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SUBMICROSCOPIC CHARACTERIZATION OF INDIUM-TIN OXIDE FILMS BY PAC

The time dependent observation of perturbed $\gamma\gamma$-angular correlation (PAC) has been used to characterize Sn-doped In_2O_3 films from the submicroscopic viewpoint of radioactive ^{111}In probe-atoms. Since the tracers do not represent impurities in ITO, the observed PAC-spectra produce true images of the sample's cation-sublattice. Therefore, typical measurements of bixbyite-In_2O_3 bulk material show the signals for the two In-sites. Deviations from this quasi-ideal PAC-signature of the In-sublattice do occur as a consequence of *electronic* or *structural* perturbations of the tracer environments which can be related systematically to measuring temperature, Sn-content, and annealing parameters of the samples.

1. INTRODUCTION AND MOTIVATION

Sn-doped In_2O_3 (ITO) finds wide-spread applications in the form of transparent conducting films, e.g. as part of solar-cell devices, and therefore many efforts have been made to investigate the electronic and optical properties of thin films (Hamberg et al. 1982). Based on these results, information about the electronic band structure and the intrinsic (e. g. O^{2-}-vacancies) and extrinsic (Sn-donors) defect pattern has been obtained (Fan et al. 1977). However, since the defect structure and details of the n-type doping mechanism of Sn in In_2O_3 are not fully understood up to now, a microscopic technique observing the local atomic and electronic environment of a radioactive probe atom might supplement existing information about this compound. Moreover, in contrast to other methods, PAC will allow the characterization of ITO-films which are already part of a device.

2. EXPERIMENTAL TECHNIQUE

The PAC of [111]In(EC)[111]Cd-atoms is advantageous in this context because the probe nuclei do not represent impurities in In_2O_3. No eventual defect accumulations at the probe's site have to be taken into account and therefore the measurements of the electric hyperfine interaction produce a true picture of the microscopic cation environments (In_2O_3: typical cation-anion distance d=0.21-0.22nm, typical cation-cation distance d=0.33-0.38nm, Marezio 1966) in the material. This hyperfine interaction between the electric field gradient of the probe's lattice neighborhood and the electric quadrupole moment of the tracer nucleus is observed by the perturbed angular correlation of the $\gamma\gamma$-cascade(171-245keV) initiated by the EC-decay of [111]In (Siegbahn et

al. 1965). Each individual lattice environment is thus identified by means of a specific electric field gradient and is represented in the PAC time function by a characteristic modulation, which can be described by two parameters: the quadrupole constant $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = V_{yy} - V_{xx}/V_{zz}$.

Generally, statistical deviations of the tracers surrounding entail characteristic line broadenings and a loss of modulation amplitude, which is referred to as a *damping* of the PAC time spectra. For an explanation, two different phenomena have to be taken into account: On the one hand, *structural* disorder of the probe's surrounding caused by the tracer implantation process (400keV IONAS/Göttingen; Uhrmacher et al. 1985) or by defects and impurities. On the other hand, *electronic* relaxation processes, which will not be explained in detail in this work. A distinction between these two phenomena is possible because of their different effects on the PAC time function (Lupascu et al.1995), and they can be separated experimentally by means of certain temperature and annealing treatments.

3. RESULTS AND DISCUSSION

The aim of this work is a comparison between the experimental results of PAC time functions in pure In_2O_3 bulk material and measurements in a commercially available Sn-doped In_2O_3(ITO)-film produced for technical applications (Flachglas AG). Since the spectra of the oxide bulk material are very well understood (Bolse et al. 1987), one is now able to look at deviations in the time spectra of thin Sn-doped ITO-films. These can be attributed to Sn-complexes or structural disorder induced by certain film preparation procedures. As it will be shown, different phenomena have to be taken into account depending on the measuring parameters.

