

Multiple Low-Temperature Interface Reactions: An Alternative Route into the Amorphous State of Metallic Alloys

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During the preparation of thin Au/In multilayers (0.39/1.2 nm, total thickness 48 nm) by ion-beam sputtering at 86 K, periodic interface reactions were observed by an *in situ* measurement of the electrical resistivity. The resulting phase was identified as amorphous Au_xIn_{1-x} with compositions x which were controlled by the choice of the individual Au and In layer thicknesses. The formation of these amorphous phases was restricted to a thin interface region (< 6 nm) and, most important, could not be obtained by long-range diffusion of thick Au/In multilayers.

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For many years, the application of a rapid quenching process has been the only experimental way to obtain an amorphous metallic state. Examples of these techniques are vapor quenching onto liquid-helium-cooled substrates [1], splat cooling of the melt [2], or even faster processes like laser quenching [3] and low-temperature ion irradiation [4]. The situation significantly changed due to experiments demonstrating the possibility of an amorphization by thermal diffusion [5] as well as by mechanical alloying [6]. But it soon turned out (for reviews see [7–9]) that these new preparation techniques hinged on severe thermodynamic constraints restricting their application to a small number of systems. For binary systems, a large negative heat of mixing as well as an anomalously high diffusion coefficient of one element within the other are demanded for amorphization by a thermally driven solid-state reaction to occur. AB systems complying with these requirements are usually brought into the amorphous state by preparing crystalline $A-B$ multilayers (the typical thickness of the individual A and B layers is 20 nm) followed by a heat treatment allowing the amorphization by solid-state reaction. For Ni/Zr, a system satisfying the above requirements, an interesting alternative preparation technique has been demonstrated [10]. After room-temperature sputtering of Ni/Zr multilayers with extremely small individual layer thicknesses (approximately 5 monolayers of each constituent), an amorphous phase could be observed without an additional heat treatment. By advancing this technique of multiple interface reactions allowing low preparation temperatures ($T \leq 86$ K) within an UHV chamber and *in situ* measurements on the growing layers, we were able to prepare for the first time the amorphous phase of a system which cannot be amorphized by a thermally driven solid-state reaction. The details of these experiments obtained on a series of Au/In multilayers will be reported in the following.

The Au/In multilayers (typical individual layer thicknesses of Au, 0.39 nm, and In, 1.2 nm) were prepared by ion-beam sputtering within an UHV chamber using 0.5-keV Ar^+ ions from a Kaufman-type ion source (total pressure prior to sputtering, 10^{-9} mbar; Ar partial pressure during sputtering, 7×10^{-5} mbar). The ions hit the

Au or In target mounted on separate faces of a water-cooled rotary holder. The sputtered atoms are collected on a fused-quartz substrate held by a liquid-nitrogen-cooled holder also containing an electrical heater and a resistance thermometer. Thus, the substrate temperature T_s can be varied and controlled between 86 and 390 K. Prior to layer deposition, electrical contacts (Ag) are prepared onto the substrate allowing the *in situ* determination of the electrical resistance during layer growth. The actual layer thickness during preparation could be measured by a quartz-crystal monitor. Typical growth rates of the layers were 0.03 nm/s. The whole preparation process as well as the data acquisition can be controlled by computer.

Figure 1 shows a typical result obtained during layer deposition at $T = 86$ K. Here, the electrical resistance is plotted versus the preparation time and the different arrows indicate the start and stop of the In or Au deposition. The most important feature of these results can be noticed by inspecting a typical In/Au bilayer (e.g., the eighth bilayer as indicated in Fig. 1): Immediately after

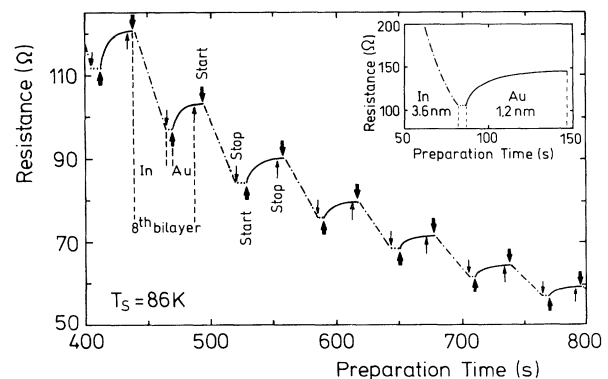


FIG. 1. Electrical resistance as observed during the deposition of the multilayer vs preparation time. The uncertainty of the data (2000 points) is smaller than the linewidth. Inset: Formation of a Au/In bilayer by Au evaporation on top of a sputtered In layer at $T = 96$ K. The Au evaporation rate is the same as in the sputtering experiment.

