Compound Formation at Cu-In Thin-Film Interfaces Detected by Perturbed γ-γ Angular Correlations

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Interface compound formation at Cu-In films is studied with the perturbed γ-γ angular correlation method using radioactive ^{111}In probe atoms. The growth of a $CuIn_2$ intermetallic interface phase is observed with a sensitivity on the scale of atomic distances in the temperature range between 220 and 340 K. This new phase is characterized by an electric field gradient (at $T = 77$ K) with $V_{zz} = 4.50(5) \times 10^{17}$ V/cm^2 and $\eta = 0.57(1)$. The activation energy of phase formation for $CuIn_2$ was determined to be 0.42(2) eV.

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The interfaces between difficult solids have attracted great interest recently, since they are of considerable fundamental and practical importance. One of the basic questions is the formation of compounds in the interface region and, connected to that, the dynamics governing the growth as well as thermal stability of such interface phases. Interface compounds are of great practical importance for the electrical and mechanical properties of thin-film systems, as for instance for Schottky barriers in metal-semiconductor contacts. For the detection of interface compounds and interfacial reactions, powerful experimental tools have been developed, all of them possessing their specific sensitivity. Interfaces within a few atomic distances of the surface can be studied extensively with electron-diffraction, Auger-electron, and photoelectron spectroscopy. Interfaces deeper inside the films can be investigated by x-ray diffraction and Rutherford backscattering, although these techniques have difficulties in resolving cases where the interfacial reaction volume is small compared to the sample volume.

In this paper we want to present the first application of the perturbed γ-γ angular correlation (PAC) method, which is based on the hyperfine interaction of radioactive probe nuclei with electric field gradients. The PAC technique exhibits a high microscopic sensitivity to changes of local structure within few atomic distances.[1] Therefore, this method offers the possibility of detailed studies of interface compound formation, as will be demonstrated for Cu-In film couples.

Film samples are produced by evaporating indium onto a glass backing at $T = 106$ K. After annealing of this In film at 260 K, copper was evaporated onto the In film at 106 K. Two different ways of deposition of the radioactive ^{111}In probe atoms were applied. In one case the ^{111}In probe atoms were evaporated simultaneously with the natural In material yielding homogeneously doped In films. In order to increase the sensitivity to interface compound formation, ^{111}In probe atoms were also deposited in a very low concentration (typically 10^{11} atoms/cm^2) onto the surface of the In film before coverage with copper. Sample preparation was carried out in an UHV chamber ($p < 10^{-9}$ mbar) providing the possibility of moving the sample from the evaporation region into a measurement position between the γ counters for the detection of PAC spectra. This position is shielded against the high background radiation from the oven to reduce accidental coincidences.

The PAC technique utilizes the isomeric nuclear state ($I = \frac{5}{2}$, $T_{1/2} = 84$ ns) intermediate between the 172–247 keV γ-γ in ^{111}Cd, which is populated through the ^{111}In decay ($T_{1/2} = 2.8$ d). The nuclear quadrupole moment of this state ($Q = +0.8$ b) senses the electric field gradient produced by the extranuclear charge distributions. This interaction splits the isomeric nuclear level, leading to transition frequencies ω_1, ω_2, and $\omega_3 = \omega_1 + \omega_2$ in the case of ^{111}Cd, which at the same time causes time-dependent modulation of the γ-γ angular correlation. This modulation can be extracted from the usual counting-rate ratio $R(t)$, which can be represented by a superposition of cosine functions containing the transition frequencies (for details, see Recknagel, Schatz, and Wichert[2]):

$$R(t) = A_{\text{eff}}\left\{s_0 + \sum_{n=1}^{3} s_n \cos\omega_n t\right\}, \tag{1}$$

where A_{eff} is an effective γ-γ angular correlation parameter. The amplitudes s_n, depending on the detector geometry and orientations of the principal-axis system of the electric field gradient, are not of special importance for our case. The largest component of the electric field gradient tensor V_{zz} can now be deduced from ω_1, since $\omega_1 \propto QV_{zz}$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ from the ratio of ω_1/ω_2 (see Ref. 2). In case fractions f_i of probe atoms are exposed to i different electric field gradients, Eq. (1) has to be modified accordingly by a weighted sum.

