EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

Local investigation with radioactive probe of wide band gap oxides thin films doped with transition metals.

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Abstract

We intend to apply radioactive ion implantation techniques to wide band gap oxides doped with transition metals. Perturbed Angular Correlations will be used, to locally investigate properties regarding defects, electron density and magnetic interactions. With specific experiments we aim to advance in fundamental research, which can be used to optimize manufacture procedures of devices while strengthening the collaboration between synergetic institutes.

Requested shifts: 3 shifts, (split into 2 runs over 1 year)

Introduction and motivation

Semiconductor and insulator oxides can be used in several technological applications such as gas sensing (important in environmental monitoring and public security)[1], as highkappa dielectric material for metal-oxide–semiconductor field effect transistor (MOSFET) devices in microelectronic industry [2] and as a promising candidate for spintronic material [3]. However, in order to be successfully used in such applications, these oxides must form nanostructured materials such as thin films with specific characteristics. The smaller systems are more important where the control of the electronic properties of their materials become critical, once defects, doping concentration as well as the extension of surface and interfaces are inversely proportional to the film thickness. In many materials is their active surface, for instance, that presents the interesting properties for some technological applications. In other cases, the material's performance is strongly affected by the interface between the film and the substrate. Therefore, preparation of high quality nanostructured materials requires characterization techniques capable to distinguish different regions inside the material at the atomic scale. Local techniques such as perturbed gamma-gamma angular correlation (PAC) spectroscopy are suitable for a precise and detailed characterization of nanoscopic materials. In this investigation we will focus on semiconductor oxides which can be used as the base material for three important technological applications: gas sensors, dielectric material and spintronics.

The effective gate insulator SiO_2 thickness of MOSFET devices has been continuously reduced to meet the scaling requirements of ultra-large-scale integrated technology. With scaling, however, in order to avoid severe short channel effects SiO_2 must be reduced to the point that leakage current becomes unacceptable. Therefore, a replacement for SiO_2 must be found [4]. HfO_2 has received attention as alternative high-k gate dielectrics for SiO_2 gate oxide in Si-based CMOS devices [5], mainly because it has a higher dielectric constant of approximately 16–45 and as a result, has been applied in both 45 and 32 nm technology nodes [6,7], which has stimulated further research to modify HfO_2, by doping with other elements, for instance, and optimize its electrical properties for possible application in more advanced CMOS technology.

In parallel, semiconductor oxides are also promising materials for another important field in the next-generation microelectronics: spintronics, which has triggered the intensification of significant research on exploring the possibilities of inducing ferromagnetism (spin functionality) in otherwise non-magnetic semiconductors by doping dilute concentrations of magnetic impurities therein. Consequently, over the past ten years or so, the field of ferromagnetism in dilute magnetic semiconductors (DMSs) and dilute magnetic oxides (DMOs) has developed into an important branch of materials science. Although most extensive research in this field has been done on two wide band-gap functional n-type metal oxides, namely TiO_2[8] and ZnO[9], several other transition-metal doped semiconductor oxides have been also studied such as SnO_2[10], In_2O_3[11,12], CeO_2[13]. Lastly, another important application of semiconductor oxides is for gas sensing, in which semiconducting metal oxides have attracted the attention of environmentalist and many others[14-16]. The principle of semiconducting metal oxide gas sensors is based on surface-chemical interaction between gas molecules and the sensor material. Chemical adsorption of oxygen under ambient conditions creates extrinsic surface acceptor states that repel conduction band electrons. Gases with reducing properties affect the amount of adsorbed oxygen; thereby changes in the electronic conductivity can serve as measurable quantity for the presence and concentration of reducing target gases[17]. Among several semiconducting oxides, SnO_2 has been intensively studied as a sensor material, which sensing performance can be enhanced by metal doping[18].

Proposed studies

a) Tin oxide

Despite the many investigations, the origin and control of ferromagnetism in DMSs and DMOs is the most controversial research topic in materials science and condensed-matter physics today. Room-temperature ferromagnetism has been reported by substituting transition elements in semiconductor hosts such as ZnO and TiO_2 [8_9]. However, a few authors have not observed ferromagnetism in the same series [19-21]. Among candidates for DMO, SnO_2 is an attractive semiconductor with a wide band gap and optical transparency in the visible region. Thin-film samples of SnO_2 doped with Fe[22] and Ni[23] were reported to exhibit room-temperature ferromagnetism. SnO_2 thin film doped with Co not only exhibit ferromagnetism with a Curie temperature close to 650 K, but also a giant magnetic moment of 7.5 μB/Co[24]. Furthermore, the possibility of using the magnetic properties of gas sensing materials instead of their conventional electrical features has increased the scientific and technological interest in dilute magnetic semiconductor nanosized oxides, especially in SnO_2. This is because, while conventional gas sensors based on nanopowder systems face some challenges in making electrical contacts and accurate measurements of the electrical responses, the monitoring of the magnetic responses of these nanostructured gas sensing materials shows no need for electrical contacts, somehow simplifying the manufacturing of devices. Therefore, in CERN our intention is to study thin films of SnO_2 doped with Fe, Co or Ni in order to investigate the occurrence of room temperature ferromagnetism and the possibility of formation of other phases with the dopant. We intend to use soft landing of ^{111}Cd or ^{117}In probes and PAC measurements to investigate the surface of films, where is expected to occur the magnetic order.

b) Hafnium oxide doped with Fe or Co

Doping HfO_2 with rare-earth element changes electronic structure, improve crystallization temperature, stabilize the high temperature cubic or tetragonal phase to room temperature, and suppress the formation of oxygen vacancies [25,26]. In collaboration with an existing LOI INTC-I-087_LOI87, we intend to complement their experiments with PAC measurements in Fe-doped HfO_2 film carried out by the IPEN group in São Paulo where previous experiments showed a fraction with a very small quadrupole frequency, which is an indication of a cubic phase. We intend to perform PAC measurements with ^{111}Cd or ^{117}In at CERN implanted in HfO_2 doped with Fe and also with Co films on silicon substrates in order to investigate the formation of the cubic phase, which it is likely to be near the silicon interface.

