

# Electric field gradient in nanostructured SnO<sub>2</sub> studied by means of PAC spectroscopy using <sup>111</sup>Cd or <sup>181</sup>Ta as probe nuclei

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**Abstract** Electric quadrupole interactions were studied in pure and Mn-doped powder samples and thin films of SnO<sub>2</sub> using perturbed  $\gamma\gamma$  angular correlation spectroscopy (PAC). The powder samples were prepared by Sol gel method and the thin film were prepared on the Si (100) substrate by sputtering technique using Sn in the oxygen atmosphere. The samples were characterized by x-ray diffraction, energy dispersive spectroscopy and scanning electron microscopy. The thickness of the film was 100 nm. The average particle size of the SnO<sub>2</sub> powder samples was determined to be smaller than 60 nm. The radioactive <sup>111</sup>In and <sup>181</sup>Hf tracers were introduced in the powder samples during the sol gel chemical process. Radioactive <sup>111</sup>In was implanted on the SnO<sub>2</sub> thin films using the University of Bonn ion implanter (BONIS). PAC measurements were carried out in a four BaF<sub>2</sub> detector spectrometer in the temperature range of 77–973 K for samples annealed at different temperatures. The PAC results for both nuclear probes show the presence of two electric quadrupole interactions. The major fractions in both cases correspond to the substitutional sites in the rutile phase of SnO<sub>2</sub>. The results are compared with previous PAC measurements.

**Keywords** SnO<sub>2</sub> · PAC spectroscopy · Electric-field gradient

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## 1 Introduction

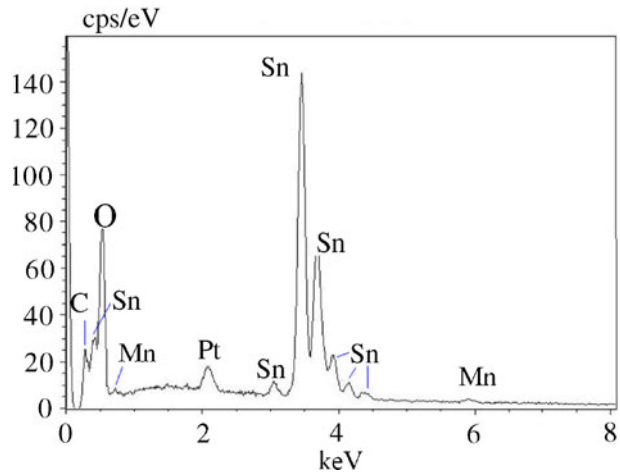
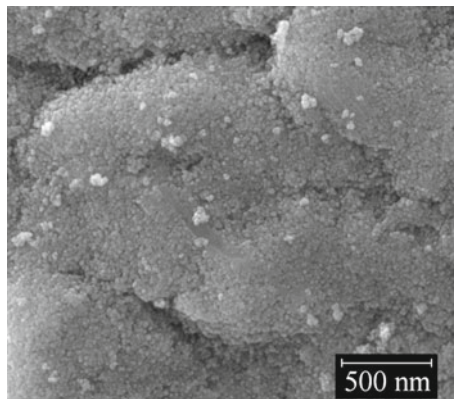
The tin dioxide  $\text{SnO}_2$  semiconductor with a wide band gap is quite attractive for the fabrication of diluted magnetic semiconductors (DMS) because of its excellent optical transparency and the fact of having native oxygen vacancies with high carrier density. DMS are a class of materials that have been studied intensively in recent years due to their main application in the area of spintronics. There are other applications such as flat panel display devices, solar cells and lasers [1–7]. Some experiments have been conducted to investigate the magnetism in  $\text{SnO}_2$  [8–11] doped with transition metals however controversial results have been reported in compounds prepared by different methods. More recently it has been observed that the sintering temperature, to which the  $\text{SnO}_2$  is submitted, can influence the magnetic ordering of the same sample [12]. Other studies concluded that the defects in the crystal structure are responsible for the ferromagnetism, instead of 3d or 4f ions doping. Recent research in this area includes experimental and theoretical investigation and involves several different metal oxides as well as experimental techniques. Whereas there are reports of several studies involving  $\text{SnO}_2$ ,  $\text{TiO}_2$  and other oxides in the literature using different experimental technique there are very few investigations which used microscopic technique such as PAC to study  $\text{SnO}_2$ .

