Coating Materials News & More

Semiconductor Device Coatings, Materials and Processes

May 2021 | David Sanchez & Samuel Pellicori

Introduction

Past Coating Materials News & More (CMN) discussions have examined optical materials and their deposition processes in terms of applicability to regions of the electromagnetic spectrum from deep ultraviolet (DUV) to infrared (IR). The thin film industry applies PVD and epitaxy processes and combinations of materials to achieve control of light and energy in specific applications. In this issue, we will connect the materials and processes as they are applied to increasingly complex solutions in the fields of manufacturing, communications, and energy efficiency.

Processes and Materials

Optical and semiconductor applications based on thin film layers involve mature process and materials engineering. Manufacturing principles for growing single-crystal Silicon (Si) and Germanium (Ge), as well as condensing Zinc Sulfide (ZnS) and Zinc Selenide (ZnSe) for use as substrates are central to advanced solid state device structures. Specialized epitaxy and CVD technologies that allow the deposition of single or multi-element compound species with precise control of crystal structure, band structure, and intricate composition are critical to the industry. In an oversimplification, during Molecular Beam Epitaxy (MBE) film growth, multiple effusion cells are used to direct impinging beams of thermally induced flux onto the substrate. The combination of high-vacuum condensation of the sublimed material and the substate temperature allow the formation of single-crystal films of complex high purity composition with controlled microstructure. The lower population of defects produced in MBE deposition results in longer free carrier lifetimes, and therefore higher emitter and sensor device efficiencies. Analogous to optical designs based on stacking of oxides or fluoride layers, this technique creates multi-layer structures like Quantum Wells, distributed Bragg Reflectors, and other critical elements for industry. These are the foundation of light-emitting diodes (LEDs), laser diodes, and multijunction solar cells that are used to power infotainment, laser machining, and energy harvesting technologies. MBE enables better control of deposition parameters than metalorganic chemical vapor deposition (CVD).

Focusing on applications related to building blocks of semiconductor lasers, Indium (In), Gallium (Ga), Arsenic (As), Phosphorous (P), and Aluminum (Al) are all key elements. Indium is perhaps most well-known for its important roles a bonding agent for sputtering targets, and the expensive component of Indium Tin Oxide (ITO) for use in transparent conducing oxide (TCO) applications. Indium world supply is rare; the metal process entails initial mining and extraction, and subsequent recovery and recycling from industry. Available world sources are limited, thus rendering Indium an expensive market entity. Similarly, Gallium is mostly a byproduct of commodity metal production; extensive efforts to recycle and refine are underway worldwide in conjunction with growing demand from the industry. Though toxic, Arsenic is perceived as a commodity metal similar to Phosphorous and Aluminum, which also have much larger markets supporting extraction, refinement and production. The boiling points and reactivities of these elements are critical to the implementation of the individual effusion cells designed for each element in the MBE tool.

In the production of semiconductor absorbers or emitters, the individual p-type or n-type character of the active layer is dictated by composition, doping, and application of the device.

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In an emitter, Arsenide, Phosphide, and Nitride layers are directly pumped with current via electrodes from a power source or energetic photons (photon energy above band gap energy) to release carriers. The electrodes might be TCO layers in the case of optical devices or metal contacts for electronic devices. The pump excites electrons in the conduction band to a higher energy state which then decays to a state near the conduction band of the semiconductor. Simultaneously holes generated in the valence band move to the top of the valence band and recombine with electrons in the conduction band, emitting characteristic photons near the designed bandgap energy. In optical devices, the back of the stack is coated with a high reflector dielectric stack with low absorption. The front of the stack is coated with a partial reflector or an index matching layer if the output is to be mated an optic. These laser emissions are coalesced by conventional gathering optics and manipulated into the desired beam shape for the intended task. Since the energy from each diode and larger package is duplexed, the power and cooling bus systems are increasingly efficient, powerful, and stable. In recent years, strides in performance, cost, and longevity of diode bar stacks have taken solid state lasers mainstream in communications, edge deletion and processing, and are emerging in sensing and telemetry applications that require challenging optical engineering solutions.

While it's true that the functional stacks and structures used in fabricating solid state lasers require MBE or MOCVD to deposit rather exotic thin film dyads, it's also true that issues such as efficient electrodes, capping layers, and device stacking schemes influence the performance of the overall package. The rear high reflector requires low absorption to assure long life. In a pure dielectric, electrons are bound and are not available for conductance. This is the case for most optical coatings and is fundamental in the treatment of laser induced damage resistant coatings. On the output side of the device beyond the partial reflector or emission facet, AR coatings on all the optics - downstream to the workpiece - need to durable or easily replaced to be increasingly adopted in industry.

Optical & Semiconductor Device Applications

Because the surface reflection loss is as high as 65% in high refractive index semiconductors, their effective quantum conversion efficiencies are low, reflection-reducing coatings are required on all semiconductor surfaces to increase the conversion efficiency. Effective AR coatings range in complexity from single- to multi-layer designs. In the case of photo-voltaic (PV) silicon for the visible-NIR solar cells, a single QW layer of Silicon Nitride (Si_3N_4) is deposited during the fabrication of the silicon devices. The single layer is effective for PV cells that produce power from wavelengths between ~400 nm and ~900 nm.

