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Multifunctional oxide nanostructures by metal-organic chemical vapor deposition (MOCVD)*

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Abstract: The development of thin films, in the context of ongoing reduction in the size of electronic systems, poses challenging questions for the materials sciences of multifunctional nanostructures. These include the limits of size reduction, integration of heterogeneous functions, and system characterization or process control at an atomic scale.

We present here different studies devoted to perovskite oxide materials (or materials with derived structure), where in specific directions of the crystal structure the atomic organization decreases down to a few nanometers, thus building nanostructures. In these materials, very original physical phenomena are observed in multilayers or superlattices, nanowires (NWs) or nanodots, mainly because strain, surfaces, and interfaces play here a predominant role and can tune the physical properties.

Metal-organic chemical vapor deposition (MOCVD) routes have been used for the synthesis of oxide materials. We first introduce the basic rules governing the choice of metal-organic precursors for the MOCVD reaction. Next we discuss the principles of the pulsed injection MOCVD system. A laser-assisted MOCVD system, designed to the direct growth of 2D and 3D photonic structures, will also be described.

Selected case studies will finally be presented, illustrating the powerful development of different oxide nanostructures based on dielectric, ferroelectric, or superconducting oxides, manganites, and nickelates, as well as first results related to the growth of ZnO NWs.

Keywords: heterostructures; MOCVD; multifunctional oxide materials; multilayers; nanowires.

INTRODUCTION

In recent decades, the rapid miniaturization of microelectronic systems to the submicron scale, following Moores's law, has led to remarkable increases in computing power, while, at the same time, new processing technologies have enabled considerable cost reduction in device manufacturing. However, as the microelectronic industry advances toward ever smaller devices, it is now believed that physical factors of current top-down silicon technology will soon limit further advances. The size of elementary

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functions of devices reaches actually a few tenths of nanometers, and further size reduction implies the use of new materials (i.e., for gate oxides or integrated memories), which have to be introduced in the fabrication processes together with several new elements. The frontier of materials research will therefore be challenged by the development of material systems made up of new components with nanoscale dimensions and by the availability of technologies able to realize new material structures at the nanoscale.

Materials based upon these concepts began to emerge with studies of low-dimensional structures such as thin films and interfaces and now encompass a wide range of material research areas, from nanostructured particles to nanostructured composites, metamaterials, superlattices, and hetero-structures with different kind of building blocks (pillars, NWs, nanodots). These new artificial materials have specific properties which can be added and embedded with the classical transistor function to address new application fields: i.e., new technologies of energy, biotechnologies, sensors of different type... The key objectives in these developments are to tailor, at the nanoscale, novel material systems with radically new functionalities which are developed when the physical dimensions of the building blocks become lower than the critical length of an analyzed property (electron mean free path or diffusion length, tunnel distance, superconducting penetration depth, magnetic correlation length, etc.). This gives rise to new materials with enhanced properties based upon an improved understanding of materials nanostructures.

In this process, revolutionary breakthroughs rather than current evolutionary progress are required. A bottom-up approach, where functional electronic structures are assembled from chemically synthesized, well-defined building-blocks, has the potential to go far beyond the limits of top-down technology by defining key nanometer-scale metrics through chemical synthesis. The use of metal-organic chemical vapor deposition (MOCVD) as a generic technique for the synthesis of a large variety of building blocks can be a good solution to tackle several of these challenges; this technique was therefore largely employed in the present studies.

Among all the oxide materials, the oxides with a perovskite structure provide a wide spectrum of enhanced functionalities and have the potential to replace whole devices, thus having an enormous impact in today's modern world. These advanced smart materials have already started to find their way into industrial applications, but there are still immense possibilities to achieve improved functionalities by further tailoring and coupling their properties in many different areas, from dielectric, ferroelectric, piezoelectric, pyrolectric, and magnetic properties to photon- or phonon-sensitive devices.