starting the In deposition, the resistance shows an almost linear decrease with a constant slope until the deposition is stopped (In layer thickness 1.2 nm). This behavior suggests a layer-by-layer growth of the In at least for the first 4 monolayers (ML). During the deposition interrupt, necessary to interchange targets, the actual resistance stays constant. The most striking behavior is observed after starting the Au deposition (total thickness 0.39 nm, corresponding to 1.5 ML). Here, a resistance increase is found in marked contrast to what is expected in a simple parallel-resistor model. The observed increase suggests an interface reaction of the deposited Au atoms with the underlying thin In layer. Using the independently determined total layer thicknesses, the corresponding resistivities can be calculated and are plotted in Fig. 2 versus the total film thickness. Clearly, after a total of roughly twelve bilayers, the bilayer resistivity approaches a constant average value of $71.5 \mu\Omega \text{ cm}$. This value gives a first clue to what phase is formed by the Au/In interface reaction. For the results presented in Figs. 1 and 2, the Au and In layer thicknesses were adjusted in a way to correspond to an average composition of the intermetallic compound In_2Au (CaF_2 structure). This composition was independently verified by Rutherford backscattering (RBS) after complete thermal reaction of the multilayers at 390 K. From earlier work [11] it is known that crystalline In_2Au films exhibit a typical resistivity of $\rho(300 \text{ K}) = 25 \mu\Omega \text{ cm}$, well below the above bilayer value. On the other hand, In_2Au can be forced into the amorphous phase by vapor quenching onto cooled ($T < 100 \text{ K}$) substrates with resistivities prior to recrystallization at T_x within the range $75 \mu\Omega \text{ cm} \leq \rho \leq 100 \mu\Omega \text{ cm}$ [11]. It is important to note that by thermal reaction of thick In/Au layers with an average composition of 2:1 at $T > 220 \text{ K}$ (this is the starting temperature of long-range diffusion in the In/Au layer system [12]) only crystalline In_2Au can be obtained, but not the amorphous phase [13]. Thus we are led to the conjecture that during the Au deposition onto an ultrathin crystalline In layer at 86 K a thin amorphous AuIn_2 layer is formed producing the observed

resistivity increase. On top of this amorphous layer, disordered crystalline In can be deposited, resulting in the observed linear resistivity decrease, and the whole process can then be repeated periodically. If this conjecture holds, the whole of the resulting film should be in the amorphous phase after the deposition is completed at $T = 86 \text{ K}$ due to these multiple interface reactions. Experimentally, this can be tested by monitoring the temperature dependence of the film resistivity during an *in situ* thermal annealing process. An amorphous phase should exhibit a sharp resistivity decrease at the recrystallization temperature T_x . Exactly such a behavior is observed experimentally as can be seen in Fig. 3, where the temperature dependence of the resistivity is shown for the film corresponding to Figs. 1 and 2. At $T_x = 200 \text{ K}$ (T_x is defined by extrapolation as indicated by the dotted lines in Fig. 3) a sharp resistivity drop is found, indicating the transition from the amorphous to the crystalline AuIn_2 phase. After annealing to 390 K the reversible linear $\rho(T)$ behavior is obtained typical of the crystalline phase. X-ray analysis of the crystalline phase revealed the CaF_2 structure of AuIn_2 ; no other lines could be detected within the experimental resolution. The above value of T_x is in excellent agreement with the recrystallization temperature observed for vapor quenched films of the same composition [11]. Furthermore, the small transition width indicates an amorphous phase of a very well defined stoichiometry. This becomes clear by studying the composition dependence of T_x . Experimentally, this can be accomplished by varying the ratio of the In to Au layer thickness, leading to different average bilayer compositions if all the interface reactions are complete. The results of such a series of experiments are presented in Fig. 4 together with the corresponding data obtained for amorphous films prepared by vapor quenching [11]. Excellent agreement is found between both preparation techniques over the whole composition range, where an amorphous $\text{Au}_x\text{In}_{1-x}$ phase can be produced. This pro-

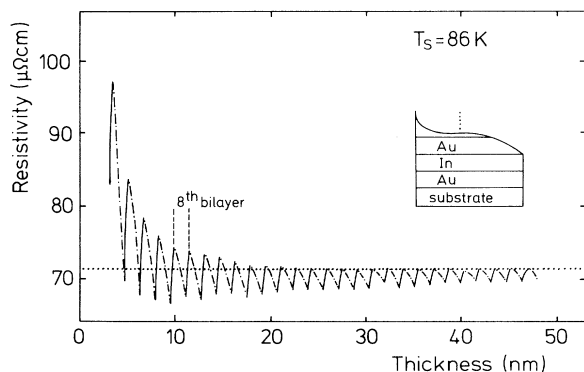


FIG. 2. Electrical resistivity corresponding to Fig. 1 related to the actual film thickness corresponding to Fig. 1.

