Co/ZnO nanorods system for magnetic gas sensing applications

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***Abstract*— The ideal chemical gas sensors would provide a device capable of being sensible, selective and stable. To improve the state of the art metal oxide gas sensors two approaches are pursued: obtaining nanosized, single crystalline metal oxide nanorods, and introducing innovative transduction principle. The first approach ensures high surface area for gas interaction coupled with the higher stability. The second approach could overcome limitations on the performances achievable and set a new milestone in the field. In this work magnetic gas sensing tests were carried out, using a MOKE (magneto-optical Kerr effect) magnetometer, showing that it is possible to exploit a new mechanism for sensing devices. The sensing layer, based on Co layer covered by ZnO nanorods, was entirely deposited by RF sputtering. The device showed very good H_2 detection at room temperature. The current work focuses on the characterization of the sensing heterostructure based on Co/ZnO nanorods by volumetric magnetization measurements and by MOKE measurements in air and in gas. A model for H_2 sensing is also formulated.**

Keywords—gas sensor; cobalt; ZnO nanorods; H_2; MOKE

I. INTRODUCTION

Metal oxide gas sensors are used since many decades to detect a gas species at high working temperature. High working temperature is needed to promote gas reaction with the oxygen ionosorbed over the semiconductor, inducing a variation in the resistance of the material [1]. A strategy to improve the sensing surface is to use nanosized materials like nanowires, nanorods and nanoparticles [2]. Indeed high temperature operation could raise the problem of the thermal stability of the sensing layer and of ignition of fuels when detecting explosive species. Hydrogen, for example, can explode when mixed with atmospheric oxygen at concentration of 4% (LEL, Lower Explosive Limit). Thus room temperature detection is very important.

Our previous work showed that it is possible to develop a magnetic gas sensor, based on a metallic-ferromagnetic Co layer covered with and coupled to semiconducting ZnO nanorods (NRs), to detect H_2 at room temperature [3]. The transducer signal is acquired by using magneto-optical Kerr effect (MOKE) magnetometer, a technique that is surface sensitive, and thus influenced by reaction taking place on the semiconductor surface. The current work clarifies several aspects of the investigated sensing phenomenon by comparing the measurements taken by MOKE with volumetric magnetization measurements of a Co layer covered by the ZnO NRs. The sensing layer structure (Co thickness and ZnO nanorod layer) was also engineered with respect to the previous one to obtain better sensing properties.

The heterostructured Co/ZnO NRs developed here differs from the wide research reported in literature on dilute magnetic semiconductors (DMS), i.e. wide band gap semiconductors doped with transition metals, like Fe, Co or Ni. The previous research is focused on obtaining a ferromagnets working at RT [4] or antiferromagnet like hematite [5]. In both cases they are impracticable to use as gas sensors since they need very large applied magnetic fields (of the order of kOe) to obtain efficient gas sensing. Magneto optical approach has been used in Surface Plasmon resonance sensors to enhance VOC detection [6], with a different system (TiO_2 and Au/Co/Au).

The current work also presents a simplified model explaining H_2 sensing.

II. EXPERIMENTAL

A. Sensing layer deposition

The sensing layer was realized entirely with RF magnetron sputtering system. A Co layer was deposited onto the 3 × 3 mm^2 Al_2O_3 substrates at RT. The thickness of the Co layer was varied between 115nm and 150 nm. To protect the Co layer, from oxidation in air, a 50 nm thick ZnO thin film was deposited at RT, with a RF power of 50 W at $7x10^{-3}$ mbar. Then we deposited a seed layer of Sn at 400°C, that acts as a catalyst for the subsequent growth of the ZnO nanorods. ZnO NRs grows from Sn seeds at 400°C: the power was varied from 200 to 100 W, with a pressure of 10^{-2} mbar. Deposition time was varied from 5 to 15 minutes. Annealing in ambient air for 20 minutes was carried out at 300°C to stabilize oxygen coverage of ZnO before sensing.

B. Characterization and sensing measurements

The heterostructured layers were characterized by SEM microscopy, Raman and photoluminescence spectroscopy.

Magnetization loops were measured at room temperature (RT) by means of a sensitive Alternating-Gradient Field Magnetometer (AGFM) operating in the ±15 kOe field range.