Over the past 20 years, a remarkable range of new functions has been discovered and developed in perovskite oxides, including high-temperature superconductivity and colossal magnetoresistance. More recently, there has been a great interest in multiferroic oxides in which the coupling of different ordering phenomena (e.g., ferroelectricity and ferromagnetism) offers the potential for a new class of devices [1,2].

Actual research is mainly focused on the development and use of these perovskite oxide materials, with a quality comparable to that achieved in semiconductors. Phenomena related to interface studies, tunneling, polarization, matching with the semiconductor substrate, or strain engineering are key issues for the emergence of these materials.

In the present paper, we review a series of advanced studies dedicated to new artificial structures or metamaterials made up from different oxide building blocks.

The generic properties of the different perovskite oxides which have been used are reported in Table 1.

| High ε_r insulators | SrTiO ₃ | $ ρ \approx 1.1013 \Omega.\text{cm}, ε_r = 20000 (4 \text{ K}) $ |
|--------------------------------------|-------------------------------|---|
| Low $\varepsilon_{\rm r}$ insulators | LaAlO ₃ | $\varepsilon_{\rm r} \approx 25 \; (300 \; {\rm K})$ |
| Conductors | Sr_2RuO_4 | $\rho_{ab} \approx 1.\ 10^{-5}\ \Omega.\text{cm}\ (77\ \text{K})$ |
| Superconductors | $Y\bar{B}a_2Cu_3O_{7-\delta}$ | $\rho \approx 0$ |
| Semiconductors | doped SrTiO ₃ | |
| Ferroelectric | PbTiO ₃ | $Pr = 80 \ \mu C/cm^2$ |
| Ferromagnetic | SrRuO ₃ | |
| Antiferromagnetic | PrNiO ₃ | |
| Ferrimagnetic | PrFeO ₃ | |
| Collossal magnetoresistance | (La,Sr)MnO ₃ | |
| High thermal conductivity | LaCoO ₃ | |
| Catalysts | La(Ti,Cu)O ₃ | |

 Table 1 Selected perovskite materials and their properties.

All these perovskites have nearly the same in-plane cell parameters: $a \approx b \approx 3.9$ Å.

SYNTHESIS OF THIN FILMS AND NANOMATERIALS BY MOCVD: TOOLS AND METHODS

MOCVD is a technique very commonly used in Si technologies and in general in electronic device fabrication for the synthesis of thin films and coatings. This technique offers several potential advantages over other physical deposition processes:

- a high degree of control in stoichiometry, crystallinity, and uniformity;
- a versatile composition control; and
- the ability to coat complex shapes and large areas.

Molecular engineering of precursors

Effective access to functional metal oxide films by MOCVD requires volatile precursors that yield pure metal oxides on a desired substrate. These precursors used for chemical vapor-phase reactions should in general meet the following properties:

- They should have an evaporation rate which is large enough, stable and constant with the time.
- The precursor molecule should be chemically and thermally stable during the transport through the gas phase to the surface.
- They should be relatively to synthesize.
- They should not be dangerous and should not produce dangerous side products.
- In the case of droplet-derived deposition processes, they must be soluble and stable in a suitable solvent without formation of precipitates.

For CVD processes, precursors like halogenides, hydrides, or alcoholates have been used in electronic chip fabrication as long as only simple materials, derived from Si, where necessary to built the complete architecture of electronic devices [3,4]. Today the new concepts developed in electronic integration require the incorporation of a large class of new materials and new elements from the periodic system. Traditional precursors are no more adapted for all the new elements taken in consideration, as, for example, those of the group 2 of the periodic system (Ba, Sr, Ca). These elements are very electropositive and therefore have the tendency to form compounds with ionic bonds and low vapor pressure. To obtain precursors with large vapor pressure, it is necessary to use molecules with small intermolecular interaction energies. Since the work of Yamane [5], chelate compounds are the main candidates for such precursors. The basic compound of the chelates is the β -diketone, which exists in

two tautomere forms, the diketone and the enol form: $R'-C(=O)-CH_2-C(=O)-R$ (diketone), R'-C(-OH)=CH-C(=O)-R (enol), where R and R' are different organic ligands.

