### Letter

### Reactions of r.f.-sputtered copper layers with Cd, Ga, Ge, Sn and Zn

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Results obtained by r.f. sputtering of copper layers on different metal substrates are presented. The copper layer reacts during the sputtering with cadmium, gallium, germanium, tin and zinc bulk or layer forming  $Cu_4Cd_3$ , CuGa and  $Cu_9Ga_4$ ,  $Cu_3Ge$  and  $Cu_5Ge$ ,  $Cu_6Sn_5$  and  $Cu_3Sn$ ,  $CuZn_4$  and  $Cu_5Zn_8$  respectively. There is no reaction with gold, aluminium or magnesium under the conditions employed.

### 1. Introduction

In our previous work it has been shown that on thermal evaporation of a copper layer onto thin gallium, indium, antimony, tin, tellurium or zinc layers the respective intermetallic compounds are formed at room temperature, but there is no reaction if the second layer is aluminium, gold, germanium, magnesium, manganese or samarium [1].

Similarly, if copper is thermally evaporated onto bulk pieces of gallium, indium or tin compound formation takes place at room temperature at each of these substrates [2].

On r.f. sputtering of copper onto bulk tellurium [3] or antimony [4], intermetallic compounds are already formed during the deposition process.

The present paper presents the results obtained from an investigation of the r.f. sputtering of copper layers onto bulk or layers of the metals gallium, germanium, cadmium, tin, zinc, magnesium, aluminium or gold, as well as thermally evaporated layers of copper on the bulk zinc or cadmium.

#### 2. Experimental details

Thin films of gallium, germanium, cadmium, zinc, tin, magnesium, aluminium, gold or copper were evaporated onto glass plates in an NRC 3117 vacuum evaporation unit [1]. The layer thicknesses monitored during evaporation were 100 nm (tin, aluminium, gold, magnesium) or 1000 nm (zinc, cadmium, gallium, germanium).

Pieces of zinc, cadmium or tin were cut from rods of 99.9999% purity and machined to dimensions of approximately  $8 \text{ mm} \times 2 \text{ mm}$ . The germanium single-crystal platelets with dimensions  $20 \text{ mm} \times 15 \text{ mm} \times 2 \text{ mm}$  were of semiconductor purity. The bulk metals were etched by means of suitable agents before evaporation [5].

The sputtering of copper was performed in a Perkin Elmer r.f. sputtering unit, model 2400 8SA. The copper cathode (diameter, 203 mm; purity, 99.999%) was at a distance of 70 mm from the substrate. Sputtering was performed at a pressure of 2.0 Pa with a cathode power of 1 kW. The thickness of the copper layers, measured after the evaporation by means of a Talystep unit, was between 160 and 1000 nm.

The bulk (or film) metal onto which a copper layer was sputtered was examined by means of an X-ray diffractometer, using nickel-filtered copper radiation. The identification of the compounds formed was made by means of ASTM cards.

# 3. Results and discussion

Thin gold, aluminium and magnesium films, the thickness of which was 100 nm, were thermally deposited in vacuum onto glass plates. On top of these films a copper layer was deposited using r.f. sputtering. The copper layers were deposited with sputtering times of 1, 3, 5 and 7 min. An examination of the prepared samples by X-ray diffractometry showed only reflections of copper and the other metal, which indicates that no reaction takes place between the copper and the metal. Since there was no reaction between the thin films, it was considered purposeless to sputter copper onto bulk pieces of gold, aluminium or magnesium.

## 3.1. Cu-Cd system

A copper layer was sputtered on top of a cadmium layer 1000 nm thick deposited on a glass plate, for sputtering times of 0.5, 1, 3, 5, 7 and 10 min, using a cathode power of 1 kW. In all these samples the compound  $Cu_4Cd_3$ was identified, the larger the sputtering time, the higher the intensity of the X-ray reflections of the compound. Copper was sputtered for 3 or 6 min onto bulk cadmium and in both samples the compound  $Cu_4Cd_3$  was identified.

There is no reaction, however, if a copper layer is thermally deposited onto a bulk piece of cadmium.

In our earlier paper [1] it was shown that a cadmium layer deposited on a copper layer, reacts at room temperature forming a new phase which could not be identified at the time. By means of the ASTM cards obtained afterwards, two compounds were identified in these earlier X-ray patterns:  $Cu_4Cd_3$  (ASTM card 20-178) and  $CuCd_3$  (ASTM card 16-17).

In the X-ray diffraction patterns of the samples consisting of cadmium film + r.f.-sputtered copper film, the intensities of reflections of the  $Cu_4Cd_3$ compound are considerably higher than in the patterns of samples obtained by thermal evaporation of copper, and they do not increase with time if the samples are stored at room temperature. These results point to the conclusion that the reaction of compound formation is much faster during r.f. sputtering, than during thermal evaporation of copper. Owing to the intense reaction of compound formation during r.f. sputtering, the compound layer makes a barrier preventing diffusion of the components and preventing further compound formation during storage of the sample at room temperature.

