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Physics Procedia 28 (2012) 90 – 94

Physics Procedia

15th Brazilian Workshop on Semiconductor Physics

A weak magnetism observed in SnO_2 doped with Fe by means of Perturbed Gamma-Gamma Angular Correlation and Mössbauer Spectroscopy

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Abstract

Nano-structured samples of SnO_2 doped with Fe prepared by the sol-gel method were studied by the Perturbed Gamma-Gamma Angular Correlation (PAC) Spectroscopy using ^{111}In (^{111}Cd) probe nuclei as well as by ^{57}Fe Mössbauer spectroscopy. The samples were prepared from very pure metallic Sn and Fe. Carrier-free ^{111}In nuclei were introduced during the sol-gel process of sample preparation for PAC measurements. The PAC measurements were carried out after annealing the samples at different temperatures and the results show a combined electric quadrupole and magnetic dipole interaction for probe nuclei that do not occupy the regular Sn sites. The hyperfine parameters revealed weak magnetic interactions.

Keywords: PAC Spectroscopy; Mössbauer Spectroscopy; Tin dioxide; Diluted Magnetic Semiconductors; ^{111}In; Doping with Fe.

1.Introduction

Currently, the search for materials with properties of a diluted magnetic semiconductor is growing in high technology research and industry. Tin dioxide is a good candidate when it is doped with a transition metal [1,2]. Tin dioxide is an n-type semiconductor with high band gap and has a tetragonal structure that belongs to the space group P42/mnm. The notable properties of SnO_2 are its high optical transparency and electric conductivity, good chemical stability, low price, high abundance and high melting and boiling points. The tin dioxide has found many applications such as gas and humidity sensors, solar cells, capacitors, varistors, displays and utensils in electronics industry [2,3]. One possible important application is in the spintronics devices using the tin dioxide as a diluted magnetic semiconductor due to its high transparency in visible region, high density of charge carriers and native oxygen vacancy.

In this work the PAC spectroscopy is used as a microscopic nuclear technique, to measure hyperfine interactions in nano-structured powder samples of semiconducting oxide SnO_2 doped with Fe. The PAC

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doi:10.1016/j.phpro.2012.03.677

spectroscopy has been used for the measurements of the magnetic hyperfine field (MHF) and the electric field gradient (EFG) using ^{111}In-^{111}Cd radioactive probes. As far as we know this is the first study in which ferromagnetism has been detected in SnO_2 doped with Fe in nano-structured powder samples using PAC spectroscopy. Ferromagnetism has however been observed earlier in thin films [4] or bulk ceramic material studied with Mössbauer Spectroscopy [5,6]. In the work reported by Junko Sakuma et al [7] while the samples measured by Mössbauer Spectroscopy did not show any magnetic interaction, magnetization measurement showed the sample to be magnetic. These authors associated the observed magnetism to the defects in the sample. In this work, we also investigate the role of the defects produced during sample preparation.

2.Experimental Procedure

The tin dioxide samples were prepared using the sol-gel method, which is a well established methodology to produce samples of nanoparticles. The samples were prepared starting from pure metallic Sn (99.9999%) and Fe (99.99%) by dissolving them separately in dilute nitric and hydrochloric acid respectively and then mixing these solutions well together. About 30 μCi of carrier free ^{111}In was added to this mixture before adding the known quantities of citric acid and ethylene glycol to form an organic complex solution. The solution was heated to 80° C for about 3 hours to form the gel which was dried for 10h at 380º C. The dry powder received thermal treatment under nitrogen atmosphere at 773 K before PAC measurements. The main advantages of the sol-gel method are the guarantee of the stoichiometry and the lower temperatures used for the preparation of compounds which are necessary for the formation of nanostructured material. More details about the sample preparation can be found in the reference [3]. Part of the samples prepared without the radioactive probe nuclei were used for the X-ray diffraction measurements. A total of four samples were prepared for this work, three of them doped with 3%, 5% and 10% Fe respectively and one pure SnO_2 sample. The PAC measurements were performed using the gamma spectrometer consisting of four BaF_2 detectors in the temperature range of 150 K to 325 K. The SnO_2 sample doped with 10% of Fe was measured by the Mössbauer spectroscopy at room temperature.

3.Experimental Results and Discussion

The X-ray diffractograms of the SnO_2 samples doped with Fe are shown in figure 1. The X-ray diffraction analysis confirmed the well-known rutile structure of the compounds. The doping of SnO_2 with transition metal did not change the crystal lattice. The average particle size was deduced from the XRD line broadening using Scherrer's equation [8]. The calculated values are 7 nm, 4 nm and 3 nm respectively for the SnO_2 samples doped with 3%, 5% and 10% Fe.

