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Implantation of cobalt in SnO_2 thin films studied by TDPAC

Juliana Schell,[1,2] Doru C. Lupascu,[2] Artur Wilson Carbonari,[3]
Ronaldo Domingues Mansano,[4] Thien Thanh Dang,[5]
and Reiner Vianden[5]
[1]*European Organization for Nuclear Research (CERN), CH-1211 Geneva, Switzerland*
[2]*Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany*
[3]*Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, 05508-000 São Paulo, Brazil*
[4]*Escola Politécnica, Universidade de São Paulo, 05508-010 São Paulo, Brazil*
[5]*Helmholtz-Institut für Strahlen- und Kernphysik, Universität Bonn, Nussallee 14-16, 53115 Bonn, Germany*

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Here we report time differential perturbed angular correlation (TDPAC) results of Co-doped SnO_2 thin films. Making use of stable Co and radioactive ^{111}In implanted at the Bonn Radioisotope Separator with energies of 80 keV and 160 keV, respectively, it was possible to study the dopant incorporation and its lattice location during annealing. The hyperfine parameters have been probed as a function of temperature in vacuum. Two quadrupole interactions were observed. At high temperatures the dominant fraction for the probe nuclei can be assigned to the Cd-incorporation at the cation substitutional site in a highly disordered structure, obtained after implantation, to high crystallinity for the measurements at 873 K and 923 K. The similarity in TDPAC spectra obtained in undoped SnO gives indirect evidence that In and Co diffuse to different depths during the annealing process. Other interpretations will be discussed. [http://dx.doi.org/10.1063/1.4983270]

INTRODUCTION

Tin dioxide is used as gas and humidity sensor, transparent electrodes for solar cells, varistors, optoelectronic devices, capacitors, flat-panel displays, as high capacity anode in lithium-ion batteries, and many other electronic devices.[1–3] SnO_2 is an n-type semiconductor with high chemical stability, optical transparency in the visible region and a band gap of 3.6 eV.[1–3] It has been reported that tin dioxide would be an excellent candidate for diluted magnetic semiconductors (DMS) when doped with cobalt.[4] DMS are a new class of semiconductor materials that have been intensively studied in recent years due to enormous technological potential. Interestingly, Fitzgerald et al[4] reported, using Mössbauer Spectroscopy, that the Co-doped (5%) bulk samples were paramagnetic at room temperature. However, Misra et al.[5] studied powder samples doped with different concentrations of cobalt using electron paramagnetic resonance, and reported both a ferromagnetically ordered component and isolated paramagnetic Co^{2+} ions incorporated into the SnO_2 lattice. In our previous work,[6,7] using time differential perturbed angular correlation (TDPAC) spectroscopy, we observed no ferromagnetism for Co-doped powder samples with concentrations in the range of (2-5%). However, there are several works reporting ferromagnetism at room temperature in Co-doped SnO_2 thin films. Gopinadhan et al.[8] observed a considerable ferromagnetic moment in thin films doped with 10% of Co, which were produced by spray pyrolysis. Ogale et al.[9] reported ferromagnetism for the films doped with 5% of Co with a giant magnetic moment of 7.5 ± 0.5 μB/Co with Curie temperature close to 650 K. This was the highest value reported for potential DMS. Apart from our previous works,[6,7] there are no other TDPAC investigations in Co-doped SnO_2 samples. Unfortunately, observation of ferromagnetism in wide band gap oxides is not a consensus yet, mainly because central issues of uniformity and reproducibility have not been solved so far. Some authors claim that the observed ferromagnetism is due to different sources other than intrinsic magnetism[10] in similar systems. Since intrinsic ferromagnetism was not observed in undoped SnO_2 in our previous work, we report here TDPAC measurements on Co-doped SnO_2 thin films.

TIME DIFFERENTIAL PERTURBED ANGULAR CORRELATIONS

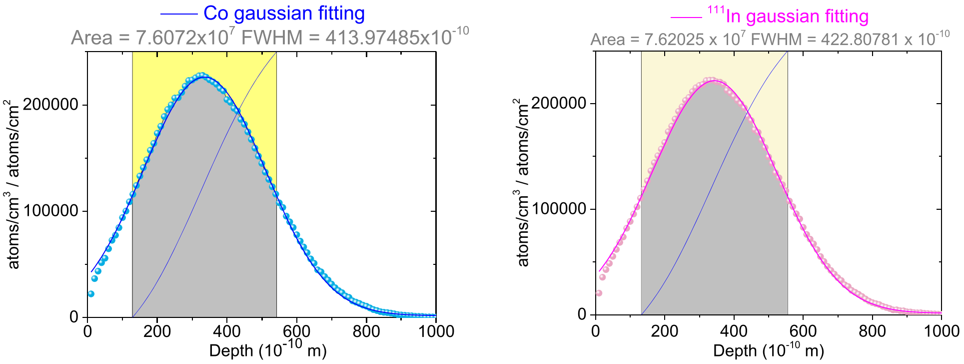
TDPAC is a very sensitive technique that provides information about hyperfine interactions of a radioactive probe nucleus placed on a particular atomic site of the crystal. While the energy separation of the nuclear sublevels can be directly measured by the resonance process in Mössbauer spectroscopy and nuclear magnetic resonance, the precession frequency is measured in the TDPAC experiment. Inherently, the precession frequency is determined from the observed modulations of perturbed gamma-gamma angular correlation spectra providing information about electric and magnetic hyperfine fields generated by the electronic and ionic environment of the probe nuclei. In addition, the axial asymmetry of the electric field gradient (EFG) tensor or deviations from it are described by the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. Moreover, the major component of the EFG tensor V_{zz} is obtained from the observable spin dependent quadrupole frequency ω_Q, which is given by the equation 1.

