times10^{-11}\exp(-0.015T_t) \tag{2}$$

T_t (K) being the melting point. The point corresponding to the diffusion coefficient value for the Au/Cu couples ($D = 1\times10^{-20}$ cm^2 s^{-1}) taken from ref. 14 satisfies the relationship (2).

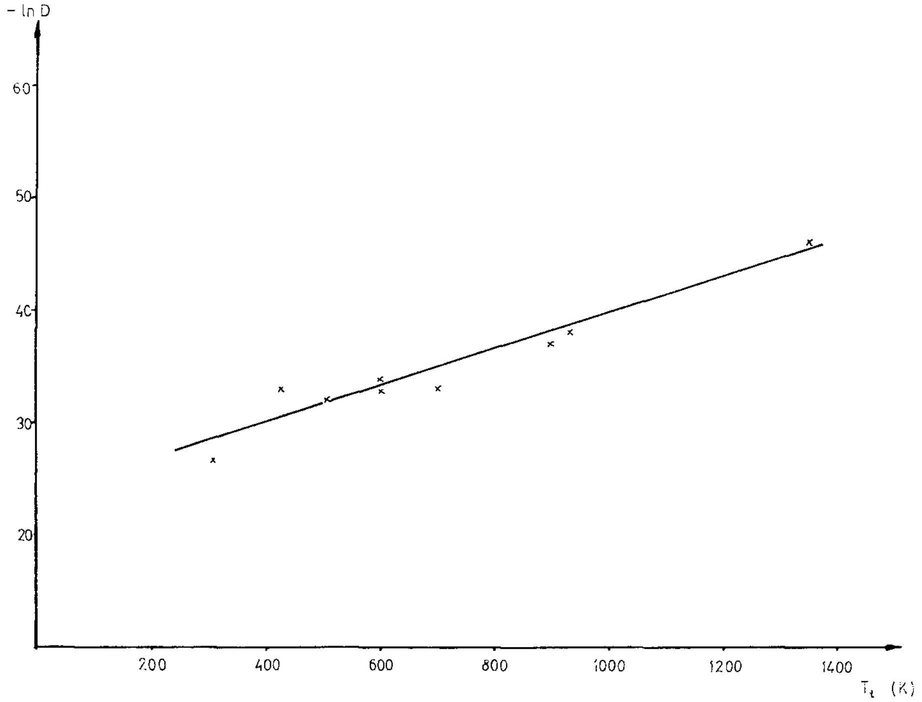

Fig. 7. Diffusion coefficient D(cm^2 s^{-1}) *vs.* melting point T_t(K) of metals reacting with gold in thin Au/metal couples:

$$-\ln D = 0.015T_t+24$$

or

$$D = 3.66\times10^{-11}\exp(-0.015T_t)$$

The experimental result that the gold reacts more rapidly with a metal if its melting point is lower could be explained by the fact[15] that the metals having lower melting points contain more structural defects responsible for a rapid volume diffusion of gold followed by the reaction of compound formation.

5. CONCLUSIONS

The kinetics of formation of compounds at room temperature in Au/Me (Me = Al, Cd, Ga, In, Pb, Sb, Sn, Zn) couples have been investigated. All these reactions were found to be diffusion controlled. Using the rate of compound formation as a measure of interdiffusion, the diffusion coefficients have been calculated for all the investigated couples. The relationship between diffusion coefficient $D\,(\mathrm{cm^2\,s^{-1}})$ and melting point $T_t\,(\mathrm{K})$ of the metal reacting with gold has been found to be

$$D = 3.66\times10^{-11}\exp(-0.015T_t)$$

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