In figure 1, typical PAC-spectra of In_2O_3 bulk material (left column) are compared to spectra of an ITO-film (right column). The top row (a) shows time functions of samples right after tracer implantation without further annealing treatments. In both spectra an exponential decay of the modulation is clearly visible which can be attributed primarily to radiation induced defect complexes in the probe surrounding. After a subsequent annealing process up to temperatures above T=750K, distinctive changes in both time functions can be observed. This is illustrated in the middle row (b). Both spectra show the two characteristic modulation, which are related to two frequency triplets of the two different cation sublattice-sites of the bixbyite-In_2O_3 crystal (site#1: ν_{Q1}=155MHz, η_1=0 point symmetry D_{3d}(site D); site#2: ν_{Q2}=118MHz, η_2=0.71 point symmetry C_2(site C),Wyckoff 1964, Bartos et al. 1993). However,the spectra of In_2O_3 bulk material show a completely *time independant* loss of modulation amplitude, while the ITO-spectra exhibit a typical *exponential damping* of the modulation. As mentioned above, two different phenomena are responsible for these distinctive superpositions. The time independent damping can be related to *electronic* relaxation processes (Lupascu et al. 1995) which have been also observed in other oxide materials (Wang et al. 1993). The exponential damping in the spectra of the film can be explained by *structural* disorder of the probe surrounding caused by the great amount of Sn (ca. 10 atomic %) in the sample (Habenicht 1995). With increasing measuring temperature another significant change is visible.

