DOSSIER DE THÈSE CIFRE

PROPERTIES AND BEHAVIOR OF INFRARED MATERIALS: TOWARDS HIGH EFFICIENCY AND HIGH DURABILITY ANTIREFLECTION COATING

RESEARCH PROJECT

REF DOSSIER : THESE 193

NOT EXPORT CONTROLLED TECHNOLOGY /
TECHNOLOGIE NON SOUMISE À CONTRÔLE DES EXPORTATIONS

Page laissée intentionnellement blanche.

TABLE DES MATIÈRES / DOCUMENT CONTENT

1 CONTEXT

This PhD topic is proposed within the framework of the PRIMEO Joint Laboratory (Partnership for Research and Innovation on Emerging Materials for Optronics), established between Safran Electronics & Defense and the Pprime Institute - UPR CNRS 3346. This collaboration, in place since 2010, enables both academic and industrial studies to be conducted, thereby addressing nearly the entire Technology Readiness Level (TRL) scale. Knowledge exchange between the teams of both entities is a key aspect, with Safran engineers regularly working within the laboratory to carry out characterizations themselves and interact with the researchers at the Institute.

Optronic systems, such as those developed by Safran Electronics & Defense, are composed of various optical components, including windows, lenses, filters, and dichroic plates. For each of these components, functionalization (optical, mechanical, electrical) is achieved through thin-film treatments. Technological differentiation largely depends on the performance that can be achieved through these surface coatings.

The front optics of these optronic systems directly contribute to the systems' performance in detection, observation, and identification. These optics operate in particularly complex environments influenced by atmospheric conditions and numerous external parameters that are inherently uncontrollable. Therefore, they must exhibit sufficient characteristics to withstand usage profiles in environments that may be harsh, corrosive, and erosive, while remaining compatible with the functions of the optronic system (i.e., providing high transmission). In the coming years, defense programs are expected to increasingly demand improved characteristics in terms of the mechanical and chemical robustness of these optics, particularly for multispectral windows, whose transmission range may extend from the visible to the far infrared.

These coatings are commonly produced using vapor-phase deposition techniques, such as the Electron Beam Physical Vapor Deposition (EB-PVD) process, which creates multilayer interference systems made of dense and uniform materials across the entire component surface. However, certain geometric configurations (e.g., large optical parts or high curvature) make it challenging to achieve uniformity at all points: variations in thickness, density, and mechanical properties can arise. These heterogeneities become particularly problematic when optical components and their coatings are subjected to severe operational conditions.

.

2 OBJECTIVES

The multilayer coatings applied to front optics aim to provide a specific optical function, typically anti-reflection, as well as protection against mechanical or chemical aggressions. The performance of these coatings, achieved via EB-PVD, is generally satisfactory for conventional optics, i.e., flat and/or with low curvature. However, recent studies have highlighted a lack of robustness in critical environments, such as saline fog, for components with complex geometries (large diameter, high curvature). The mechanisms involved are not yet fully understood, but they result in multiple forms of degradation, including chemical attack and delamination. The technical specifications required for the optronic devices of SAFRAN Electronics & Defense are becoming increasingly stringent, and conventional thin-film deposition technologies must be further characterized to enhance their performance levels.

The decline in optical performance and the lack of mechanical robustness are largely attributed to the significant challenges in achieving uniform deposition across complex components, leading to considerable variability in properties:

- Microstructural: thickness, density, roughness
- Chemical: stoichiometry, surface energy
- Mechanical: stress, adhesion, hardness

The objective of this PhD work is to develop coatings for substrates with highly complex geometries, resulting in uniform properties and resistance to operational stresses.

To achieve this, the optimal deposition conditions will need to be identified by adjusting influential parameters and potentially employing advanced deposition systems, such as uniformity masks or mechatronic systems enabling growth under variable incidence. Additionally, new materials may be considered based on an exhaustive literature review conducted at the project's outset. This research will primarily focus on fluorides for use in anti-reflective architectures (e.g., YbF_3, DyF_3, CeF_3) and surface protective materials to explore new optimization pathways (cf. the discussion in section 4 on the current state-of-the-art MgF_2, commonly used for multispectral applications).

The project also aims to design and develop a new type of multilayer architecture by integrating:

- New materials
- Novel interfaces to enhance thermo-mechanical stability (e.g., composition gradients, buffer layers)
- Consideration of the mechanical properties of individual layers, such as mechanical and intrinsic stress, adhesion energy, and thermal expansion coefficient.

