

Nanostructured thin layers of vanadium oxides doped with cobalt, prepared by pulsed laser ablation: structure, chemistry, morphology, and magnetism

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ABSTRACT

Cobalt-doped vanadium oxide thin layers prepared by pulsed laser ablation are investigated by (i) X-ray photoelectron spectroscopy, (ii) the local atomic order by X-ray absorption near-edge structure (XANES), (iii) the morphology of the films was investigated by atomic force microscopy (AFM), and (iv) magnetic properties were quantified by magneto-optical Kerr effect (MOKE). In most cases, the chemical composition of the host matrix was found to be the vanadium (5+) oxide V_2O_5 at the sample surface and lower ionization states (+2 and +3) in the bulk. Co ions are found either in high ionization state Co^{5+} (for samples synthesized in high vacuum condition, denoted by VO1), or with Co in lower ionization states Co^{4+} (for samples synthesized in a mixture of argon and oxygen atmosphere, denoted by VO2). Consistent information was obtained from chemical shifts from individual core level scans in XPS, compared with existent data in literature, and the amplitude of the pre-edge peak in XANES, which is a sign of quadrupole $1s \rightarrow 3d$ dipole-forbidden transition and whose amplitude is proportional to the number of $3d$ vacancies per atom. AFM revealed big particles with sizes $> 100 \mu m$ for VO1 samples, whereas smaller nanoparticles with sizes ranging between 20 and 30 μm were observed for VO2 samples. VO1 samples presented very high coercitive fields with a relatively low saturation magnetisation at room temperature, whereas VO2 samples presented double-loop hysteresis curves, indicating the coexistence of exchange bias between two kinds of magnetic moieties with strong anisotropy.

Keywords: vanadium oxide; pulsed laser deposition; XPS; XAFS; magnetic properties

1 INTRODUCTION

The synthesis of Diluted Magnetic Semiconductors (DMS) is amongst the outstanding results of the last two decades in materials physics [1,2]. The last years (2003-2007), diluted magnetic semiconductors were successfully synthesized based on (nonmagnetic) transition metal

oxides (ZnO , TiO_2) doped with magnetic ions (Cr-Ni). Recently, also our group succeeded PLD synthesis of cobalt doped ZnO which has shown definite room temperature ferromagnetism (manuscript in preparation).

In DMS, magnetic ordering is produced between isolated magnetic ions via the double exchange or RKKY interaction [3], where the magnetic ions interaction is mediated by the charge carriers from the matrix. Hence, possibility of control of magnetic ordering via the density of the charge carriers is provided by these systems. A wide range of applications may be foreseen starting with this phenomenon, such as induced ferromagnetism by light irradiation [1], DMS based spintronic devices [2], ferromagnetism control *via* applied electric fields, particularly the possibility of domain wall displacement by varying the charge density. A novel application was demonstrated in the possibility of ferromagnetic ordering *via* molecular adsorption at surfaces [4], by using carriers donated by molecular species for mediating ferromagnetism by double exchange.

This Contribution deals with investigating the possibility of synthesis of materials where magnetic ions are isolated in matrices which exhibit Mott-Hubbard metal-insulator transition (MIT) [5]. The chosen host materials are in this study vanadium oxides, where MIT can be achieved at temperatures interesting for applications, in the range $-50 \text{ }^\circ\text{C}$ up to $+60 \text{ }^\circ\text{C}$ [6,7]. Indeed, first explorations revealed interesting magnetic properties, such as uniaxial magnetic anisotropy or persistent orbital currents on materials starting with doped vanadium oxide [8]. The practical realization of such materials would open controlling possibilities of the ferromagnetic ordering occurrence through the strong variation of charge density following the Mott-Hubbard transition from the insulating to the metal state.

2 EXPERIMENTAL

The materials were synthesized by pulsed laser deposition (PLD) in NILPRP Magurele. The targets were synthesized by sintering a mixture of vanadium oxide (VO_2) and cobalt oxide (CoO), in various proportions.

