Basic Research of Intrinsic, Tamper-Indication Markings and Patterns Defined by Pulsed Laser Irradiation: FY 14 Update

SAND2020-3678PE

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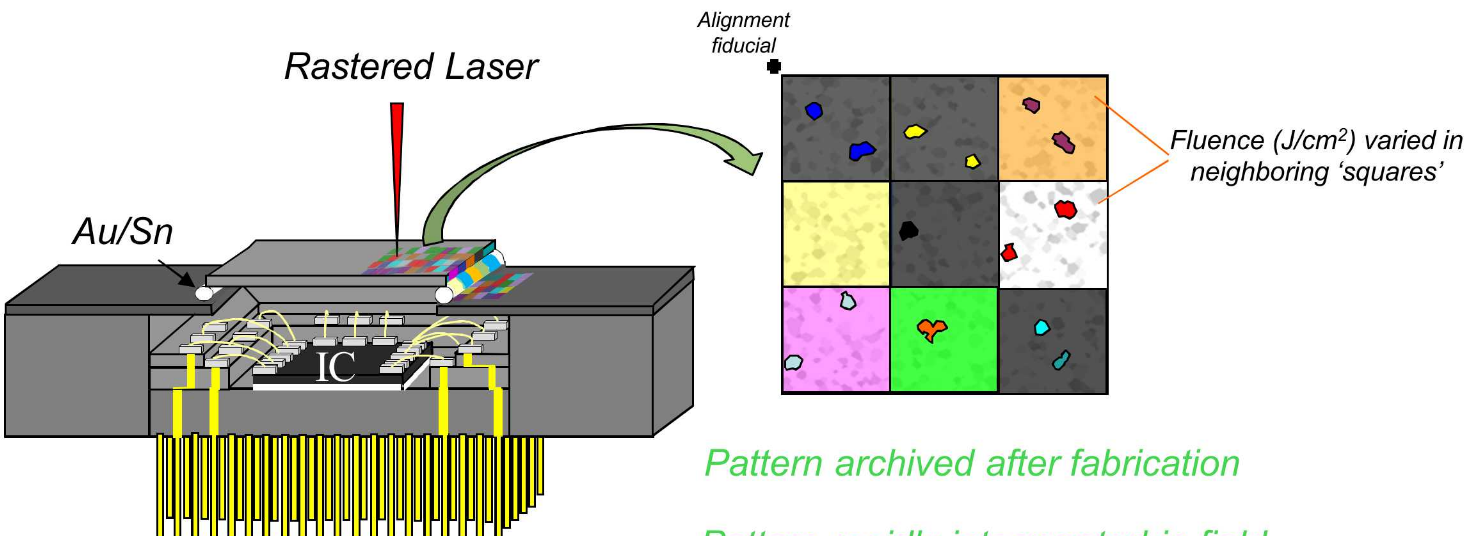
Novel Materials for Unattended Sensing to Support Future Treaties

Primary Objective (from BAA): "Identify microscale or nanoscale structures and phenomena in materials that can provide ***passive*** or active indicators of interference with unattended monitoring or sensing to support compliance with treaties."

OUR APPROACH: Research how short (ns) and ultra-short (fs, ps) pulsed laser light interacts with surfaces to create <u>color patterns</u> and complex morphological features for use as passive indicators of interference/tamper



Pattern archived after fabrication

Pattern rapidly interrogated in field and compared to determine authenticity

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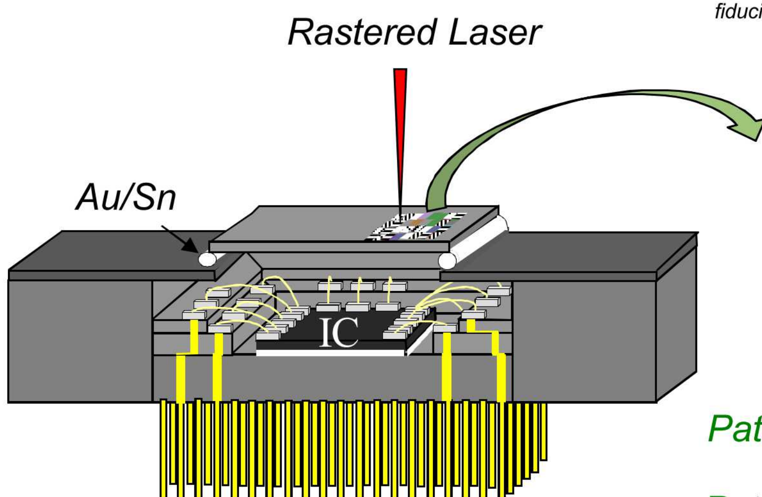

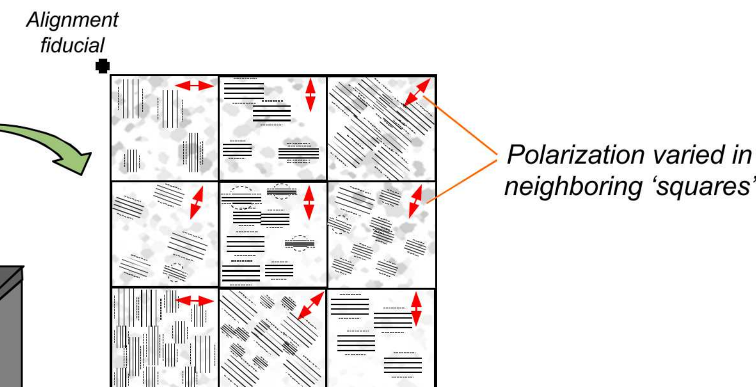

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Pattern rapidly interrogated in field and compared to determine authenticity

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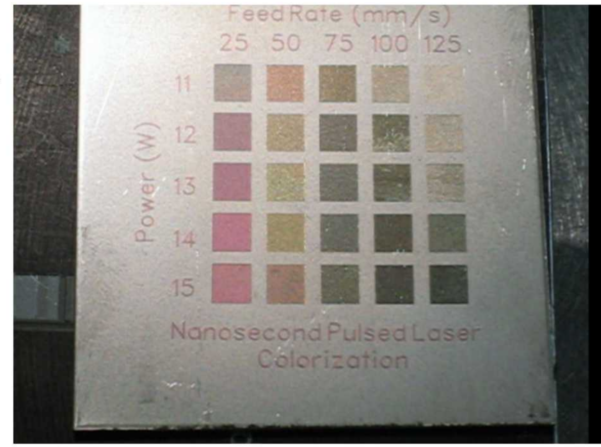
Rapid laser color marking processes are desired for fabricating complex markings and patterns.