To date, metal β -diketonates, especially 2,2,6,6-tetramethyl-3-5-heptanedionate (thd), have mainly been used for MOCVD routes to perovskite oxides. Other complexes following the same behavior are also well adapted: that is the case for Ti(OⁱPr)₂(thd)₂ as a generic precursor for Ti (Fig. 1).



Fig. 1 Typical precursors of Sr and Ti used for the MOCVD of perovskite oxides.

The evaporation enthalpy ΔH is approximately equal to the binding energy between the precursor molecules in the liquid or solid. ΔH can be estimated by the formula [6]

$$\Delta H = -\frac{3kT}{\left(4\pi\epsilon_{o}\right)^{2}r^{6}} \left[\frac{\mu^{2}}{3kT} + \alpha_{o}\right]^{2} - \frac{3\alpha_{0}^{2}I}{4\left(4\pi\epsilon_{0}\right)^{2}r^{6}}$$
(1)

where *r* = distance between molecules, α_0 = polarizibility, *I* = ionization energy, μ = dipole of the molecule, *T* = temperature.

This formula explains qualitatively that:

- The absolute value of ΔH increases and the vapor pressure decreases when the dipolar moment between metal and oxygen increases (when their difference in electronegativity increases). We have, therefore: $p(Mg(thd)_2 < p(Cu(thd)_2) and p(Ca(thd)_2) < p(Pb(thd)_2))$.
- The ionic radius of the metal atom determines its distance to oxygen and the value of the dipolar moment $\mu = q \cdot d$ (q charge of the atoms, d distance between O and the metal atom). In the case of lanthanide complexes, the electronegativity differences are similar and the vapor pressure therefore decreases with increasing radius: $p(Yb(hd)_2) > p(Tm(thd)_2) > p(Er(thd)_2) > etc. > p(Sm(thd)_2) > p(Nd(thd)_2)$. A similar relation is found for the vapor pressures of thd compounds with elements from the 2nd group and for the acac (acetylacetonate) compounds of the 9th and 10th group where the radius increases from Mg to Ba, from Co to Ir, and from Pt to Ni.

The vapor pressure of chelates with large metal atoms (like Ba) can be modified by association effects. The formation of tetrameres $Ba_4(thd)_8$ is therefore possible. The association effects can be minimized by addition of further ligands, e.g., tetraglyme or phenentrolyne by the formation of Ba(thd)₂tetraglyme or Ba(tmhd)₂Phen₂ [7].

The size and the number of ligands determine also the vapor pressure. Large ligands can induce large London forces (last term in eq. 1). On the other hand, large molecules can produce a larger screening of the Coulomb forces. Al or Cr chelates illustrate the first case, where the vapor pressure decreases with the length of the ligand: $p[M(acac)_3] > p[M(thd)_3] M = Al$, Cr. But screening is probably more important in the case of Pb compounds: $p[Pb(acac)_3] < p[Pb(thd)_3]$.

The substitution of H by F, with a smaller polarizability and therefore small dispersion forces, increases the vapor pressure.

In injection MOCVD, a liquid precursor solution is needed and solid precursors are therefore associated with chemically compatible organic solvents (i.e., monoglyme, diglyme...). The final film

stoichiometry is adjusted by adjusting the respective concentrations of the precursors in the precursor liquid source [e.g., $Ba(thd)_2$ -triglyme, $Sr(thd)_2$ -triglyme, and $Ti(O^iPr)_2(thd)_2$ for BST films]. An active research is also performed on bi-metallic precursors, where the final stoichiometry of the desired compound is directly adjusted in the metal-organic precursor itself.

Film deposition engineering: The advantages of injection MOCVD

All films described in this survey were produced by injection MOCVD [8,9]. This technique is based on the computer-controlled injection of microdroplets of precursor solution into the evaporator system. The droplets are produced by means of a high-speed electro-valve. The frequency of the injection as well as the time of the injection can be adjusted so as to reach the appropriate growth rate for each deposited material (Fig. 2).



