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INVESTIGATION OF DIFFUSION AND SOLID-STATE REACTIONS IN THIN FILM SYSTEMS

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Abstract

Diffusion and solid state reactions in Pd/Cu, Pd/Ag and NiPt/a-Si thin film systems have been investigated. The process of complete homogenization in the diffusion couples of Pd/Cu and Pd/Ag at such a low temperature (120-310 °C), where the volume diffusion does not play a significant role were followed. The Pd/Cu system behave quite similarly from the point of view of diffusion to the Pd/Ag system, except that in the latter system phase-formation does not occur. Thus, by the comparison of these two systems we can examine the effect of phase formation on the development of the intermixing. Samples that had been prepared by magnetron sputtering were annealed under vacuum conditions and analyzed later on by SNMS. Furthermore the processes controlling the formation of a continuous compound layer that grows at the interface of the NiPt/a-Si system were also studied. The samples were prepared by a custom built magnetron sputtering system and were annealed later on. We followed the growth rate of the continuous compound layer in the above system by a combined method developed by the members of our department that include SNMS and profilometer measurements.

I. Introduction

The total intermixing in diffusion couples at remarkably low temperatures have already been reported [1, 2]. Several models were developed in order to gain a deeper understanding of the underlying procedures (e.g. diffusion-induced grain boundary motion (DIGM), diffusion-induced recrystallization (DIR)) yet some details remained unexplained. We investigated the Pd/Cu and Pd/Ag systems in order to unfold this problem and achieve a better insight.

The Ni-Si system is present in many electronic applications during the last decade as contact material [3, 4]. Thus the physical characteristics of the different compounds that appear during the variant processes in this system hold a great interest and worth to deal with. The nucleation of these phases is just as important as their latter growth and as a proof of this numerous experiments were concerned with this system formerly [5]. Our goal was to obtain more precise information about the nucleation and the growth of the NiSi phase by our new method.

II. Experimental details

The samples were prepared by magnetron sputtering. In case of the Pd/Cu system I prepared samples with two different layer thickness ratios. Samples with layer thicknesses corresponding to the atomic ratio of the CuPd and Cu_3Pd phases (62.5 nm / 50 nm, 33.6 nm / 80 nm) were prepared to examine the role of the initial layer thicknesses in the nucleation of the different phases. The samples were annealed under vacuum conditions at 250-280 °C for 1 hour. Depth profiles were gained by SNMS. In order to elucidate the effects of the developing stress we are going to perform the annealing of the samples under high pressure conditions (200 bar) in high purity (99.999%) Ar atmosphere. The new annealing chamber that can tolerate such extreme circumstances is still under construction and testing. This chamber will be connected directly to a high pressure Ar storage cylinder. Prior to the pressurizing of the chamber we

pump it down to 0.1 mbar. The chamber is equipped with a built-in furnace that can reach 800-900°C and it is connected to a water cooling system from the outside.

The Figure 1 shows the schematic figure of the annealing system.

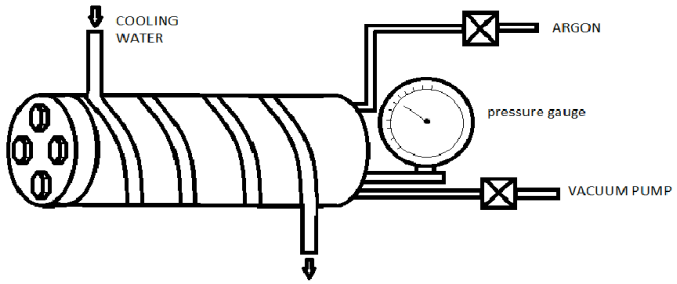


Figure 1.

Pd (15 nm) / Ag (15 nm) and Pd (30 nm) / Ag (30 nm) samples were prepared on single crystal Silicon substrate. I performed heat treatments in the vacuum chamber under $1*10^{-5}$ mbar for 1-8 hours in the 100-180°C range. Depth profiles were recorded by SNMS.

$Ni_{95\%}Pt_{5\%}$ (40 nm) / a-Si (100 nm) samples were prepared on single crystal Silicon substrate. The 5 at% Pt within the Ni were designed to stabilize the establishing of the NiSi phase during the annealing. Prior to the heat treatments of the samples I performed preliminary measurements in order to define the ideal time and temperature window for my research to avoid the recrystallization of the sample. Since the recrystallization affects the phase growth. These preliminary measurements were achieved in a vacuum chamber equipped with a 4 wire resistance measuring unit. For example as it can be seen on Figure 2. one can see that after 5 hours of annealing a clear mark of recrystallization appears that indicates a significant change in the sample's resistance .