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Pulsed laser deposition was performed by using an excimer laser (KrF) with fluence of 9 J/cm^2 , in controlled atmosphere: (i) in vacuum ($10^{-5} \text{ mbar} = 10^{-3} \text{ Pa}$); (ii) in oxygen atmosphere ($10^{-3} \text{ mbar} = 10^{-1} \text{ Pa}$). Depositions were realized on single crystal Si(001) and quartz SiO₂(001). Substrates were heated during deposition, in order to improve crystallinity and to avoid the formation of macroscopic droplets.

X-ray photoelectron spectroscopy (XPS) was performed by using a VG-ESCA MK II installation of NIMP Magurele with Al K_α radiation and a hemispherical electron analyzer with 100 mm radius, operating at pass energy of 100 eV for overview spectra, and at 50 eV for individual core level spectra. Room temperature magneto-optical Kerr effect (MOKE) measurements were performed in NIMP Magurele by using a MOKE system with He-Ne laser radiation and a pizoceramic modulator. X-ray absorption fine structure (XAFS: EXAFS and XANES) measurements were performed at the Doris storage ring facility in Hasylab, Hamburg, Germany (Al beamline), by using a Si(111) double crystal monochromator. The measurements on Co-doped vanadium oxide thin layers were performed in fluorescence mode by using a Si:Li detector and selecting the channels corresponding to the fluorescent radiation of interest (Co or V K_α). For consistent data interpretation, standards of metal Co and of Co(II)O were measured in the same run, in transmission mode on a 5 μm Co foil for the metal and of a pressed pellet of CoO powder mixed with cellulose. Atomic force microscopy (AFM) was performed in the University of Iasi by using a home-made equipment.

3 RESULTS AND DISCUSSIONS

Although several investigations were performed, in the following we discuss mainly on the differences presented

by samples prepared in high vacuum conditions (10^{-5} mbar) and in oxygen atmosphere (10^{-3} mbar).

3.1. X-ray photoelectron spectroscopy (XPS)

Figure 1 presents overview XPS spectra on the two samples of interest (VO1, synthesized at 10^{-5} mbar and VO2, prepared at 10^{-3} mbar). One notices the presence of V, O and Co photoelectron and Auger electron signals, and of carbon contamination from the inherent contamination layer. A first observation is that the carbon contamination visibly decreases when the synthesis is performed in oxygen atmosphere; at the same time, in this case, the Co 2p, V 2p, and O 1s signals show noticeable increases.

One observes also the presence of Cu and, for the VO1 sample, of Zn - but this is connected to the copper or brass plates on which the samples were mounted. The most intriguing result here is the presence of the N 1s level in both samples. Usually, this level does not come from the contamination layer. Therefore, it may be inferred that in this case nitrogen is present in the sample itself. The integral amplitude of this level is $4,5 \pm 0,5 \%$ from the oxygen level. Therefore, it may be inferred that the synthesized samples are nitrogen doped from the very preparation moment.

Figure 2 presents the V 2p and O 1s core level electron distribution curves (EDC). One notices that there is no observable chemical shift between both samples. The resulting binding energies (BE) are 17,64 eV for V 2p_{3/2}, 525,16 eV for V 2p_{3/2}, and 531,0 eV for O 1s. Also, the O 1s spectrum contains a "shoulder" due to the oxygen from the contamination layer, at BE of around 533 eV, corresponding to oxygen in ionocovalent bindings C=O, C-OH, etc. The position of the principal O 1s component from the EDC is close to the reported value in literature for O²⁻. With the levels of vanadium, we have performed a complete analysis of the reported data in literature.