Fig. 2 Basic scheme of injection MOCVD deposition.

For microelectronic applications, specifically for digital applications and advanced circuits, compact homogeneous layers and multilayer structures with very flat surfaces are required. In view of the short critical lengths involved in new physical devices, only smooth surfaces on structurally "perfect" layers can allow planar technology, reproducible etching structures, and the achievement of small spreads of the device characteristics. Therefore, the surface quality is very important and the operating conditions must be adapted to preserve a clean and smooth surface for multilayer growth or superlattices. For this purpose, the thermodynamic driving force in CVD processes (supersaturation) has to be controlled. With increasing effective supersaturation and mass transport toward the substrate, one can observe changes in the growth-rate-limiting factors from surface kinetics driven processes to volume diffusion (2D or further 3D) growth processes. In heteroepitaxy also, the misfit between the substrate and the layer influences strongly the surface nucleation and the growth modes. Misfit reduces the possibility of layer-by-layer growth and enhances island formation (2D nucleation) [10]. Thus, the misfit acts in the same way as supersaturation. The strain caused by misfit may be relaxed by formation of dislocation or cracks, thus having an impact on the physical properties. In the specific case of microelectronic devices, slow growth rates (low supersaturation) and perfectly matching substrates have therefore to be used in general. For the growth of corrugated layers, island, or NW growth, radically different growth conditions have to be adapted.

In the case of multilayers, two separate precursor solutions are used—one for the first type of layer [SrTiO₃ (STO), $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), or $YBa_2Cu_3O_{7-\delta}$ (YBCO)] and one for the second layer [BaTiO₃ (BTO), STO, or $PrBa_2Cu_3O_{7-\delta}$ (PBCO)]. Therefore, two injectors are commonly used. The periodicity of the superlattices is simply regulated by changing the concentration in the starting solutions and the number of injections for each material. The growth rate of each superlattice is generally set around 1 Å/s by using an injection frequency of 1 Hz and an injector opening time smaller than 1 ms.

Post-annealing can play a crucial role in order to obtain the right oxygen stoichiometry and so to optimize the physical properties of the thin films and superlattices.

NANOMATERIALS AND NANOSTRUCTURES BY MOCVD

The following case studies illustrate typical results which have already been obtained on

- new artificial materials with tailored properties obtained by the combination of perovskite oxides building blocks;
- new metamaterials for photonic applications realized in a UV-assisted system; and
- oxide nanomaterials with a morphology controlled from 2D to 1D by mastering the MOCVD growth conditions.

Tailoring properties by the combination of perovskite oxide building bocks

Most perovskite oxides are correlated electronic systems, which offer a rich spectrum of physical properties such as superconductivity, ferromagnetism, ferroelectricity, semi-conducting, or metallic behavior. Such properties are present in compounds with the same crystal structure, allowing the engineering of new epitaxial multifunctional devices. The first part of this chapter is dedicated to demonstrate the different types of artificial structures that can be realized by combining different oxide building bocks.

As reported in Table 1, the perovskite materials have all a,b in plane lattice parameters close to the same value of 3.90 Å. The growth of superlattices along the *c*-axis of the perovskite structure is therefore possible since epitaxial conditions are fulfilled along this direction.

Several modulated structures have been grown by alternating, on a nanometer scale, different perovskite building blocks with intrinsic varying properties [8].

The superlattice period: $\Lambda = d_{ox1} + d_{ox2}$ (where d_{oxi} is the individual thickness of a building block) (Fig. 3) was characterized by X-ray diffraction (XRD) [9], X-ray photoelectron spectroscopy (XPS), or transmission electron microscopy (TEM) in correlation with the specific related physical properties.



Fig. 3 (a) Superlattice made of two different oxides. (b) High-resolution TEM image of a $(LSMO/STO)_n$ superlattice showing sharp interfaces between individual layers. (c) XRD pattern (Synchrotron) showing well-resolved satellite peaks characteristic of the superlattice period.

