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TDPAC STUDIES OF AFTER-EFFECTS IN In_2O_3 PRECIPITATES IN A SILVER MATRIX

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We present a series of time-differential perturbed angular correlation measurements of the time-dependent interaction associated with the aftereffects processes which follow the electron capture decay of the ^{111}In embedded in In_2O_3 precipitates in a silver matrix. The In_2O_3 precipitates were obtained by internal oxidation of indium-silver alloys. We study the atomic recovery probability dependence on the precipitate size and temperature. We analyze the influence of the surface charge density built-up at the metal semiconductor contact on the electron availability. The experimental results allow us to suggest a tentative description of the recovery processes in the precipitates.

1. Introduction

In recent papers [1 – 4], the hyperfine interaction at ^{111}In sites of an In_2O_3 compound has been investigated by means of the TDPAC technique. In particular, a fluctuating interaction was observed and studied as a function of temperature [1 – 4] and free carrier concentration [4]. This interaction originates in the atomic relaxation processes which follow the nuclear electron capture of ^{111}In (usually called after-effects). From our last results [4] we can argue that this perturbation is ultimately produced by a hole trapped in the impurity center introduced by the decay product ^{111}Cd in the band gap of the semiconductor. The analysis of TDPAC spectra with a convenient parametrization allows the extraction of the hole lifetime, which has a typical value of 30 ns at room temperature. Two different electron-hole recombination mechanisms were identified: electrons coming from the conduction band mostly dominate the recombination processes at low temperature (15 K – 200 K), while thermal excitation of electrons from the valence band is the most important source of electron supply at higher temperatures. This last fact made it possible to compute, in the frame of our model, the position of the cadmium impurity level, which turns out to be 0.16_4 eV above the valence band.

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On the other hand, In_2O_3 precipitates have been identified in internal oxidation studies of AgIn alloys [2,5,6]. The fluctuating interaction due to aftereffects was observed when the formed In_2O_3 precipitates are of considerable size, while this interaction was absent in smaller precipitates [2]. This fact was tentatively attributed to the influence of the metallic matrix, but more information is still necessary in order to fully explain this behaviour.

In this paper, we report a series of TDPAC measurements of In_2O_3 precipitates in a silver matrix, obtained by internal oxidation of AgIn (1 at.% and 7 at.%) alloys. The dependence of the hole lifetime on the precipitate size is shown. At room temperature, the hole lifetime (which is much shorter for small precipitates) tends to the values measured in pure In_2O_3 samples when the precipitate size is increased. We studied the temperature dependence of the hole lifetime in the largest precipitates and found that it is systematically shorter than that measured in In_2O_3 samples in the studied temperature range (RT – 1000 K). This reveals that even for large precipitates, the metallic matrix does modify the electron supply to the Cd acceptor level.

2. Experimental procedure and data treatment

The TDPAC measurements were performed through the well-known 173–247 keV $\gamma-\gamma$ cascade in ^{111}Cd. The radioactive probe nuclei of ^{111}In (which populate nuclear levels of ^{111}In by electron capture) were obtained in the Ag matrix by the nuclear reaction ^{109}Ag(α, 2n)^{111}In, using the 56 MeV α-particle cyclotron beam of the CNEA, Buenos Aires.

The AgIn alloys were prepared by melting the irradiated silver foils together with appropriate amounts of inactive high-purity indium metal in an Ar atmosphere in quartz tubes. Afterwards, the samples were rolled down to their final thickness. The oxidation treatments were performed by heating the samples in quartz tubes open to air in a conventional electric oven, stable within 4 K at the proper temperature. In this way, In_2O_3 precipitates are built-up inside the silver matrix with sizes which are functions of the oxidation temperature, oxygen partial pressure and oxidation depth. Varying these parameters, it is possible to have control of the mean diameter of the precipitates. The relative mean diameter of the In_2O_3 precipitates at two different temperatures and oxygen pressures for alloys of the same composition were computed following a study of the dynamics of internal oxidation of impurities in silver and size effects by Ehrlich [7]. Assuming a spherical shape for the precipitates, the relative mean diameters (rmd) are given by:

$$\frac{\mathrm{rmd}\,(T_1, p_1)}{\mathrm{rmd}\,(T_2, p_2)} = \left(\frac{C(T_2)\,D'(T_2)\,D''(T_1)}{C(T_1)\,D'(T_1)\,D''(T_2)} \; \frac{\xi_1\, p_2^{1/2}}{\xi_2\, p_1^{1/2}} \right)^{1/2} , \tag{1}$$

where $C(T) = C_0 \exp(-(E/RT))$ is the oxygen concentration at the sample surface, $D'(T) = D'_0 \exp(-(E'/RT))$ and $D''(T) = D''_0 \exp(-(E''/RT)$ are the oxygen and indium diffusion coefficients in the alloy; ξ_1 and ξ_2 are the final depths of the oxidation front at temperatures T_1 and T_2, respectively; p_1 and p_2 are the oxygen partial pressures in each case.

