

Temperature dependence of electron-capture aftereffects in the semiconductor In_2O_3

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We present a series of measurements of a fluctuating perturbation in the angular correlation of ^{111}Cd in In_2O_3 powder samples. We analyze the temperature dependence of the associated hyperfine parameters and conclude that this perturbation arises from "aftereffects" following the electron capture of ^{111}In . We discuss the connection of perturbed-angular-correlation measurements of aftereffects with local electric properties at impurity sites of semiconductors.

In a recent paper¹ we have reported on a time-differential perturbed-angular-correlation (TDPAC) measurement of the parameters that characterize the quadrupole hyperfine interaction of ^{111}Cd at In sites in crystalline In_2O_3 . The crystalline structure of In_2O_3 consists of In ions coordinated by six oxygen ions in two different geometries.² Besides the two static interactions associated with two different indium sites, a strong time-dependent perturbation was seen at room temperature (RT).

In this Rapid Communication we present a series of TDPAC measurements of this fluctuating interaction and identify it as arising from "aftereffects" (AE) following the electron capture in the decay of ^{111}In in the compound In_2O_3 . We analyze the temperature dependence of the hyperfine parameters associated with the AE phenomena and discuss the connection of TDPAC measurements of AE with local electric properties at impurity sites of semiconductors.

The so-called AE are the electronic relaxation processes which follow the creation of an electron hole in an inner atomic shell. During its diffusion towards the atomic surface this initial hole creates additional holes (due to Auger transitions). Because the mean life of the holes in the outermost atomic shells depends strongly on the atomic environment, the attenuation of the angular correlation will vary with the character of the probe surroundings.

The fluctuating interaction, present in chemically prepared In_2O_3 , was also found in In_2O_3 precipitates in a silver matrix.¹ This time-dependent contribution to the perturbing field increases with increasing size of the In_2O_3 precipitates. It is absent in thermally oxidized 1-at. % AgIn alloys while it is clearly evident in 7-at. % AgIn alloys, oxidized at 823 K, where the precipitates are considerably bigger. This is in agreement with the well-known fact that when the radioactive atom is embedded in a metal it returns to its atomic ground state in a very short time (less than 10^{-12} s).^{3(a)} On the other hand, in semiconductors the recovery time is expected to be long enough to give rise to measurable effects in the angular correlation.⁴ Indeed, in the 1-at. % AgIn alloys, the In_2O_3 precipitates seem to be small enough to profit from the proximity of the metal matrix regarding the atomic recovery, while bigger precipitates (7 at. %) show the expected nonmetallic behavior.

In order to study the fluctuating hyperfine field we used In_2O_3 powder samples. In_2O_3 is a *n*-type semiconducting compound with a bixbyite-type $T_h^7(1a_3)$ crystal structure.

The unit cell has 80 atoms with two different indium sites with relative populations 3:1. The maximum observed oxygen vacancy concentration is less than 1% (Ref. 5) and the solubility of indium interstitials at 573 K is about 1 at. %.⁶ Powder samples were chemically prepared in the following way: a natural cadmium foil was irradiated with 28-MeV deuterons to produce ^{111}In via the nuclear reaction $^{110}\text{Cd}(d,n)^{111}\text{In}$, and then dissolved in HNO_3 together with some indium metal. Next, H_2S was introduced into the solution and the yellow precipitate of CdS was eliminated by centrifugation. This process was repeated until no visible CdS was present. The solution was then evaporated and the In_2O_3 was obtained by calcination of $\text{In}(\text{NO}_3)_3$ at about 773 K. Finally, the compound was annealed in air at 1273 K for six hours.

The suitability of the described process was checked through x-ray analysis of the resulting product. The Debye-Scherrer pattern showed the characteristic lines of In_2O_3 reported by Swanson, Gilfrich, and Ugrimic,⁷ only. Additional proofs of the reliability of the preparation method are the results of TDPAC experiments performed on different sources which gave in all cases the same static hyperfine parameters.

The TDPAC measurements [a complete description of the technique can be found in Ref. 3(b)] were performed with the 173-247-keV γ - γ cascade of ^{111}Cd . A conventional automatic two-detector apparatus, with one NaI(Tl) and one CsF scintillator, was used. The movable detector changed its position every 1800 s between $\theta = 90^\circ$ and 180° with respect to the fixed one. The time spectra of coincidence $N(180^\circ, t)$ and $N(90^\circ, t)$ were stored in subgroups of a multichannel analyzer. We evaluated from these time spectra, corrected for accidental counts, the asymmetry ratio:

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)} \quad (1)$$

The A_4 coefficient of this γ - γ cascade can be neglected. The asymmetry ratio is then given by $R(t) = A_2^{\text{expt}} G_2(t)$, where A_2^{expt} is the measured angular-correlation coefficient and $G_2(t)$ is the perturbation factor which contains the relevant information about the interaction between the nucleus in its intermediate state and the perturbing extranuclear fields.