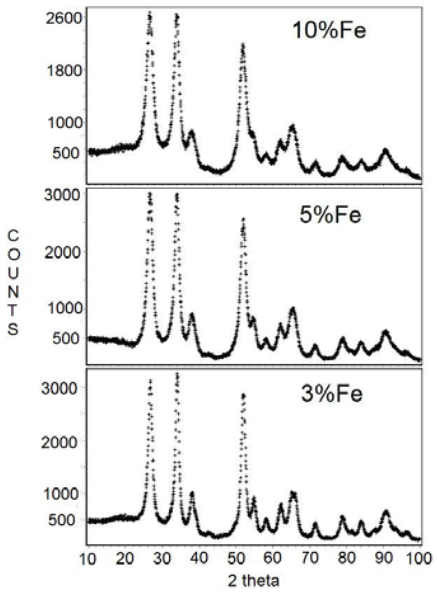

Figure 1. X-ray diffraction patterns of SnO_2 doped with Fe.

The PAC spectra for the sample doped with 3% Fe measured at different temperatures are shown in figure 2. The experimental results were analyzed using a combined electric quadrupole and magnetic dipole interactions and showed two different sites for the probe nuclei. The major fraction (60%) was identified with the probe nuclei occupying regular Sn sites [3] and show magnetic interaction. The quadrupole frequency for this site remains practically unaltered (ν_Q ~120-128 MHz) in the temperature range 100-325 K, which is in agreement with the earlier observation [3]. In this case, the magnetic frequency and the correspondent magnetic hyperfine field B_{hf} decreases with increasing temperature as shown in figure 3. For the measurement at 150 K the observed value is ν_m ~15 MHz (B_{hf} ~7 T). The magnetic frequency drops to nearly zero at about 325 K. The minor fraction most probably is due to the probe nuclei in the interstitial sites or defects. The electric quadrupole frequency for this site also changes very little (ν_Q ~147-150 MHz) between 100 K-295 K. The sample doped with 5% of Fe does not shows magnetic interaction. The electric quadrupole interaction shows parameters similar to those of the sample doped with 3% of Fe. The quadrupole frequency for the regular Sn site remains practically constant (ν_Q ~115 MHz) while for the minor fraction the quadrupole frequencies vary in the range 120-160 MHz between 100 K-295 K.

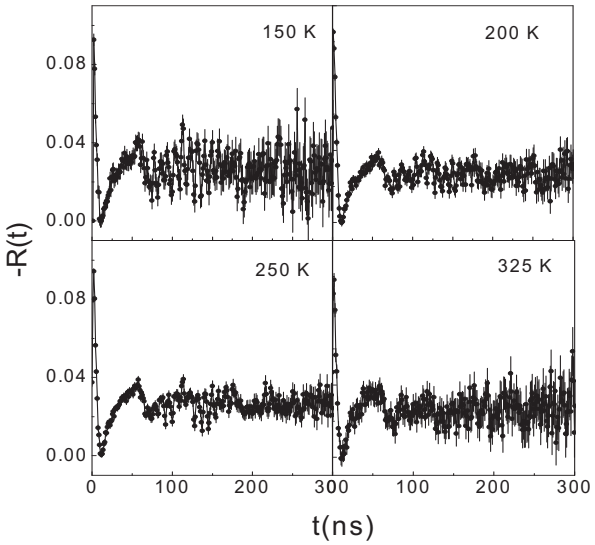

Figure 2. PAC spectra of SnO_2 samples doped with 3% Fe. Samples annealed at 773 K

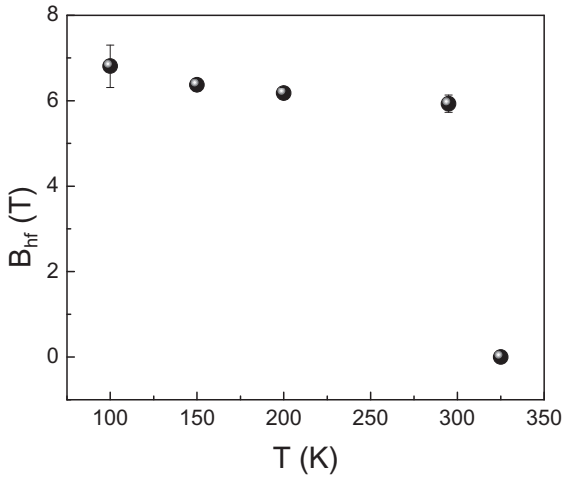

Figure 3. Temperature dependence of the magnetic hyperfine field B_{hf} for SnO_2 doped with 3% Fe