- Our approach:
  - rastered, focused laser spot (1064 nm)
  - nanosecond pulse duration for local heating
  - metal reacts with air to form coating

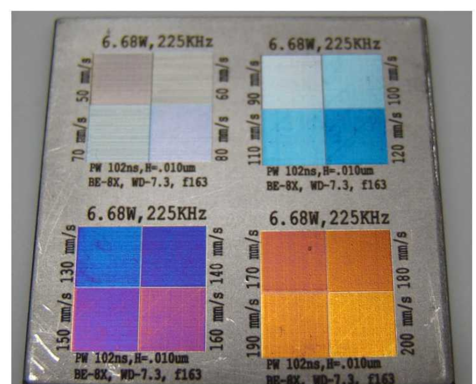
Stainless Steel 304L



- Variety of bulk materials form color layers
  - Stainless steel 304L R ~ 0.73
  - Dual phase steel (50% ferrite) R ~ 0.72
  - Titanium CP2 grade R ~ 0.57
  - Titanium alloy Ti_6Al_4V R ~ 0.37
  - Kovar[TM] (FeNiCo) R ~ 0.63
  - Georo[TM] ($Au_{88}Ge_{12}$) R ~ 0.74
  - Copper R ~ 0.97

- FY 14 work has expanded to study coloring of thin metal films
  - Titanium R ~ 0.57
  - Chromium R ~ 0.62
  - Vanadium R ~ 0.54

Bulk Titanium (CP2 grade)



1 cm

Titanium film (3 microns)

0.5 cm

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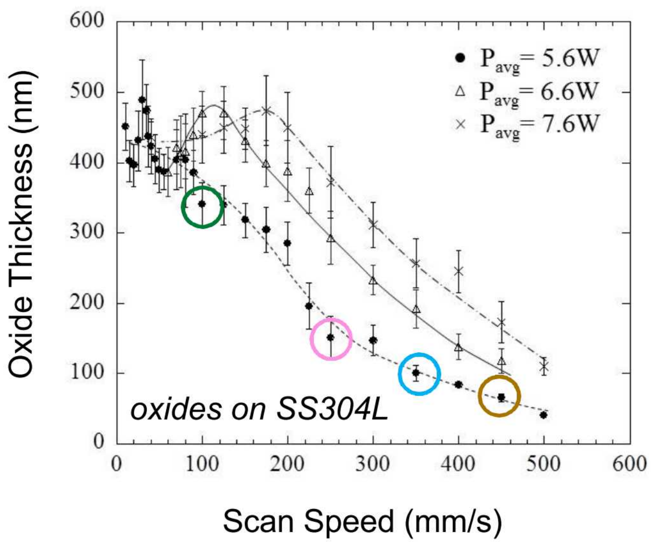
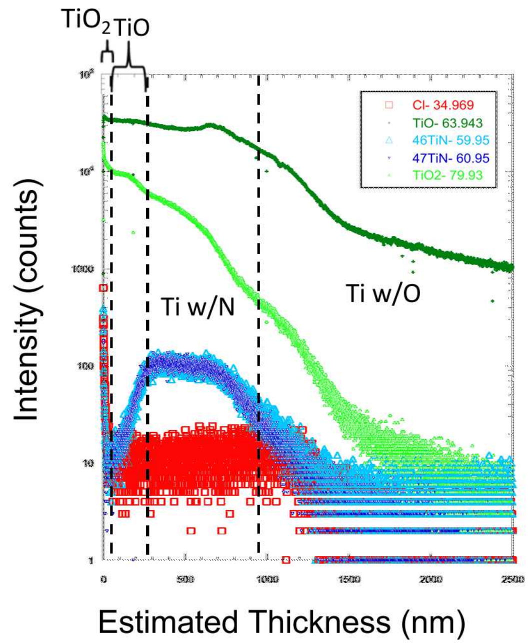
Our research of laser-fabricated color oxides has investigated the physical origins of color and spectral reflectance and their relation to processing.

