Discontinuous Precipitation in the Copper-Indium System from the Viewpoint of Nuclear [111]In Probes in Grain Boundaries

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We employ the discontinuous precipitation occurring in a supersaturated solid solution of indium in copper in order to prove that ^{111}In nuclear probes are successfully placed in deeply buried grain boundaries by means of low-temperature diffusion. The observation of perturbed angular correlations of γ rays in the decay of ^{111}In to [111]Cd yields the signal of the intermetallic δ phase (Cu_7In_3) as a clear manifestation of the phase transformation. Experiments with either diffused or implanted samples allow us to distinguish and characterize different stages of the precipitation process.

Grain boundaries (GB's) have considerable influence on the mechanical properties of polycrystalline metallic systems. In polycrystalline semiconducting materials employed, e.g., in thin-film solar cells GB's, to a large extent, determine the electronic properties and thus the performance of the respective devices. Therefore it is highly desirable to develop nondestructive experimental methods which yield information on the structural and electronic properties of GB's, preferably on an atomic scale.

Based on specific hyperfine interactions, information of this type is available from nuclear probe methods like $\gamma\gamma$ perturbed angular correlations (PAC) or Mössbauer spectroscopy. Both these methods have, in the last decade, been successfully applied to surfaces [1–3], interfaces [4], and buried layers [5]. The application to GB's is hampered by the problem of placing the nuclear tracers in the GB's quantitatively. Only if this problem is solved can full advantage of the properties of the nuclear probe methods be taken and an exclusive submicroscopic sensitivity to GB's obtained.

In this Letter we demonstrate the successful application of PAC to GB's by working in the regime of exclusive GB diffusion (Harrison's type-C kinetics [6]) in the Cu-In system. The Cu-In system has recently attracted considerable interest, since metallic Cu-In films are frequently used as precursors for photovoltaic devices based on either $CuInSe_2$ or $CuInS_2$ light absorbers. For the present study, the system offers several advantages. First, solid solutions of In in Cu exhibit the discontinuous precipitation (DP) reaction which starts at GB's [6,7]. This effect allows us to prove that our tracers are indeed probing GB's. Second, the favorable PAC probe ^{111}In does not represent an impurity in the system and is, therefore, chemically indistinguishable from the overwhelming majority of the inactive indium atoms. Therefore, PAC produces a true image of the In-containing phases here. This is the major difference to the only previous PAC study of GB's in which the ^{111}In probe acted as an impurity

[8]. Third, there exists a large body of PAC data for copper [9], indium [10], and the Cu-In alloys including the δ phase (Cu_7In_3) [11,12].

The DP in the Cu-In system is governed by a solid-state reaction, which reads $\alpha_0 \rightarrow \alpha + \delta$, and which preferentially starts at large angle GB's in a supersaturated solid solution of In in Cu (α_0 phase, here: 8.7 at.% In) [7]. The DP proceeds by GB diffusion of In atoms, and GB's become migrating reaction fronts behind which the α_0 phase decomposes into the intermetallic δ phase and the depleted solid solution α. As a result, a two-phase region with a typical lamellar structure is produced. A metastable phase α_m with medium indium concentration is expected by theory to occur during this type of precipitation process [13]. However, the existence of the α_m phase hitherto could not be proven by experiment for the Cu-In case. We performed two types of experiments in order to observe this process, by means of PAC, either from the viewpoint of In atoms in bulk material or in GB's. For this purpose, ^{111}In PAC probes were either implanted or diffused into the samples, respectively.

Following the electron-capture decay of [111]In (half-life $T_{1/2} = 2.8$ d), the PAC is observed using the 171 and 245 keV γ rays emitted during the deexcitation of [111]Cd to its nuclear ground state [14]. Thus the quadrupole interaction of the 245 keV isomeric state ($T_{1/2} = 85$ ns, quadrupole moment $Q = 0.8 \times 10^{-24}$ cm^2) with an extranuclear electric field gradient (EFG) becomes observable. The diagonalized EFG tensor is conveniently described by its largest component V_{ZZ} and by the dimensionless asymmetry parameter η. The PAC spectrum of a polycrystalline sample, $R(t)$, shows typical modulations with frequencies proportional to $\nu_Q = eQV_{ZZ}/h$ (h is Planck's constant), the quadrupole interaction frequency, and has the following form:

$$R(t) = AG(t) = A\sum_{i=1}^{N} f_i G_i(t). \tag{1}$$

A is the experimentally observed γ anisotropy, and $G(t)$ denotes the time dependent perturbation factor which is split into N factors $G_i(t)$, if N different lattice sites with specific parameters ν_{Qi} and η_i and the probability of occupation, f_i, are accessible for the ^{111}In probes. If, e.g., a fraction of the probes, f_δ, are located in the Cu-In δ phase which has six equally populated In sites, f_δ is split into six fractions, $f_\delta = f_i + f_{i+1} + \cdots + f_{i+5}$ [12]. The explicit form of $G_i(t)$ is as follows:

$$G_i(t) = s_{oi} + \sum_{n=1}^{3} s_{ni} \exp[-(c_{ni} b_i t)^m / m] \cos(c_{ni} \nu_{Qi} t).$$

