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POSSIBILITY OF AND CONDITIONS FOR THE ROOM TEMPERATURE FORMATION OF COMPOUNDS AT THE BULK METAL/THIN METAL FILM INTERFACE

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Summary

It has been shown experimentally that compounds can be formed spontaneously at the bulk metal/thin metal film interface. Compounds were formed at room temperature on bulk silver, gold, copper, gallium, indium, lead and tin, but no compounds were observed on aluminium.

1. Introduction

A procedure frequently used for the preparation of binary compounds consists of fusion and annealing of stoichiometric amounts of the constituents in an evacuated silica tube. Similar results can be obtained if two different thin films are successively evaporated in a vacuum and are then annealed at a suitable temperature. It has been observed that in some cases [1] compounds are formed spontaneously at room temperature at the interface between two evaporated films (gold and lead). Systematic investigations of this phenomenon began in 1973 and many papers have been published since then. We have shown that the spontaneous formation of intermetallic compounds at the interface between two freshly evaporated thin films of different metals is not unusual. We have shown that about 50 binary compounds can be formed by combining about 20 metals with each other at room temperature [2–4], compared with the formation of about 300 compounds when the same metal couples are heated to elevated temperatures.

Since a large number of compounds are spontaneously formed at room temperature on the boundary between two different polycrystalline thin films, it is of interest to determine whether compounds would be formed on the boundary between a thin metal film evaporated on the surface of another bulk metal in a vacuum. In addition it is of interest to know under what conditions the spontaneous formation of binary compounds occurs, whether there is a difference in behaviour depending on whether the substances are poly-

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crystalline or single crystal and what would happen if two metal pieces were kept in contact for a longer time at room temperature.

The formation of compounds in some of the examples mentioned above is of both theoretical and practical importance. In this paper we present the results of a study of the conditions under which compounds are formed at the boundary between a polycrystalline or amorphous bulk metal sample and a thin film of another metal. No such data could be found in the literature.

2. Experimental details

The following bulk metals were used: gold (purity, 99%); silver, aluminium, copper and indium (purity, 99.99%); gallium, lead and tin (purity, 99.9999%). Aluminium and copper were used as foils and silver and gold were cast and rolled into sheets. The other metals were used in the irregular shapes supplied by the manufacturers (Koch-Light; Johnson-Matthey). If necessary, one side of these specimens was flattened and/or polished.

The surface was cleaned before evaporation using one of the following three methods: washing with absolute alcohol, mechanical treatment followed by washing with absolute alcohol treatment or etching with or without previous mechanical treatment. Owing to the very low melting point of gallium it was polished using different types of writing paper. The resulting polished surface was usually polycrystalline, but it was also possible to prepare it in an amorphous state. The results presented in Section 3 were obtained using maximally cleaned bulk metal surfaces.

The following metals were used for the evaporated films: gold (purity, 99.99%); silver, aluminium, gallium, indium and tellurium (purity, 99.999%); cadmium, copper, lead, tin and zinc (purity, 99.9999%). The films were evaporated to thicknesses of 500 or 1000 Å using the procedure described earlier [2–4].

The X-ray diffraction patterns of the specimens were determined immediately after evaporation and a number of times during the following 3–5 months. In some cases additional X-ray diffraction patterns were determined after longer periods. The compounds were identified from the ASTM cards.

3. Results

The conditions under which interactions take place at the bulk metal/thin film interface were investigated using two groups of bulk metals. The first group contained silver, aluminium, gold and copper which are characterized by relatively high melting points, unambiguous metallic properties and high crystal symmetry (*i.e.* f.c.c. lattice). The second group consisted of metals characterized by low (indium, lead and tin) and very low (gallium) melting points, a cubic lattice (lead) or symmetry lower than cubic. All these materials are extensively used in electronic and semiconductor techniques, so that their behaviour is of interest from both theoretical and practical viewpoints. A total of 31 bulk/film couples were prepared and analysed to establish whether any interaction took place and, if so, whether it was a sporadic or a frequent phenomenon. The metal couples chosen for investigation were those which reacted at room temperature in the form of thin film couples to produce compounds [2–4]. The compounds formed in the systems investigated are given in Table 1.