Growth of superlattices

 $(BTO/STO)_n$ superlattices. In order to study the feasibility of superlattices of different periodicity, films with a thickness ratio of about 3:1 of d_{STO} : d_{BTO} (in each bilayer) were deposited [13,14]. Even in the case of a periodicity of 4.0 nm, when the superlattice consists of 15 layers of 2.9-nm-thick STO and 1.1-nm-thick BTO sublayers, the first-order satellite peaks in XRD are still visible (as in Fig. 3c), thus proving that no interdiffusion between the BTO and the STO films occurs.

In order to study the influence of the different stacking thicknesses on the dielectric properties, superlattices with various periodicities were deposited. While keeping the thickness of the STO sublayer constant ($d_{\text{STO}} \approx 7.8 \text{ nm}$), the thickness of the BTO sublayer was increased from $d_{\text{BTO}} \approx 4.8 \text{ nm}$ to $d_{\text{BTO}} \approx 24 \text{ nm}$. In this way, one obtains multilayers with periodicities varying from 12.6 to 31.8 nm.

Dielectric measurements carried out on these samples qualitatively show only a weak temperature dependence of the dielectric constant over a wide range of temperature [1]. Furthermore, no typical Curie–Weiss behavior is observed at the temperatures where one would expect a decay of the dielectric constant. In general, these superlattices have lower losses than reported elsewhere [16].

 $(LSMO/STO)_n$ superlattices. Multilayers alternating manganites and ferroelectric materials $[(LSMO/STO)_n]$ were grown on LAO substrates [17–19]. The presence of satellite peaks reveal a good coherence over the stacking which is also confirmed by TEM cross-section images, where the perfect interfaces between adjacent layers extend on a very large scale (Figs. 3b and 3c).

Such multilayers or superlattices will be required for future spin electronic devices which challenge the present conventional electronics [20–22]. The ultimate goal will be to prepare devices that operate with a single, spin-polarized electron. Device concepts currently investigated for this purpose are:

- Spin valves consisting of two ferromagnetic (FM) layers of different coercive fields that are separated by an insulating (I) or a non-magnetic metallic spacer (M). Spin valves can be of both types: (FM/I/FM) or (FM/M/FM).
- Spin-polarized quasi-particle injection device based on a FM layer and a superconducting layer (HTS) electrically isolated: (FM/I/HTS).

 $(YBCO/PBCO)_n$ superconducting superlattices. In the case of superconductors, varying the thickness and the nature of the stacking components can artificially modulate the anisotropic nature of high T_c materials. The study of these artificially modulated structures can contribute to the understanding of the basic properties of high T_c superconductors. The superconducting superlattices which have been studied are: (YBCO/PBCO)_n. This structure is very convenient because of the direct material compatibility, which allows switching from a superconductor to a metal/semi-conductor/insulator, just by changing one element without structural change.

PBCO exhibits a semi-conducting behavior, with a 100 K resistivity close to 0.5 Ω .cm. YBCO is superconducting at 90 K with a resistivity $\rho_{(300\text{K})} = 150 \ \mu\Omega$.cm and a resistivity ratio $R = \rho_{(300\text{K})}/\rho_{(100\text{K})} = 3$.

Different superlattices have been constructed by varying the thickness of YBCO with a constant thickness of PBCO. XRD shows that all multilayers are grown epitaxially with a cube-on-cube relation with the substrate [23].

When the thickness of YBCO layer decreases from 29.4 to 3 nm, T_c decreases from 90.2 to 40 K. For a YBCO thickness equal to 29.6 nm (about 28 cells) or 18.5 nm (about 19 cells), superconducting properties of the multilayers are equivalent to bulk's one ($T_c > 89$ K). In the case of thinner YBCO layers (≤ 15 cells), T_c and ΔT_c of the multilayer are strongly affected.

These multilayers have been studied in great details in order to determine the complex physical properties generated by this artificial stacking of insulating and superconducting sublayers [24].