(2)

The quantities s_{ni} and c_{ni} ($n = 0, \ldots, 3$) are the tabulated weighting and scaling factors, respectively, which only depend on η_i. Sometimes a lattice site no longer can be described by one sharp EFG, but rather shows a distribution of EFG's due to, e.g., defects or lattice distortion. In many cases, good approximations are obtained by assuming frequency distributions of Lorentzian ($m = 1$) or Gaussian ($m = 2$) shapes, which lead to the exponential term in Eq. (2).

The starting material in our experiment was a Cu (8.7 at.% In) alloy which was prepared at the MPI Stuttgart (Germany). The material was homogenized for 28 days at 670 °C under Ar atmosphere and then quenched to room temperature (RT) in a water bath. In this manner, a supersaturated, homogeneous solid solution of In in Cu (α_0 phase) at RT was obtained. This was checked by different metallurgical methods [7]. For specimens we used ground polished and cleaned slices of 10 mm diameter and 1 mm thickness which had been cut from a cylindrical ingot. The mean grain size was 120 μm.

In the first part of the experiment, ^{111}In was implanted into the samples at RT by means of the IONAS facility in Göttingen. A typical implantation dose was $10^{13}/\text{cm}^2$ at an implantation energy of 400 keV. This leads to a mean implantation depth of ≈ 60 nm and a probe concentration of ≈ 10 at. ppm in the implanted volume. Thus the tracer concentration is negligible compared to the background In concentration.

Figure 1 shows PAC spectra of an implanted sample, all measured at RT. The spectrum of the as-implanted state [Fig. 1(a)] shows a broad distribution of quadrupole frequencies which is fitted (solid line) very well by a distribution of Gaussian shape for 100% of the probes [cf. Eqs. (1) and (2)]. In order to remove possible lattice damage due to the implantation process, the sample was first annealed at 680 °C for 1 h and then water quenched. The PAC spectrum which is shown in Fig. 1(b) was fitted by the same parameters as the spectrum of Fig. 1(a), indicating the negligible influence of implantation defects. Therefore we attribute the respective parameters [$\nu_Q = 17(2)$ MHz, $b_G = 7(2)$ MHz, and $\eta = 0.5$] to the undisturbed α_0 phase. The DP is induced by annealing treatments at 350 °C and 400 °C, and the respective PAC
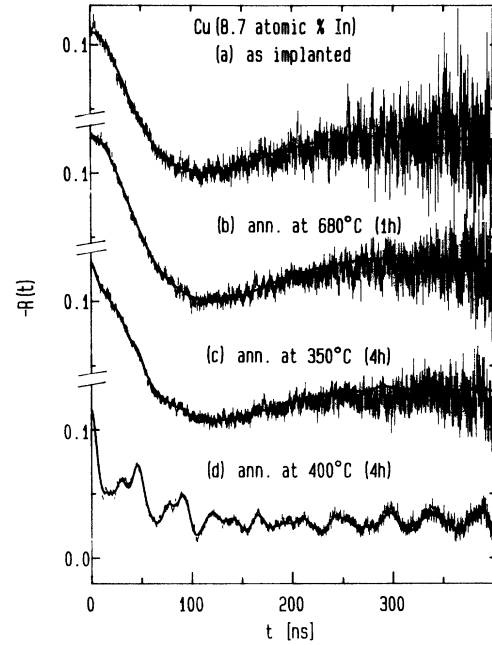

FIG. 1. PAC spectrum of a supersaturated solid solution of In in Cu after ^{111}In implantation (a) showing a distribution of quadrupole frequencies which is not affected by high-temperature annealing (b). The DP is thermally induced at lower temperatures and is monitored by the signal of the intermetallic δ phase which induces characteristic modulations in (c) and, more prominent, in (d).

spectra are shown in Figs. 1(c) and 1(d). The prominent modulation which is visible in the spectrum of Fig. 1(d) is well described by the PAC parameters of the δ phase [12] for $f_\delta = 67(2)\%$ of the probes. The analysis of spectrum (c) of Fig. 1 also indicates a small contribution of the δ phase of $f_\delta = 14(1)\%$.