4. Discussion

Table 1 shows that compounds were formed in 27 out of the 31 bulk/film couples investigated. No compounds were formed in the bulk Au/Al film, bulk Al/Au film, bulk Cu/Sb film or bulk Cu/Te film couples.

4.1. Number of compounds formed

In 22 of the 27 couples in which compound formation takes place only one compound per couple was formed. Two compounds per couple were found in three couples and three compounds per couple were formed in two couples. The number of compounds formed in the bulk/film couples is generally less than that reported for the corresponding film/film couples. For example in the bulk Ga/Au film couple only one compound was found, although in the corresponding film/film couple four compounds were formed. Such examples are numerous. The reason for this difference in reactivity is as follows. The concentration of the constituents in the film/film couples can be changed at will, whereas only those compounds in which the bulk metal concentration is predominant can be formed in the bulk/film couples. Thus only Ag_2In is formed in the bulk Ag/In film couple and only $AgIn_2$ is formed in the bulk In/Ag film couple. However, both compounds can be obtained in the corresponding film/film couple by varying the concentrations of the metal film components. The same explanation holds for the Au/Ga and Sn/Au couples.

If only one compound is formed in a film/film couple, the same compound is formed in the bulk metal/thin film couple regardless of which bulk metal is present. For example, Ag_3Ga is formed in both the bulk Ag/Ga film and the bulk Ga/Ag film couples. Similar behaviour is observed for the bulk Ag/Sn film and bulk Sn/Ag film couples where Ag_3Sn is formed in both cases, and for the bulk Sn/Cu film and bulk Cu/Sn film couples where Cu_6Sn_5 is formed. In these three examples only one compound is formed regardless of the concentrations of the constituents.

4.2. Reaction rate

The formation of compounds in the bulk/film couples takes place at different rates. In some cases compounds are formed within 24 h of evaporation. In the majority of cases, however, compound formation is observed a few days after evaporation. The compound formation process is complete when the evaporated layer disappears, but this is observed for only a few couples. In

TABLE 1

Compounds formed at the bulk metal/thin metal film interface at room temperature

Bulk metal	*Thin film*											
	Ag	*Al*	*Au*	*Cd*	*Cu*	*Ga*	*In*	*Pb*	*Sb*	*Sn*	*Te*	*Zn*
Ag	—[a]	—	—	—	—	Ag_3Ga	Ag_2In	—	—	Ag_3Sn	Ag_2Te	—
Al	—	—	○[b]	—	—	—	—	—	—	—	—	—
Au	—	○	—	$AuCd_3$	—	$AuGa_2$ AuGa Au_2Ga	$AuIn_2$ AuIn	$AuPb_3$ $AuPb_2$	$AuSb_2$	AuSn	—	$AuZn_3$ AuZn
Cu	—	—	—	Cu–Cd	—	CuGa	CuIn	—	○	Cu_6Sn_5	○	$CuZn_4$
Ga	Ag_3Ga	—	$AuGa_2$	—	CuGa	—	—	—	—	—	—	—
In	$AgIn_2$	—	$AuIn_2$	—	CuIn	—	—	—	—	—	—	—
Pb	—	—	$AuPb_3$	—	—	—	—	—	—	—	PbTe	—
Sn	Ag_3Sn	—	AuSn $AuSn_2$ $AuSn_4$	—	Cu_6Sn_5	—	—	—	—	—	—	—

[a] Not studied because the reactivity has not been reported in the literature or because the compound formed by the film/film couple has not yet been identified.

[b] The compound anticipated, *i.e.* the compound formed by the film/film couple, was not formed in the bulk metal–film interaction.

general the evaporated layer can be identified even after several months, indicating that the process has not terminated.

The rate of compound formation in the bulk/film samples is less than that in the film/film samples. The rates in the film/film and bulk/film couples are compared in Table 2 for three groups of samples. The first group contains couples in which the compound formation is completed within 24 h of evaporating the film. The second group contains couples in which compound formation in the film/film samples is complete within 1 week of evaporating the film. However, in the bulk/film samples compound formation requires a rather longer time and the process is incomplete even after several months. In the film/film couples in the third group compound formation is observed within 1 month, but completion of the process requires years. No compound was observed in the corresponding bulk/film samples during the period of investigation.