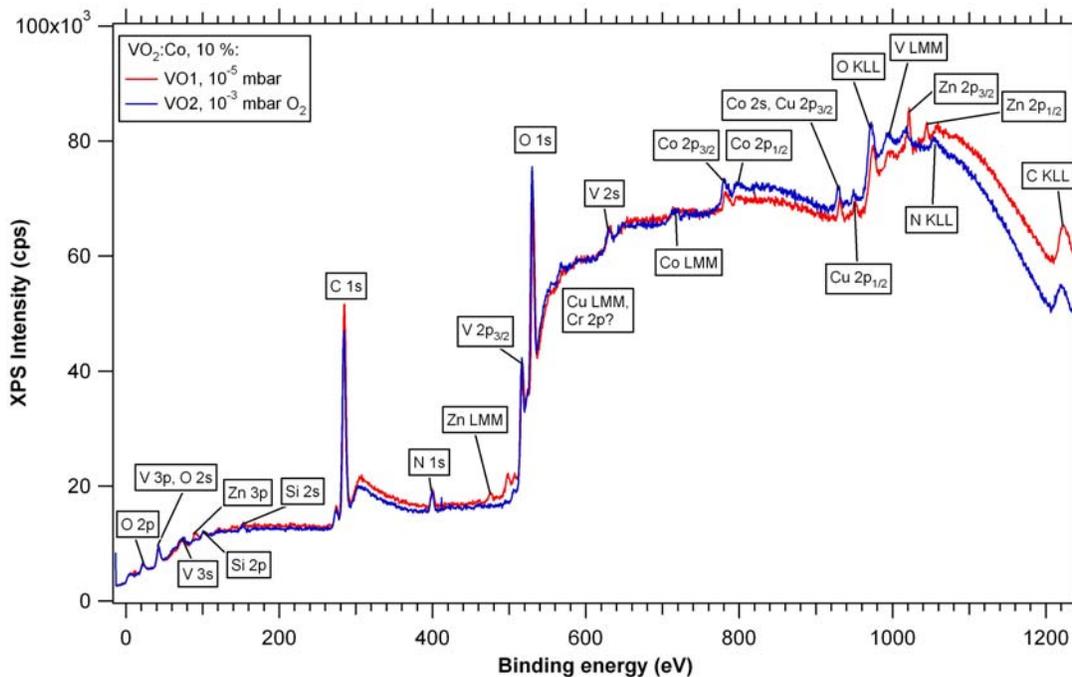


Figure 1: overview XPS scan of the two samples of interest VO1 and VO2, synthesized at different oxygen pressures.