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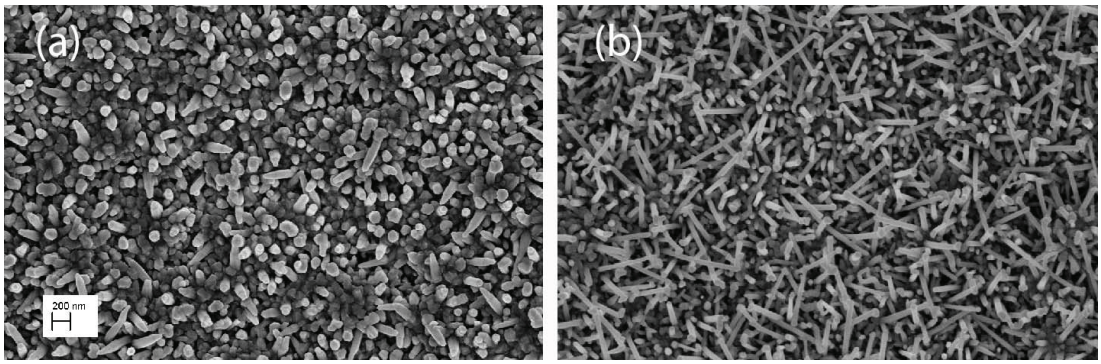

Fig. 1. : SEM image of the top surface of ZnO NRs. The NRs covers densely the Co underlying layer. (a) Power 200W; (b) Power 150W.

The diamagnetic contribution given by the probe and the substrate were subtracted from the measured signal.

For sensing measurements at RT we used MOKE magnetometer in longitudinal geometry, i.e. with the applied magnetic field lying on the plane of the sample and of the incident and reflected light, using an *s*-polarized He-Ne laser (633 nm). The light is linearly polarized and passes through an optical chopper which modulates its intensity at a frequency of 400 Hz. The light reflected from the sample, passes through a second crossed polarizer, rotated close to the extinction. The Kerr signal is recorded through a Si photodiode and a lock-in amplifier. The electromagnet used allows to apply a maximum magnetic field of 50 Oe. The magnet and the samples are fitted into stainless steel chamber with gas inlet and outlet. A quartz window ensures easy access for optical measurements. Gas carrier was humid air at 50% and gas used was H_2.

III. RESULTS AND DISCUSSIONS

Figure 1 reports the SEM image of two sensing devices, showing the morphology difference between ZnO NRs deposited at 200 W and 150 W RF power: in both cases we observe a dense coverage of Co layer by ZnO NRs. For 200 W growth condition (a), the NRs emerge mostly vertically from the surface, while few of them are tiled. For 150W growth condition (b) the NRs are thinner and longer and mostly they are tilted randomly with respect to the surface. The diameter is around 80 nm (200 W) and 50 nm (150 W). The ZnO NRs are polycrystalline.

Figure 2 (Left) reports the volumetric magnetization measurements of the Co layer covered by the ZnO NRs. It shows strongly anisotropic magnetization curve reflecting a predominant in-plane anisotropy. The coercivity higher than in MOKE measurements [3], reflects an higher vertex field H_{max} (15 kOe). In-plane hysteresis loop (Figure 2-Right) reveals the presence of two magnetic phases contributing in the magnetization process, as evidenced by the presence of two maxima in the dM(H)/dH curve (inset refers to upper branch of M(H)).

The setup used for MOKE characterization in presence of gases is shown in Figure 3: the MOKE technique offers the great advantage to be surface sensitive, therefore the measured signal is not affected by paramagnetic and diamagnetic contributions of the substrates, seen in the AGFM measurements. The RT magnetic gas sensing properties of the Co/ZnO NRs can thus be evaluated by measuring the saturation magnetization (M) in air and in gas for different concentrations of H_2 (up to 400 ppm in dry air). Data in Figure 3 Right reports the relative response of the system to hydrogen $[MM_s(air)-MM_s(gas)]/MM_s(air)]$, showing linear correlation between response and H_2 concentration in this range.

We formulated an itinerant-electron model that explains the observed reduction of Co magnetization with H_2 concentration. The interaction of H_2 is expected to be by physisorption interaction with oxygen species on the surface of ZnO, that releases electron into the metal oxide conduction band.

The Co density of states (DOS) is spin-splitted around the Fermi energy E_F; only the spin-up 3-d sub-band is completely filled: Spin-up and spin-down electrons (per unit volume of Co) generated by reaction in the ZnO layer are equal in number. Spin-up electrons entering Co will populate the s-electron sub-band only, while spin-down electrons can populate both the s-electron and the d-electron sub-bands. The d-electron sub-band has a much higher DOS at the Fermi level (E_F). As a consequence, most of the electrons entering Co populate the spin-down subband; spin-up electrons released by the ZnO layer and not entering Co remain in the semiconducting layer where they thermalise (i.e., one half of their initially up spins quickly reverses).