Two sequences of TDPAC measurements at different temperatures were performed using two samples prepared in

the above described way. With one of them, three measurements, at 14 K, 75 K, and RT were done in vacuum (better than 10^{-3} torr). The same sample was previously measured at RT in air. With the second sample the following sequence of measurements was performed in air: RT, 473, 823, 1073, 473, RT, and 623 K. The same results were obtained with both samples at RT in air. The results for the first sample at RT were also the same in air and in vacuum. No change was observed in the $R(t)$ spectra between 14 K and RT, whereas dramatic variations were observed between RT and 1073 K. Typical results are shown in Fig. 1.

The "structured" part of the $R(t)$ spectra can be decomposed into two undamped periodic oscillations. These arise from the two static quadrupole interactions associated with

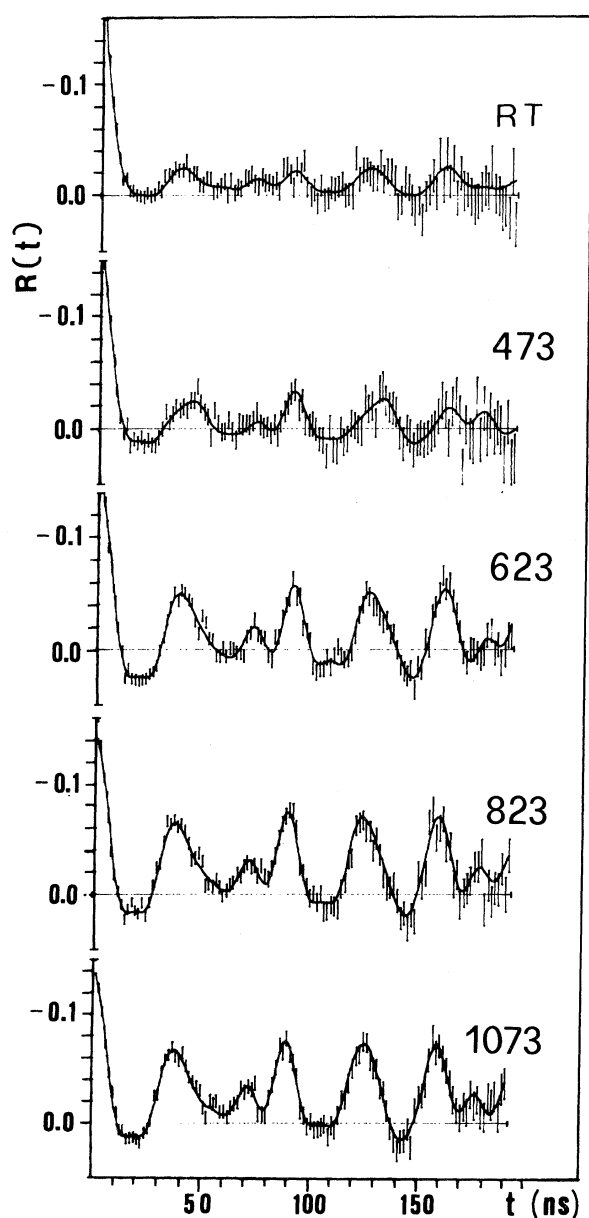


FIG. 1. TDPAC spectra labeled according to the temperature of measurement (in K). Full lines show the curves fitted to the data.

the different indium sites of the crystal structure. It is important to note that only after the thermal treatment at 1273 K well-defined static quadrupole frequencies are observed. This may be connected with Meyer's observation⁸ that a high-temperature treatment is necessary to eliminate residual nitrogen oxides whenever In_2O_3 is obtained by calcination of $\text{In}(\text{NO}_3)_3$. A time-dependent interaction is also present with its characteristic exponential shape. Its magnitude can be estimated from the difference between the $R(t)$ values at $t=0$ and its next maximum.

The analysis of our data was performed using the theoretical functions $G_2(t)$ derived by Baverstam *et al.*⁹ on the basis of the Abragam and Pound¹⁰ theory. The authors in Ref. 9 have shown that the basic assumptions of the Abragam and Pound theory are satisfied in AE processes and derived a modified perturbation factor taking into account the fact that the fluctuating field is turned off when the atomic ground state is reached. To do so, two simplifying assumptions were made:

(i) The probability for an atom to reach its ground state is $P_g(t) = \lambda_g \exp(-\lambda_g t)$. This assumption implies that all the atomic recovery processes are characterized by a single exponential recovery time λ_g^{-1} .

(ii) The mean interaction strength averaged over all excited atoms is constant along the recovering process.

The time-dependent contribution to the perturbation factor can then be written as

$$G_2^*(t) = \frac{\lambda_g}{\lambda_g + \lambda_{2r}} + \frac{\lambda_{2r}}{\lambda_g + \lambda_{2r}} \exp[-(\lambda_g + \lambda_{2r})t], \quad (2)$$

where λ_{2r} is the Abragam and Pound relaxation constant.