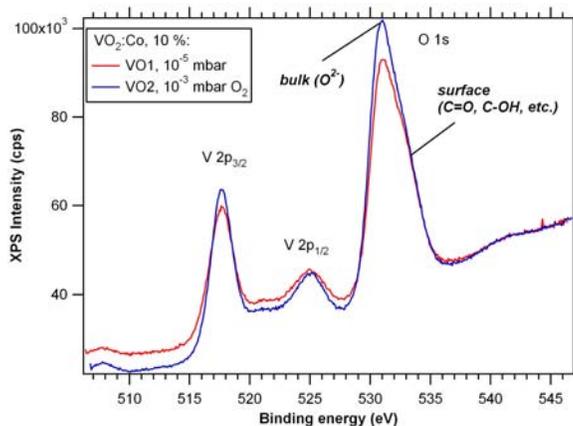


Figure 2: V 2p and O 1s EDC on samples VO1 and VO2

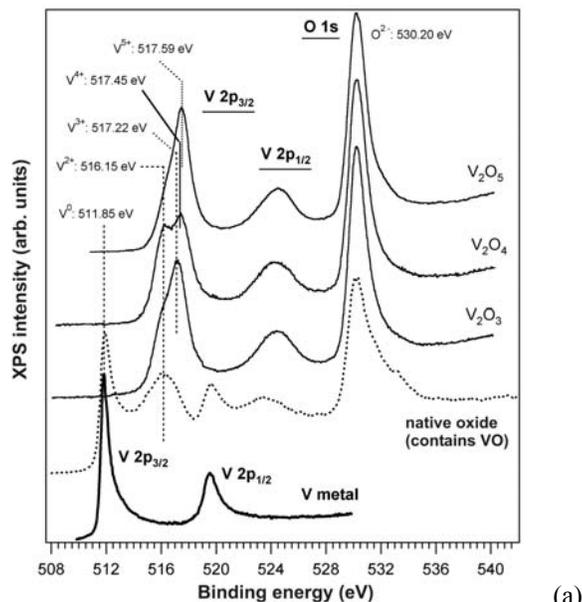


Figure 3: V 2p and O 1s EDC on several vanadium oxides (a)

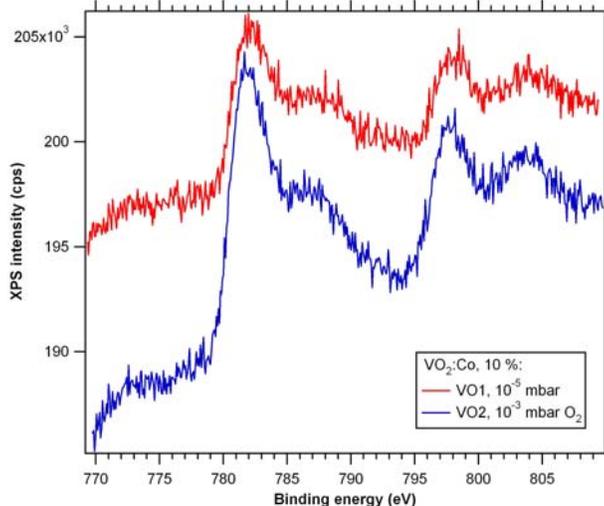


Figure 4: Co 2p EDC for VO1 and VO2

Figure 3 shows the analysis of the V 2p data from different vanadium oxides, as vanadium exist in several oxidation states, from (II) to (V). The data are extracted from Ref.

[9]. By comparing these data with the experimental BE derived from Fig. 2, one may infer the presence of vanadium in a (+5) ionization state, therefore by forming the compound V_2O_5 . This result is a bit deceiving, since this compound does not present Mott-Hubbard transition.

Figure 4 presents the Co 2p EDC for both samples. Comparing with data from literature [9], cobalt here is found in a (IV-V) ionization state; the ionization state seems to be a bit lower when the sample is prepared in oxygen atmosphere (+4.7 for VO1, +4.3 for VO2).

3.2. X-ray absorption near-edge spectroscopy

Figure 5 presents the V K-edge XANES on both samples. From the analysis of the pre-edge region, where dipole forbidden transitions $1s \rightarrow 3d$ manifest [10], one derives the average number of 3d vacancies and hence the vanadium oxidation state. From Figure 5, different ionization states may be inferred for vanadium, namely +5 for VO2 and around +2 (+3) for VO1, which corresponds to vanadium (II) or VO, and to vanadium (III) or V_2O_3 . A similar compound is actually identified in the vanadium native oxide on surfaces in vacuum (see Fig. 2) and was recently evidenced for thin films prepared by using a plasma atomization source [11].

This result seems to contradict XPS results, but one has to take into account that the investigated depth is around 1-2 nm in XPS owing to the photoelectron escape depth [12], whereas in X-ray absorption recorded in fluorescence mode, the investigated depth is several hundreds of nm (up to micrometer range). Therefore, although at the surface vanadium pentoxide is formed in both cases, by varying the oxygen pressure one may succeed to synthesize vanadium oxides with V in lower ionization states, such as VO or V_2O_3 , which exhibit Mott-Hubbard transition.