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \tag{1}$$

with Q being the nuclear quadrupole moment and I the nuclear spin. Here we present the electric quadrupole interactions in terms of the lowest transition frequency ($\omega_0 = k\omega_Q$), where k = 6 for a half integer spin and k = 3 for an integer spin. Further details about the TDPAC technique can be found in Refs. 11 and 12. In this paper we focus on electric hyperfine interactions, since there is no clear evidence of magnetism involved in our studies.

EXPERIMENTAL

SnO_2 thin films were-deposited on Si (1 0 0) p-type wafers using sputtering. A 0.05 T magnetic field was applied to the target 10 cm away from the Si wafer substrate using the processing gases Ar (99.999%) and O (99.998%). The substrate temperature did not exceed 363 K during deposition. The thin films were implanted with Co at the Bonn Radioisotope Separator with an energy of 80 keV and 1.5 x 10^{16} atoms/cm^2 fluency, which corresponds to 10 % in atoms (related to the peak concentration in the implantation profile). Finally, ^{111}In(^{111}Cd) was implanted at 160 keV and no annealing was carried out before the TDPAC measurements. The implantation profiles are displayed in the Figure 1.



(a) (b)

FIG. 1. Implantation profile of ^{59}Co (a) and ^{111}In (b) as a function of depth obtained by SRIM simulations for implantation energies of 80 keV and 160 keV, respectively. Gaussian functions were fitted to the data points (lines) to determine the area and FWHM.

RESULTS AND DISCUSSION

Figure 2 displays the TDPAC spectra measured as a function of temperature without previous thermal treatment. Spectra were fitted by a model considering that probe nuclei occupy two site fractions with pure electric quadrupole interactions, hereafter identified as site 1 and site 2. The sequence of the spectra corresponds to the sequence of measurements, and, with this, a structural rearrangement is observed at 573 K. Therefore, it is verified that defect recovery starts at 573 K, implying a decrease in the asymmetry parameter of the site 2.

By increasing the measurement temperature, it is observed that at 873 K the structure is reordered so as to resemble the structure observed in the spectra of both the thin film of SnO without dopant and that of the non-doped SnO_2 powder sample.[6,7,13–15]

Figure 3 shows subsequently TDPAC spectra at 873 K and 923 K intercalated with measurements at room temperature, so that the sequence of the spectra corresponds to the sequence of measurements. The amplitudes of the spectra decrease in the measurement at room temperature (295 K) as observed after the measurements in high temperature (873 K and 923 K). The hyperfine parameters are displayed in Figure 4. With the reduction of the amplitude of the spectra at 295 K, a lower value for the fraction of the site 1 is observed. No magnetic hyperfine interaction is observed.

To help the discussion, the hyperfine parameters obtained will be quoted by simple "EFG". The sites 1 or 2 are distinguished by EFG_1 and EFG_2, respectively. Interestingly, the hyperfine parameters show an irreversible but progressive behavior indicating this process is due to a cumulative, maybe incomplete, thermal effect of defects recovery. The parameters shown in the zone B are related to the completely disordered crystalline structure. After partial recovery of implantation defects at 573 K, in the zone C, the frequency distribution of EFG_1 and EFG_2 parameters decrease monotonically, as conventionally expected. The minor fraction could be assigned to defects, an effect of having often internal strain which can lead to a distribution of damped EFG_2.

Interestingly, the quadrupole frequency for nuclei at site 2 is similar to those reported before for probes at Sn sites in the SnO structure in thin films.[14] However, the same parameter for site 1 is quite smaller than those reported for probes at Sn-sites in SnO_2 and SnO.[6,7,13–15] The EFG_2 ($V_{zz} = 8.5 \text{ x } 10^{21}$ V/m^2 and $\eta = 0.56(6)$) at 923 K can be associated to a charged state of rutile in SnO[13,14] (with 1 electron added to the whole super cell). For comparison, on the V_{zz} calculation we used the old Q value of 0.83(13) b.[16] However, the current one is 0.683(20) b.[17] Such differences in the hyperfine parameters are ascribed to the presence of defects caused by Co impurities at the

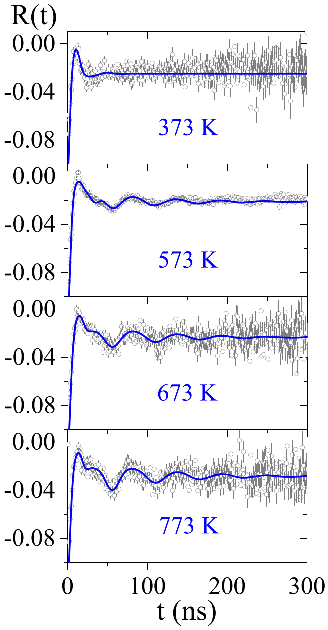


FIG. 2. TDPAC spectra of Co-doped SnO_2 thin film as a function of temperature using ^{111}In(^{111}Cd) as probe nuclei.