In a first step, a sample consisting of a film couple of 300-Å In homogeneously doped with ^{111}In and 135-Å Cu (equivalent to an atomic ratio Cu:In = 1:1) was studied. PAC spectra were recorded at 77 K after annealing at different temperatures T_A (annealing time:

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10 min). Figure 1 displays three PAC spectra together with their Fourier transformations. At annealing temperatures below 240 K, only the well-known electric field gradient for ^{111}Cd (populated by ^{111}In) in In[3] is present,[4] as expected [Fig. 1(a)]. At $T_A = 280$ K [see Fig. 1(b)] a new field gradient can be observed in addition, denoted by the fraction f_{CuIn_2}. Finally the fraction is dominant at a temperature $T_A = 340$ K [see Fig. 1(c)]. This new field gradient is characterized by $\omega_1 = 107(1)$ Mrad/s, $\omega_2 = 155(1)$ Mrad/s, leading to $V_{zz} = 4.50(5) \times 10^{17}$ V/cm^2 and $\eta = 0.57(1)$; it is very well defined, showing the existence of a new ordered structural phase in our Cu-In film sample. The subscript CuIn$_2$, indicating the stoichiometry of this phase, will be justified later. No fraction for ^{111}In in Cu with $V_{zz} = 0$ caused by the cubic crystal structure is detected, which excludes In diffusion in Cu in our annealing temperature range, as expected from known diffusion data.[5] Figure 2 summarizes the isochronal annealing experiments, showing the dependence of the fraction f_{CuIn_2} (left scale) for the new phase as a function of annealing temperature. Above $T_A = 320$ K all our ^{111}In probes[4] share the new phase; for annealing temperatures $T_A > 380$ K, the new phase decomposes into less-defined structures accompanied by In precipitations, which were not further investigated here.

The appearance of a new structural phase in the Cu-In film system raises the question of an interface compound, whose thickness, stoichiometry, and crystal structure has to be determined.

The stoichiometry can be obtained by study of samples with different Cu:In atomic ratios. For the above-mentioned case of Cu:In = 1:1, we observed all ^{111}In probes being incorporated in the new phase above 320 K, which means that there was enough copper to convert the In film completely into the new phase. Therefore, we have studied a sample with Cu deficiency, namely films of 2400-Å In doped with ^{111}In and 270-Å Cu corresponding to an atomic ratio Cu:In = 1:4. The fraction f_{CuIn_2} saturates above 320 K as before; however, now with $f_{\mathrm{CuIn}_2} \approx 50\%$. From this we conclude that all Cu atoms have migrated into the In film, producing the new phase containing half of the probe atoms and therefore also occupying only half of the In volume. Additional evaporation of another 270-Å Cu on top of this sample and annealing at 320 K produces a fraction $f_{\mathrm{CuIn}_2} \approx 100\%$, justifying therefore the stoichiometry Cu:In = 1:2 in the new intermetallic compound.

Now it is possible to relate the CuIn$_2$ fraction to an average thickness of the grown CuIn$_2$ phase. According to the stoichiometry, our sample with 300-Å In would have been saturated by a 70-Å Cu coverage. Therefore, we can identify $f_{\mathrm{CuIn}_2} \approx 100\%$ with 370-Å thickness of the CuIn$_2$ film—however, under the assumption of volume conservation during phase formation (see below). This thickness calibration is added in Fig. 2 (right scale). The depth sensitivity becomes clear now: Because of an uncertainty of typically 1% for the determination of the fractions, the film thickness resolution is in the order of 10 Å. This sensitivity can, however, be drastically improved by deposition of our ^{111}In probe atoms at the interface, which is feasible[6] and will be demonstrated below.

