MATERION

MATERION ADVANCED CHEMICALS
COATING MATERIALS NEWS
March 2011 Volume 21 Issue 1

A LOOK BACK AT 20 YEARS OF COATING MATERIALS DEVELOPMENTS

This month we celebrate the 20th anniversary of the publication of Coating Materials News (CMN) in coincidence with the reorganization and rebranding of CERAC and the entire Brush Wellman and Williams Advanced Materials organizations as Materion Corporation. The Advanced Chemicals business unit of Materion gathers the coating materials from Milwaukee, Albuquerque, Brewster, Buffalo and Tucson facilities into one focused and dynamic group. With Milwaukee at the center, Materion Advanced Chemicals will continue their dedication to guiding and supporting trends in the coating industry and its commitment to the principles of CMN.

The origin of CMN was the result of a cooperative effort between me and CERAC's president and founder, Dr. Ervin Colton. We often had long discussions on key coating materials issues within optical industry. One day in a general conversation, he suggested that I write a newsletter that discussed coating materials and deposition processes. This was the birth of CMN. The preamble expressed in Vol. I Issue I, outlined the objective of the newsletter, namely "to inform old and new users of coating materials of progress in the development of materials for thin films…" and to "…provide information on the recommended techniques for the optimum deposition…." Having matured and expanded to its current circulation, the newsletter takes the issues of Coating and Materials across the globe – reminding of efforts past and looking into challenges of the present and future.

What started as a "news letter" has evolved into a "guide" to assist educating the coating technician and engineer in choosing materials, and deposition techniques for specific applications. In the first two issues, we presented an outline discussion of the most frequently used coating materials for general applications, i.e., those optimal for use in specific spectral regions. The list has not significantly changed since then, but the materials have been improved. We also provided guidance on evaporation parameters and deposition techniques for the commonly used compounds.

Over the past two decades, CMN has discussed a great variety of topics related to optical coating materials developments and improvements. Questions from our readers play an important role in guiding the topics reported in CMN. For example, when reviewing fundamentals of pertinent deposition techniques we often report thin film optical and physical (mechanical) properties by highlighting current published works from key conferences in conjunction with insight from my peers and personal experience.

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We review some examples where the collection of experience, new market pressures, conference proceedings and direct CERAC sponsored trials and reports have converged in CMN to respond to challenges of the optics community.

A topic for fervent discussion has been ophthalmic AR and protective coatings. Anti-reflection coatings are applied to virtually every glass or plastic optically functioning surface. The proliferation of polymer substrates and lightweight, high style eyewear has pushed process and material enhancements. Producing durable AR coatings on polymer surfaces after exposure to ambient environments presents challenges for deposition processes and materials. Resistance to wet, cold and hot, and abrasive conditions requires dense adherent coatings. Since polymers cannot tolerate the high temperature associated with densifying film layers, high-energy low temperature processes such as Ion Assisted Deposition (IAD) or sputtering are employed. Along with the low temperature process, coating materials have been developed that are compatible with maintaining low deposition temperature. $LaTiO_3$ is one example of the high-index layer material that has been refined for the application by CERAC to provide dense hard ophthalmic coatings. The reader is encouraged to refer to archived technical publications at our website. They can be found in the Resource Center under the Advanced Chemicals Business.

Similarly, exotic high-energy laser applications have seen remarkable growth in military, medical and high energy laser fusion systems. For the IR region, ZnS, YF_3, YbF_3 and ThF_4 and alternate fluoride compounds are under constant process pressure to meet increasingly complex performance or regulation demands. CMN has reported on how high multi-layer counts of ZnS/YF_3 stacks for demanding filters and AR coatings on Ge and ZnSe substrates has required the development of advanced drying and melting procedures for the production of YF_3 and called for a new hyper-stable ZnS raw material. In addition, that report went on to address how the new YbF_3 formulation dramatically reduced spitting and improved water band performance over the conventional YbF_3 on the market.