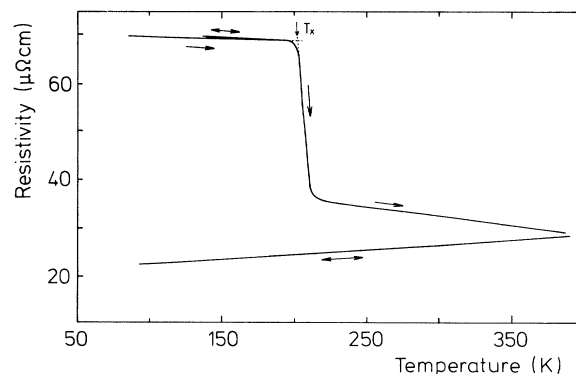


FIG. 3. Temperature dependence of the resistivity during annealing of the multilayers shown in Fig. 2. Arrows (double arrows) indicate irreversible (reversible) behavior.

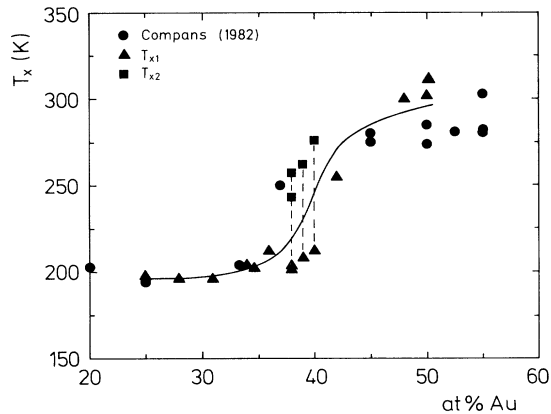


FIG. 4. Crystallization temperatures T_x , defined as indicated in Fig. 3, of the Au_xIn_{1-x} multilayers vs the Au concentration x in percent. For $0.38 \leq x \leq 0.4$ two separate transition temperatures T_{x1} and T_{x2} were obtained (the corresponding values are connected by a dashed line). For all the other values of x only one transition temperature T_{x1} is observed.

vides clear evidence that in our case the observed interface reactions at 86 K lead to an amorphous phase (a phase), proving the above conjecture.

Since this is the main result of the present work, the following remarks appear to be necessary: The above conclusion is based on both the qualitative and quantitative resistivity behavior during preparation as well as the result of the annealing procedure exhibiting a sharp resistance drop at T_x . These concentration-dependent temperatures coincide with the crystallization temperatures of Au_xIn_{1-x} phases, which have been proven to be amorphous by independent electron-diffraction experiments [13]. In addition, after the preparation of crystalline Au_xIn_{1-x} phases by thermal interface reactions, their annealing behavior was characterized by a resistance decrease over a much broader temperature range (190 K) [14] than the above drop at T_x , supporting the interpretation of the formation of an amorphous phase in the latter case.

A serious objection against the interpretation of a chemically driven interface reaction into the amorphous phase could result as the consequence of the applied sputtering technique. Here the relative high energy (typically 10 eV) of the deposited atoms could lead to a short-range collisional mixing at the interfaces. To exclude this possibility, an additional evaporation experiment was performed. In this case, on top of a sputtered thin In layer, the corresponding Au layer was evaporated at 96 K from a resistively heated W crucible at the same rate as in the sputtering experiment. The result is shown in the inset of Fig. 1. A resistance increase indicating the interface reaction is obtained which is identical to the case of Au sputtering, proving that the reaction is not due to collisional interface mixing.

