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Functional nanostructured oxides

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ABSTRACT

This contribution reports on novel physical properties of specific oxides in their nano scaled configuration. This includes the ultrafast optical limiting of VO_2 thin films, the magneto-optical tunability of the ESR response of α-Cr_2O_3 nano-spheres, and the reversible control of the surface tension of ZnO oriented nano-rods as well as the validation of the synthesis of high crystalline stoichiometric of rare earth nanostructures by the so called local gas feeding beam pulsed laser deposition.

1. Introduction

As defined by Woodword et al. and in addition to the series of major literature [1–18], binary or multi-component metal oxides play a significant role in several fields, including inorganic and materials chemistry, solid state physics, materials science, electrical engineering and recently the trans-disciplinary field of nanosciences/nanotechnology. The significance of metal oxides resides in their variety, their chemical stability, and their diverse chemical as well as their physical properties. Metal oxides display rich properties ranging from piezoelectricity, multiferroicity to superconductivity, from negative thermal expansion to super-ionic conductivity. Metal oxides are used as optical coatings, transparent conducting electrodes, gas sensors, and catalysts among the large variety of applications. They are full integrated components in Lithium ion batteries, fluorescent lights, and fuel cells. An important focus of the scientific community is to understand the origin of the properties of the various oxides and to learn how to manipulate them via modification of their composition, crystal structure, their defects and recently their size as well as their shape at the nanoscale. This requires an understanding of the electronic band structure, which, on the one hand, is the link between composition and crystal structure and on the other hand with the chemical and the physical properties. The optical and electrical transport properties can be understood directly from the electronic structure. The chemical reactivity and catalytic properties depend upon the energy levels and symmetry of electronic states near the Fermi level. Even the dielectric and mechanical properties can be traced to the chemical bonding that is the origin of the electronic structure.

Vanadium dioxide (VO_2), α-phase of chromium oxide (α-Cr_2O_3), zinc oxide (ZnO) and rare earth oxides (RE_2O_3) are attracting further interest in view of their multi-functionalities in their nanoscaled form. VO_2 which is a special oxide exhibits a pure 1st order phase transition. Indeed, as reported recently [19], the photo-induced phase transition by femtosecond laser pulses in VO_2 has allowed to shed light not only the so long disputed nature of the transition itself (electronic or phononic), distinguishing hence the Mott–Hubbard like transition from the electron trapping in homopolar bonds. The dynamic and the duration of such a phase transition were found to be of about 180 fs [19]. This 1st order phase

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transition characteristic of VO_2 at about 68 °C, makes it an optical coating candidate of choice for ultrafast optical switching devices [21], field effect transistors and electro-optical gates [22] as well as ultrafast tunable nano-plasmonics among others [23,24] as well as optical limiting in the IR spectral region [25]. As demonstrated by Sasaki et al. [31], chromium (III) oxide, α-Cr_2O_3 is considered as a potential candidate in the quest for magnetic materials which can be applied in ultrafast magneto-optical switching [27–30]. This later target in the case of α-Cr_2O_3 is based on several specific characteristics of such an oxide [31–39]. Due to its multi-functionality, ZnO is an additional peculiar oxide [40]. Recently, Ngom et al. have reported an interesting behavior of highly oriented ZnO nano-rods in terms of optical control of their surface wettability [41]. In addition to the three above mentioned oxides, RE_2O_3 structures in their nano-scaled configuration are gaining more interest and are expected to play an important role in the emerging high κ-based nano-electronics and nano-phosphors.

This contribution reports on (i) novel nonlinear properties of nano-structured VO_2 thin films as ultrafast optical limiter, and (ii) magneto-optical tunability in α-Cr_2O_3 nano-spheres, (iii) as well as reversible control of the surface tension of ZnO oriented nano-rods, (iv) in addition to the validation of the synthesis of high crystalline stoichiometric of RE_2O_3 nano-structures by the so called local gas feeding pulsed laser deposition.