A sample with 15 000-Å In homogeneously doped

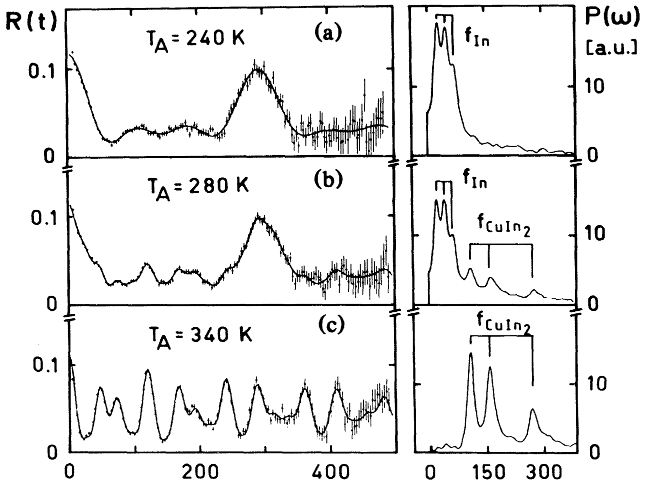

FIG. 1. PAC spectra with their Fourier analyses of a 300-Å In(^{111}In)/135-Å Cu film couple for different annealing temperatures. The time spectra are fitted by Eq. (1).

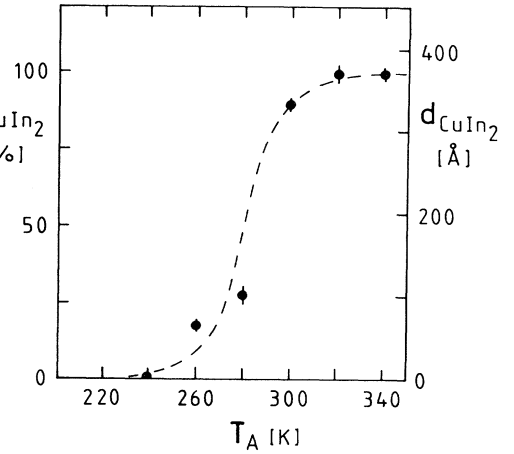

FIG. 2. Fraction of ^{111}In probe atoms in the CuIn$_2$ interface phase (left scale) of a 300-Å In(^{111}In)/135-Å Cu film couple as a function of annealing temperature. On the right side this fraction is translated into the thickness of the interface phase.

with ^{111}In and 3380-Å Cu, according to the stoichiometry $CuIn_2$, was used to determine the growth kinetics and crystal structure. The phase $CuIn_2$, and therefore the crystal structure, are not known in the bulk phase diagram.[7] Now isothermal treatment was applied; the average thickness of the $CuIn_2$ layer was measured for several time intervals Δt at three different temperatures. These thicknesses d_{CuIn_2} are plotted versus $\Delta t^{1/2}$ in Fig. 3. The linear dependence supports the fact that the $CuIn_2$ compound formation is mainly governed by diffusion processes. A least-squares fit of

$$d_{CuIn_2} = [D_0 \exp(-E_a/k_B T)]^{1/2} \Delta T^{1/2} \qquad (2)$$

to the experimental data yields an activation energy $E_a = 0.42(2)$ eV and a diffusion constant $D_0 = 1.0(3) \times 10^{-6}$ cm^2/s. After the isothermal procedure for this sample, a film of about 18 400-Å thickness, only consisting of $CuIn_2$, is obtained. Now an x-ray diffraction experiment was carried out, supporting a tetragonal crystal structure with $a = 6.645(1)$ Å and $c = 5.376(2)$ Å and a symmetry of group D_{4h}^{18} ($I4/mcm$), such as was found for $AgIn_2$.[8] This structure is also consistent with the measured η value. On the basis of this structure and lattice constants, a density for $CuIn_2$ of 8.2 g/cm^3 is obtained, quite close to the average density of 7.86 g/cm^3 used before for the thickness calibration.