Silicon-based sensing devices have a large market presence in terrestrial solar cells, commercial cameras, cell phones, and LIDAR imagers. Silicon generates photoelectrons in response to light of wavelengths greater than 300 nm to ~1100 nm. Commercial camera focal planes include a short-wave pass filter that eliminates response to wavelengths less than 700 nm (Near-IR). LIDAR systems that use the 905 nm laser diode wavelength can use silicon imagers. The 905 nm wavelength is not eye-safe and is potentially damaging to retinal cells. Therefore, the pulsed output is restricted to acceptable power, which then limits the range of the LIDAR. Operation at 1550 nm is eye-safe since the vitreous humor in the eyeball absorbs this wavelength before it can reach the retina. The longer wavelength requires a more expensive Indium Gallium Arsenide (InGaAs) imaging sensor.

Semiconductor materials are used to fabricate MW and LWIR sensors. Because many sensor types require cooling to reduce intrinsic noise generation, they also require coating materials that have small, thermally induced intrinsic and extrinsic stresses and strains. Suitable coating materials include ZnS and a fluoride such as Yttrium Fluoride (YF_3), Ytterbium Fluoride (YbF_3), or IRX. ZnS layers grow with compressive stress; fluoride layers grow with tensile stress. In multi-layer coatings, the total internal stress would be effectively compensated by the opposing strain imposed by the alternating material layers. However, low-index layers, namely the fluoride layers, are always thicker (approximately2x) than the high-index ZnS. Therefore, excess tensile stress remains to be accommodated. Coating design and deposition process can address and minimize the probability of adhesion failure.

In addition to optical and thermal requirements, the electrical properties of the coating can interact with the band structure of the semiconductor surface and must be designed and deposited to prevent the shunting of charges that are intended as photoelectric signals. Amorphous morphology and complete stoichiometry are important layer properties and are influenced by the deposition conditions. [1]

Transparent Semiconductor Coating Materials

There are applications where it's desired to have electrical conduction and visible-region transparency. A small variety of transparent conducting oxide materials (TCOs) are available for many applications. The most familiar TCO is ITO, Indium Tin Oxide. Variations are Indium-doped Zinc Oxide: IZO, Aluminum-doped Zinc Oxide: AZO, Fluorine-doped Zinc Oxide: FZO, etc. In TCO materials, conduction of electrons and ions is produced by the creation of electronic defects and vacancies that include holes and mobile charge carriers. Deposition of a TCO layer with the desired optical and electrical properties requires the correct starting material and appropriate deposition process. Some TCOs can be thermally evaporated (ITO), others require

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sputter deposition (ITO, AZO, IZO, etc.). Layer resistivity is determined by variables such as deposition energy and might include high temperature annealing after deposition in the applications where a minimum resistivity is required. Sputter deposition often eliminates the need for thermal annealing. Resistivity is measured as ohmic sheet resistance. Sheet resistance requirements are dictated by the specific application and can range from a <10 Ohms/square for RF shielding to kOhms/square to dissipate charge accumulation on electronic devices and insulators. ITO has been used for decades to de-ice aircraft windows. High sheet resistance coatings on solar cell covers prevent static charge accumulation on solar cell panels that could otherwise lead to arcing and cell circuit failure. TCO layers are also components of LEDs, OLEDS, and touch panels. [2-8]

TCOs have the property that as wavelength increases, their characteristics change from transparency to reflectance. The transition occurs near their band gap which is between 1200 nm and 1500 nm depending on material. At this "plasma frequency", the material properties change from transmission to reflection. This property of ITO and other TCOs is applied in thermal control (energy conserving) to windows to admit visible wavelengths and reflect IR energy that causes heating of internal space.

Summary

This issue of CMN & More used examples of semiconductor laser diodes and their basic fabrication principles to compare the differences and similarities between wafer level epitaxy and conventional optical coatings. Though exotic and somewhat geographically or industrially sequestered these critical materials may be, the importance of the devices they enable is central to advancing lasers in science and industry. Just as these "Epi" wafers are key engines of emissive and energy conversion applications, these devices can be stacked in-situ with wafer-level processes or physically combined to meet ever increasing engineering challenges. The role of electronic structure and its relationship to optical film layer material and process has also been briefly touched upon. Now, with a better understanding of lithography and epitaxy principles, future articles can more easily describe the challenges specific to VCSELs, LWIR sensing and directed energy.

We have presented a sampling of functional applications, materials and processes that are inherent in the optical coating of semiconductor materials. Semiconductor devices and their applications range from everyday consumer electronics to advanced, high-tech space, medical and military instrumentation. Future issues of CMN & More will expand on this.

Laser Diodes can be used directly for work or to pump crystals, discs and fibers for an increasing number of industrial applications.

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