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Search for aftereffects in tin oxide films

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Time-differential perturbed-angular-correlation measurements made using ^{111}In probes, which decay through electron capture to ^{111}Cd, have been performed on SnO_2 films in order to check the existence of electron-capture aftereffects. Two different substrates were employed for the SnO_2 films: an insulating quartz plate and a silver film. Measurements at room temperature coincide with previous results in powder samples. The results show no evidence of a fluctuating interaction arising from electron-capture aftereffects.

Early in the development of the time-differential perturbed-angular-correlation (TDPAC) technique, the question of whether the electron-capture (EC) aftereffects (AE) will or will not perturb the angular correlation in semiconductors and insulators became a controversial one.

The so-called AE are the electron 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 by Auger transitions. Since the mean lifetime of the holes in the outermost atomic shells strongly depends on the atomic environment, the effect on the angular correlation will vary with the local electron availability in the probe's surroundings.

From our results on this subject[1-4] we can argue that this perturbation is ultimately produced by a hole trapped in the impurity acceptor center introduced by the decay product in the band gap of the semiconductor.

In a recent paper[5] we have reported a TDPAC study of tin oxide using $^{111}\text{In} \xrightarrow{\text{EC}} {}^{111}\text{Cd}$ probes. Although in this system a perturbation arising from the AE can be expected, we have not found any evidence of its presence in our measurements. Nearly simultaneously with the publication of the preliminary results of that investigation,[6] Wolf *et al.*[7] reported TDPAC measurements on ZnO and SnO_2. They claim that the temperature dependence of the intensity of the quadrupole interaction observed in their spectra reveals the decay AE. The fact that in a hydrogen-doped sample they find a faster increase of the intensity with the temperature seems to confirm their hypothesis.

The striking disagreement between the results of both groups motivates the continuation of our investigation of this subject.

As we mentioned above, AE depend strongly on the local electron availability at the probe's site. There are many ways of varying the local electron availability in a semiconductor. The most currently used are (i) temperature treatments, (ii) impurity doping, and (iii) metallic junctions. The first two methods have been employed in the above-mentioned work on tin oxide;[5-7] here we used the third.

The metallic contact can be made by embedding the semiconductor in a metallic matrix as we did with In_2O_3 in silver,[3] or evaporating a thin film of the sample on a metallic backing as done by Bolse, Uhrmacher, and Lieb for In_2O_3 on an Al substrate.[8] In both cases, the Ohmic character of the metal-semiconductor junction predicted by a simple calculation in terms of the work functions and electron affinities was confirmed by the experimental results. A similar calculation using an electron affinity value of 4.8 eV for SnO_2 and a silver work-function value of 4.2 eV (both from Ref. 9) predicts also an Ohmic contact. In this case electrons will flow from the metal to the semiconductor and a thin double layer of higher charge density is created to make the Fermi level of the two materials coincident at thermal equilibrium. Hence, the local electron availability at the probes' sites in the semiconductor will increase with the metal contact.

We present here a TDPAC study with ^{111}In in SnO_2 films on two different substrates: (I) an insulator and (II) a metallic silver film.

The films were prepared by thermal evaporation of high-purity metallic tin (99.999% purity) in a vacuum chamber following the method described in Ref. 10. The chamber was evacuated up to 10^{-5} Torr and, before evaporation, a pure-oxygen flux was introduced and kept at a pressure of about 5×10^{-3} Torr. Sample I consisted of a SnO_2 film on a rectangular quartz plate optically polished substrate. In sample II the substrate consisted of a silver coating on a quartz plate. In both cases, commercially obtained carrier-free $^{111}InCl_3$ diluted in distilled water was dropped onto the films and then dried using an infrared lamp. Then, new films were evaporated onto them, so that the activity remained between the two films, both having approximately the same thickness.

We estimate a total thickness of about 7000 Å in both cases and the amount of ^{111}In is less than 10^{-3} at. ppm. In sample II, another silver coating was evaporated in order to ensure the metal contact on both faces of the Sn-O films.

Finally, the ^{111}In was diffused into the films by annealing them in an oven at 770 °C for 2 h in air, ensuring, at the same time, the complete oxidation of the tin films. The resulting product, monitored by electron Mössbauer spectroscopy, was revealed as polycrystalline SnO_2, with no traces of either SnO or metallic Sn.

The TDPAC measurements (a complete description of the technique can be found in Ref. 11) were performed using the well-known 173–247 keV γ-γ cascade of ^{111}Cd. A conventional automatic two-detector apparatus with two CsF scintillators was used providing a time resolution of 1.6 ns full width at half maximum (FWHM). After subtraction of the chance-coincidence background, the asymmetry ratio

$$R(t) = 2\frac{N(180°,t) - N(90°,t)}{N(180°,t) + 2N(90°,t)} \qquad (1)$$

was calculated.