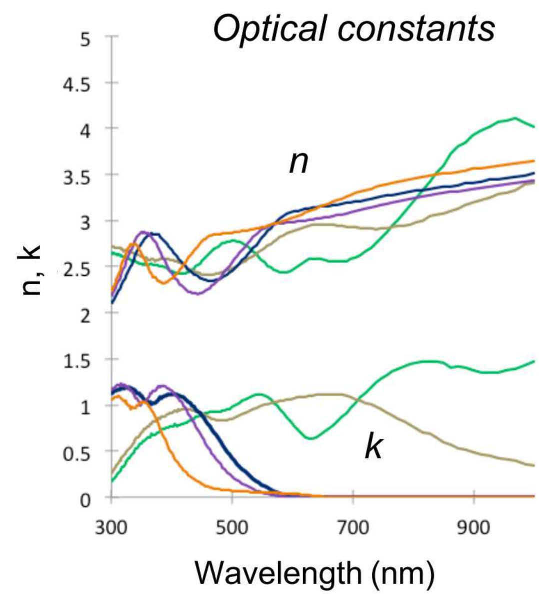
Coating thickness



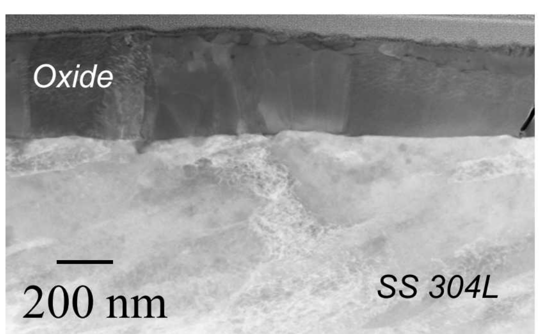
Composition

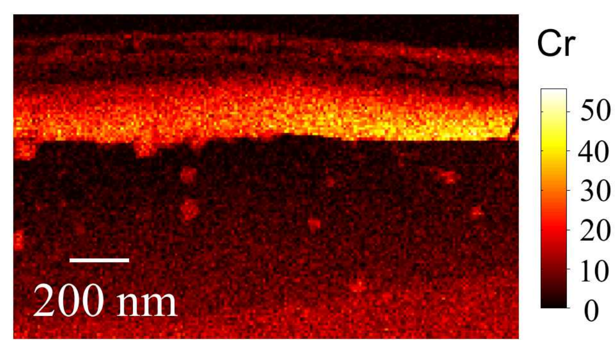


Optical constants



Phase and Microstructure





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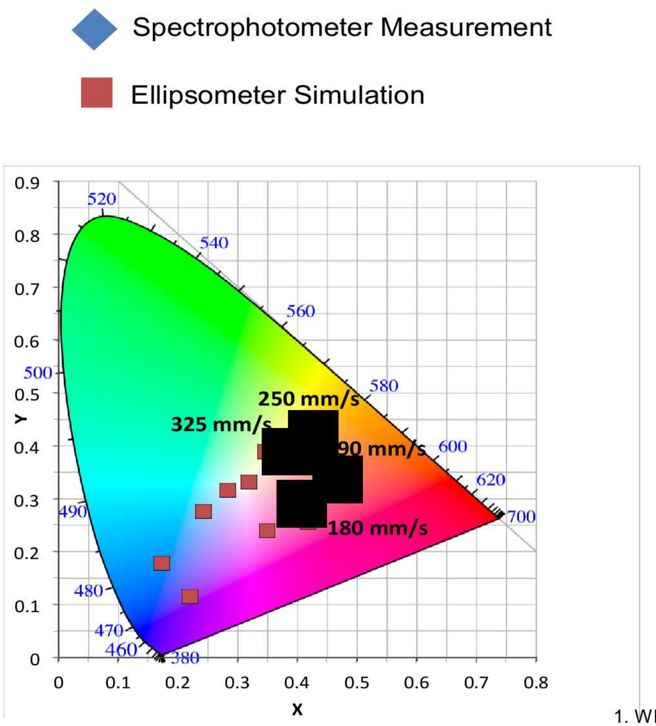
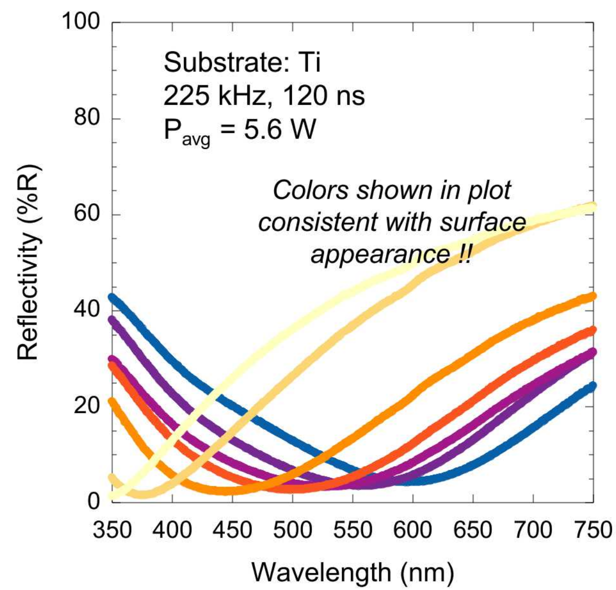
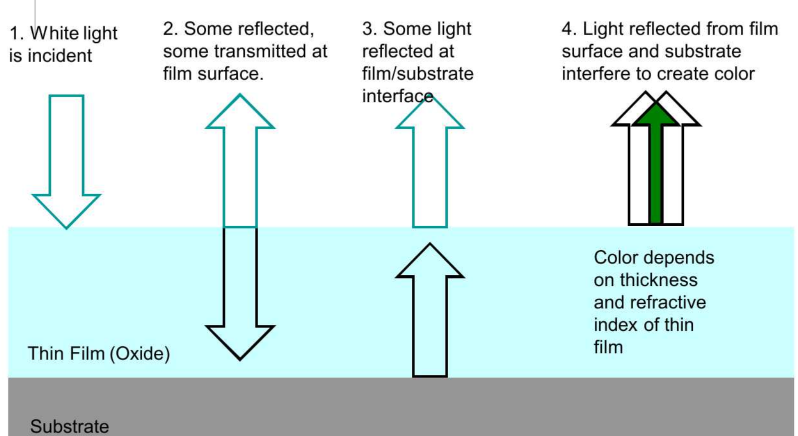
Colored appearance can now be predicted using measured optical constants (of film, substrate) and oxide layer thickness, roughness.

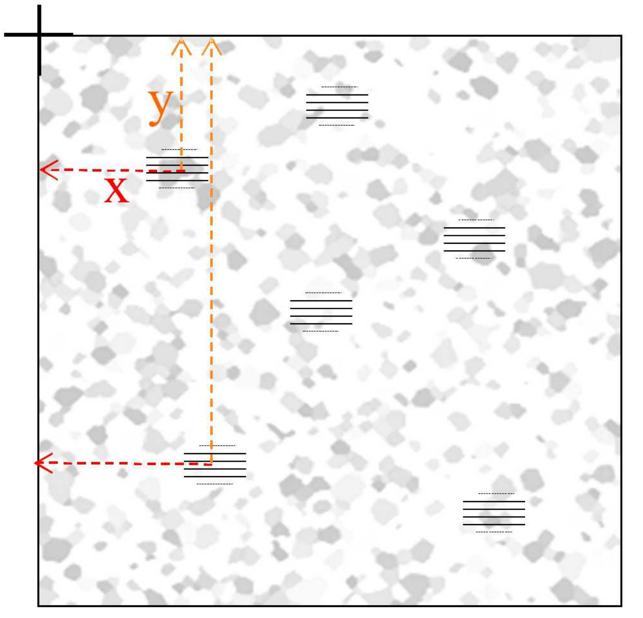






Alternative laser-based processes have been developed to pattern alternative intrinsic markings.

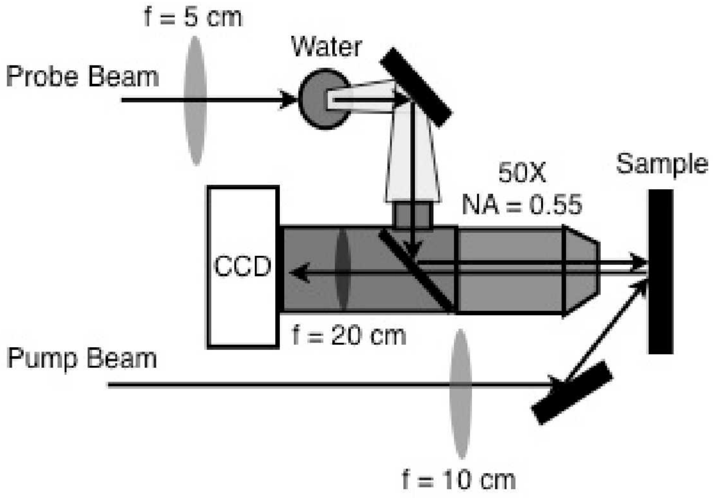
- Our approach:
  - rastered, pulsed laser spot (ns, ps or fs)
  - formation of complex, periodic ripple patterns
  - desire to control some characteristic of pattern (for including encrypted information much like a barcode)
  - also would benefit from randomly formed or placed features for validation of authenticity of marking
- Applicable to materials that do not form colored oxides.

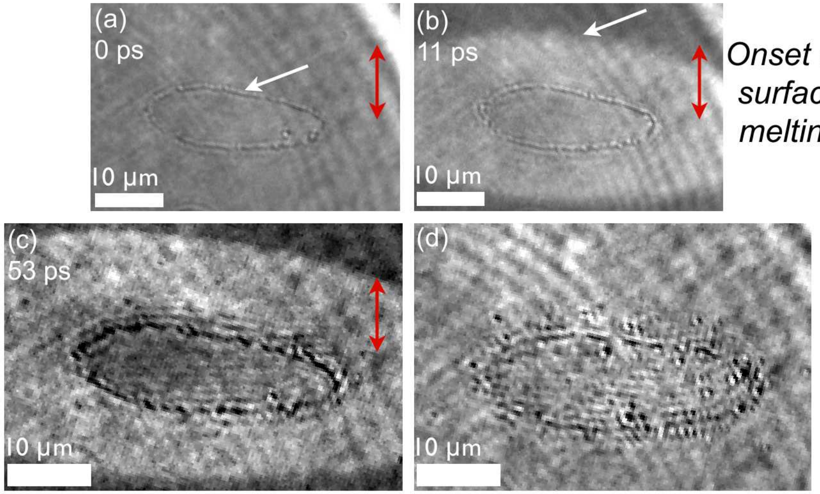


Initial hypothesis: formation of ripples at random sites . Archive their locations

Key discoveries from our research of laser-induced periodic surface structures (LIPSS).

- First study to:
  - identify timescales for ripple formation (pump-probe)
  - show that a combination of Fresnel diffraction and surface plasmon polaritons affect LIPSS formation.
  - investigate the effects of polarization with respect to pre-existing feature orientation (Fresnel diffraction).
  - discover the effects of surface asperity height on EM field periodicity and amplitude.

