

**DIFFUSION IN Pd-Cu THIN FILMS****G. Molnár<sup>1</sup>, G. Erdélyi<sup>1</sup>, G. A. Langer<sup>1</sup>, A. Csík<sup>2</sup>, G. Katona<sup>1</sup>, L. Daróczy<sup>1</sup>,  
M. Kis-Varga<sup>2</sup>, A. Dudás<sup>3</sup>, D. L. Beke<sup>1</sup>**

<sup>1</sup>Department of Solid State Physics, University of Debrecen, P.O. Box 2,  
Debrecen H-4010, Hungary

<sup>2</sup>Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI),  
P.O. Box 51, Debrecen H-4001, Hungary

<sup>3</sup>Semilab Semiconductor Physical Laboratory, H-1117 Budapest, Prielle  
Kornélia Street 2, Hungary

**Abstract**

Diffusion in polycrystalline Pd-Cu thin film system was investigated in the temperature range of 120-310 °C, by SNMS depth profiling technique. Depending on the annealing parameters, an almost complete homogenization was detected even at temperatures where the volume diffusion was frozen in. The detected Cu profiles were typical C-kinetic regime grain boundary profiles in the Pd layer. Because of the much higher grain boundary diffusivity on the Cu-rich side, the Cu grain boundaries saturated with Pd after very short times. On the Pd-side, from the time evolution of C-type depth profiles, we determined the Cu grain boundary diffusion coefficients at different temperatures. The high concentration level in Cu-side could be interpreted supposing moving boundaries that leave behind regions with high Pd concentration.

Though the intermetallic phase formation in this system under similar conditions was proved, the shape of our depth profiles do not show any effects of a reaction layer formation near the original interface. Our findings remain compatible with the previous results, if we suppose an unconventional type of growth

mode: phase formation takes place in and around grain boundaries, by means of transport along interface/grain boundaries.

## I. Introduction

There are experimental evidences that a complete mixing or homogenization may take place in thin film systems at rather low temperatures, even when the bulk transport is frozen and atomic movements are restricted to grain boundaries (GBs) only [1,2]. In order to understand the low-temperature homogenization, two processes are usually taken into consideration: i) diffusion-induced grain boundary motion (DIGM) [3,4]; ii), diffusion-induced recrystallization, (DIR) [5,6]. During DIR new grains are formed with composition discontinuously different from the surrounding original grains, while in case of DIGM, a zone with changing composition is left behind a sweeping boundary.

In our work we present results on the time evolution of depth profiles in Pd/Cu bilayer system at low temperatures. Recently, the kinetics of interdiffusion, stress development, concentration depth profiles, phase formation were thoroughly investigated in this system [7,8], but there are still numerous open questions left. Chakraborty et al. showed that using selected area diffraction at low temperatures (175-250 °C) interdiffusion is accompanied by compound formation: at first  $\text{Cu}_3\text{Pd}$ , afterward  $\text{CuPd}$  phase are formed [8]. However, the authors interpreted the measured concentration depth profiles as a result of GB and volume diffusion processes and they deduced volume and GB diffusivities from their experiments [8].

Using a different technique, Secondary Neutral Mass Spectrometry (SNMS) and studying the intermixing in a wider temperature range, we have shown [9,10] that the measured depth profiles need a completely different interpretation, because the volume diffusion transport is completely frozen in the investigated temperature range. The high Pd concentration in the Cu layer can be elucidated by supposing moving interfaces/GBs e.g. in DIGM process. As a report of my PhD research activities I summarize these results below.

## **II. Experimental details**

Pd(20nm)/Cu(30nm) bilayer samples were prepared by DC magnetron sputtering onto Si wafers and onto polished MgO single crystals. Pd films were deposited always as a top layer. In the second deposition run we prepared bilayer samples with different thicknesses (Pd(30nm)/Cu(50nm)) on Si substrates too. In the case of film preparation onto MgO, the temperature of the previously mentioned substrate was held at 200 °C during the copper film deposition, in order to get a copper layer with larger grain size. During the deposition of layers onto Si, the substrate temperature was kept at room temperature. The grain size of the as-deposited samples was estimated by taking TEM images. Our samples were annealed under vacuum ( $1 \cdot 10^{-4}$  Pa) at temperatures, ranging from 120 to 310 °C. The time evolution of the intermixing process was studied between 20 minutes and 11 hours. The concentration profiles were measured by a Secondary Neutral Mass Spectrometer (SPECS INA-X).