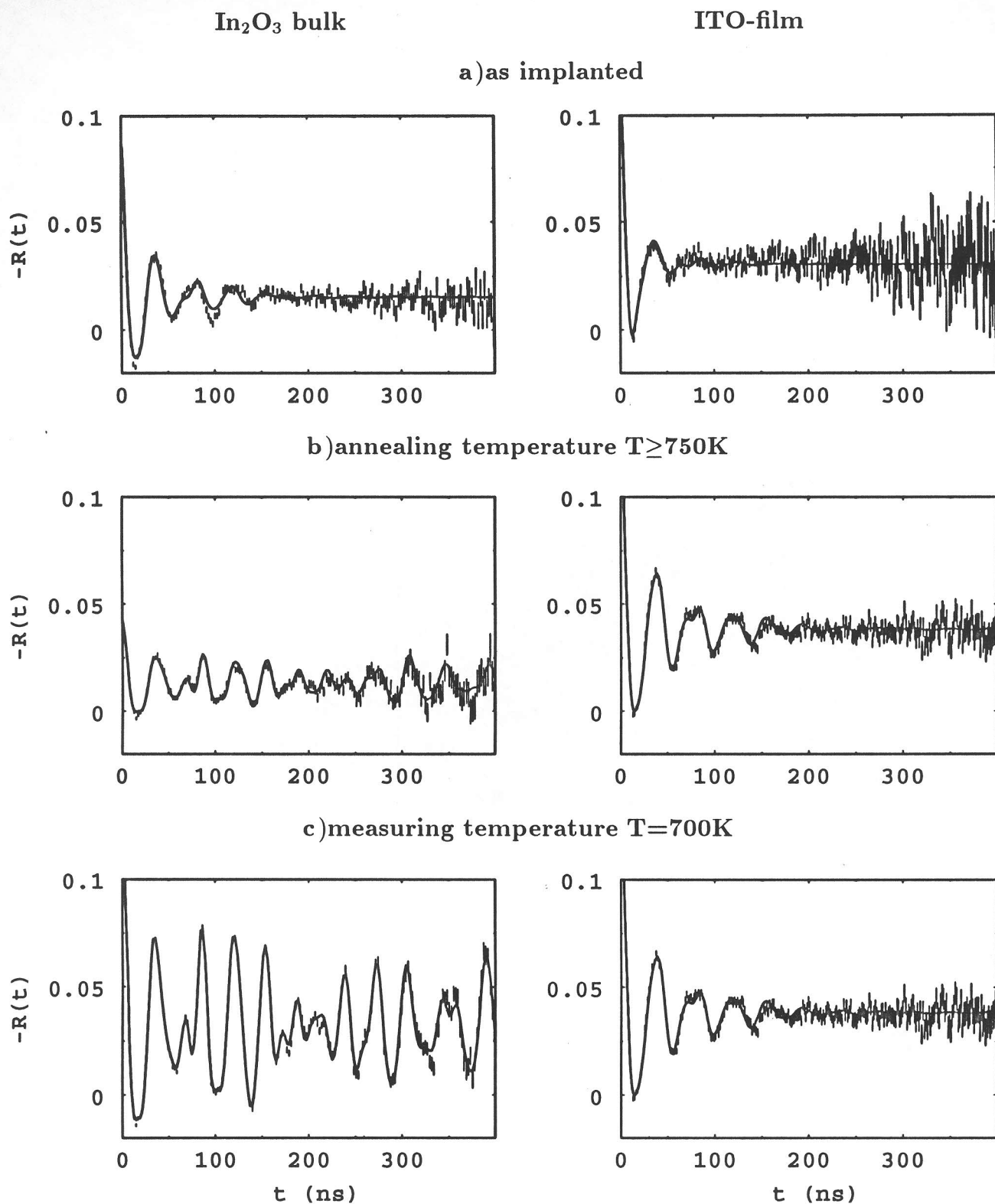**In₂O₃ bulk**   **ITO-film**

Figure 1: PAC time- and fourier-spectra of In₂O₃ bulk samples (left column) and ITO-films (right column) at different measuring parameters. The top row (a) shows PAC-spectra right after tracer implantation, the middle row (b) spectra after annealing treatments above 750K, and the bottom row (b) spectra at high measuring temperatures.
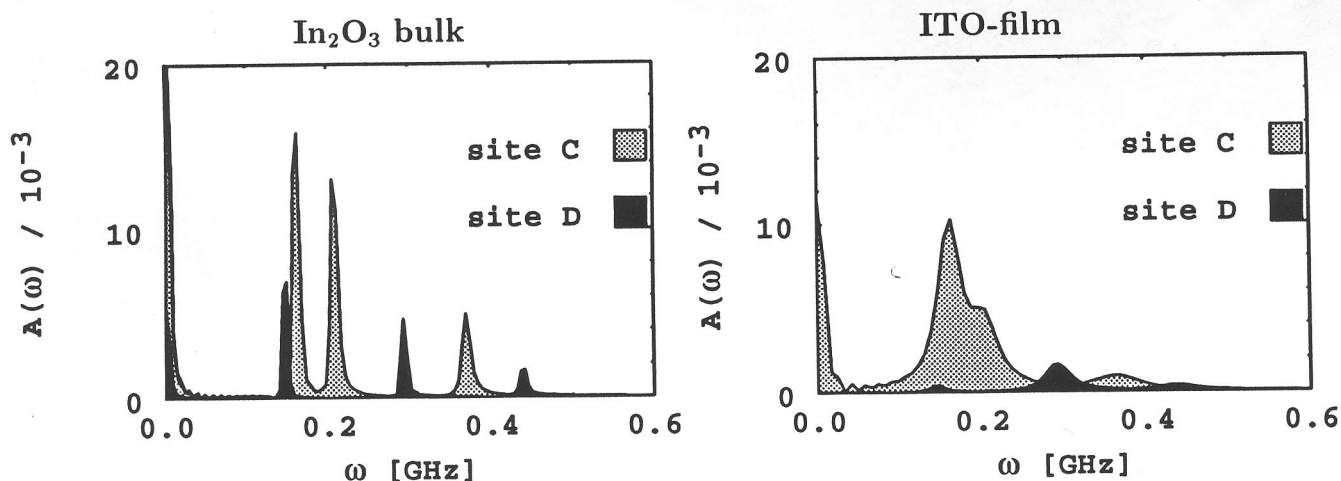
Figure 2: Fouriertransform of PAC-spectra for bulk material (left) and for an ITO-film (right) at high measuring temperatures. The two frequency triplets of the two cation sites D and C are marked in both spectra.

In the bottom row (c) PAC-spectra at a measuring temperature of 700K are shown. While thers is no change in the film's time function, the time independant damping of the bulk spectra has completely vanished. This behaviour is fully reversible and typical for an electronic process. Thus, a clear distinction between structural and electronic phenomena is possible. These results illustrate the differences between In_2O_3 bulk material and ITO-films on a submicroscopic scale. Further experiments with ITO-films of lower Sn-content are in progress. Based on these results a comparison of film properties of technical interest, e.g. conductivity and optical transmission with hyperfine parameters will be possible.

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