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Editorial

Special Issue "Thin Films and Nanostructures by MOCVD: Fabrication, Characterization and Applications—Volume II"

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In our world dominated by global communications, data centers, travels and environmental concerns, there is an increasing need for the deposition of materials with competitive quality, thruput, and relatively low cost/impact, to be implemented in smart devices capable of integrating complex systems, such as the emerging Internet of Things (IoT). So, it is not just a matter of coating a surface with a certain material, but, in most cases, the deposition of one or more materials with functional properties for a very broad range of applications, including photonics, micro-nanoelectronics, sensors, energy conversion, devices for automotive and data storage/processing. To just cite one example, the ultimate trend of semiconductor nanotechnology requires the use of advanced epitaxial growth techniques; in particular, besides the need of fabricating low-dimensional structures, such techniques must assure high structural, optical, and electrical quality materials with easy industrial transferability. Other requirements include the possibility of changing composition within a period of a few angstroms in at least one dimension, growing high-purity layers (with unintentional impurity levels of a few parts per billion), as well as introducing electronic doping. Last, it must be possible to grow or self-assemble different alloys, even with 3D geometry, under uniform and reproducible conditions.

In this respect, the Metalorganic Chemical Vapor Deposition process (MOCVD, MOVPE when Vapor Phase Epitaxy is involved), introduced by Manasevit in 1968 [1], has been assuming increasing importance as a key enabling technology, being related to the study and fabrication of many materials and devices of scientific and commercial interest, without which today's world would not be the same. It belongs to the wider class of CVD (VPE) processes, in which an inert carrier gas, such as ultrapure H_2 or N_2, containing the precursor species, is forced to flow on a substrate, where a chemical-physical reaction takes place at a proper temperature, leading to the growth of the desired material. The vapor phase transport in MOCVD is realized by suitable metalorganic compounds and/or hydrides of the atomic species to be deposited, which can be featured by electronic-grade purity. Such compounds act as molecular precursors for the deposition, whose high vapor pressures allow lower reaction temperatures with respect to other conventional CVD systems and a very high control of the reactant molar flow (within µmol/min), with the possibility to tune the material composition, even outside the stoichiometric ratios. The growth temperature is necessary to thermally dissociate the precursors transported by the carrier gas (pyrolysis); this frees elemental species to be deposited at a high enough partial pressure in the growth chamber. Thereby the supersaturation conditions are reached, hence pushing the thermodynamic system to deposit the desired material, so to approach the equilibrium conditions. Different possibilities are available in terms of process activation, especially when the deposition temperatures need to be sensibly lowered so that hot wire, plasma-enhanced, laser-assisted and radical-assisted MOCVD can be used, or proper precursors exploiting Lewis acid–base reactions, allowing even the room temperature deposition, without the need for the thermal dissociation of reactants.

Nowadays, the scientific and commercial importance of MOCVD is well recognized, since it yields state-of-the-art devices that benefit from high process control, and encompasses

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a wide range of materials, from single elements to multinary compounds, in the form of films, monolayers, multilayers, superlattices, nanowires, nanodots, or complex 3D nanostructures, and in different structural phases, from amorphous to crystalline and epitaxial materials, which can be grown and even self-assembled with excellent doping control, abrupt interfaces and uniformity. Moreover, being a chemical technique, MOCVD enables conformal growth with convenient deposition rates even on large areas (300 mm wafers), which is particularly useful when the film coating of complex substrate recesses or nanostructures is required. Such advantages cannot be easily found in other advanced methods, such as Physical Vapor Deposition (PVD) and particularly Molecular Beam Epitaxy (MBE).

Ellipsometry and other optical-based spectroscopy techniques are currently being proposed to reduce the advantage that the MBE process had in the past, namely the use of Reflection High-Energy Electron Diffraction (RHEED). A particularly effective in situ monitoring technique for MOCVD is Reflectance Anisotropy Spectroscopy (RAS), which measures the difference in reflectance between two axes of a crystal surface as a function of time/photon energy; the cubic symmetry of III-Vs compounds makes negligible the isotropic contribution of the bulk so that the anisotropic contribution of the surface provides much useful information on the growth in real-time.

Other key factors for the wide diffusion of MOCVD are due to the flexibility in the choice of the chemical precursors, good control of the (many) process parameters, no need for ultra-high vacuum, and suitability for industrial implementation. For these reasons, MOCVD has allowed the growth of the whole range of II-VI and III-V-nitrides semiconductor alloys and related quantum-confined heterostructures, some of which have led to the fabrication of blue-white diodes and laser diodes [2], and for which S. Nakamura, I Akasaki and H. Amano were awarded the Nobel Prize in 2014. For more than 20 years, the availability (mass production) of white LEDs has been suppressing the use of incandescent bulbs, with great benefits in terms of illumination, duration, consumption and carbon emission.