Strain and surface engineering

Two-phase, horizontal nanocomposite heteroepitaxial films offer great promise for multifunctional device applications. More specifically in oxide materials, which are highly correlated systems, the inter-

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faces which are induced are very complex due to the collective nature of the electronic behavior. They offer new application possibilities with respect to conventional semiconductors since many physical properties can be related to the quality of these interfaces and their stress state. In the case of perovskite oxides, strain manipulation and control can be applied by using not perfectly matching substrates combined with thin oxide films [25] (Fig. 4).



Fig. 4 Depending on its lattice parameter, the perovskite ABO_3 film can be either in compression or in extension on the various substrates mentioned on this scale.

Strain enhanced physical properties. The effect of biaxial strain on the properties of epitaxial ferroelectric thin films and superlattices was demonstrated on single-layer ferroelectric films of biaxially strained $SrTiO_3$ and $BaTiO_3$ films. Measurements of the effect of biaxial strain on the paraelectric-to-ferroelectric transition temperature (*T*–C) have demonstrated the ability of percent-level strains to shift *T*–C by hundreds of degrees [26,27]. Similar results have been obtained by MOCVD on PbTiO₃ [28,29] where the transition can be shifted from more than 200 °C when PTO is deposited on STO with a misfit stress of 1.1 % (Fig. 5).



Fig. 5 Phase transition in PbTiO₃ and for a thin film deposited in SrTiO₃ as seen from the XRD data.

Strain stabilize nickelate phases. Rare earth nickelates with the generic formula RENiO₃ (RE = rare earth) have attracted a lot of research interest since the report of a sharp metal-to-insulator (MI) transition whereof the critical temperature TMI can be tuned with the rare earth size. These phases are difficult to stabilize (only under high pressure) [30]. Nevertheless, they can be stabilized by epitaxy. In the case of SmNiO₃, when an in-plane expansion is applied at the interface by a substrate with higher lattice parameter (STO), the first atomic layers give a coherent interface which is rapidly destroyed in a direction parallel to the surface. As a consequence, the MI transition disappears. However, with a

compressive stress (LAO), the epitaxial growth is coherent over the whole thickness of the film. The cubic SmNiO_3 phase is fully stabilized and the MI transition is clearly present. (Fig. 6). Thus, in RENiO₃ nikelates the MI transition can be finely tuned by chemical substitution and strain stabilization [31,32].



Fig. 6 Stabilization of SmNiO_3 (SNO) by epitaxy. On STO substrates, the SNO phase is under extension and is not stabilized. On LAO substrates, SNO is under compression and the cubic phase is stabilized.

Strain manipulation, on a selection of phases with the appropriate elastic moduli, opens up a new avenue for strain control in thin or thick films and also promises new forms of ordered nanostructures for multifunctional applications. In order to finally achieve practical devices, a number of hurdles need to be overcome, including the creation of ordered structures (and their formation on a large scale), achieving different combinations of materials and control of strain coupling between the phases.

Photonic crystals by laser-assisted photolytic deposition

The fabrications of 2D and 3D periodic arrays of high optical index materials have raised a considerable interest in the last years for photonic applications [33–35]. Currently, most of the methods for making such photonic crystal structures are based on lithography and ionic abrasion techniques producing patterns on the scale of visible light wavelengths. Up-scaling of these techniques to low-cost mass production of 3D photonic crystals (eventually also made up from a large variety of materials) remains, however, a challenge.

On the basis of early experience in MOCVD, the possibility to perform the growth of a submicronic periodic structure by the chemical decomposition of gaseous species in a 3D holographic field was developed.

For this purpose, a MOCVD reactor was coupled to an optical set-up [36] providing an interference field of UV light, where chemical reactions of the suitable species can be achieved, very locally, either by thermal decomposition or photolytic reaction.

In this optical arrangement, the primary polarized UV laser beam (of 8 mm diameter) is divided into four parallel beams, in such a way that three beams surrounding a central beam point to the three vertices of a regular triangle. The geometry of the four wave vectors gives rise to a pseudo fcc symmetry, with a unit cell of 922 nm for laser wavelength of 355 nm.