### 3.2. Cu-Ga system

Copper layers were sputtered on gallium films (thickness, 1000 nm) thermally evaporated in vacuum. The cathode power was 1 kW in all experiments, but the time was varied from 2 to 12 min. If the sputtering time was shorter (2 or 4 min), the copper reacted with the gallium layer forming the compound CuGa. The same compound was formed in the sample in which both layers had been thermally evaporated. If the sputtering time was longer (5 to 12 min), in addition to the compound CuGa (52 wt.% Ga), another compound, Cu<sub>9</sub>Ga<sub>4</sub> (32.78 wt.% Ga), was formed. The intensities of the X-ray reflections increase with sputtering time, the CuGa reflections being much more intense. In this case there is the phenomenon of formation of two compounds, indicating that the first compound formed does not form a barrier and the diffusion of the reactants continues unhindered.

## 3.3. Cu-Ge system

Copper layers were sputtered on layers of germanium 200, 500 and 1000 nm thick and on pieces of bulk germanium 1 and 2 mm thick (sputtering time, 2-16 min; cathode power, 1 kW). Sputtering times of 2 to 8 min on the layers or 6 to 16 min on the bulk metals, result in the formation of a single compound, Cu<sub>3</sub>Ge, identified on the basis of the ASTM card 6-0693. Longer sputtering times, for both the layer and the bulk samples, lead to the formation of another, not yet identified phase, in addition to the Cu<sub>3</sub>Ge compound. In the X-ray diffraction patterns of the samples consisting of germanium layers with copper layers sputtered for 10 min on top of them, pure  $Cu_3Ge$  is observed. But the sample sputtered for 16 min shows the reflections of the unidentified phase, along with those corresponding to the Cu<sub>3</sub>Ge compound. The Cu-Ge phase diagram [7] contains, in addition to Cu<sub>3</sub>Ge, another phase with higher copper content (Cu<sub>5</sub>Ge). It can be assumed that this compound has been formed in our samples, because it is formed when longer sputtering times are used, leading to a higher copper content.

### 3.4. Cu-Sn system

The tin layers evaporated onto glass plates were 100 nm thick, and the tin plates had dimensions of  $11 \text{ mm} \times 9 \text{ mm} \times 2 \text{ mm}$ . Copper layers were sputtered on these samples, with sputtering times ranging from 1 to 12 min and with 1 kW cathode power. For shorter sputtering times, only the Cu<sub>6</sub>Sn<sub>5</sub> compound is formed on the 1000 nm thick tin layer and on the bulk tin surface, but for longer sputtering times two compounds, Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn, are formed. On the thinner tin layer (100 nm) and when using a longer sputtering time (7 min), only Cu<sub>3</sub>Sn is formed. This can be readily understood:

the tin concentration is low and there is enough copper to form the compound of higher copper concentration.

# 3.5. Cu-Zn system

Copper layers were sputtered onto pieces of zinc  $(8 \text{ mm} \times 2 \text{ mm})$  (sputtering times, 1.5, 3, 6 min; cathode power, 1 kW). There was no reaction on the Cu-Zn interface for samples sputtered for 1.5 min, but a longer sputtering time led to the formation of the CuZn<sub>4</sub> compound.

When a copper layer was thermally evaporated onto a bulk piece of zinc no reaction took place.

Copper layers were sputtered onto zinc layers (thickness, 1000 nm) thermally evaporated onto glass substrates (sputtering times, 3, 6, 9 and 12 min; cathode power, 1 kW). Sputtering for 3 min allows the completion of the reaction between copper and zinc and two compounds,  $CuZn_4$  and  $Cu_5Zn_8$  are formed. Using a sputtering time of 6 min leads to the formation of only  $Cu_5Zn_8$ . In both cases all the zinc has been consumed and zinc reflections could not be identified in the X-ray pattern. Longer sputtering times cannot lead to further reaction because there is no more zinc left. However, the thicker copper layer obtained by longer sputtering shields the compound and therefore its reflections are less intense in the samples obtained after sputtering for 9 and 12 min than in those obtained after sputtering for 3 and 6 min. If a shorter sputtering time is used, the compound  $CuZn_4$  is formed in the zinc layer until all the zinc has been consumed; further addition of copper leads to a structural transformation:

 $2CuZn_4 + 3Cu \longrightarrow Cu_5Zn_8$ 

Therefore in the sample sputtered for 3 min both compounds are identified. With a further addition of copper the reaction is completed, *i.e.* all the  $CuZn_4$  is consumed by reaction with copper to form  $Cu_5Zn_8$ . Further addition of copper has no effect on the reaction.