It would be very difficult to provide an exhaustive picture of all the other applications, materials, and devices, as well as fundamental and industrial research involved in MOCVD in this editorial. However, it is useful to present in the following an overview of the most interesting devices that have been realized in ongoing research, thanks to this important technology.

A major role is played by high-efficiency, multijunction solar cells (mainly III-V semiconductors), which are fundamental in space applications, as well as in earth installations, when coupled with solar concentrators, with the added value of exploiting the cooling liquids for co-generated heat. At the same time, thermophotovoltaic converters (such as chalcogenides, and perovskites) are also important for energy harvesting from heat and refrigerating systems (Peltier coolers).

In the field of information technology and wireless communication, III-V-nitride semiconductors for power RF applications are relevant, such as high-frequency, high mobility transistors (HEMTS) and those for optoelectronic devices, such as quantum dot lasers, amplifiers and fiber optics communications lasers at 1.3 and 1.55 µm. Great contribution is also given by materials for high-power Laser emitters (ultraviolet, based on AlN, quantum dot lasers, Vertical Cavity Surface Emitting Lasers, VCSELs). For in-memory computing, memristive devices (containing 2D Transition Metal Di-Chalcogenides, TMDC) are being grown to emulate the brain behavior, thus contributing to the boosting field of artificial intelligence.

Another important application field is given by materials for sensors (even for gesture recognition) and X-ray/Infrared radiation detectors (with III-V, II-VI semiconductors, perovskites, Ga_2O_3).

Moreover, it should be noted that different metals, metal nitrides, oxides and ceramic coatings are realized by MOCVD for industrial purposes. Among oxides, a special mention should be made to the MOCVD growth of ZnO, from thin films to nanostructures, which is a fundamental and multifunctional material, also including neutron detection and biomedical applications.

Basic research, on the other hand, is always introducing new materials and systems, often involving the world of new and intriguing material properties and crystal growth modes (such as Van der Waals Epitaxy), from quantum confinement to spintronics and valleytronics.

Therefore, 2D materials exhibiting a wide variety of electronic properties, such as TDMCs (MoS_2, WS_2, WSe_2, $MoTe_2$, etc.), graphene, mono-elemental Xenes crystals (antimonene), topological insulators (typically Bi-Sb-Se-Te alloys) are being grown by MOCVD. Finally, focused studies are conducted to allow the effective integration of III-V, nitride semiconductors and silicon carbide on silicon, thus allowing full CMOS compatibility for mass production.

The list could be much longer, but what has been mentioned above is already enough to give an idea of the enormous field of applications of the materials and devices enabled by MOCVD growth; more details on the process and related products can be found in Refs. [3–5].

For the sake of objectivity, it has to be said that the MOCVD technology, just like any other advanced deposition technology, is not free from limitations, such as the complex chemical-physical processes (still not well understood) that rule the growth and the highly reactive atmosphere employed for the vapor phase, the instrumentation cost and potential environmental impact, therefore efforts to improve the performance of materials and devices grown by MOCVD are being made, mainly directed toward the realization of better and cheaper reactors, novel and less harmful chemical precursors, improvement of in situ characterization and larger area growth. Future research trends are also directed toward optimizing materials for further electronic applications, such as high-critical temperature superconductors, dielectrics and piezoelectrics.

To further testify to the large spread of MOCVD employment, and also due to the COVID-19 pandemic, the 2023 MOCVD global market is reported to be around USD 1088.1 million in 2022 and is expected to reach USD 2024.2 million by 2028 [6].

Following the successful edition of Volume I [7], this Special Issue, Volume II intends to collect potential contributions from the many different applications areas of MOCVD-related research, providing an anthology of the most recent and promising results of the field, especially in correlation with the functional properties and applications of materials and devices meeting the future technological trends. The involved topics include the MOCVD of the following materials (and/or study of related devices): semiconductors, complex oxides, magnetic and topological insulators, thermoelectric, superconductors and phase change alloys. Concerning the possible typologies, studies on functional coatings, epitaxy, multilayers, nanocomposites and nanostructures will be welcome. At the same time, large room will be left for specific growth-related aspects, such as surface chemistry, catalyzed and selective area deposition, process simulation and in situ monitoring.

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