## 2 Experimental

The powder samples of pure and 3 and 5 % Mn-doped  $\text{SnO}_2$  were prepared using the sol gel method [1]. The resulting powders were pressed into pellets and submitted to a thermal treatment at 1173 K for 12 h. Thin films of  $\text{SnO}_2$  were prepared on silicon substrate (100) with sputtering technique using 99,999 % pure Sn target in Argon and oxygen atmosphere. The thickness of the film was  $\sim 100$  nm, measured with a white-light-interferometer (Filmetrics Model F40 230–243). The samples were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) at the Polytechnic Institute, University of Sao Paulo using samples without radioactive nuclear probes. The radioactive probe  $^{111}\text{In}$ - $^{111}\text{Cd}$  was introduced in the samples during the sol gel chemical process by adding carrier free  $^{111}\text{InCl}_3$  solution with an activity of  $\sim 20\mu\text{Ci}$ . In a similar process the probe  $^{181}\text{Hf}$  was introduced by adding the  $^{181}\text{HfF}_4$  solution, obtained by dissolving a small quantity ( $\sim 0.1$  mg) of neutron irradiated Hf metal in a few drops of dilute hydrofluoric acid [1]. Radioactive  $^{111}\text{In}$  was implanted into thin film using University of Bonn ion implanter BONIS with beam energy of 160 keV. A rapid thermal annealing ( $T_A$ ) was carried out at 873 K for 10 min before PAC measurements. The PAC measurements were performed using a spectrometer consisting of four conical  $\text{BaF}_2$  detectors and a slow-fast coincidence system for measuring the delayed gamma-gamma coincidence spectra.

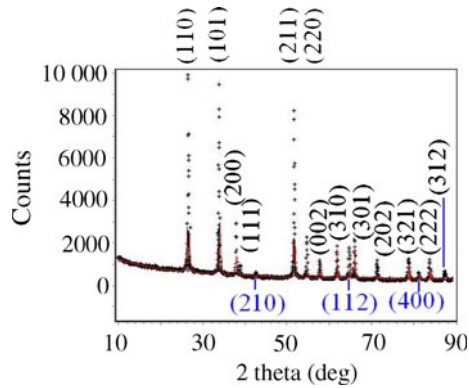
## 3 Results and discussion

The EDS, SEM and XRD results for 3 % Mn-doped powder sample are shown in Figs. 1, 2 and 3, respectively. The EDS spectra show mainly the presence of Mn in

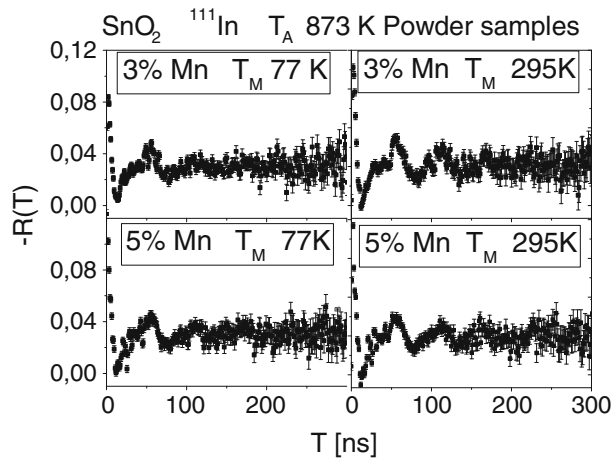
**Fig. 1** SnO<sub>2</sub> 3 % Mn powder sample EDS image**Fig. 2** SnO<sub>2</sub> 3 % Mn powder sample SEM image