The spatial modulation of the electromagnetic energy intersecting the substrate surface allows us to achieve, at each laser pulse (6 ns at 100 mJ/cm²) a temperature modulation of very high contrast (up to 1000 °C). Therefore, a thermal decomposition of gaseous precursors might be expected at the hot points, following the energy modulation of the 3D interference network. Unfortunately, for this type of

experiment, the substrate must have a high absorption of UV light, as well as very low reflectivity and thermal conductivity, and the growth of 3D pattern was not possible up to now.

The growth of a solid phase was nevertheless possible by a photolytic decomposition of adsorbed molecules [chromyl chloride (CrO_2Cl_2)]. This precursor can be photolytically decomposed in the gas phase into CrO_2 and Cr_2O_3 under UV–vis light at wavelengths less than 565 nm [37]. Deposition was made on SiO₂ glass substrates or on different single-crystalline substrates: (001)Si, (0001)Al₂O₃, and (001)TiO₂. Photolytic deposition times ranged between 5 and 20 min (i.e., 3000–12000 laser pulses) and the UV energy was in a range of 5–20 mJ/cm².

Figures 7a and 7b present two patterns obtained under these conditions in a 2D or 3D configuration.



Fig. 7 Optical principle of the laser interferences and periodic patterns of material deposited from a photolytic decomposition of CrO₂Cl₂: (a) 3D pattern from a 4-beam interference. (b) 2D pattern from a 3-beam interference.

The present experimental results indicate that a vapor-phase decomposition of precursor leading to a 3D periodic nanostructure can be obtained at room temperature on a substrate intersecting a 3D interference field of UV laser light. These 3D periodic oxide nanostructures are very promising for photonic applications.

From film (2D) to nonowires (1D): The case of ZnO

The fine-tuning of growth conditions in MOCVD experiments enables the preparation of a large variety of microstructures and nanostructures. A typical example is given by the growth of ZnO where, depending on the required applications, either thin films or NWs can be produced.

By using Zn(acac) and propanol as solvent in injection MOCVD, the deposition conditions can be varied in such a way that the surface morphology is drastically affected. The main parameters governing either film growth or NWs growth are the total pressure in the reactor, the temperature, and the oxygen partial pressure.

When the total pressure in the reactor is relatively high (5-10 Torr) ZnO thin films are formed between 300 and 400 °C with a surface roughness strongly affected by temperature.

When the total pressure is lower than 2.5 Torr, NWs can be obtained under conditions which are mainly controlled by temperature and oxygen partial pressure. Increasing the partial pressure of oxygen or decreasing the substrate temperature leads to ZnO nanostructures with larger diameter. Conditions can be isolated leading to ZnO coatings composed of several micrometers-long NWs and with diameter as small as 15 nm (Fig. 8).



Fig. 8 Scanning electron microscopy (SEM) of ZnO NWs grown at 460 °C.

These NWs are further studied and exploited to improve the quality and efficiency of dye-sensitized solar cells recently proposed as alternatives to Si-based photovoltaic devices [38,39].

CONCLUSIONS

The different oxide nanostructures, which can be prepared today with a large variety of oxide building blocks, are extremely powerful candidates to be integrated in emerging device concepts. Thanks to the development of new materials and of new processing technologies, the fundamental electronic, magnetic, or photonic properties of perovskite oxide materials can be combined today at a nanoscale and can also be triggered with stress, surface, or size effects. The different examples of multilayers, hetero-structures, nanostructured patterns, NWs, or nanodots, which have been obtained by MOCVD in the present work, demonstrated that new multifunctional materials are actually available for magnetic or photonic data storage, as nanoscaled arrays for ultimate device integration or optimized structures in hybrid solar cells. For all these applications, the liquid-source MOCVD processes used in these studies are suitable for the preparation of high-quality oxide films at an atomic scale. A large variety of oxide nanostructures can further be investigated today, mainly with the aim to simplify, densify, and increase the number of functions integrated in the current device architectures.

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