Summarizing, only at CERN-ISOLDE will it be possible to perform further investigations on semiconductor oxides doped with magnetic elements using, in particular PAC probes for which the measurements are carried out on the implanted element without elemental transmutation (^{111m}Cd/^{111}Cd) to be compared with results obtained with standard PAC probes, e.g., ^{111}In(^{111}Cd). Our priority of using the CERN facilities are for the following samples: 1) SnO2 thin film doped with Fe or Co or Ni; 2) HfO_2 thin film doped with Fe or Co, using (^{111m}Cd/^{111}Cd), ^{111}In(^{111}Cd), and ^{117}Cd(^{117}In) probes and subsequent PAC measurements.

Thin film sample preparation

High quality thin film samples will be prepared by electron beam evaporation in IPEN and by magnetron sputtering in the Engineering College at São Paulo University, where they will be further characterized by x-ray diffractrometry (XRD) and scanning electron microscopy (SEM). Samples will be also prepared by magnetron sputtering in CBPF, Rio de Janeiro. All samples will be characterized by Rutherford backscattering (RBS) in the Physics Institute of São Paulo University.

Summary of requested shifts:

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We estimate the total amount of ISOLDE beam time needed to accomplish the above-described tasks to be 3 shifts, distributed according to table I:

Table I: Beam time request

Required isotope	Implanted beam	PAC experiment	Intensity [at/μC]	Target / Ion source	Comments	nº of shifts
^{111m}Cd	^{111m}Cd	$\gamma-\gamma$	10^8	molten Sn, plasma		1
^{117}Cd	^{117}Ag	$\gamma-\gamma$	10^8	UC$_2$, RILIS (Ag) UC$_2$ – only used with surface ionization (In)	Nb or Ta ion source cavity to decrease In surface ionization contamination for Ag. Any UC2 target using W or Ta transfer line can be used for In.	1
^{111}In	^{111}Cd	$\gamma-\gamma$	10^8			1

All of our beam times consist of collections to be measured off-line and can in this way be easily shared with other users. We stress the particular case of the ^{111m}Cd beam time, where collections should run day and night with a period of about 4-5 hours between collections that usually last for 15-30 min. There are actually four PAC setups co-shared during beam times and the samples can be implanted on the same collective sample holder used with other users which are also doing PAC experiments.

For these PAC experiments, the number of implanted atoms per sample range from $5{\cdot}10^8$ up to 10^{11}, depending on half-lives, coincidence efficiency and on the fluence limit for proper recovery of the implantation damage. All isotopes will be collected in the general-purpose implantation chambers at GLM and/or GHM new collection point at the ISOLDE hall, building 170. All $\gamma-\gamma$ PAC measurements will be performed off-line, outside the ISOLDE hall, in the new Solid State Laboratory in building 115.

Several furnace systems exist already at ISOLDE for annealing treatments under vacuum or gas flow at atmospheric pressure at the new SSP lab.

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• Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	**Availability**	**Design and manufacturing**
SSP-GLM chamber	☒ Existing	☒ To be used without any modification
Existing equipment on the solid state labs in building 115 and 275 - 6 detector PAC standard setups - annealing furnaces - glove boxes	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed SSP-GLM chamber and building 115 installations.

Additional hazards:

Hazards	*SSP-GLM*	*Building 115*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]		
Vacuum	10-6 mbar at SSP chamber 10 during collections		
Temperature	295 K, room temperature collections		
Heat transfer	-		
Thermal properties of materials	-		
Cryogenic fluid		Liquid nitrogen, 1 Bar, few litres used during the PAC measurements on appropriate dewar	
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			
Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☒ Produced at ISOLDE 111mCd (48m) 117Cd(2.5h)	Sources to be measured at 115 and 275 r-011	
• Sealed source	☒	22Na sources provided by RP services at CERN, used at 115 and 275 r-011	
• Isotope	111mCd (48m) 117Cd(2.5h)		
• Activity	111mCd (48m) < 3 e 7 Bq 117Cd(2.5h) < 8 e 6 Bq		
Use of activated material:	none		
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			

Non-ionizing radiation			
Laser	none		
UV light	none		
Microwaves (300MHz-30 GHz)	none		
Radiofrequency (1-300MHz)	none		
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful		Acetone (ICSC: 0087), ethanol (ICSC: 0044) and methanol (ICSC: 0057). Less than few centilitres per chemical, used on cleaning samples on ventilated fume hood on building 115. The respective ICSC forms have been printed and will be handled during preparation and experiments.	
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]		
Mechanical			
Physical impact or mechanical energy (moving parts)	[none]		
Mechanical properties (Sharp, rough, slippery)	[none]		
Vibration	[none]		
Vehicles and Means of Transport	[none]		
Noise			
Frequency	[frequency],[Hz] Ambient noise at the ISOLDE Hall, building 170		
Intensity	Ambient noise at the ISOLDE Hall, building 170		
Physical			
Confined spaces	[none]		
High workplaces	[none]		
Access to high workplaces	[none]		
Obstructions in passageways	[none]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or	

	fume houses on building 115 r-007	fume houses on building 115 r-007	
Poor ergonomics	[none]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

There is no additional equipment with relevant power consumption on these small-scale experiments.