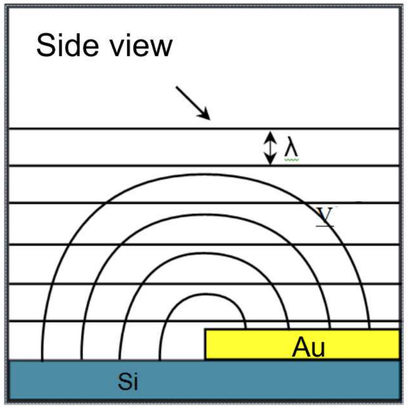


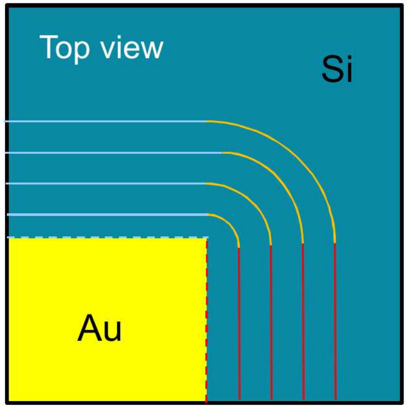


Onset of surface melting

Ripple formation at ~ 50 picoseconds

Final surface morphology





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Tasks for FY14

- **Modeling the formation of laser-induced periodic structures**

  Sub-task 2.4 Investigate roles of surface plasmon polaritons, effects of fluence, site specificity.

  Sub-task 2.5 Model light solid interactions using EM solver multi-source scattering, interference.

- **Investigate stability of laser-defined markings**

  Sub-task 6.4 Corrosion testing that implements salt fog / spray.

- **Research methods for feature interrogation**

  Sub-task 7.1 Investigate light-based methods for pattern inspection and authentication. This includes microspectrophotometry and speckle.

Work completed in FY14 involved modeling of light – solid interactions and validation experiments.

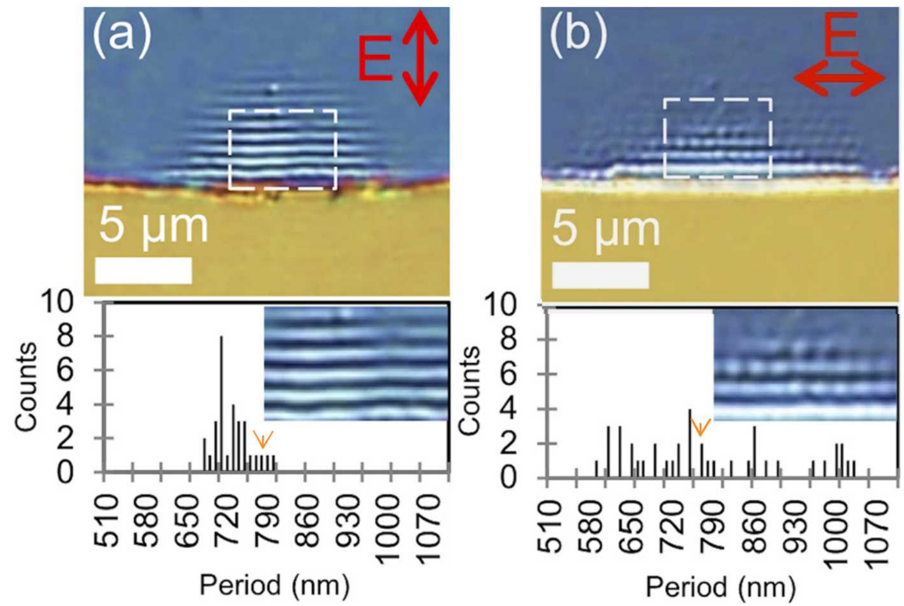
- Experiments with pre-fabricated (well defined) mesa structures

  - light polarization orientation w/ respect to edge

  - fluence (which can drive plasmon intensity)

- Modeling (COMSOL, Lumerical) accounts for

  - incident wavelength
  - pulse duration
  - fluence
  - feature geometry (height, etc.)
  - Fresnel diffraction
  - surface plasmon excitation



ᵛ Fundamental wavelength of incident beam

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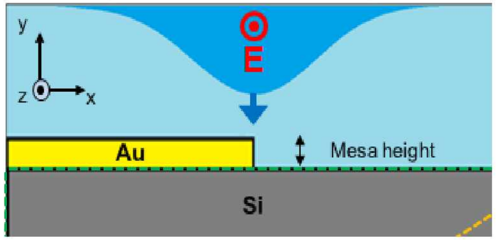
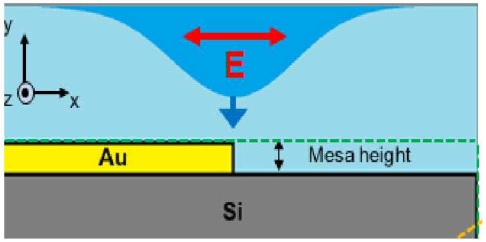
The amount by which the surface period is shifted from the fundamental wavelength of incident radiation varies with laser fluence.

Modeling completed in FY14 explains many of the observed complexities of markings.

- Vary alignment of polarization direction with respect to step edge to activate surface plasmons to different degrees (similar to expts.)
- Vary step height of mesa
- Predict field variations across surface
- Compare with measured ripple patterns



a. Fresnel diffraction



b. Fresnel diffraction & surface plasmon excitation

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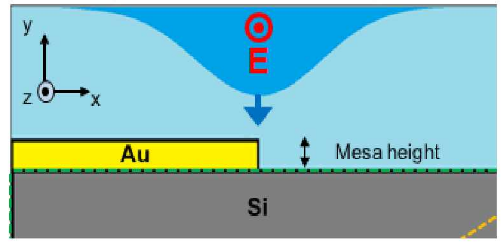
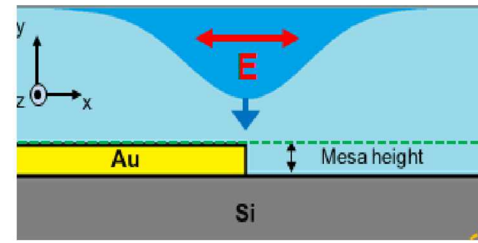