## **III. Results and discussion**

Figure 1-5 show the Pd and Cu concentration-depth profiles of samples that were annealed in the temperature range of 150–310 °C.

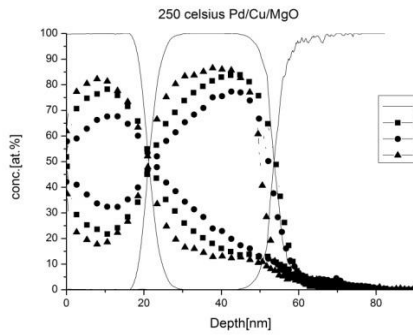


Figure 1

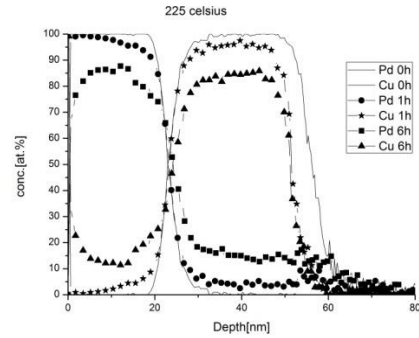


Figure 2

The profiles of the as-deposited specimen show some smeared interfaces (5-7 nm). This can be explained by some intermixing during the sample preparation process, initial interface roughness and additionally preferential sputtering due to different atomic masses of Cu and Pd atoms. Detectable Pd penetration occurs on the Cu-side, already at 120 °C, at the shortest annealing time (20 minutes), as Figure 3 shows.

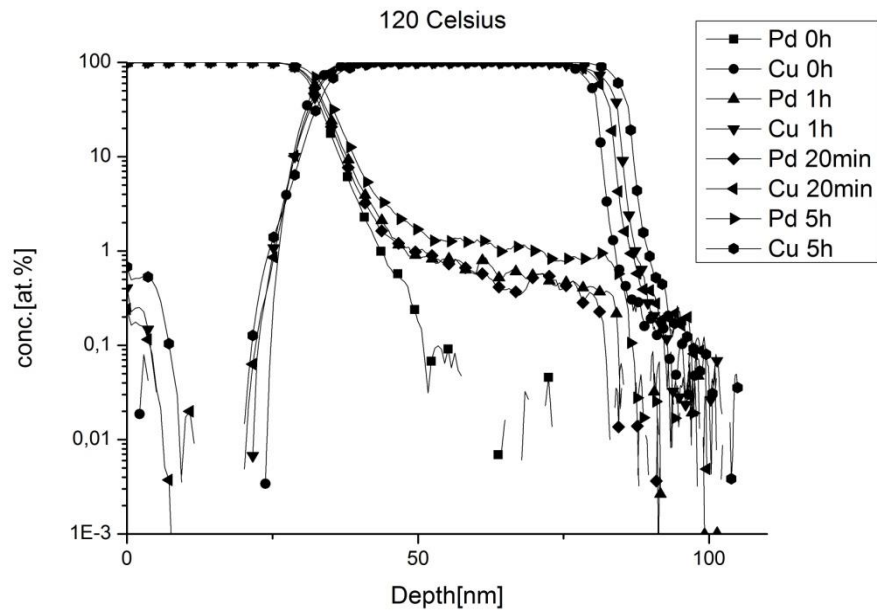


Figure 3

Near the initial interface the average concentration drops with decreasing slopes, inside the Cu film the emergence of a plateau region can be observed. The Pd concentration in the plateau region increases with the annealing time and saturates at about 10-15 at.% (Fig. 2, Fig 4).