the sample apart from some C and Pt which come from the sample holder materials. The SEM photograph shows that the particle size is smaller than 10 nm. The particle size is in agreement with previous results [13]. Yanes et al. [14] have reported that in some of their SnO<sub>2</sub> samples particle size was as small as  $\sim 2.5$  nm, which is close to the value of the Bohr atomic radius. This property makes SnO<sub>2</sub> semiconductor particles, or quantum dots (QD). These QD due to their small particle size exhibit unique catalytic electrical properties due to complete depletion of nano grains per charge carriers and also due to the high surface area. The optical transition from the valence band to the conduction band of these nanoparticles allows the thin dioxide prepared by sol-gel method to be a candidate for other technological applications such as fluorescence markers, light emitting laser and photonic integrated devices. The XRD pattern and calculated lattice parameters are in agreement with those found in the literature for the standard tetragonal rutile structure of SnO<sub>2</sub> [15] representing the space group P42/mnm. The average particle size of the sample doped with 3 % Mn was evaluated to be 5 nm from the broadening of the peak (110) and calculated using the Scherrer equation [16].

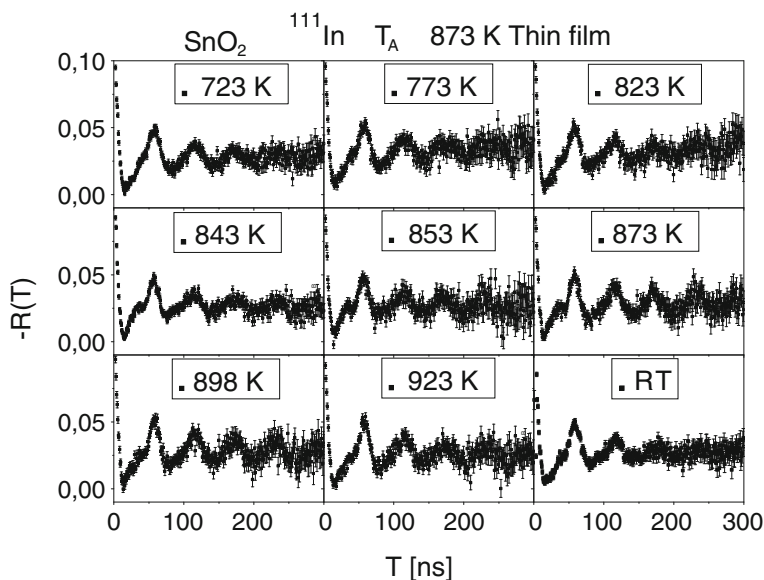
**Fig. 3**  $\text{SnO}_2$  3 % Mn powder sample XRD pattern



**Fig. 4** The perturbation functions for  $^{111}\text{In}$  probes in  $\text{SnO}_2$  doped with 3 % (*top*) and 5 % of Mn (*bottom*). The measurement temperature ( $T_M$ ) were 77 K (*left*) and 295 K (*right*)