The occurrence of the modulation of the δ phase shows the sensitivity of PAC to the DP process in the case of randomly distributed probes with no spatial correlation to GB's. For the following discussion it is essential to determine the maximum fraction of probes in the δ phase, $f_{\delta,\max}$, after the DP reaction is completed. In this *final state*, the mole fraction of the δ phase, X_δ, is calculated by means of the lever rule, which yields $X_\delta = [\text{In}(\alpha_0) - \text{In}(\alpha)]/[\text{In}(\delta) - \text{In}(\alpha)]$. Here, $\text{In}(\alpha_0)$, $\text{In}(\alpha)$, and $\text{In}(\delta)$ denote the atomic concentrations of In atoms in the pure α_0, α, and δ phases, respectively. Now we have to take into account that, in this type of PAC experiment, the sensitivity to a phase is proportional to its mole fraction *and* to its In content. Therefore $f_{\delta,\max}$ is given by $f_{\delta,\max} = X_\delta \text{In}(\delta)/\text{In}(\alpha_0)$. The factor $1/\text{In}(\alpha_0)$ is used to ensure proper normalization. When these relations are combined, we obtain the following:

$$f_{\delta,\max} = [1 - \text{In}(\alpha)/\text{In}(\alpha_0)]/[1 - \text{In}(\alpha)/\text{In}(\delta)]. \quad (3)$$

Equation (3) shows that the measurement of $f_{\delta,\max}$ will allow a sensitive determination of In(α), since the starting concentrations In(α_0) and In(δ) are well known [7,15]. From the data of Geber and Haasen [7] we estimate that the DP process should be completed after ≈ 35 h at 350 °C. Shown in Fig. 2(a) is the PAC spectrum of an ^{111}In-implanted Cu (8.7 at. % In) sample which was annealed at 680 °C (1 h) and at 350 °C for 66 h after implantation. For comparison Fig. 2(b) shows the PAC spectrum of an ^{111}In implanted Cu_7In_3 sample (nominally 100% δ phase), annealed at 580 °C (1 h) after implantation. Both spectra show the modulation of the δ phase for 98(2)% (a) and 72(2)% (b) of the probes [16]. The spectrum in Fig. 2(a) is the largest, clearest, and best resolved PAC signal of the δ phase we were able to obtain so far [11,12]. It shows that the phase transformation via DP leads to crystallites of high quality. Furthermore, by means of Eq. (3) we now obtain a *maximum* concentration of In in the α phase at 350 °C to be In(α) = 0.5%, a value much lower than the previous literature value of 2% [15]. This means that it is impossible, under the present experimental conditions, to observe the α phase by PAC due to a too low In concentration. Otherwise we could not have observed practically 100% of the probes in the δ phase as a result of the DP.
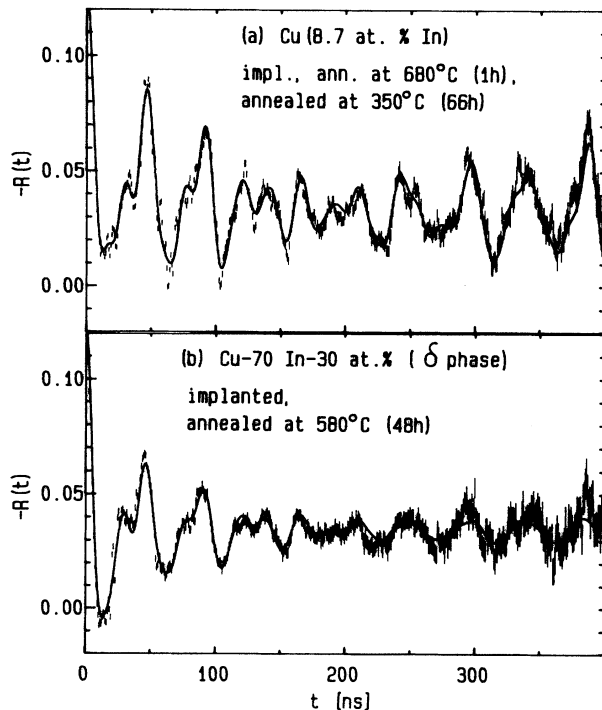
In the second part of the experiment, the ^{111}In tracers were introduced by diffusion. A carrier-free solution of [111]InCl$_3$ on 0.04 molar HCl was dried on the polished sample surface, and the probes were diffused into the samples at 350 °C under H_2 atmosphere. Figure 3(a) shows the PAC spectrum after a diffusion time of 4 h. A clear modulation due to the occurrence of the δ phase is visible, which remains practically unchanged after the sample was ground polished and a surface layer of 3.0(5) μm was thus removed [Fig. 3(b)]. Therefore we can safely exclude surface effects and have shown that the probes penetrate the sample via GB diffusion. An estimate of the diffusion lengths of GB and bulk diffusions [6,7] leads to values of 25 μm and 40 Å, respectively. This measurement was completed by an annealing treatment at 400 °C (1 h), the PAC result of which is shown in Fig. 3(c). The least-squares fit yields f_δ = 55(5)% for all three spectra. The remaining fraction is characterized by a frequency distribution of Lorentzian shape around $\nu_Q = 0$ with $b_L = 7(2)$ MHz and $\eta = 0$.