A conventional automatic two-detector aparatus, with one NaI(Tl) and one CsF scintillator was used, providing a time resolution of 2.4 ns FWHM. After subtraction of chance coincidence background, time spectra coincidence corresponding to angles 90° and 180° between detectors were combined to form the ratio:

$$R(t) = 2\,\frac{N(180°, t) - N(90°, t)}{N(180°, t) + 2N(90°, t)} \cong A_2^{\exp}\, G_2(t)\,,$$

$A_2^{\exp}$ being the measured angular correlation coefficient and $G_2(t)$ the perturbation factor containing the relevant information about the hyperfine interaction.

Theoretical functions of the form $A_2 G_2(t)$, folded with the measured time-resolution curve, were fitted to the experimental $R(t)$. We use a perturbation factor of the form:

$$G_2(t) = \left(\frac{\lambda_g}{\lambda_g + \lambda_r} + \frac{\lambda_r}{\lambda_g + \lambda_r} \exp-(\lambda_g + \lambda_r)t\right) \cdot \left(f_1\, G_2^1(t) + f_2\, G_2^2(t)\right), \tag{2}$$

where $G_2^i(t)$ are static quadrupole perturbation factors corresponding to each of the two inequivalent In-sites in the In_2O_3 crystalline structure. They are well-known functions of the quadrupole frequencies $\omega_{Q_i} = eQV_{zz}^i/40\hbar$, the asymmetry parameters η_i and the relative widths δ_i (FWHM) of a Lorentzian distribution of frequencies around ω_{Q_i}. The factor containing λ_g and λ_r takes into account an exponential attenuation of the angular correlation, originated at the fluctuating environment and characterized by the Abragam–Pound relaxation constant λ_r [8], which affects a decreasing fraction of probes ($\exp - (\lambda_g t)$) as their complete atomic recovery is achieved [9]. A more complete description of the $G_2(t)$ factor can be found in refs. [3] and [4].

We have already used this parametrization to analyze our results on In_2O_3 and In_2O_3:Sn compounds. This previous work led us to the following interpretation of the parameters which characterize the fluctuating interaction (see ref. [4]).

The parameter λ_r takes into account all the fluctuating interactions which are present during the atomic recovery process, for example, the spin-lattice relaxation and the electronic disturbances in the probe's surroundings. Since the correlation times arising from these mechanisms are all contained in the single quantity λ_r, it is very difficult to obtain any quantitative information about the processes involved from the measured λ_r. Nevertheless, it can be worth mentioning that the measured value of 0.12 ns^{-1} is consistent with a calculated estimation of the magnitude of the Abragam–Pound constant associated with a pure magnetic interaction produced by a hole in the 4d shell of the Cd atom.

The parameter λ_g is the probability, per unit time, for an atom to reach its ground state (the normal ionization state Cd^{2+}). We showed in ref. [4] that only the holes trapped in levels above the valence band will perturb the angular correlation, and then λ_g^{-1} provides the lifetime of a hole trapped at the Cd impurity level of the semiconductor.

3. Results and discussion

Figure 1 shows typical $R(t)$ spectra, at RT, for three different precipitate sizes in 1 at.% In alloys. Spectrum (a) corresponds to precipitates which have been taken as unit diameter. The two static quadrupole interactions, with relative ratio 3:1, associated with the two inequivalent indium sites in the bixbyite-type crystalline structure of the indium sesquioxide, are clearly seen. Here, no fluctuating interaction is observed. Spectrum (b) corresponds to precipitates with an average diameter three times larger than the preceding one, obtained by oxidizing the alloys at 823 K in air. The exponential shape characteristic of the fluctuating interaction can be observed. This exponential shape dominates spectrum (c), which corresponds to precipitates nineteen times larger than (a), obtained after oxidation at 1150 K. This spectrum does not differ from the ones taken with In_2O_3 powder samples at RT, shown in refs. [3] and [4].