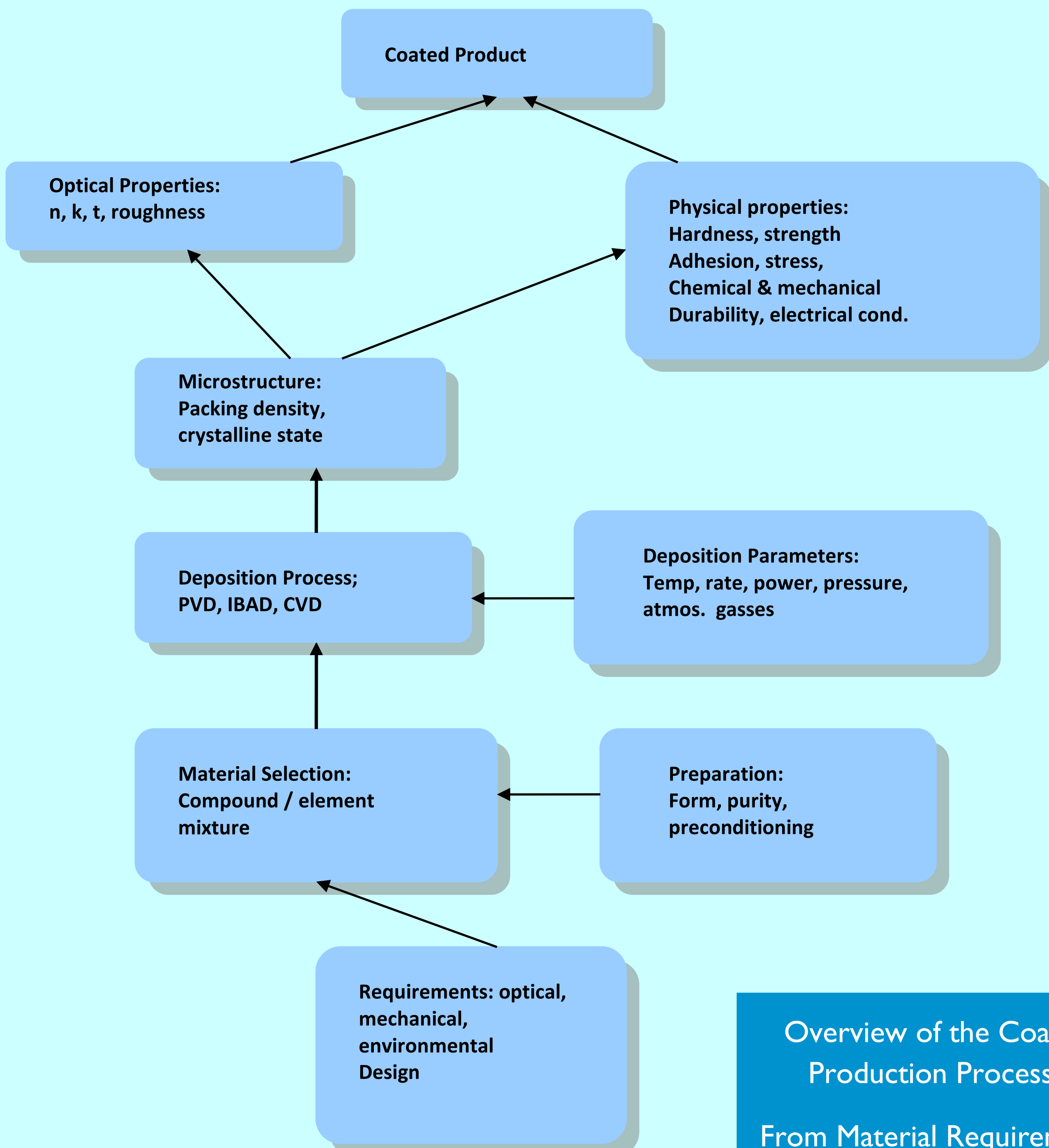
Demands from NIF, CERN, Medical Lasers and Microelectronics have pushed designs in the UV/DUV. CMN has reported on the improved fluoride products for the DUV/UV and the dangers/benefits of IAD for denser layers. Often deposition process improvement is realized through specific preparation of the starting materials. Such pre-processing consists of attention to form, composition control, and density. CMN has reported on the importance of pre-conditioned oxides for evaporation to improve Laser Induced Damage Threshold (LIDT) and reduce operator/tool variance in the plant. While the IP is immense, the advancements in the Oxides and their stability and control have advanced the state of the art in materials preparation and deposition. Readers are encouraged to refer to Technical Data Sheets available on line at our website. They can be found in the Recource Center under the Advanced Chemical Business. Specific process results for pre-melted forms and cone shaped inserts are given in CMN V14, Issues 2 and 4 (2004) and V15 Issue 1 (2005).

The confidence that has been gained by evaporation approaches yielding reasonable LIDT has also rekindled reactive deposition of the metals to produce the oxide compound. We hope that future CMN articles will compare and contrast the performance of filters made from these new reactive deposition techniques to that of pre-conditioned oxides. Past CMN articles summarize the reports of groups who have been researching various techniques for improving laser induced damage threshold - these articles remain available on our online technical database.