Since the A_4 coefficient of this γ-γ cascade can be neglected, the asymmetry ratio is then given by $R(t) \approx A_2^{\text{expt}} G_2(t)$, 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 nuclear intermediate-state moments and the perturbing extranuclear fields.

The $R(t)$ spectra measured with both samples at room temperature are displayed in Fig. 1. They appear to be very similar. The main feature of both spectra is a strong damping of the angular correlation. The spectra are well reproduced by a least-squares fit (see solid line in Fig. 1) using a theoretical function of the form

$$G_2(t) = \sum_i f_i \sum_{n=0}^{3} S_n \exp(-\delta_i \omega_n t) \cos(\omega_n t)\,, \qquad (2)$$

where f_i are the relative fraction of nuclei that experience a given perturbation. The frequencies ω_n are related by $\omega_n = F_n(\eta)\omega_Q$ to the quadrupole frequency $\omega_Q = eQV_{zz}2\pi/40\hbar$.

The F_n and S_n are known functions[12] of the axial-asymmetry parameter defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{ii} are the principal components of the electric-field-gradient tensor. The exponential function accounts for a Lorentzian frequency distribution of relative width δ around ω_n.

The fits reveal the presence of two static-quadrupole interactions. In sample I, the highest fraction $f_1 = 85_5\%$ is exposed to a hyperfine interaction characterized by $\omega_1 = 28.78_{1.00}$ Mrad/s and $\eta_1 = 0.52_5$, and the remaining probes are submitted to a hyperfine interaction characterized by $\omega_2 = 14.9_6$ Mrad/s and $\eta_2 = 0.58_6$. In sample II, the two interactions are characterized by $f_1 = 82_3\%$, $\omega_1 = 23.9_{3.00}$ Mrad/s, and $\eta_1 = 0.69_{34}$; $f_2 = 18_1\%$, $\omega_2 = 14.3_7$ Mrad/s, and $\eta_2 = 0.37_8$. In both samples the two interactions have a distribution of around 15%. These interactions coincide with the ones we found with SnO_2 powder samples reported in Ref. 5.

Furthermore, high-temperature measurements were performed with both films. Again, no dependence with the substrate nature is observed. We find here the same temperature dependence of the quadrupole interactions in both samples which, in fact, agree with what was found with powder samples.[5] As we said in Ref. 5, we assign these interactions to In probes substitutionally replacing tin with a singly or doubly ionized oxygen vacancy as a near neighbor. In this picture, the change in the $R(t)$ spectra with increasing temperature arises from the ionization of the oxygen second-donor level. As expected, this evolution is independent of the film substrate.

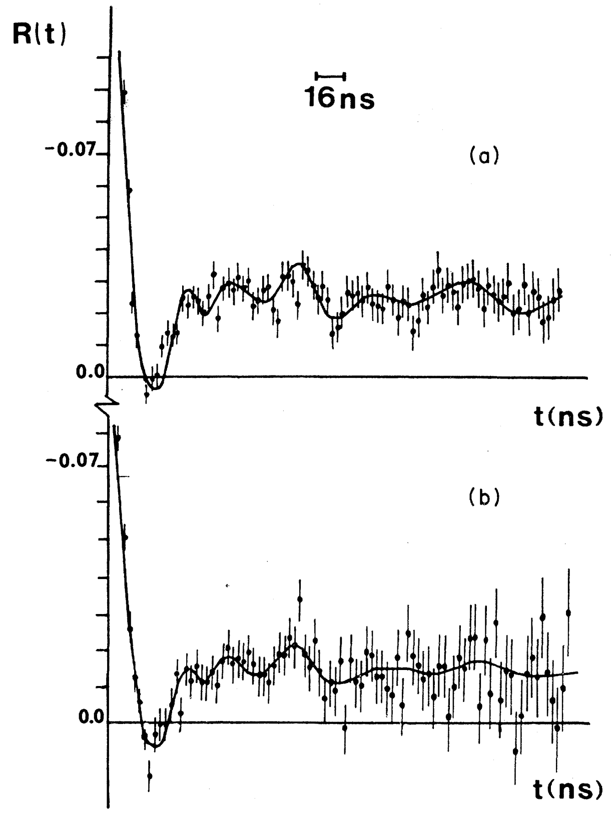

FIG. 1. TDPAC spectra of ^{111}In taken at room temperature of (a) sample I and (b) sample II. Solid lines show the results of least-squares fits of Eq. (2) to the data.

In order to make a further check on the existence of a fluctuating interaction arising from the decay AE, we have fitted all our spectra with a theoretical perturbation factor including an exponential term. In none of our spectra did we observe an improvement of the fits using this theoretical function.

We find, therefore, that there is no evidence of the presence of any time-dependent interaction arising from AE in our SnO_2 samples. In our model of aftereffects, this implies that the lifetime of the holes trapped in the Cd impurity centers must be shorter than 1.6 ns at room temperature. This prompt recombination is consistent with the prediction of the shallow character of all the Sn site acceptors in the SnO_2 semiconductor.[13]

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