Like optical principles, these new designs will require modeling through numerical (e.g., Abaqus, Ansys) and/or analytical simulations to optimize the architecture using a holistic approach.

The robust solution must meet the following requirements (applicable environments according to ISO 9211-4:2012 and ISO 9022:2002 standards):

- Severe abrasion: ISO 9211-4-01-03
- Adhesion: ISO 9211-4-02-02
- Solubility: ISO 9211-4-04-02
- Cold: ISO 9022-2-10-09-1
- Dry heat: ISO 9022-2-11-06-1

- Humid heat: ISO 9022-2-12-06-1
- Acetone resistance: ISO 9022-87-04-1

Complementary Testing Methods

Standardized tests often yield binary results (compliant/non-compliant). To better distinguish the behaviors of different architectures and deposition conditions, new tests will be implemented:

- Thermal Shock:
  The optical component and its coating must withstand 5 cycles of 2 hours each (1 hour at -40°C followed by 1 hour at +90°C), with a transition ramp of 30°C/min.

- Cross-Hatch:
  A grid of scratches will be created, followed by an adhesion test, both before and after exposure to humid heat.

- Mercedes Indentation Test (VDI 3198 Test):
  Similar to the scratch test, indentation could serve as a valuable tool for understanding adhesion and adhesion energy. An imprint is created via micro- or nano-indentation and then analyzed using microscopy techniques (optical, electronic, interferometric, or near-field, such as AFM) to observe fractures or delamination.

3 ORGANIZATION OF RESEARCH WORK

The coatings studied within the framework of this PhD project will largely be developed using the production and development facilities available at the Safran E&D site in Saint Benoît (86), significantly promoting subsequent Technology Readiness Level (TRL) advancement. The thin films will primarily be created using a physical vapor deposition technique, specifically thermal evaporation (EB-PVD – Electron Beam Physical Vapor Deposition). A dedicated development system (called the B23 unit) will be used for producing mono- or multi-layer stacks. However, specific depositions may also be carried out using the DIVA deposition system at the Pprime Institute.

A variety of materials are envisioned for integration into next-generation anti-reflective architectures, including:

- A sulfide: Typically ZnS, a crucial material for the intended applications.
- Fluorides: YF_3, currently the most widely used material, with bibliographic research expected to identify alternatives such as YbF_3, DyF_3, or CeF_3.
- A protective material: Here, another fluoride, MgF_2, commonly used on flat optics, although oxides might also be explored.
- Materials for buffer or adhesion-promoting layers: Such as oxides like HfO_2.
- Hybrid materials: With complex, graded compositions (e.g., compositional gradients at interfaces).

The project involves varying influential deposition parameters to control microstructural properties (thickness, density, roughness), mechanical properties (residual stress, adhesion, hardness), chemical properties (stoichiometry, surface energy), and optical properties (refractive indices n and k).

The physico-chemical characterization of coatings will primarily be conducted at the Pprime Institute, using advanced tools such as spectroscopic ellipsometers, scanning electron microscopy (SEM), near-field microscopy (AFM), interferometric techniques, and mechanical or thermo-mechanical characterization tools like nano- and micro-indenters.

Two distinct approaches will be pursued concurrently, as outlined below. The scope and breakdown of these studies were defined in collaboration with Pprime Institute researchers:

1. Physical Properties & Growth Phenomena at the Material Level (Single-Layer Films)

This approach aims to better understand the properties of various materials of interest for visible and infrared domains (fluorides, sulfides), particularly when deposited at an angle (moderate, related to substrate curvature). The goal is to comprehend growth phenomena in complex fabrication processes involving multiple evaporation sources and/or ionic assistance, epicyclic substrate motion, use of uniformity masks, growth under oblique incidence.

Various characterizations will be performed at the single-layer level to understand the intrinsic properties of materials as a function of deposition parameters. The focus will include uniformity across complex surfaces, particularly:

- Microstructural properties: Thickness, density, porosity.
- Mechanical properties: Residual stresses, hardness.
- Chemical properties: Stoichiometry, presence of impurities.

- Optical properties: Refractive indices $n\&k$

Additionally, mechanical and thermal properties such as Young's modulus, Poisson's ratio, and the coefficient of thermal expansion (CTE) will be studied to refine performance predictions for newly designed treatments.