The Fermi energy of Co increases by dE_F owing to the dn electrons generated by the reaction and entering the metal; dE_F is proportional to dn. The magnetization of Co is reduced by a quantity dM because the increase in spin-down electrons acts to reduce the difference between majority and minority electrons. A linear relation is expected between dM and dn. An increase of H_2 concentration brings about an increase of dn and a stronger effect on the magnetization of Co.

IV. CONCLUSIONS

In this work we investigated a new transducing mechanism for RT gas sensing of hydrogen which involves an heterostructure of Co layer protected and covered by a ZnO NRs. The preparation by RF sputtering prevents oxidation of

the Co layer thus ensuring good properties of the magnetic interface, while the ZnO NRs take care of interaction with gas species. The surface area of the NRs can be easily modified by varying preparation conditions, as well as the Co thickness.

Volumetric magnetization measurements showed that in-plane magnetization is obtained and that there are two magnetic phases contributing in the magnetization process.

The sensing tests indicated that H_2 detection is linearly proportional to H_2 concentration. The reduction of Co magnetization with H_2 concentration was explained by a increase of the Fermi energy of Co owing to the dn electrons generated by the reaction of H_2 with ionosorbed oxygen and entering the metal.

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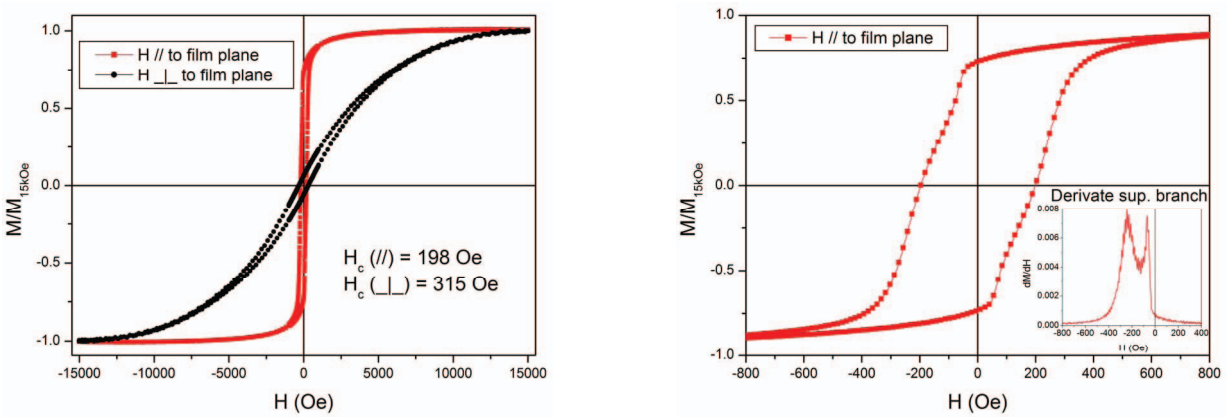

Fig. 2. (Left) Hysteresis loops measured by Alternating Gradient Force Magnetometer (AGFM); (Right) In plane hysteresis loops ; Inset: first derivate of the superior branch.

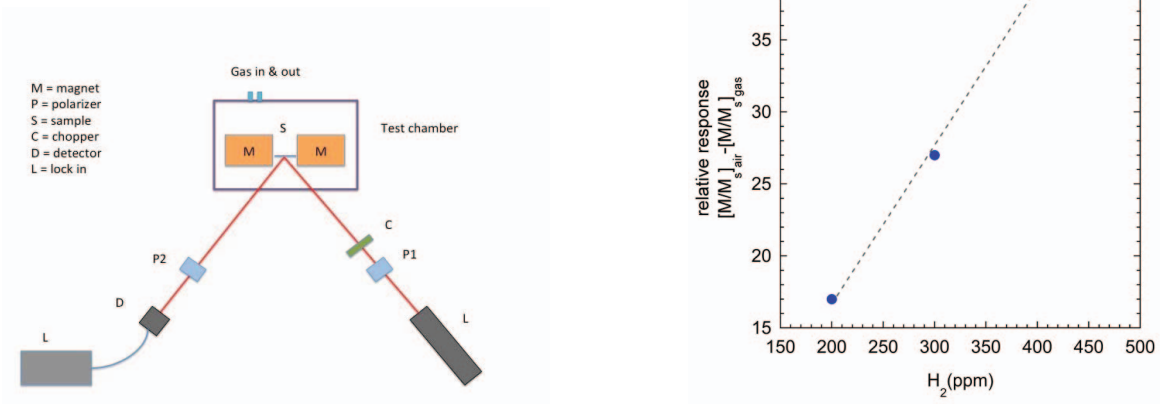

Fig. 3. (Left): Scheme of MOKE setup for measurements with gases; (Right) Relative response of Co/ZnO NRs to H_2 at RT.