As already pointed out, the sensitivity to interface compound formation can be greatly increased by deposition of the ^{111}In probe atoms at the interface region. Such an experiment was done with a 400-Å In/200-Å Cu film sample. After preparation of the In film, carrier-free ^{111}In (about 10^{11} atoms) was deposited onto the In surface at $T = 100$ K by evaporation from a carefully heated, ^{111}In-doped Cu crystal in our oven. This procedure was checked by measurement of the surface electric field gradient at In.[6] After deposition of about $\frac{1}{3}$ monolayer of Cu, the surface field gradient vanishes, and a broad distribution around $V_{zz} = 7 \times 10^{17}$ V/cm^2 occurs, which is due to the fact that the ^{111}In probe atoms are now decorated statistically by Cu atoms. An additional 200-Å Cu deposition does not produce more defined electric field gradients. Now isochronal annealing leads to the appearance of only two definite field gradients, denoted by the fractions f_{In} and f_{CuIn_2}. f_{In} and f_{CuIn_2} are the fractions of probe atoms in In bulk and in the $CuIn_2$ interface compound, respectively, recognized by the electric field gradient parameters. The results are shown in Fig. 4, where both fractions[4] are plotted versus the annealing temperature T_A. Inserted on top of the figure is a schematic illustration of the film structure indicating the distribution of the ^{111}In probe atoms (black dots) and the interface layer at different annealing temperatures. Because of the higher sensitivity, the $CuIn_2$ interface compound formation is now already detectable above 220 K. At $T_A = 240$ K about 20% of the ^{111}In probe atoms[4] are incorporated in $CuIn_2$, which has an estimated averaged thickness of two monolayers at most.

We have shown that the PAC method can be utilized to measure the interface alloy formation up to a

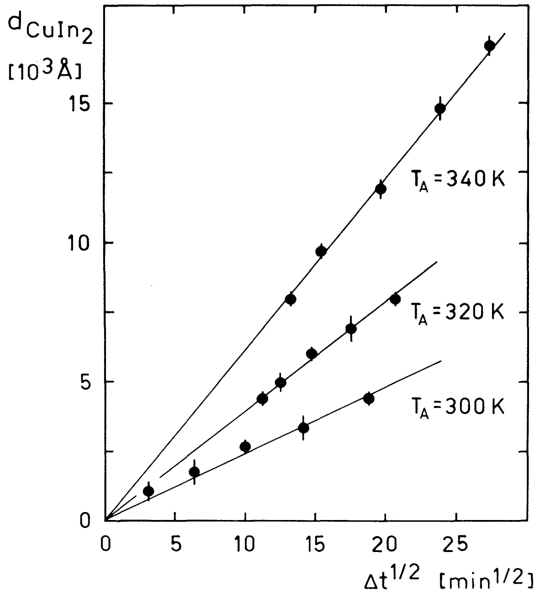

FIG. 3. Thickness of the $CuIn_2$ interface phase in a 15 000-Å In(^{111}In)/3380-Å Cu film couple as a function of $\Delta t^{1/2}$ in an isothermal annealing program for different temperatures.

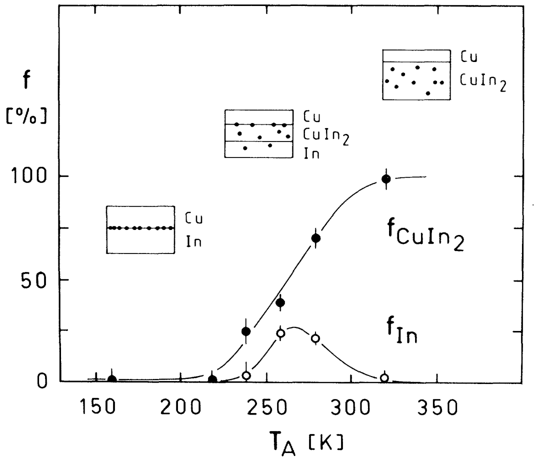

FIG. 4. Fractions of ^{111}In probe atoms in In and $CuIn_2$, respectively, for a 400-Å In/200-Å Cu film couple with ^{111}In deposited at the interface, for different annealing temperatures. The inset illustrates the interface phase formation and distribution of ^{111}In probes (black dots).

sensitivity on the scale of atomic distances. Properties of interface phases can be investigated in detail; besides the thickness, it is possible to determine stoichiometry, crystal-structure symmetries from the electric field gradient tensor, and the growth kinetics. This is applicable to all film thicknesses, and therefore the PAC technique is a powerful complementary method for studies of interface phases.

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