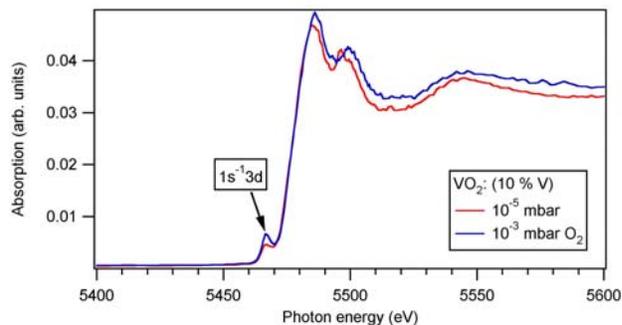


Figure 5: Vanadium K-edge X-ray absorption near-edge structure (XANES)

3.3. Magneto-optical Kerr effect investigations

Figure 6 presents MOKE hysteresis loops obtained on both samples. Sample VO1 exhibits a strong (super) paramagnetic behaviour, with superposed a weak ferromagnetic component with strong coercive field,

suggesting the presence of two magnetic phases: one which is superparamagnetic (might originate from vanadium oxide aggregates), the other being a kind of DMS (cobalt ions interacting by double exchange). The hysteresis cycle obtained for sample VO2 suggest the occurrence of a strong anisotropy, superposing a ferro- and an antiferromagnetic phase, possibly interacting by exchange bias [8,13]. Due to the lack of space, we shall not discuss here AFM data; we just mention that these images support the co-existence of two distinct phases in both kind of samples (isolated nanoparticles in VO1, percolated nanoparticles in VO2).

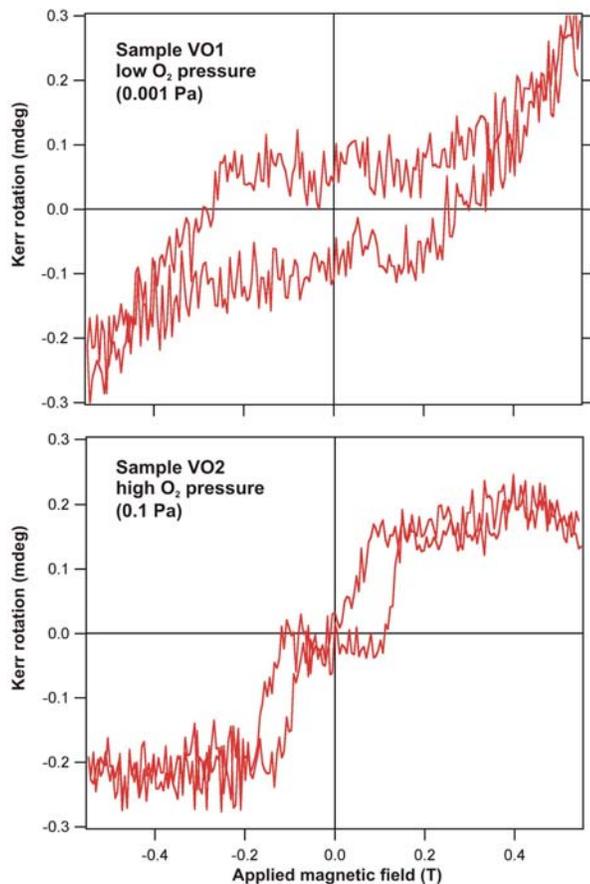


Figure 6: Magneto-optical Kerr effect

4 CONCLUSION

Very first results have been presented, by correlated reactivity and chemical composition measurements (XPS) with electronic structure (XANES), magnetism (MOKE) and morphology (AFM) for samples formed by magnetic ions embedded in a Mott-Hubbard material (vanadium oxide). We identified composition variations between surface and bulk of materials; the bulk composition seems to be tunable through preparation parameters. Promising ferromagnetic behaviour is observed, also dependent on the preparation conditions. It

is suggested that the VO2 hysteresis loops might be connected to the percolation threshold of nanoparticles evidenced by AFM, whereas the ferromagnetic phase from VO1 might be connected to the presence of vanadium suboxides (VO, V₂O₃) which provide carriers for intermediating ferromagnetism and hence is a true DMS behaviour.

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