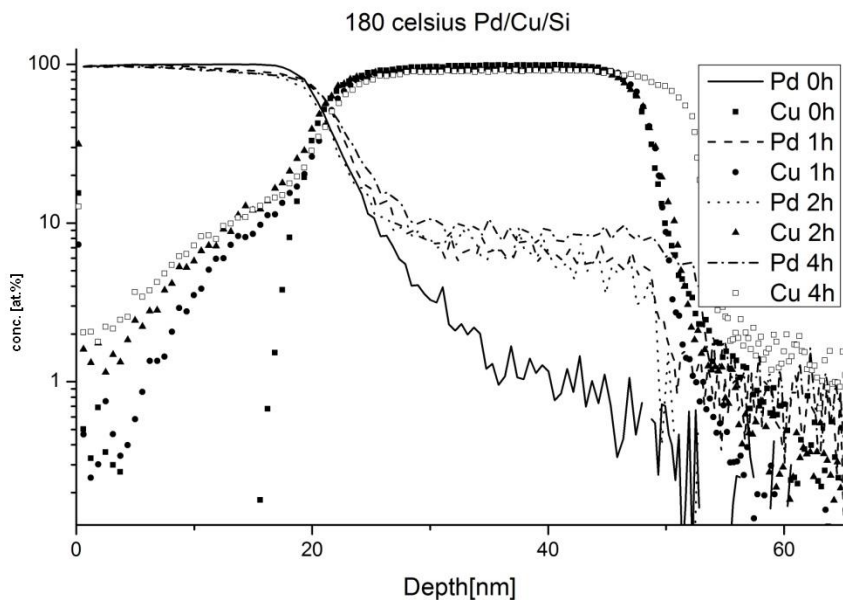


Figure 4

The time evolution of the Cu profiles can nicely be observed at higher temperatures (Fig. 4). If diffusion take place in grain boundaries only, (C-type diffusion regime), the average concentration profiles can approximately be described by Gauss- or complementary error functions, in that case, if the grain boundary penetration depth is less than the film thickness. Considering the shape and the amplitudes of the Cu-profiles, one can recognize that these are likely C-type profiles. Some Cu enrichment at the topmost surface and a concentration minimum can also be observed. The concentration minimum of Cu is visible at longer times and at higher temperatures (Fig. 1, Fig. 2). At the highest temperature (Fig. 5) a complete homogenization takes place.

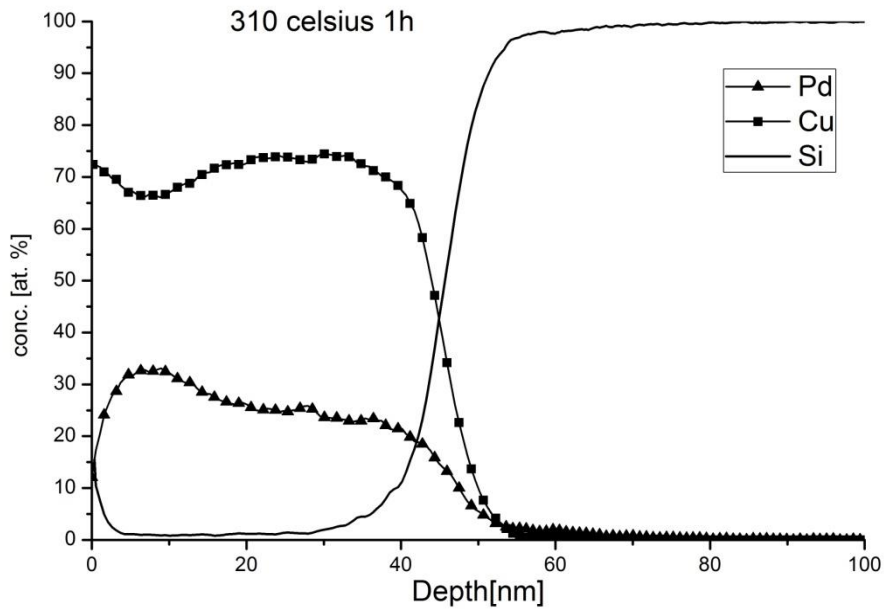


Figure 5

At a given temperature the Pd volume diffusion coefficient in Cu matrix is close to the bulk Cu self-diffusion coefficient [11,12]. This relationship is true in a wide temperature range, the activation energies of bulk self- and Pd impurity diffusion processes are practically the same.

According to the tracer data of Maier [12], Cu volume self-diffusion coefficients at temperatures 150 °C and 250 °C are  $5 \cdot 10^{-30}$  m<sup>2</sup>/s and  $2.2 \cdot 10^{-25}$  m<sup>2</sup>/s, respectively. Considering some hours annealing time ( $t=10^4$  s), the volume penetration depth ( $\sqrt{D \cdot t}$ ) at 250 °C is  $4.4 \cdot 10^{-11}$  m. This means that the condition of C-kinetic regime is strictly fulfilled,  $\sqrt{D \cdot t} \ll \delta$ , where  $\delta$  is the grain boundary width ( $\delta=0.5$  nm), so the transport in Cu below 250 °C is restricted to the grain boundaries. These considerations are still qualitatively valid for the annealing carried out at 310 °C, where the estimated volume penetration depth is still lower than 0.5 nm.