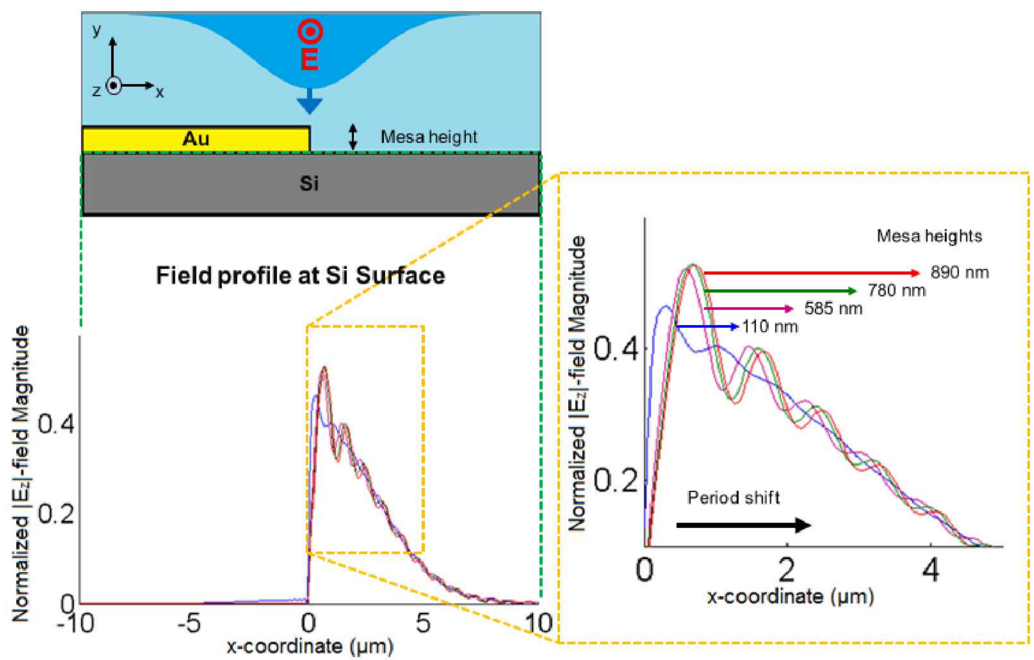
a. Fresnel diffraction



b. Fresnel diffraction & surface plasmon excitation

Example where surface plasmon excitation is minimized

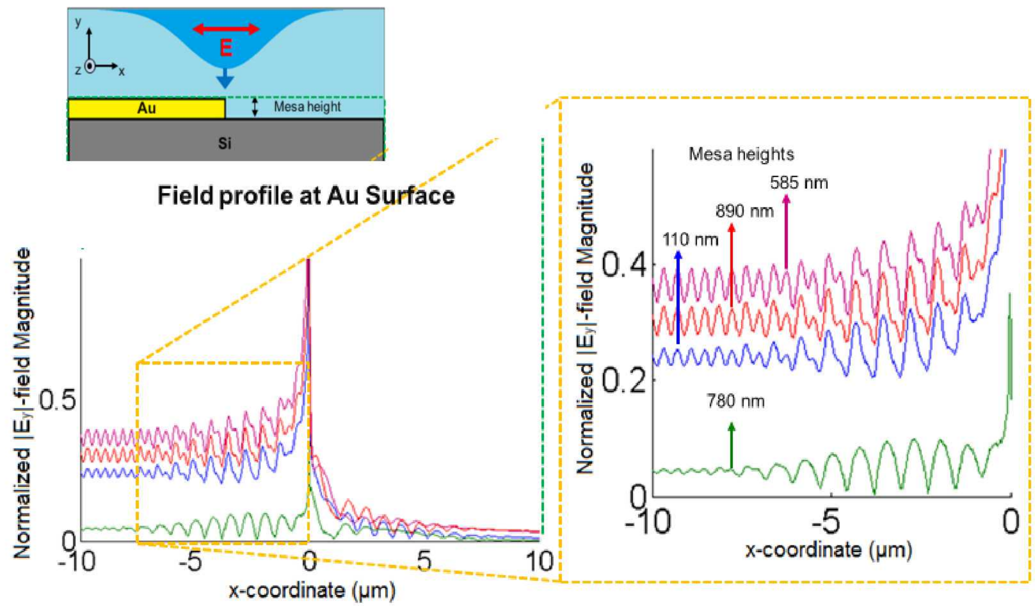
- Predictions:
  - no EM field variation on Au (similar to experiments)
  - shifted period with increased mesa height (not validated in lab).



Modeling has explored effects of surface plasmon excitation.

Predictions :

- Periodic field variations on Si and Au (similar to ripple patterns formed in lab).
- Periodic field variations extend to greater distance from step edge (similar to ripple patterns formed in lab).
- In-plane periodicity of EM field variations shifts to dimensions below the primary wavelength of incident light (similar to ripple patterns formed in lab).
- Second harmonic in periodicity due to traveling wave from opposing edge.



Orient light polarization perpendicular to mesa step edge to maximize effects of surface plasmon polariton excitation.

Surface ripple patterns produced on real surfaces are complex markings with intrinsic features.

- User controlled features

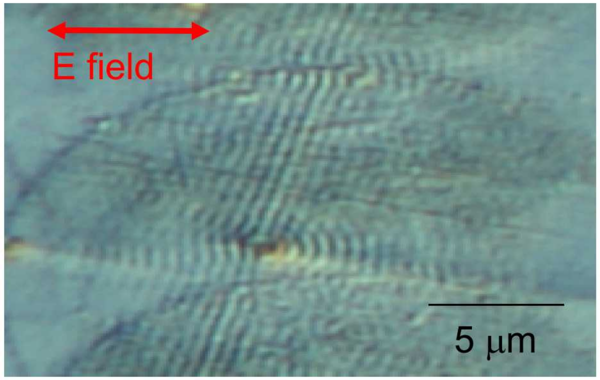
  - average wavevector of ripples (via polarization)

- Spontaneous characteristics

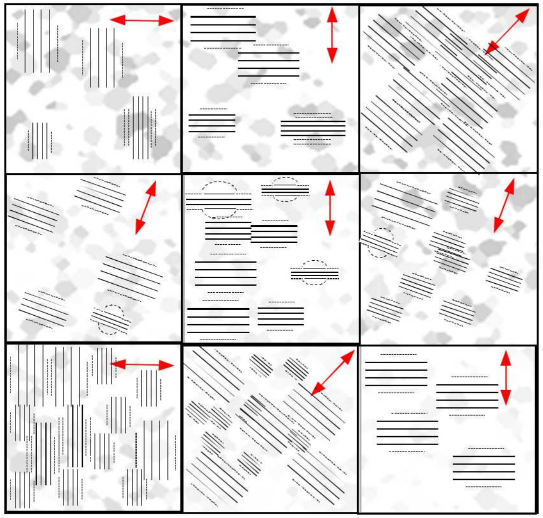
  - location (maps to initial asperity location)

  - ripple period (attributed to degree of plasmon excitation which relates to orientation of polarization to local step edge).

Periodic ripple pattern on Stainless Steel 304L formed around an initial surface defect



Example wherein polarization is varied in discrete square macro-areas and ripples form at asperities with unique periods (due to relative alignment).



Polarization varied in neighboring 'squares'

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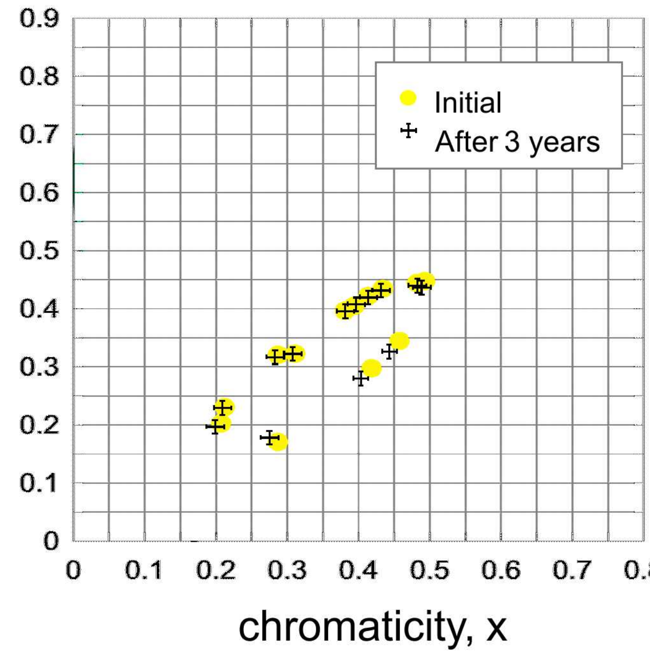
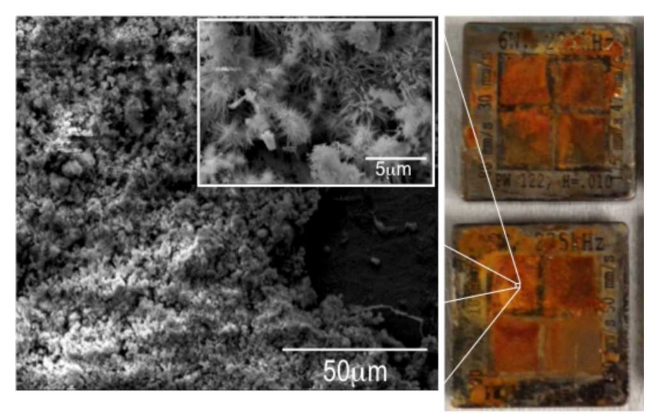
Colored oxide coatings do not change in humid environments but exhibit poor resistance to corrosion when immersed in salt water.