To produce a metastable amorphous phase by interface

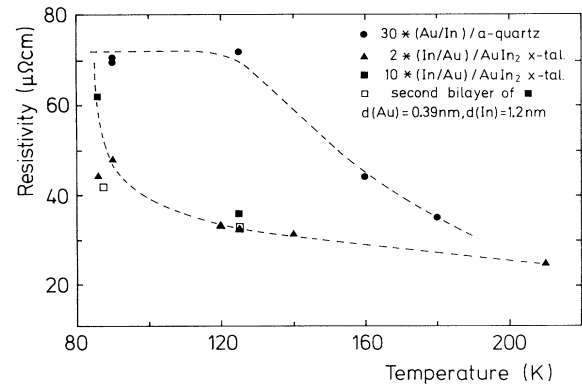


FIG. 5. Average resistivity of different prepared Au/In multilayers vs preparation temperature. The inset gives information on (number of bilayers) * (layer sequence)/(type of substrate) and on the fixed individual layer thicknesses.

reactions, thermodynamic driving forces are needed like a negative heat of mixing supported by an increase of the interface entropy. Additionally the kinetics of the reaction must provide a barrier to hinder the formation of the stable crystalline phase [15]. To study how this barrier can be influenced by temperature and crystalline nucleation centers, the following experiments were performed. Standard systems of thirty Au/In bilayers (0.39/1.2 nm) were prepared at different substrate temperatures T_s and the resulting bilayer resistivities determined *in situ* as described above. The results are shown in Fig. 5 by the solid circles. Clearly, at $T_s = 125$ K the amorphous bilayer value still can be obtained, indicating the formation of the a phase at this temperature. For higher substrate temperatures the bilayer resistivity is drastically reduced, approaching the crystalline $AuIn_2$ value for $T_s > 180$ K. (For $T_s \geq 220$ K long-range diffusion is possible, which in the AuIn system always leads to a crystalline phase. Thus, the result obtained at $T_s = 220$ K can serve as a reference for crystalline $AuIn_2$.)

To study the influence of nucleation centers for crystallization on the formation of the a phase, multilayers were prepared on top of crystalline $AuIn_2$ films. The results are included in Fig. 5. The most impressive consequence of the enhanced nucleation possibility is found at $T_s = 125$ K. At this temperature, amorphization by an interface reaction on top of crystalline $AuIn_2$ is no longer possible; rather, the crystalline $AuIn_2$ phase is formed, in contrast to the result obtained for multilayers on amorphous quartz substrates at the same temperature. The corresponding resistivity behavior during preparation (not shown here) also exhibits a periodic resistivity increase and decrease, indicating interface reactions, but in this case the crystalline $AuIn_2$ phase is formed as can be deduced from the resistivity value of $35 \mu\Omega \text{ cm}$ approached after approximately three bilayers. This limiting value

exhibits a slight increase for growing numbers of bilayers, suggesting a growing degree of disorder of the resulting crystalline phase. In this context, it is important to note that on top of crystalline AuIn₂ the layer sequence plays a dominant role. Only for In/Au, where the more mobile Au atoms react with the underlying first thin In layer, does nucleation at the substrate lead to the crystalline phase. For the opposite sequence (Au/In) on top of crystalline AuIn₂, the arriving In atoms do not react with the total thickness of the first Au layer and the influence of the underlying crystalline substrate is strongly reduced. As a consequence, after approximately three bilayers, their resistivity approaches the amorphous value in this case. The effect of disorder accumulation for an increasing number of bilayers is much more pronounced at lower temperatures T_s . At 86 K the resistivity of the tenth bilayer is about 50% larger than the value of the second (solid and open squares in Fig. 5), while at $T_s=125$ K this difference is only 10%. Thus, the influence of a crystalline AuIn₂ substrate to act as a nucleation center clearly increases at higher temperatures.

It would be interesting to test experimentally whether there is a low-temperature limit for the above interface reaction to occur. Unfortunately, in our preparation system we are restricted to temperatures above 85 K.

In conclusion, we have demonstrated that an amorphous phase can be prepared at low temperatures by an interface reaction for a system which cannot be amorphized by long-range thermal diffusion. By repeating the interface reaction periodically, thick amorphous films can be grown. On the other hand, as has been shown in [14] each interface reaction is restricted to a maximum Au layer thickness of 1.5 nm, corresponding to a maximum reacted interface region of approximately 6 nm. Above this limiting value no further reaction takes place [14] in agreement with recent theoretical considerations [16,17].

We feel that the observed interface amorphization is not restricted to the studied AuIn system, but rather may occur at every A - B interface, if the corresponding AB system can be forced into the amorphous phase by, e.g., a

rapid quenching process. Thus, the reported phenomenon may have an important bearing on magnetic multilayers, where for many systems amorphous phases are known to exist. But this conjecture still has not been proven experimentally.

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