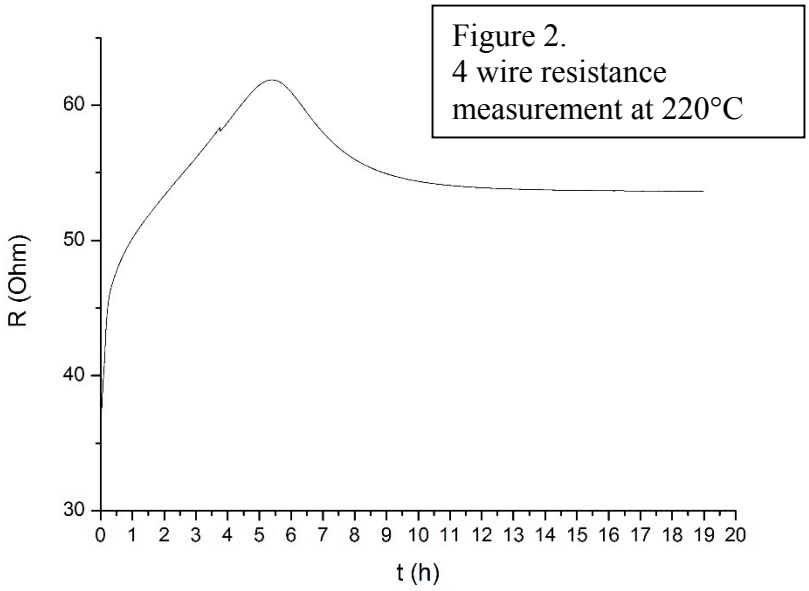


Figure 2.
4 wire resistance measurement at 220°C

For conducting a successful measurement I needed a “quite wide” product layer (5-20 nm), thus I decreased the annealing temperature since this way I had the possibility following the process at a longer time range. On Figure 3. one can see the repeated experiment at 200°C that shows a promising 13 hours long annealing time before the recrystallization.

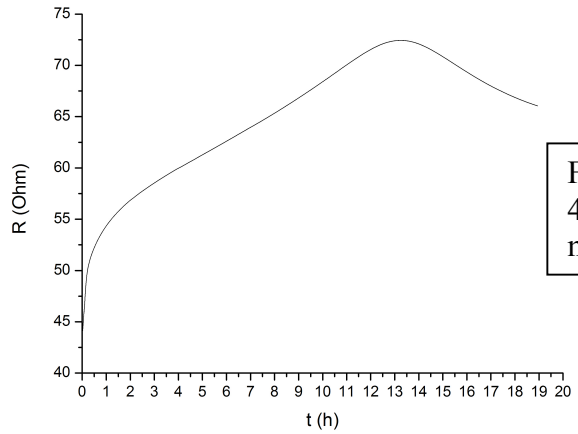


Figure 3.
4 wire resistance measurement at 200°C

As the result of these measurements I concluded that the best temperature is 200°C for my investigation.

Since we can stop the ion-etching during the SNMS measurements at any desired moment and later on we can measure the depth of the obtained craters by the profilometer, we can acquire the essential width value, with our new method, of the growing product layer as it can be seen on Figure 4.

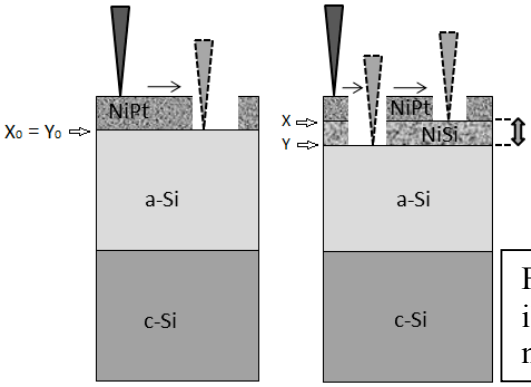


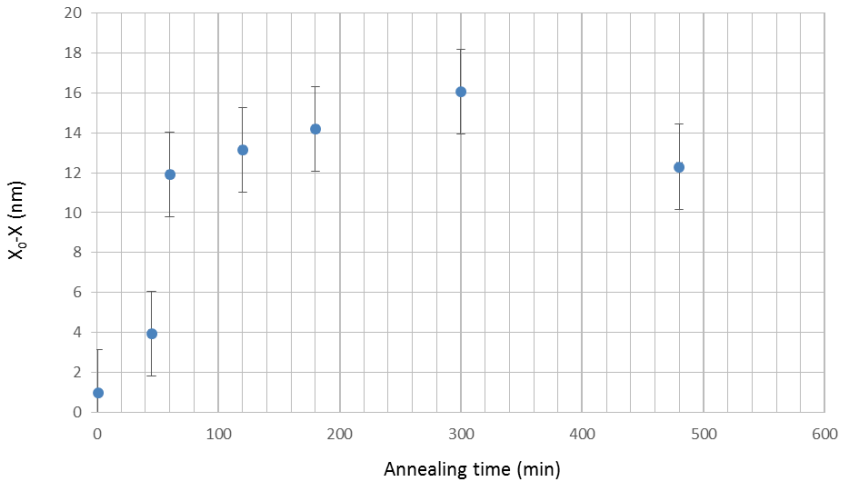
Figure 4. Schematic illustration of the measuring method