2. Nano-structured VO_2 and ultrafast optical limiting

Within the thermochromic vanadium based family there are several optically active vanadium oxides among which VO, V_2O_3 and VO_2. These later oxides are known for their metal/insulator–semiconductor (M/I–S) phase transition characteristics and hence exhibiting effective changes in their electrical resistivity at specific temperatures [26,42–47]. This noteworthy characteristic makes them optically active under external stimuli such as temperature, pressure, or light. One should single out vanadium dioxide (VO_2) which exhibits a singular ultrafast 1st order type phase transition at the vicinity of ~67.8 °C with several orders of change in the electrical resistivity due to its strong electron correlation behavior. Such a large electrical resistivity modulation as a function of temperature is accompanied by a reversible M/I–S transition. This latter behavior causes a remarkable reversible change in the optical response, specifically in the infrared region. From theoretical point of view, this phase transition has been, initially, interpreted in terms of Mott–Hubbard like transition [48] or electron trapping in homopolar bonds. The very recent ultrafast spectroscopy investigations shed-lighted, on how fast is such a phase transition as well as on the electronic band structure changes [18,19]. Using a femtosecond laser pump-probe geometry, the relaxation processes in VO_2 substantiated that the light-induced phase transition was as fast as the laser pulse duration of 100 fs itself. As shown in Fig. 1, possible mechanism in relation to the phase transition is likely to be due to changes in the 3d band structure correlated to the crystal structure changes. More precisely, the upper d||—an unoccupied in conduction band of semiconductor phase is within the broad π*-band which is empty, but more strongly hybridized with oxygen 2π-orbitals and lies above the Fermi level E_F. In the metallic phase, however, all 3d-bands are close to Fermi-level. Upon the laser excitation, the main transitions related to ultrafast light-induced phase transition are from occupied d||-valence band to unoccupied d||–π* mixed conduction band followed by resonant transitions to unoccupied excited states of metallic phase. As a result the screening of the charge transfer by conduction electrons in metallic phase takes place by ultrafast laser excitation. The additional complementary recent work of Lysenko et al. [20] indicated that upon a laser excitation, an instantaneous

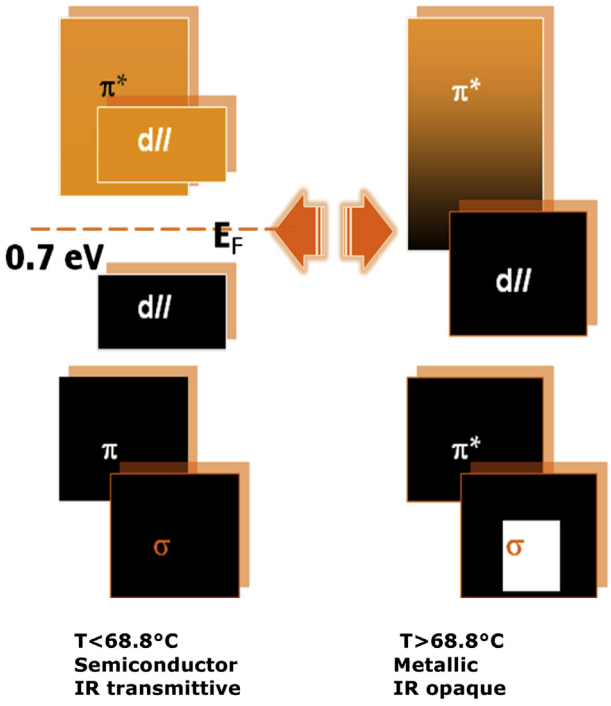

Fig. 1. Reversible opening/closing of the VO_2 band gap versus external thermal stimuli such a temperature.

response in the transient reflectivity and transmission was observed followed by a relatively longer relaxation process. The observed phase transition has been then associated with the optical interband transition in VO_2. This singular phase transition characteristic of VO_2 at about 68 °C, makes it an optical coating candidate of choice for smart windows applications [47,49], thermal sensors [50], optical switching devices [43], field effect transistors and electro-optical gates [22] as well as ultrafast tunable nano-plasmonics among others [24,25]. This contribution reports on ultrafast optical limiting of pulsed laser deposited VO_2 films in the IR spectral region; more specifically at 1.064 μm.

The reversible semiconductor–insulator/metallic transition of VO_2 is followed by a reversible optical transition which would be translated by a significant reversible modulation in the refractive index and dielectric constants ε(ω). The temperature dependence of the standard real and imaginary parts have been calculated. The limit dielectric constants ε(0) and ε(∞) for bulk VO_2 are 43 and 10.0 in the dielectric regime, respectively, and 18.3 and 9.0 in the metallic regime. In the near infrared, ε(ω) has values of approximately 8.64 and 5.7 in the dielectric and metallic states respectively.

From experimental point of view, the determination of the thermal variation of the dielectric constant ε(ω,T) and hence the refractive index n(ω,T) is ideally determined ellipsometry measurements. In this case, a Jobin Yvon–UVISEL spectroscopic ellipsometer with an attached temperature cell was used to characterize the optical properties of a set of VO_2 thin films deposited on glass substrates. The instrument is mainly composed of a Xenon source, a polarizer, an analyser, and a monochromator handling the dispersion and the selection of the wavelength to a photomultiplier. The ellipsometric measurements were performed at two incident angles: 70° (reflection) and 90° (transmission) as a function of the wavelength (spectral range 200–1600 nm) for various temperatures ranging from 30 to 85 °C. the ellipsometric angles ψ and Δ, which are respectively the amplitude attenuation and the phase