Since there are no experimental Pd GB diffusivity data in Cu available, especially at low temperatures, we supposed that these data can also be close to the Cu GB self-diffusion data. Supposing furthermore, that the segregation factor of Pd is about unity, the following expression, deduced from low-temperature tracer GB self-diffusion measurements in Cu [13], may roughly give the order of magnitude of the Pd GB diffusivity in Cu:

$$\delta D_{gb} = 1.16 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1} \cdot \exp(-84.75 \text{ kJmol}^{-1} / RT) \quad (1)$$

A fast estimation shows (see Table 1) that the GB penetration depth at 225 °C for the shortest heat treatment ( $t=3600$  s) is about 3290 nm, i.e. it is much larger than the Cu film thickness itself.

T[°C]	$\delta D_{gb}$ [m <sup>3</sup> /s]	$D_{gb}$ [m <sup>2</sup> /s]	$\sqrt{D_{gb} \cdot 3600s}$ [nm]
120	$6,3 \cdot 10^{-27}$	$1,2 \cdot 10^{-17}$	207
150	$4,0 \cdot 10^{-26}$	$7,9 \cdot 10^{-17}$	533
180	$2,0 \cdot 10^{-25}$	$3,9 \cdot 10^{-16}$	1180
225	$1,5 \cdot 10^{-24}$	$3,0 \cdot 10^{-15}$	3290
250	$4,0 \cdot 10^{-24}$	$8,0 \cdot 10^{-15}$	5370

Table 1

It means that in the Cu-film GBs are saturated with Pd in the first few minutes of heat treatments. In order to study the initial stages of mixing we prepared samples with smaller grain size and larger thickness (Table 2).



Substrate	Si	MgO	Si
Cu thickness/grain size [nm]	30/10	30/50	50/10
Pd thickness/grain size [nm]	20/5-8	20/15	30/5-8

Figure 2

The profiles shown in Fig.3 and in Fig.4 are similar to those ones measured in specimens with larger grain size. In order to observe the stage prior to saturation, we carried out a series of annealing at 120 °C as well, see Fig.(3). During the shortest annealing (20 min.) a plateau develops, i.e. saturation takes place completely, indicating that the Pd GB penetrating depth is larger than the increased Cu film thickness (50 nm), see Table 1.

Systematic volume self-diffusion measurements at low temperatures are not available in Pd. However, the well-known empirical rule on self-diffusion may help us to estimate the role of volume diffusion transport in Pd matrix [14]. According to this rule, the diffusivities of fcc metals, when they are plotted in a homologous temperature scale ( $T/T_m$ , where  $T_m$  is the melting point), are almost the same. Since the melting point of Pd is considerable higher than that of Cu, the bulk diffusion coefficients in Pd in the investigated T-range should be some orders of magnitude lower than the bulk diffusion data in Cu. Thus, we can preclude the role of volume diffusion in the Pd layer too. The rule of thumb, mentioned above, is valid for the GB diffusivities in Pd and in Cu as well. The observed C-type Cu-profiles (Fig.4) shows that GB diffusion in Pd is much slower than in Cu.

Fortunately, in the Pd layer the Cu profiles show that the GB penetration depth of Cu is comparable or less than the Pd film thickness i.e. we could observe the depth profiles prior to the saturation of GBs see Fig.(4). Supposing a columnar grain structure and using our numerical procedure published recently [15], we determined the grain boundary diffusion coefficients, which are able to fit qualitatively the observed profiles. The evaluated GB diffusion coefficients, and the input parameters, necessary for the numerical procedure are shown in Table 3.

T[°C]	120	150	180
Dgb[m <sup>2</sup> /s]	< 5*10 <sup>-22</sup>	1*10 <sup>-21</sup>	7*10 <sup>-21</sup>
Pd thickness [nm]	30	20	20
Pd grain size [nm]	5	5	5

Table 3

At the lowest temperature, Cu GB diffusion in Pd is practically frozen in (Fig.3). Interestingly, the appearance of some Cu at the topmost surface indicates that along fast boundaries or triple junctions, Cu atoms are able to reach the Pd surface.