The comparison of the spectra of Figs. 1(c) and 3(b), which were both measured after a reaction time of 4 h at 350 °C after either probe implantation or GB diffusion, demonstrates the peculiarities of the experiment. The 4 times larger fraction of the δ phase observed for the diffused sample is an independent indicator for the fact that the probes are located in GB and can thus produce a signature of the initial state of the DP. In this state, the majority of the In atoms is still located in the α_0 phase
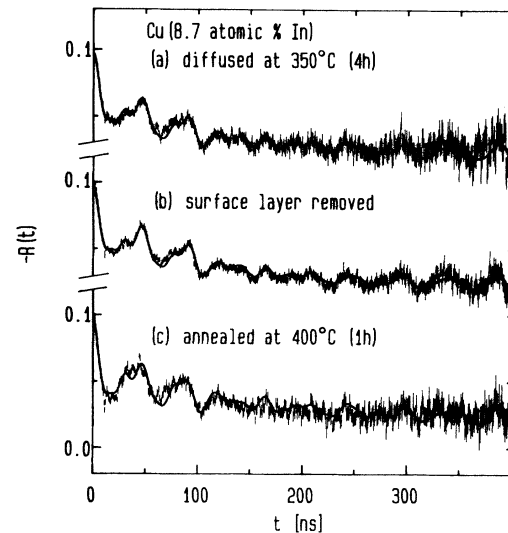
FIG. 2.   (a) PAC spectrum of Cu(8.7 at. % In) after complete precipitation that reveals a very clear signal of the δ phase for practically 100% of the nuclear probes.   (b) For comparison, a spectrum for the nominally pure δ phase is shown.

FIG. 3.   PAC spectra of a Cu-In sample which was doped with ^{111}In by means of GB diffusion.   (a) The pronounced modulation of the δ phase indicates the enhanced sensitivity to GB's [cf. Fig. 1(c)].   (b) The removal of a 3-μm-thick surface layer does not change the signal.   (c) The fraction f_δ remains constant also after an additional annealing. The probes of the fraction $1 - f_\delta$ are incorporated in the metastable α_m phase.

which is, as expected, observed for the implanted but not for the diffused sample. In the latter, however, 45(5)% of the probes are not located in the δ phase but are rather subjected to a distribution of small EFG's, and their signal is more similar to that of pure copper ($\nu_Q = 0$) than to the one we have determined for the α_0 phase. We assign this fraction to a metastable (at 350 °C) solid solution of In in Cu, α_m, having a mean In concentration between that of the α_0 and the one of the equilibrium α phase: In(α) < In(α_m) < In(α_0). We exclude, for this fraction, sites in GB's, since much larger EFG's are expected and were determined for these [8]. The constant fraction of $f_\delta = 55(5)\%$ for the diffused sample also after an additional thermal treatment at 400 °C indicates that this fraction is the maximum f_δ for the *intermediate* state of the DP. We can, therefore, insert this value into Eq. (3), if we replace In(α) by In(α_m) and can thus determine In(α_m) to be 4(1)%.

In conclusion, we have successfully employed the DP process in the Cu-In system in order to *prove* that PAC with ^{111}In tracers allows the *exclusive* probing of GB's. Moreover, we were able to characterize and distinguish different stages of the DP process. By means of ^{111}In-implanted samples we determined the PAC signal of the supersaturated solid solution of 8.7 at. % In in Cu (α_0 phase), observed the well-known signal of the intermetallic δ phase as a clear manifestation of the DP process, and showed that the equilibrium α phase has an In concentration below 0.5%, a value much lower than previously reported [15] giving rise to a larger driving force of the DP process. A low-temperature (350 °C) diffusion process was utilized to place the ^{111}In probes in GB's. The enhanced sensitivity to GB's in this type of experiment is clearly demonstrated by the observed 4 times larger fraction of the δ phase as compared to implanted samples after an identical heat treatment (350 °C, 4 h). We presented evidence for the occurrence of a metastable solid solution of In in Cu (α_m) with a mean In concentration of 4(1)%. This result is in accordance with Cahn's model [13] of the DP process. Finally, we expect that the proposed method of exclusively probing GB's by PAC will find further interesting applications to polycrystalline metallic and semiconducting systems.

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