•Previous year's research showed excellent mechanical properties (hardness, toughness, work of adhesion) for color coatings made on steel, titanium, etc.



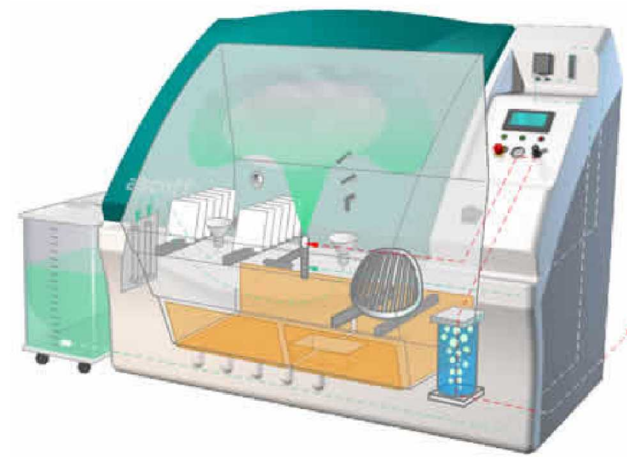
•Continued research demonstrates no change in chromaticity (colored appearance) after 3 years of room temperature aging.

•Initial work involving immersion in salt water solution for 25 days showed poor corrosion resistance (SS 304L oxides) in extreme environments.



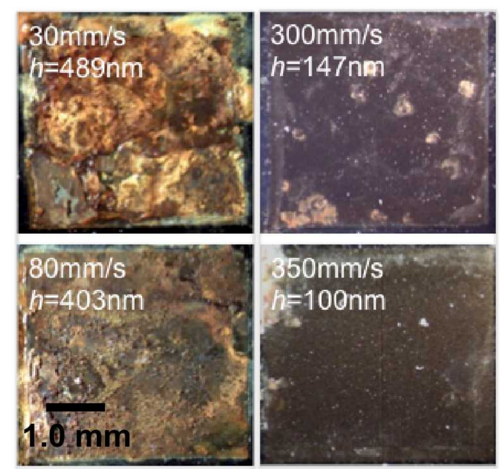
Motivation for current FY task:
Investigate corrosion resistance in salt fog environments.

Work in FY14 involved additional corrosion testing including salt fog experiments.



- Salt fog test conforms to ASTM B117 standards.
- Exposure time of 100 hours for each sample.
- Colored oxide layers made to different thickness.

- Salt Fog testing results:
  - Steel (SS304L): For a range of oxide thickness ~ 150 nm, there was no corrosion. Corrosion when thickness > 200 nm.
  - Titanium (CP2 grade): No indication of corrosion to date.



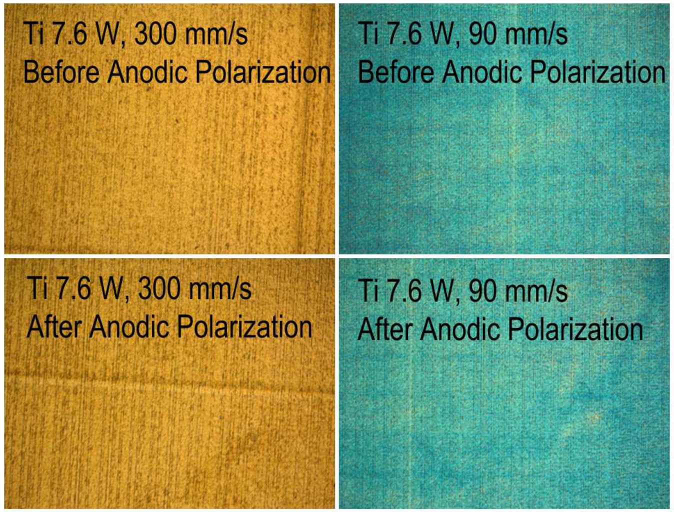
Results from salt fog tests; color layers on stainless steel

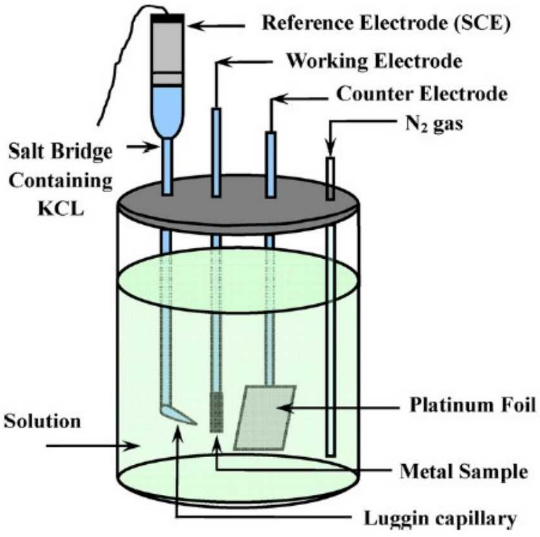
Additional corrosion testing has included anodic polarization tests for localized attack.

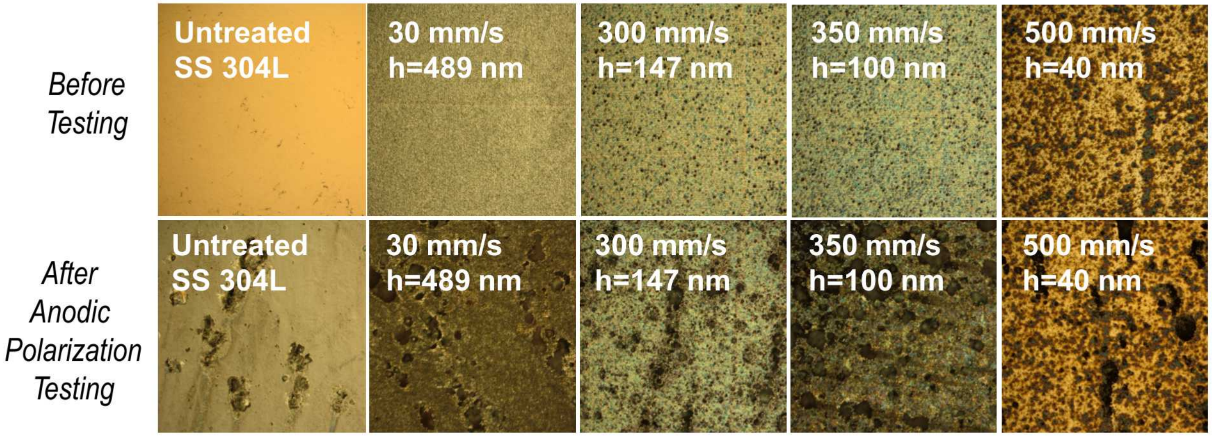
- Anodic testing results:

  - Titanium (CP2 grade): no corrosion attack (thin, thick coatings).