When the atoms reach the ground state, the hyperfine in-

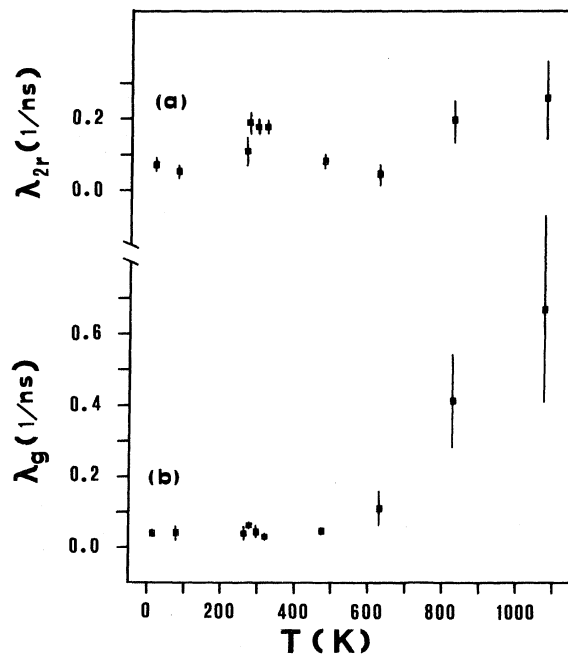


FIG. 2. (a) Relaxation constant λ_{2r} and (b) recovery constant λ_g , as a function of the temperature of measurement. The data points for the four measurements at RT are slightly displaced for the sake of clarity.

teraction will be static. Since this interaction is much weaker than the time-dependent one, $G_2(t)$ can be expressed as the product $G_2(t) = G_2^*(t)G_2^{\dagger}(t)$.⁹ The $G_2^*(t)$ is the typical static electric quadrupole perturbation factor.¹ The hyperfine parameters which characterize the static component of the perturbing field are: $\omega_1 = 18.5_{1.0}$ Mrad/s, $\eta_1 = 0.70_1$, $\delta_1 = 0.010_2$; $\omega_2 = 24.5_{1.0}$ Mrad/s, $\eta_2 = 0.12_4$, and $\delta_2 = 0.010_2$, where ω_i is the nuclear quadrupole precession frequency, η_i is the asymmetry parameter, and δ_i is the relative Lorentzian frequency distribution. These parameters correspond to the two different sites of the In ions in the In_2O_3 lattice. It is important to mention that our measurements showed no variation, within the quoted error limits, of these static parameters in all the studied temperature range (14–1073 K). This indicates that there are no phase transitions in this temperature range and that the thermal expansion of the lattice can be neglected.

Concerning the time-dependent component of the perturbation factor, its characteristic parameters are λ_{2r} and λ_g . The parameter λ_{2r} takes into account the rapid fluctuation of the field originating in the spin-lattice relaxation, the filling of the electron holes [there can be up to 7 holes in ^{111}Cd [Refs. 3(a) and 11]] and the associated electronic disturbances in the probe's surrounding. The correlation times arising from these mechanisms are all contained in the single quantity λ_{2r} . This is the reason why it is very difficult to pull out any quantitative information about the processes involved from the fitted λ_{2r} values, shown in Fig. 2(a).

The recovery constant λ_g accounts for the time the atomic system needs to fill its valence holes with electrons from the conduction band or by hole diffusion. The measured recovery time λ_g^{-1} varies from 27 ± 4 ns at 14 K to 1.5 ± 0.6 ns at 1073 K. Figure 2(b) shows the dependence of λ_g on temperature, which was found to be reversible. Between 14 and 473 K it remains constant while it clearly increases at higher temperatures. The increase of λ_g implies that above 470 K the atomic recovery time becomes shorter with increasing temperature. This indicates a higher local electron availability at the probes sites in that temperature region.

It is hard to say how this electron availability is connected with macroscopic electrical parameters such as electron concentration (n) and mobility (μ). TDPAC measurements provide information about the electronic properties in the close vicinity of the probe. The macroscopic parameters depend on the conditions of the compound preparation.⁵ There are discrepancies in the reported measurements of n , μ , and conductivity as well as in their temperature dependence. Above 1073 K a strong increase of the compound conductivity is seen.^{5,12–14} De Witt^{5(b)} and Weiher¹² show that this high-temperature region is extended to lower temperatures by doping with divalent impurities (Ca and Zn, respectively). It is then possible that the presence of Cd impurities arising from the source preparation procedure could affect the electric properties of our sample in the same way. If so, the increase of λ_g above 470 K could be related to the onset of the high-temperature behavior.

In any case, the dependence of λ_g with temperature indicates that TDPAC measurements of AE can provide information about local electric properties at impurity sites in semiconductors. Further experiments are in progress in order to establish the scope and applicability of the technique in this field.

During the revision of this manuscript we took notice of another TDPAC measurement on In_2O_3 in the same temperature range.¹⁵ Even though the authors found a time-dependent interaction that is removed with increasing temperature, their spectra differ from ours as far as the magnitude of the frequency distribution is concerned. We have found very similar spectra with a large frequency distribution for In_2O_3 samples without the final annealing at 1273 K, as mentioned above. This fact and the theoretical function $G_2(t)$ used to analyze their data do not allow a direct comparison.

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