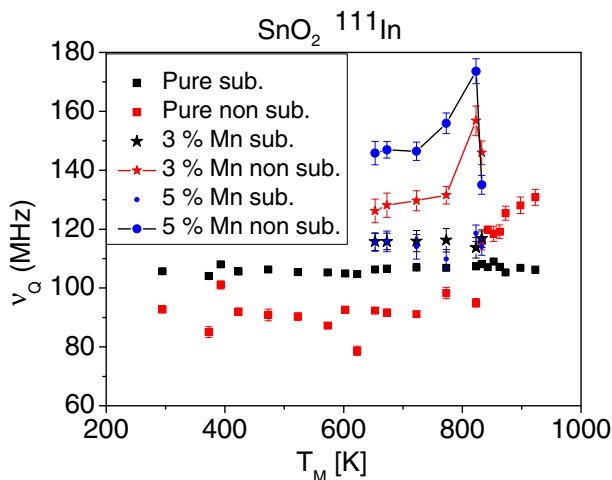


PAC measurements for powder samples were carried out, in the temperature range 77–1000 K, after thermal annealing at 873 K for several hours. Examples of PAC spectra for 3 and 5 %-Mn doped samples measured with  $^{111}\text{In}$ - $^{111}\text{Cd}$  probe at 77 and 295 K are shown in Fig. 4. In one of the earlier work on  $\text{Sn}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$  samples [10] the authors reported a magnetic moment of the order of  $0.11 \mu_B$  at Mn ion at 295 K. In the present work no magnetic interaction was observed and therefore the data were fitted with a theoretical perturbation function for pure quadrupole interaction that included two sites. The major fraction ( $\sim 75\%$ ) with well-defined quadrupole interaction was assigned to the probes in the substitutional Sn sites. The quadrupole frequencies ( $\nu_Q$ ) for the pure as well Mn-doped samples are quite similar ranging from  $\sim 115$  MHz for pure  $\text{SnO}_2$  to  $\sim 120$  MHz for 3 and 5 % Mn-doped  $\text{SnO}_2$  samples and shows very weak temperature dependence. The observed minor fractions show highly distributed quadrupole interaction ( $\delta \sim 30\%$ ). The origin of these minor fractions is not well known but most probably they correspond to probe nuclei in the interstitial sites or defects. A slight increase in the minor fraction above 823 K was observed and may be attributed to the probe migration to the surface of the microcrystals. Some typical PAC spectra for  $^{111}\text{In}$ -implanted thin films of



**Fig. 5** The perturbation functions for  $^{111}\text{In}$  probes in  $\text{SnO}_2$  thin film after a thermal treatment at 873 K. RT is room temperature and this spectrum was made after the measurements up to 923 K

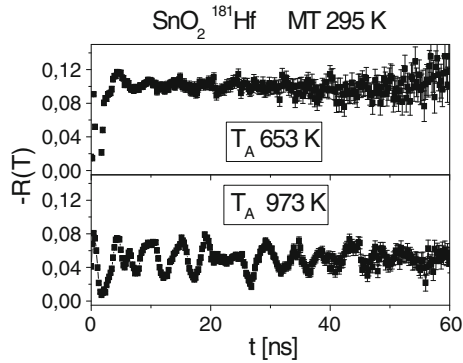
**Fig. 6** Measurement temperature dependence of the electric quadrupole frequency for the  $\text{SnO}_2$  using  $^{111}\text{In}$  as probe nuclei. The *squares punts* belong to the  $\text{SnO}_2$  thin film. The *star punts* belong to the sample doped with 3 % of Mn. The *circular punts* belong to the sample doped with 5 % of Mn. Thermal treatment were made at 873 K



$\text{SnO}_2$  taken at different temperatures are shown in Fig. 5. The observed quadrupole frequencies in thin film are very similar to those observed in powder samples and are shown in Fig. 6.

The PAC spectra for the  $\text{SnO}_2$  powder sample measured at room temperature using  $^{181}\text{Hf}$  probe are shown in Fig. 7. The measurements were carried out after the sample was annealed at 653 and 973 K respectively. It can be clearly seen that incorporation of the probe  $^{181}\text{Hf}$  in the sample considerably improves after the sample is annealed at 973 K. Once again two sites were identified. The site,

**Fig. 7** The perturbation functions for  $^{181}\text{Hf}$  probes in  $\text{SnO}_2$  powder sample after a thermal treatment at 653 K (*top*) and 973 K (*bottom*)



**Table 1** The PAC parameters for the samples after the heating at 973 K and measured at 295 K

	$\eta$ (sub.)	$\eta$ (non. sub.)	$\delta$ (sub.) (%)	$\delta$ (non. sub.) (%)	Frac. (sub.) (%)	Frac. (non. sub.) (%)
A	0.4 ( $\pm 0.005$ )	0.2 ( $\pm 0.02$ )	8.5 ( $\pm 8$ )	38 ( $\pm 2$ )	74 ( $\pm 7$ )	26 ( $\pm 2.5$ )
B	0.1 ( $\pm 0.01$ )	0.5 ( $\pm 0.02$ )	10 ( $\pm 0.6$ )	18 ( $\pm 1$ )	48.4 ( $\pm 3$ )	51.6 ( $\pm 4$ )
C	0.1 ( $\pm 0.01$ )	0.6 ( $\pm 0.02$ )	9 ( $\pm 0.8$ )	22 ( $\pm 1$ )	57 ( $\pm 3$ )	43 ( $\pm 2$ )
D	0.4 ( $\pm 0.03$ )	0.7 ( $\pm 0.05$ )	1 ( $\pm 0.1$ )	31 ( $\pm 3$ )	63 ( $\pm 5$ )	37 ( $\pm 3.5$ )