In addition to topics on materials and applications, we discussed at length issues and problem solving techniques for important problems such as stress in coatings. CMN touched on the most typical causes, effects, and control of these stresses. In addition to temperature, substrate preparation and optical design, I was able to add my own personal history stemming from my early cooperation with Dr. Colton in the development and introduction of CERAC's CIROM IRX™ and IRB™ fluoride compounds. While these pre-reacted compounds were developed specifically to replace radioactive ThF_4 they serve as a demonstrative example of using specific 'dopant' materials in with the 'host' compound to modify stress and/or growth behavior in a technical optic. Management of stress and the need to deposit many layers or a durable multi-layer system with minimal defects have influenced the development of other mixed materials and of specialty oxides such as $LaTiO_3$ and Ti_3O_5. The properties of coatings based on these mixtures or specialty sub-oxides with and without ancillary IAD have been compared in numerous CMN articles, and address the potential benefits to the process in addition to managed stress. As a reminder of the complexity of the process, Figure 1 presents an illustration of the general coating procedure and the interplay of the steps/decisions involved in producing a coated optic. The development of intrinsic stress in coatings is an important topic. We have discussed and reported success with techniques for reducing mechanical strain and thereby stabilizing coatings against thermal and other imposed environmental stresses. The techniques involve the choice of material combinations, often employing mixed composition varieties and stress management interlayers, and the particular deposition process.

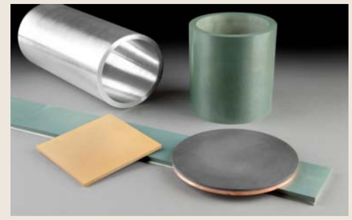
Discussion about the evolution, changes – stable and cyclic --of the coating industry would not be complete without a look at the burgeoning PV marketplace. Twenty years ago, Copper Indium diSelenide (CIS) and Copper Indium Gallium diSelenide (CIGS) based cells were dominated by the cost and efficiency advantages of silicon in the great PV debate. Transparent electrodes made from layers of PVD ITO or spray pyrolysis SnO would dominate FPD and TCO's and silicon PV would be limited to incremental improvement and constrained by raw materials availability for years. In recent times, improvements in materials and processes have given new life to photovoltaic solar cell alternatives to silicon, in particular thin film photovoltaics (TFPV) arrays offer manufacturing advantages and the promise of competing conversion efficiencies.

Growing demand for PV and accelerated development within the specialty optics and large area coating communities regarding CdS, CdTe, CIS and CIGS based cells has invigorated the Semiconductor and Optics industries. Refinements to those materials in terms of purity and form have resulted in increased efficiencies. Transparent conductive coatings are in continual development, with current emphasis on evolving alternatives to ITO. A global scarcity of indium has inspired such alternatives based on doped: ZnO. Common applications in addition to transparent solar cell electrodes include thermally insulating automobile windshields, architectural windows, and touch panel switches. This area of development has driven improved sputter target materials development. Even as Silicon swings into action (motivated by trades-offs between production cost and cell PV conversion efficiency) advances in evaporation, sputtering, and deposition sciences will have a significant impact on the Coatings and Hybrid Circuit worlds. CMN will be there to tackle the complicated issues around evaporation techniques, raw material risk aversion, safe handling and recycling of materials and upfront reporting on the trends that shape our industry.



Overview of the Coating Production Process -

From Material Requirements to Finished Product



PRIMARY MARKETS SERVED

- Large Area Coatings
- Optical & Semiconductor Coatings
- Alternative Energy
- Medical
- Specialty Inorganic Chemical Applications
- Research & Development
- LED Lighting
- Specialty Battery

KEY PRODUCTS & SERVICES

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- Phosphor Materials
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- High Purity Chemicals
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- New Product Development Partnering

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- Reactive Gas Processing
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Materion Advanced Chemicals encompasses the capabilities of Williams Advanced Materials' CERAC incorporated and Academy Corporation subsidiaries with the support of its Thin Film Technology business and other resources now integrated under the Materion brand. We are proven providers of specialty materials and innovative solutions with decades of experience in inorganic chemical synthesis and material transformation.

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Coating Materials News is a quarterly publication for Materion Advanced Chemicals.

For a free subscription to CMN, please email your name and address to AdvancedChemicals-Info@materion.com or send a fax at 414.289.9805.

Guest articles or topic suggestions are welcome.

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