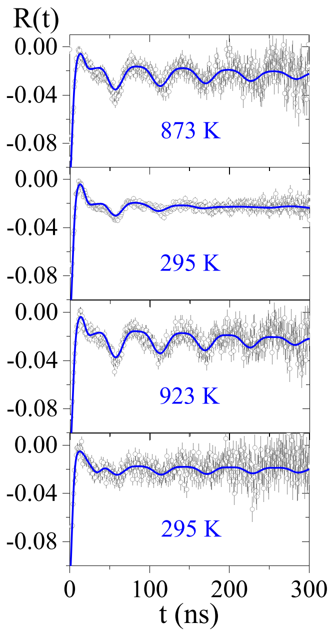


FIG. 3. TDPAC spectra of Co-doped SnO_2 thin film as a function of temperature using $^{111}In(^{111}Cd)$ as probe nuclei.

second nearest neighbor site of probes. The investigation of the defects in tin dioxide is not new because of the variety of technological applications of this semiconductor. In the dioxide form, the charge state of tin is Sn^{4+}, but Co can have two possible charge states Co^{2+} ($3d^7$) and Co^{3+} ($3d^6$). It influences the defects production and is favourable when more oxygen vacancies are introduced in the sample, since defect chemistry of SnO_2 may play an important role for the ferromagnetic properties. However, defects are difficult to control in sample preparation. In the case of bulk samples, there are not as many defects as in thin films. There is no evidence of ferromagnetism through the hyperfine parameters, even with the presence of defects caused by implantation. Nevertheless, observation of ferromagnetism in diamagnetic oxides is not a consensus yet, mainly because central issues of

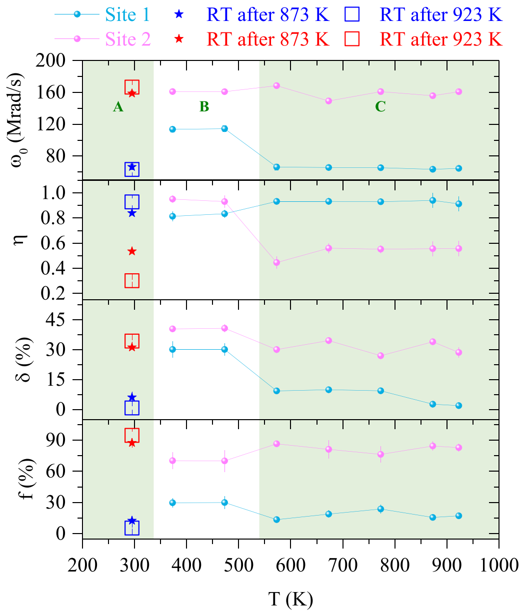


FIG. 4. Graphic representation of the hyperfine parameter temperature dependence. Solid lines are a guide to the eye and the shaded areas define zones (A, B, C) of different states of rutile.

uniformity and reproducibility have not been solved so far. Regarding the observation of the damped EFG at room temperature, it can be consistently assigned to dynamic interactions.

Even with the absence of ferromagnetism, the electrical properties of metal-doped SnO_2 are relevant for a plenty of applications, such as optical and electro-optical devices[18] related to the telecommunication or optical storage industry.[19] Metal doping appears in this concept to tailor the optical bandgap achieving an adequate absorption band in addition to a high specific surface area. There are relevant properties for photocatalysts.[20]

CONCLUSIONS

In summary, we have considered a two-fractions fitting model with probes interacting with two main EFG_1, EFG_2 distributions. One of them presents hyperfine parameters similar to those on non-doped SnO samples. Interestingly, since no annealing has been done prior to the TDPAC measurements, the EFG parameters show an irreversible but progressive behavior indicating this process as due to a cumulative, maybe incomplete, thermal effect of defects recovery. It is verified that defect recovery starts at 573 K, implying a decrease in the asymmetry parameter of the site 2. We have shown that there is no evidence of ferromagnetic ordering under the measurement conditions. However, we don't discard the possibility that In and Co diffused to different depth zones during the measurements, then not coexisting in the sample volume. Future self-diffusion measurements[21] would be helpful and are foreseen. Additional TDPAC measurements using ^{111}In co-implanted with ^{111m}Cd by overheating the transfer line of the ISOLDE target,[22] would allow to study more closely the formation or trapping of defects, such as oxygen vacancies as a function of temperature.

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