TABLE 2

Comparative data for the reaction rates in three sets of film/film and bulk/film samples

Couple	*Sample*	*Compound observed*	*Process completed*
Ag/Ga	Ag film/Ga film (24% Ga or 49% Ga)	1st day	1st day
	Bulk Ag/Ga film	1st day	1st day
	Bulk Ga/Ag film	1st day	2nd day
Cu/Ga	Cu film/Sn film (20% Sn or 85% Sn)	2nd day	5th day
	Bulk Cu/Sn film	9th day	Not completed after 3 months
	Bulk Sn/Cu film	30th day	Not completed after 2 months
Au/Al	Au film/Al film	5th day	After more than 1 year
	Bulk Au/Al film	No compound observed	
	Bulk Al/Au film	No compound observed	

4.3. Solid state transformation

Solid state transformations have been observed in bulk/film couples in which more than one compound was formed. The transformations are identical with those taking place in the corresponding film/film couples. The mechanism of the transformation is as follows. One compound is formed initially and is then slowly transformed into another compound containing more of the metal originally present in the bulk form, *e.g.*

$$AuGa_2 + Au \rightarrow 2AuGa$$

$$AuGa + Au \rightarrow Au_2Ga$$

In this example the process stops at this point although in the corresponding film/film couple it continues until the Au_7Ga_2 compound is formed.

Solid state transformation in the bulk/film couples proceeds much more slowly than in the corresponding film/film couples. For example, the

$AuIn_2 + Au \rightarrow 2AuIn$ transformation requires 115 days in the bulk/film couple but only 28 days in the film/film couple. The explanation for this difference is probably the same as that proposed above for the difference in reaction rates.

4.4. *Effect of surface preparation*

The purpose of surface preparation of the bulk metal is to remove any foreign coatings which might affect compound formation after film evaporation. For example, oxide coatings may be present on bulk copper, indium or lead, carbonate coatings may be present on bulk lead and sulphide coatings may be present on bulk silver. Therefore several surface preparation techniques have been used.

Treatment with absolute alcohol was found to be adequate for almost all film evaporations on bulk gold (except for the Au/Al and Au/Sb couples) and for a number of film evaporations on copper (Cu/Cd, Cu/Ga, Cu/In and Cu/Zn). However, when bulk silver was treated in this way the rate of compound formation in the Ag/In and Ag/Te couples became very slow.

A more efficient surface treatment consists of mechanical grinding and polishing followed by washing with absolute alcohol. This method was used for couples in which no compound formation was observed after treatment with absolute alcohol only. Compounds were formed in the Au/Sb couples, in all couples containing bulk silver and in the bulk Cu/Sn film couple. The same treatment was applied to bulk indium samples of irregular shape that had to be flattened. Compound formation was observed in the In/Ag and In/Au couples, but only trace quantities were formed in the In/Cu couple.

Compounds were formed in the Ga/Ag, Ga/Au and Ga/Cu couples after the application of a particularly elaborate surface treatment.

Etching with suitable reagents resulted in compound formation in those cases where the methods described above were not successful. In this way compounds were formed on bulk tin (Sn/Ag, Sn/Au and Sn/Cu), bulk lead (Pb/Te) and bulk indium (In/Cu).

Therefore if no compound is formed even after applying all the above treatments, the reason must be something other than an insufficiently clean bulk surface.

5. Conclusions

Reactions at the bulk metal/thin film interface to form intermetallic compounds take place spontaneously at room temperature. These reactions are quite common as they were observed on seven out of eight bulk metals investigated and in 27 out of 31 couples analysed. It can be assumed with reasonable certainty that in the majority of cases in which no compound formation was observed the reaction does occur but requires a long time.

All compounds identified in the bulk/film couples were also obtained in the corresponding film/film reactions. The bulk/film reactions produce fewer compounds than the corresponding film/film reactions which, in turn, produce fewer compounds than obtained by fusion at elevated temperatures. Compound formation in the bulk/film couples proceeds more slowly than that in the film/film couples. Structural transformations analogous to those observed in the corresponding film/film couples take place in the bulk/film couples but proceed at a slower rate. It can be assumed that the mechanism of the reaction in the bulk/film couples is the same as that of the reaction in the film/film samples and that the compounds are formed because one of the constituents is in the form of a thin film. However, the rate of the reaction is reduced because there is only one film.

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