The results of the least-squares fits to the experimental $R(t)$ ratio, at RT, for the 1 and 7 at.% alloys are reported in table 1. A fixed value of $\eta_2 = 0.12$ was adopted. No dependence of the static quadrupole parameters with the precipitate size is observed, with the exception of a slight increase of the frequency distribution in the smaller precipitates. As was the case in In_2O_3 samples [4], the Abragam–Pound relaxation constant λ_r was found to be somewhat dispersed around a mean value of 0.12 1/ns, which has been used in the final fits. For each indium concentration, relative mean diameters (rmd) were calculated using eq. (1). We have taken as unit reference the ones corresponding to the smaller precipitates that present the two static hyperfine interactions characteristic of indium sesquioxide. Both unit precipitates (for 1 and 7 at.% alloys) should be of similar size and then a direct comparison of both sets of experimental data is possible. This is done in fig. 2, where the λ_g values versus rmd of the precipitates are shown. The atomic recovery probability strongly depends on the precipitate size in the range of small rmd. For larger precipitates, it becomes roughly constant around a mean value very close to that of In_2O_3 powder samples (0.035 1/ns) [4]. This result can be understood in the frame of the following very simple picture: as it is well-known, when a metal and a semiconductor are brought

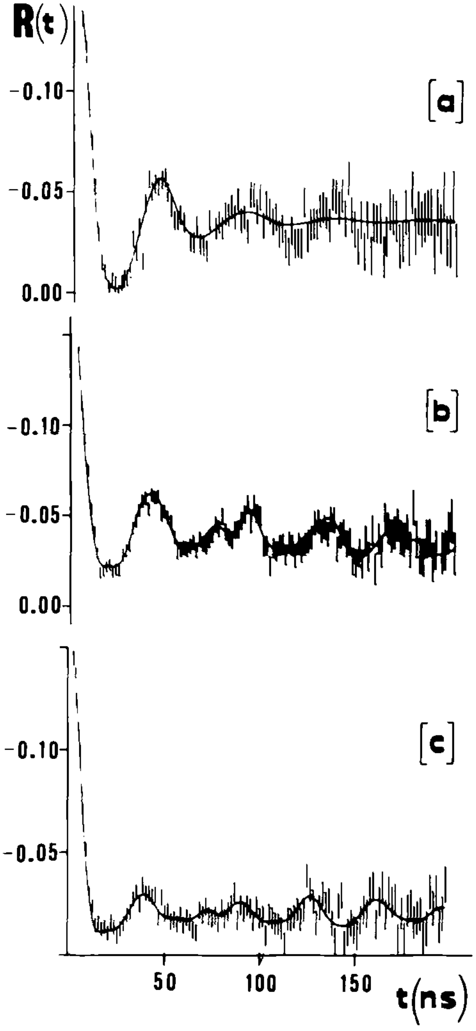

Fig. 1. TDPAC spectra, measured at RT, corresponding to internally oxidized 1 at.% AgIn alloys for three different precipitate sizes: (a) rmd = 1, (b) rmd = 3, (c) rmd = 19. The full line curves are least-squares fits of eq. (2) to the data.

Table 1

Fitted hyperfine parameters for RT measurements of In_2O_3 precipitates of different mean sizes obtained by internally oxidizing 1 and 7 at.% AgIn alloys at different temperatures in air (except for the sample oxidized at 1150 K, where the oxygen pressure was 0.08 Torr). The calculated relative mean diameter (rmd) is shown.

Nominal concentration (% In)	T_{ox} (K)	rmd	ω_1 (Mrad/s)	η_1	δ_1 (%)	ω_2 (Mrad/s)	δ_2 (%)	λ_g (1/ns)
1	820	3	18_1	0.74_2	4_1	24_1	1_1	0.19_2
7	820	10	18_1	0.69_3	5_2	24_1	1_2	0.06_1
1	1150	19	18_1	0.71_3	2_1	24_1	2_4	0.035_{10}
7	870	24	19_1	0.68_4	0_2	27_1	0_1	0.018_5
7	970	29	18_1	0.72_4	6_2	24_1	1_2	0.030_6
7	970	33	18_1	0.73_4	1_2	24_1	0_3	0.013_6