When the copper is sputtered on bulk zinc, only  $CuZn_4$  is formed. This happens because in these samples the zinc is always in excess (with respect to the copper layer) and any addition of copper always leads to a compound with high zinc content; *i.e.* to  $CuZn_4$ .

 $Cu_5Zn_8$  has been identified on the basis of the X-ray diffraction pattern [8].

Table 1 presents a survey of the substrates with which a sputtered copper layer reacts, as well as the compounds thereby formed. It can be seen that in the cases in which two compounds are formed on the same substrate, the compound formed first is the one having the lower melting temperature and the compound having higher melting temperature is formed later. This behaviour is consistent with our results obtained with the Au-Me couples [6].

# 4. Conclusion

During the r.f. sputtering of copper layers on different metal substrates (cadmium, gallium, germanium, tin, zinc), reactions on the substrate-layer

TABLE 1

Substrate	Sputtering time (min)	Compound formed	Melting temperature of the compound (°C)
1. Cd film	1 - 10	Cu4Cd3	594
Cd bulk	3 - 6	$Cu_4Cd_3$	
2. Ga film	2 - 4 6 - 12	CuGa CuGa	254
		Cu9Ga4	836
3. Ge film	2 - 10 12 - 16	Cu₃Ge Cu₃Ge	570
		Cu <sub>5</sub> Ge	823
Ge bulk	6 - 16 16 - 25	Cu <sub>3</sub> Ge	
	10 * 25	Cu <sub>5</sub> Ge	
4. Sn film	1	Cu <sub>6</sub> Sn <sub>5</sub>	415
	3	$Cu_6Sn_5$ $Cu_3Sn$	676
	7	Cu <sub>3</sub> Sn	
Sn bulk	3	Cu <sub>6</sub> Sn <sub>5</sub>	
	6	Cu <sub>6</sub> Sn <sub>5</sub> Cu <sub>3</sub> Sn	
5. Zn film	3	CuZn <sub>4</sub>	5 <b>9</b> 8
	C	$Cu_5 Zn_8$	834
	0	Cu <sub>5</sub> Zn <sub>8</sub>	
Zn bulk	1.5		
	ა 6	CuZn <sub>4</sub> CuZn <sub>4</sub>	

Reactions of sputtered copper layers with various substrates (1 kW sputtering power)

interface take place leading to the formation of intermetallic compounds. The reactions are faster on layers than on bulk metals used as substrate materials.

By comparing these results with those obtained in our earlier work [1, 2] in which the copper layers were deposited on identical substrates, but using thermal evaporation, the following conclusions can be drawn.

1. Intermetallic compound formation is faster when the copper layer is deposited by r.f. sputtering than when it is thermally evaporated.

2. Intermetallic compound formation takes place when sputtering copper on bulk zinc, cadmium and germanium, but is absent if copper is thermally evaporated. The same behaviour is observed by r.f. sputtering copper on bulk tellurium [3] or antimony [4].

3. During r.f. sputtering of a copper layer on another metal layer more compounds are formed than in the corresponding couple in which the copper layer is thermally evaporated. Thus in the Cu–Ga couple two compounds, CuGa and Cu<sub>9</sub>Ga<sub>4</sub>, are formed simultaneously. The second compound can also be formed by a structural transformation from the first formed. Thus short duration r.f. sputtering of copper on tin, germanium or zinc leads to the formation of Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>3</sub>Ge or CuZn<sub>4</sub> respectively. By using longer sputtering times Cu<sub>3</sub>Sn, Cu<sub>5</sub>Ge or Cu<sub>5</sub>Zn<sub>8</sub>, respectively, are exclusively or predominantly formed. In all these cases the melting temperature of the compound formed second is higher than that of the compound formed first.

All these phenomena can be interpreted on the basis that the r.f. sputtering energy of the particles is considerably higher and the temperature is somewhat higher than is the case when thermal evaporation is used. The higher energy of r.f. sputtering accelerates or provokes the reaction, or a structural transformation of the compound formed first into the second having higher melting temperature.

- 1 V. Simić and Ž. Marinković, J. Less-Common Met., 72 (1978) 133.
- 2 V. Simić and Ž. Marinković, J. Less-Common Met., 95 (1983) 1.
- 3 V. Simić and Ž. Marinković, J. Less-Common Met., 106 (1985) 287.
- 4 Ž. Marinković and V. Simić, Thin Solid Films, 129 (1985) 315.
- 5 C. J. Smithels, Metals Reference Book, Vol. 1, Butterworths, London, 1976.
- 6 Ž. Marinković and V. Simić, J. Less-Common Met., 115 (1986) 225.
- 7 M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
- 8 S. S. Gorelik, L. N. Rastorguev and Yu. A. Skakov, Rentgenograficheskii i elektronograficheskii analiz metallov, gosudarstvennoe nauchno-tekhnicheskoe izdatel'stvo literatury po chernoi i tsvetnoi metallurgii, Moskva, 1963.