We repeat the series of measurements and we improved its reliability and its punctuality in each and every time. The first problem was the uncertainty of the time of the annealing. The cooling rate of the samples inside a vacuum chamber is always a matter of debate in such measurements since we cannot control the cooling rate adequately in this case. As the temperature of the samples dropped by heat radiation only because we could not cool the sample holder directly the uncertainty of these heat treatments are high and any precise evaluation of these measurements became impossible. We built a new furnace to solve this problem. In this furnace a halogen bulb heat a copper block, that is lying on springs, from the inside and when it reached the annealing temperature we push the sample holder onto its surface. Thus, the temperature of sample will equalize within 5-10 minutes. At the end of the annealing, we lift up the sample holder from the copper block and push it onto a cold (room temperature) metal plate. The sample cool down approximately in 10 minutes. With this system we could eliminate the uncertainty of the heat treatment. We found two other problems in the measuring method that caused inaccuracy. Firstly, the depth of the craters etched by the SNMS with 2 mm diameter cannot be measured accurately enough within the error of 1-2 nm. I eliminated this problem by using a dense copper mesh, with hole-width of 40 μm, during the SNMS measurements. This way I obtained numerous smaller craters instead of a large one. The shape of these smaller holes were better not mentioning that this way I had the opportunity to average their depth values which in turn granted a much better result. Secondly, stopping the ion etching at the interface position with high accuracy (within 1-2 nm) is always a problem. Obtaining the real positions of the interfaces I did correction calculations. From the time-intensity curves of the full sample and the individual interface positions recorded during the SNMS measurements of the sample I got a ratio from which later on I could determine the correct positions for each and every interface by correcting the measured depth values with this ratio.

With these corrections I could improve the reliability of the repeated measurements.

III. Results and discussion

Formerly we investigated in details the Cu/Pd system and created a model [6] (GBDIREAC – grain boundary diffusion induced solid-state reaction) that can explain the reported experimental results [7, 8]. The goal of the Pd/Cu and the Pd/Ag experiments this time have been determining the speed of the motion of the grain boundaries which is actually included in the above mentioned model that originates from previous studies [6].



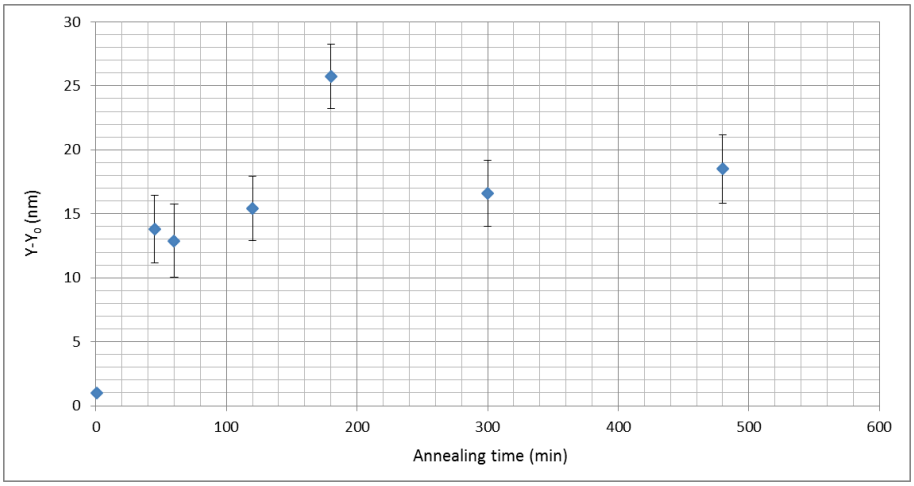


Figure 5 and 6 show the interface positions as a function of the annealing time.

The position X_0 and Y_0 indicate the original NiPt/a-Si interface measured from the sample surface. X is the position of the border of the phase closer to the surface and Y is the other border on heat-treated samples as it can be seen on Figure 4. Figure 5-6 show the data points of first approach of the experiment. You can see that there is no possible optimal fit for these points since the deviation of the points are too high. This is the consequence of the errors of the measuring method. We have been repeating a new series of measurements ever since with the improved method.

Acknowledgement

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