  - Steel (SS304L): localized pitting at cracks in oxide coatings.



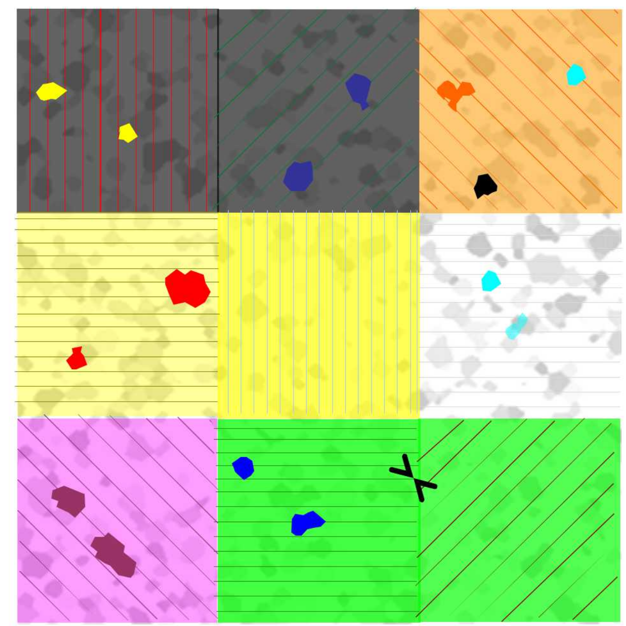




Strategy for future: development of new processes for stainless steel oxides that prevent cracking (pre-heating, post-anneal, multi-scan laser processes)

Research of speckle analysis for feature detection and pattern validation at long standoff distances.

- Laser scan direction can be varied in color features independently of color (which is controlled by fluence).
- Scan direction gives rise to large scale features ~ 50 μm period which are detected by speckle.
- Long working distance (up to meter) utilized.



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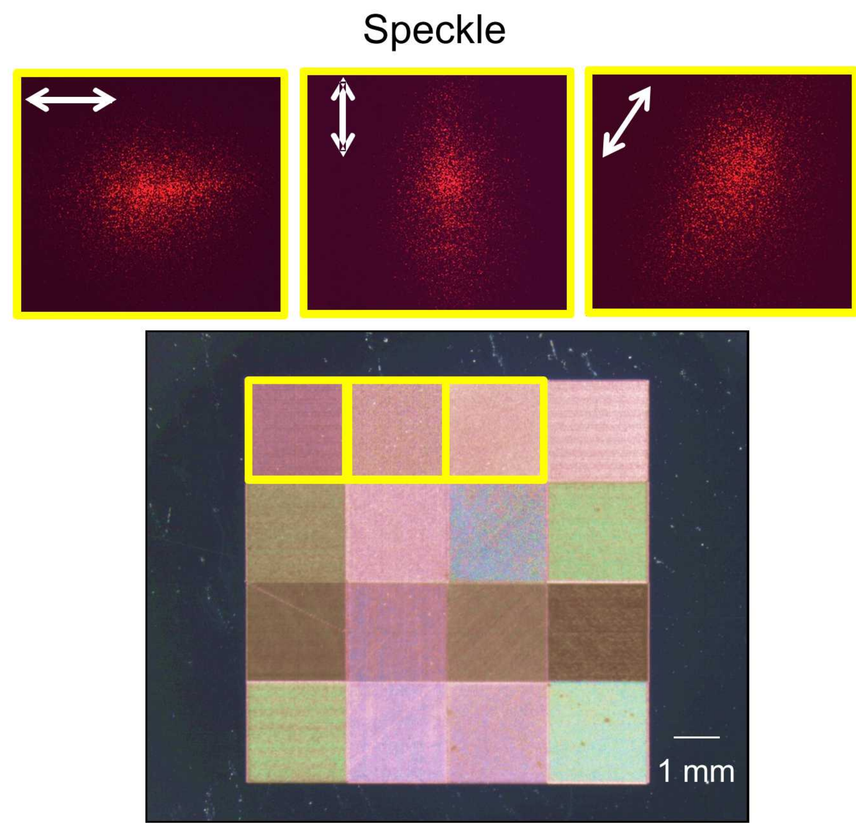
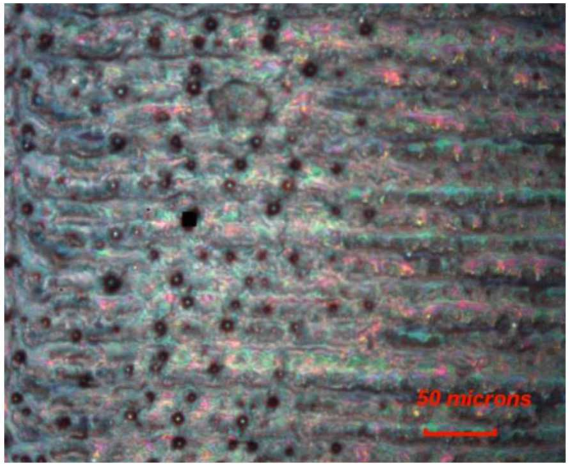
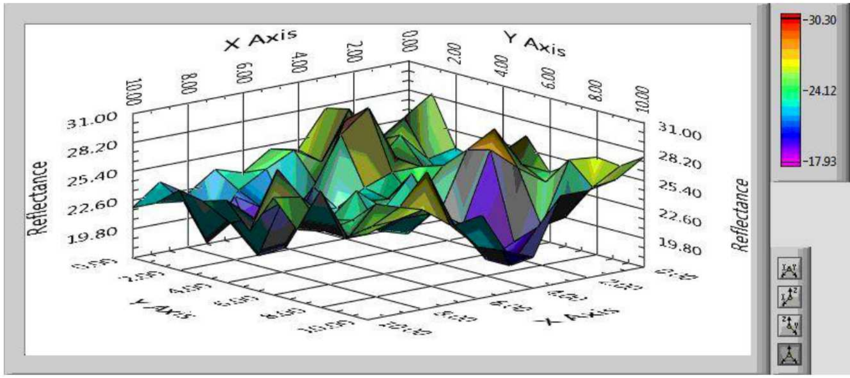


Work in FY14 involved investigation of microspectrophotometry as a method for mapping and validating uniqueness of markings.

- Utilized a Craic Inc. UV-Vis-IR microspectrophotometer
- Measurements spanned millimeter areas.
- Detected large color islands with unique reflectance spectra (compared with the surrounding material).