The sample doped with 10% of Fe was measured by the Mössbauer spectroscopy at room temperature. The measurements were made during almost one week due to low concentration of ^{57}Fe isotope in the samples (10% natural iron) besides the high probability of gamma absorption due to presence of Sn in the sample. From the results of the Mössbauer spectra shown in figure 4 one can infer that there is no magnetic interaction. The observed doublet indicates that no FeOx phase was formed which would show a sextet. This fact also indicates that iron is in the substitutional sites in the sample. From the analysis of results one observes two sites with different quadrupole interactions: Q_1= 0.40 mm/s (f = 48%) and Q_2= 0.97 mm/s (f = 52%). Both quadrupole interactions indicate Fe as Fe^{+3} since the observed isomer shifts (IS) of 0.2670 mm/s and 0.2190 mm/s respectively are typical for Fe^{+3} ion. One can therefore rule out the possibility of the presence of Fe^{+2}, which has larger IS of the order of 1.01 mm/s. It can be concluded that in this case, doping replaces the Sn^{+4} with Fe^{+3} in the crystal lattice. The sharper quadrupole doublet would correspond to the Fe^{+3} in substitutional Sn sites while the other wider doublet is due to a distortion of the structure of SnO_2 introduced by the Fe substitution. These results partially agree with previous measurements of Mossbauer spectroscopy in Fe-doped SnO_2 samples of thin film [5] and powder nanoparticles [6]. Both works observed similar quadrupole interactions which agree with our results, however both papers report the occurrence of magnetic interaction with fraction of 23 % for 14% doped film with 190 nm thickness [5] and 5% doped nanoparticles with 20 nm average size [6]. For the nanoparticles it was observed that the ferromagnetism vanishes with the increase of the annealing temperature when going from 350 ºC to 600 ºC [6], which disagrees with thin films results for 507 ºC annealing. These works also report different values for TC, 610 K for thin films [5] and 850 K for nanoparticles [6]. Comparing our results to the previous results we can conclude that the magnetic properties of Fe-doped SnO_2 are strongly sample dependent.

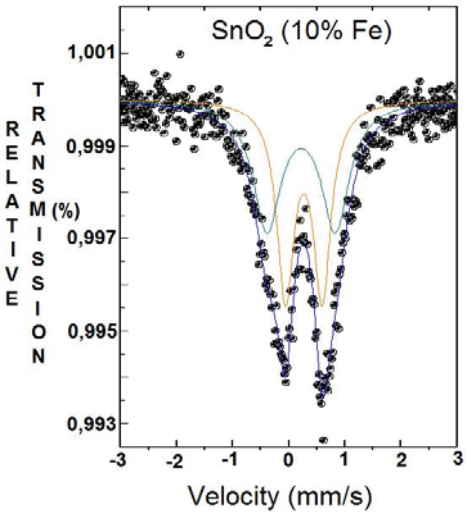

Figure 4: Mössbauer Spectrum for SnO_2 (10% Fe) at room temperature.

The PAC results reveal therefore a week magnetic interaction not seen before [3] in the pure SnO_2 sample, in the non substitutional site. This interaction is caused probably by the formation of defects. These defects were induced by changing the methodology of sample preparation (changing the acid that dissolves the Sn).

4.Conclusion

Sample characterization by XRD reveals nanostructure of the samples and the doping of SnO_2 with Fe does not change the crystal lattice. In all PAC measurement, two distinct electric quadrupole interactions were observed. One of them with (ν_Q ~ 120 MHz) was assigned to the substitutional site [3]. The second interaction is characterized by a widely distributed frequency and may be associated to interstitial sites or defects. The results show a weak

magnetic interaction in the sample doped with 3% of Fe. The Mössbauer spectrum shows only electric quadrupole interaction in the sample doped with 10% of Fe. We conclude that the weak magnetism found using PAC spectroscopy may be assigned to the defects produced during the sample preparation.

ACKNOWLEDGMENT

A.W.C. and R.N.S. thankfully acknowledge the financial support by CNPq in the form of research fellowships. J.M.R. acknowledges the graduate fellowship provided by CNEN. M. S. C. acknowledges the financial support from (CAPES). Partial support for this research was provided by the FAPESP and CNPq. Scientific collaboration of Centro Brasileiro de Pesquisas Físicas (CBPF) is thankfully acknowledged.

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