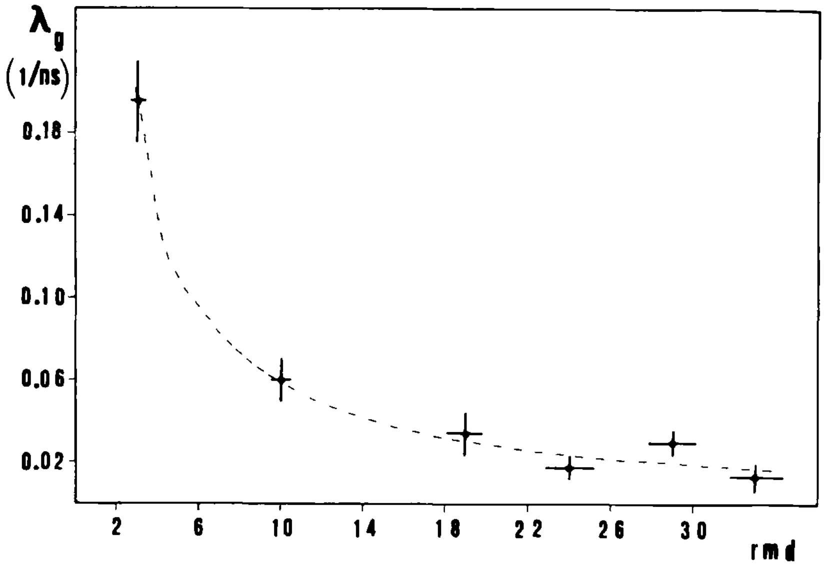

Fig. 2. Dependence of fitted atomic recovery probability λ_g with the relative mean diameter. The dashed line corresponds to the surface-to-volume ratio normalized to the first experimental point. Horizontal error bars are mainly due to uncertainties in ξ_1 and ξ_2 [eq. (1)].

into contact with each other, the Fermi level in equilibrium has to be constant and generally a space-charge double layer will build-up in the interface region [10]. This is the case when a semiconductor precipitate is formed in a metallic matrix through internal oxidation. Our results are consistent with an ohmic-type junction, since the increase of the atomic recovery probability reveals a higher electron availability at the impurity site. In an ohmic junction, electrons will flow from the metal to the semiconductor. It is reasonable to think that the influence of the charge lying in the metal-semiconductor contact on the atomic recovery probability will be proportional to the surface-to-volume ratio of the precipitate. The dashed line in fig. 2 shows the surface-to-volume ratio normalized to the first experimental point. As can be seen, the agreement is quite good.

We performed a series of measurements as a function of temperature for precipitates in which the λ_g value at RT is close to the one obtained with In_2O_3 powder samples, that is, precipitates with relative diameters in the range 20 to 33. Results are shown in fig. 3, where λ_g values obtained with In_2O_3 pure samples are also plotted for comparison. The atomic recovery probability is systematically higher

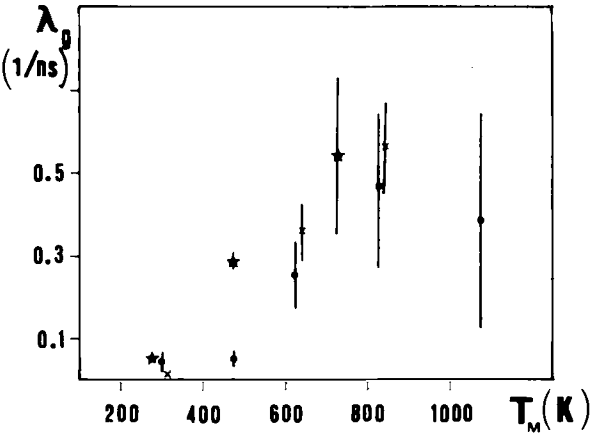

Fig. 3. Temperature dependence of the fitted atomic recovery probability in the temperature range RT < T_M < 1000 K. The (•) belongs to the λ_g values obtained with In_2O_3 powder samples reported in ref. [2]; (×) corresponds to In_2O_3 precipitates with rmd = 24; (★) corresponds to In_2O_3 precipitates with rmd = 19.

in the range RT < T_M < 1000 K. Once more, this reveals at each temperature that more electrons are available to recombine with the hole trapped in the Cd impurity level. Another temperature-dependent mechanism of electron supply is present in addition to the thermal excitation of electrons from the valence band. We assign this additional source of electrons to the presence of the metallic matrix. Actually, the equilibrium surface charge will vary with temperature and then the influence of this charge density on the electron availability in the semiconductor will also change.

4. Conclusions

In the frame of our model for the perturbation mechanism, we have obtained the atomic recovery probability for cadmium impurities in In_2O_3 semiconductor precipitates in a silver matrix as a function of the precipitate's size and temperature. The experimental results reveal that the metallic matrix increases the hole recovery probability. The effect depends on the precipitate's surface-to-volume ratio. The effective influence is an enhancement of the electron availability at the Cd impurity site. We assign this additional source of electrons to the presence of the surface charge density at the metal-semiconductor contact.

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