After determining thermo-mechanical characteristics, mechanical behavior will be assessed through numerical (e.g., Abaqus, Ansys) and/or analytical modeling at the single-layer and partial or complete architecture levels. This modeling will provide a better understanding of stresses and deformations under applied conditions, an aspect currently underdeveloped by optical designers but critical for achieving both optical and mechanical efficiency.

2. Mechanical Behavior Under Mechanical or Environmental Stress

This approach will investigate both model systems (single or bi-layer films) and complete multilayer architectures, such as external anti-reflective coatings. Tests will simulate operational environments to evaluate robustness, including adhesion tests, moderate/severe abrasion tests, thermal cycling, humid heat exposure, salt fog exposure.

These conventional tests, while useful, lack sufficient discrimination to fully describe mechanical behavior. The objective is to better understand degradation mechanisms during testing, including insufficient robustness of specific materials, cracking, fragile interfaces caused by low adhesion energy.

Detailed characterizations will be conducted on test samples to identify degradation causes, which will strongly depend on deposition conditions such as temperature, deposition rate, and applied ion power. While Safran has existing expertise in this area, collaboration with Pprime researchers will enhance result interpretation and guide optimization efforts.

Substrates and Preliminary Results

Different substrates will be used based on spectral domains and characterization requirements, including silicon, germanium, BK7 glass, chalcogenide glass (GASIR), and zinc sulfide (ZnS).

		Si	Ge	GASIR	ZnS	BK7	Lame BK7
Spectro-photométrie UV-Vis-SWIR	T(λ), R(λ), A(λ)				X	X	
Spectro-photométrie IR	T(λ), R(λ), A(λ)	X	X	X	X		
Ellipsométrie UV-Vis-SWIR	Epaisseur, n(λ), k(λ)	X	X	X			
Ellispométrie IR	Epaisseur, n(λ), k(λ)		X				
MEB	Morphologie, composition chimique	X	X	X			
Indentation	Adhérence	X	X				
Mesure de courbure	Contrainte	X		X			X
Diffraction des rayons X	Cristallinité	X					

Preliminary tests on single layers deposited on these substrates have shown significant differences in microstructure and mechanical properties. The influence of post-deposition thermal treatments on microstructure control and optimization will also be studied using in-situ techniques such as spectroscopic ellipsometry and X-ray diffraction (for crystalline deposits).

Roadmap :

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12
Etude des propriétés en monocouche	■	■	■	■								
% Propriétés optiques, microstructurales, mécaniques & chimiques												
Etude paramétrique sur matériaux classiques: T°C, vitesse dépôt, IAD	■	■	■	■								
Nouveaux matériaux: YbF3, DyF3, IR-F900			■	■								
Etude du comportement mécanique sur structure élémentaire	■	■	■	■	■	■						
Caractérisations selon tests classiques normalisés et nouveaux tests discriminatoires	■	■	■	■								
n&k, porosité, contraintes, composition chimique...												
Modélisations du comportement mécanique					■	■						
Origine des contraintes, fragilité d'interface...												
Dispersion des propriétés sur surfaces courbes					■	■	■	■				
Nouvelles architectures pour amélioration de la tenue mécanique			■	■	■	■	■	■	■	■	■	
Etude paramétrique suite étude monocouche & structure élementaire			■	■								
architecture "conventionnelle" sous différentes conditions T°C, vitesse, IAD												
Intérêt de couches "tampon"					■	■						
sur architecture conventionnel												
Gradient de composition aux interfaces					■	■	■	■				
Etude préliminaire: faisabilité de réalisation et d'analyse												
bi-déposition, mélange & diffusion thermique												
Architecture "optimisée mécaniquement"							■	■	■	■	■	
Prise en compte du comportement thermo-mécanique global												
Reporting & Synthèse avancement												
Réunion d'avancement plénière	X	X	X	X	X	X	X	X	X	X	X	
Compte-rendu annuel				X				X				
Rédaction du manuscrit									■	■	■	■

POWERED
BY TRUST

Safran Electronics & Defense

2, boulevard du Général Martial Valin
75015 Paris - France
Tél. : + 33 (0)1 55 60 38 00
Fax : + 33 (0)1 41 09 01 85
SAS au capital de 45.570.621,90 €
480 107 911 R.C.S. Paris

www.safran-electronics-defense.com

SAFRAN