with major fraction and well defined quadrupole interaction, was associated with  $^{181}\text{Hf}$  replacing Sn at the substitutional positions. The minor component with highly distributed quadrupole frequency could be due to probe substitution at interstitial or defect sites. It was suggested in an earlier study [4] that this minor site could also be due to the presence of some tin di-oxide  $\text{SnO}$  in the sample. This phase was not detected in the XRD analysis of present samples. The value of  $\nu_Q$  is in the range of 690 and 790 MHz for the substitutional site and the non substitutional site presents  $\nu_Q = 939$  and 933 MHz for 973 and 1173 K respectively. The spectrum of the measurement made at 653 K indicates frequency values of  $\nu_Q = 740.6$  MHz for the substitutional site and  $\nu_Q = 971.5$  MHz for the other site.

The PAC fitted parameters in Fig. 6 shows that the electric quadrupole interaction remains constant for the site which the  $^{111}\text{In}$  probe replaces the tin atom for all samples. This interaction was first interpreted as small  $\text{In}_2\text{O}_3$  clusters, but this frequency appears even when we changed the method of the insertion of the indium probe on the samples. In this work, we used two ways of insertion, diffusion during the preparation of the sample and implantation. Also this frequency distribution is narrow in the range of  $\delta = 6\text{--}12\%$ . Therefore we expect that this interaction can be assigned to the  $^{111}\text{Cd}$  atoms replacing the Sn [1] on  $\text{SnO}_2$  structure.

The second interaction grows up above 823 K and is highly distributed with  $\delta$  in the range of 8–22 %. We expect that this growth occurs due to the migration of indium atoms to the surface of the film what accompanies the increase of particle size [1]. The  $\text{SnO}_2$  crystallization process which forms cassiterite crystals occurs normally at temperatures above 973 K [15] which does not justify the growth of the frequency.

For the powder samples, an increase of the non substitutional interaction could also be assigned to the migration of indium atoms to the surface of the particles.

The PAC parameters for the samples after the heating to 973 K and measured at 295 K are shown in Table 1. The asymmetry parameters  $\eta$  shows that for the substitutional sites there is more symmetry as for the non substitutional sites. The major fractions belong to the substitutional sites, which are characterized by narrow distributed frequencies.

An increasing in the value of the frequencies for the samples doped with Mn has been also observed when it was compared with the value of the pure SnO<sub>2</sub> samples. In the work of Dr. Gopinadhan et al. [10], it was observed on Sn<sub>1-x</sub>Mn<sub>x</sub>O<sub>2-δ</sub> samples a magnetic moment of 0.11  $\mu_B$ /Mn ion at 295 K [10]. As show in the Fig. 2 the spectrum made at 77 K is different from the spectrum made at 295 K that could be assigned as a weak ferromagnetic interaction. In future work magnetization measurements will be done in order to check if our samples exhibit this ferromagnetic behavior and to confirm the DMS theoretical predictions [5].

## 4 Conclusion

In this work we have studied pure and Mn-doped SnO<sub>2</sub> samples by means of PAC spectroscopy using <sup>111</sup>In and <sup>181</sup>Hf probes. The results show the presence of two electric quadrupole interactions. The major fraction that shows weak temperature dependence of the electric quadrupole interaction was assigned to the probe nuclei at the substitutional site for the powder sample and for the thin film. We assigned the second interaction which increases slightly above 823 K due to the probe at the interstitial sites or defects. The slight increase in the population of non substitutional sites at higher temperature may be due to migration of indium atoms to the surface of the particles. Results with <sup>181</sup>Hf probe confirmed previous measurements where two electric quadrupole interactions were also observed. The major fraction was assigned to the substitutional site on SnO<sub>2</sub> structure while the minor fraction was assigned to the <sup>181</sup>Hf replacing the Sn on the interstitial sites or sites on the impurity SnO phase. The doping with Mn reviews an increasing on the frequencies values. We propose that this increase could be a ferromagnetic interaction. In future work it will be checked by means of magnetization.

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