Using x-ray diffraction and transmission electron microscopy (TEM), Chakraborty et al. convincingly proved that under the same conditions, in Pd/Cu bilayer film, intermetallic phases are formed [7]. Surprisingly, in their TEM micrograph no reaction layer could be detected in the vicinity of the original interface. We did not observe the effects of such reaction layer in our depth profiles. Further investigations are in progress in order to get crystallographic information on the Pd-rich region.

Our experimental findings and earlier results suggest that instead of nucleation and growth of a product layer, parallel to the original interface, compound phases may form without participation of volume diffusion, mediated by DIGM. By means of this mechanism, the high concentration regions with compositions close to the stoichiometric composition may develop and grow behind moving GBs. The grain boundary network in thin films, even at low temperatures, is able to supply enough material to reach a complete homogenization or phase formation in the whole volume of the film.

While in [9] we focused on the first stages of the intermixing, the result obtained at longer annealing times are also very interesting. Indeed, at later stages the average compositions inside both initial layers increases and the final result is an almost homogeneous 50/50 CuPd compound formation (see the curve at 4 h in Figure 1). It is important to note that the final result of such kind of low temperature homogenization can be different depending on the initial grain size, the ratio of the initial film thicknesses, the temperature and stress distribution

influenced by the substrate too, in accordance with the predictions as described in [2]. Indeed, as illustrated in Figure 5 [10], it is also possible to arrive at a different homogeneous state by changing the substrate (to Si (001) with native SiO<sub>2</sub>) and the annealing temperature (to 310°C). Here the final state corresponds to the Cu<sub>3</sub>Pd compound.

#### **IV. Conclusions**

Interdiffusion in polycrystalline Pd-Cu thin films were investigated in the temperature range of 120-310 °C by SNMS depth profiling technique. Complete homogenization/phase formation was observed in Pd/Cu system at low temperatures where volume diffusion contribution was negligible. The Cu-side profiles could be interpreted supposing moving boundaries, which leave behind regions with high Pd concentration. From the time evolution of C-type depth profiles, measured in the Pd part of the couple, we determined the Cu GB diffusion coefficients at different temperatures.

In the temperature range of our investigations interdiffusion is accompanied by the formation of Cu<sub>3</sub>Pd and CuPd phases. According to our depth profiles reaction layer parallel with the original interface, can not be detected. It means that compound formation may take place along grain boundaries.

#### **Acknowledgement**

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#### **References**

- [1] Schmitz G, Baither D, Kasprzak M, Kim TH, Kruse B. Scripta Mater 2010; 63:484-487.

- [2] Kosevich VM, Gladkih AN, Karpovskiy MV, Klimenko VN. *Interface Sci* 1995; 2:261-270.
- [3] Hillert M, Purdy GR. *Acta Metall* 1978; 29:333-346.
- [4] den Broeder FJA. *Thin Solid Films* 1985;124:135-148.
- [5] Kajihara M. *Scripta Mater* 2006;54:1767-1772.
- [6] Inomata S, O M, Kajihara M. *J Mater Sci* 2011;46:2410-2421.
- [7] Chakraborty J, Welzel U, Mittemeijer EJ. *J Appl Phys* 2008;103:113512-15.
- [8] Chakraborty J, Welzel U, Mittemeijer E J. *Thin Solid Films* 2010;518:2010-2020.
- [9] G. Molnar et. al.; *Vacuum*(2013),  
<http://dx.doi.org/10.1016/j.vacuum.2013.04.015>
- [10] D.L. Beke, G.A. Langer, G. Molnár, G. Erdélyi, G.L. Katona, A. Lakatos and K. Vad; *Phil.Mag.*,2012, DOI:10.1080/14786435.2012.732712
- [11] Peterson NL. *Phys Rev* 1963;132:2471-2476.
- [12] Maier K. *Phys Stat Sol(b)* 1977;44:567-576.
- [13] Surholt T, Herzig Chr. *Acta Mater* 1997;45:3817-3823.
- [14] Beke DL, Erdélyi G. *Scripta Mater* 1977;11:957-963.
- [15] Makovec A, Erdélyi G, Beke, DL. *Thin Solid Films* 2012;520:2362-2367.