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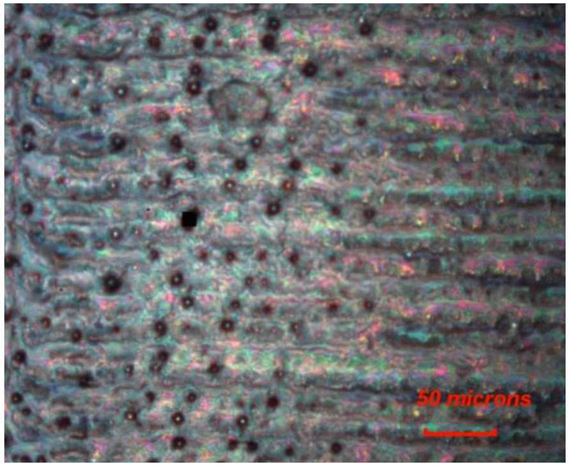

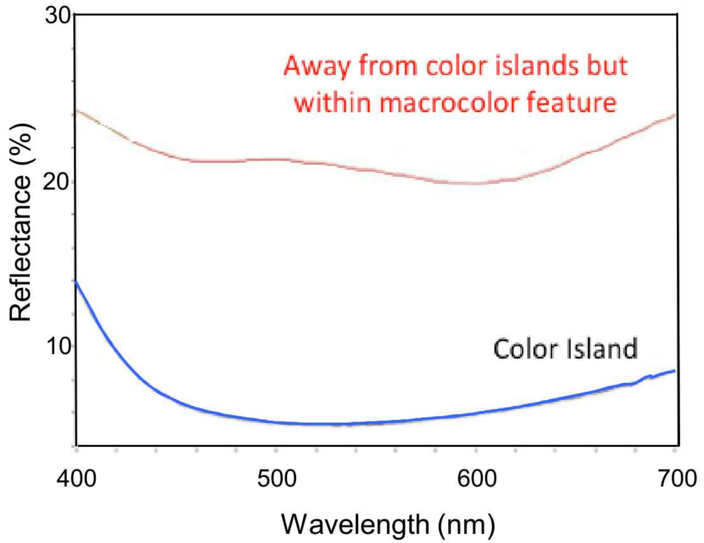

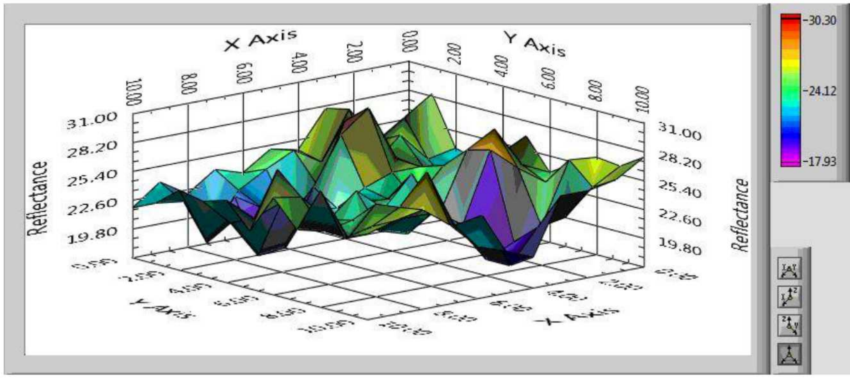

Reflectance Map at λ =

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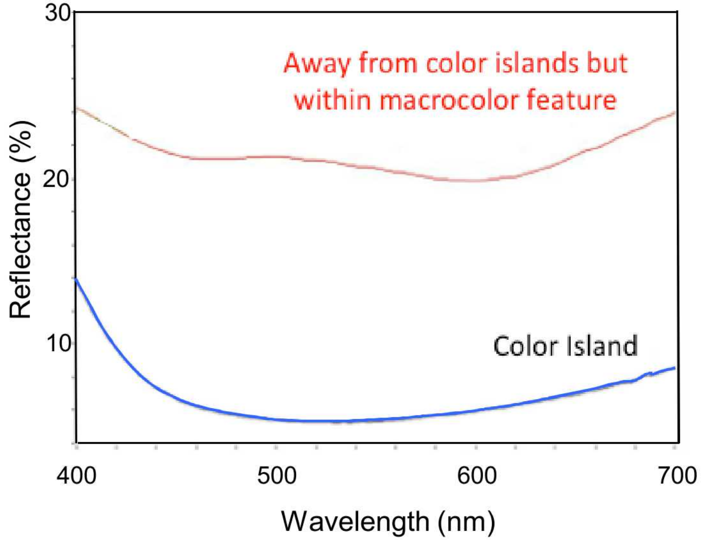

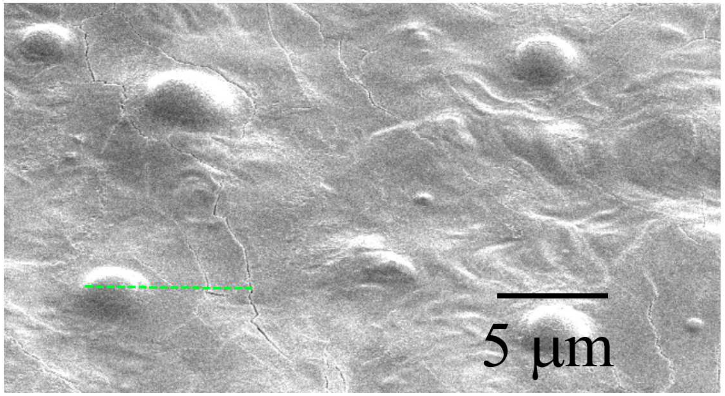

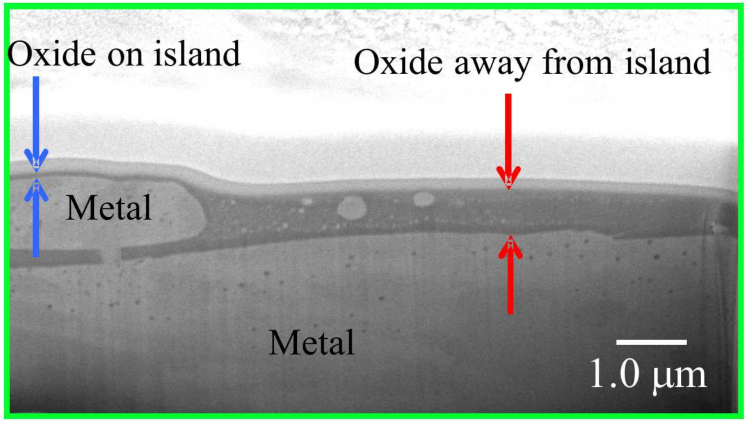

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Four presentations were delivered in past year, and two received presentation awards.

2nd Place

1. S. Lawrence et al. at the *Internat. Conf. on Metal Coatings and Thin Films* (San Diego, CA, 4/28/14)
   Title: Electrochemical and Chemomechanical performance of Laser Oxide Coatings on Metallic Substrates.

1st Place

2. G. Neiser et al. *at* the *Rio Grande Symposium on Adv. Materials* (Albuquerque, NM, 10/3/13)
   Title: Stability of Colored Oxide Films fabricated on Ti.

3. S.K. Lawrence et al. at the *Gordon Conf. on Thin Film & Small Scale Mechanical Behavior* (Waltham, MA, 7/13/14)
   Title: Development of Mechanically and Environmentally Stable Oxide Coatings by Pulsed Laser Irradiation.

4. R. Murphy et al. at *Surface Analysis 2014* (Albuquerque, 6/11/13)
   Title: Ellipsometric Analysis of Laser Fabricated Oxides on Ti.

Total Number of Presentations for project (to date) = 25.

Multiple peer-reviewed publications and a patent.

"Method of Intrinsic Marking" U.S. Patent # 8,685,599 (1 Apr 2014).

"Polarization dependent formation of femtosecond laser-induced periodic surface structures near stepped features", R.D. Murphy et al. , App. Phys. Lett. 104 (2014) Article #: 231117. *Published*

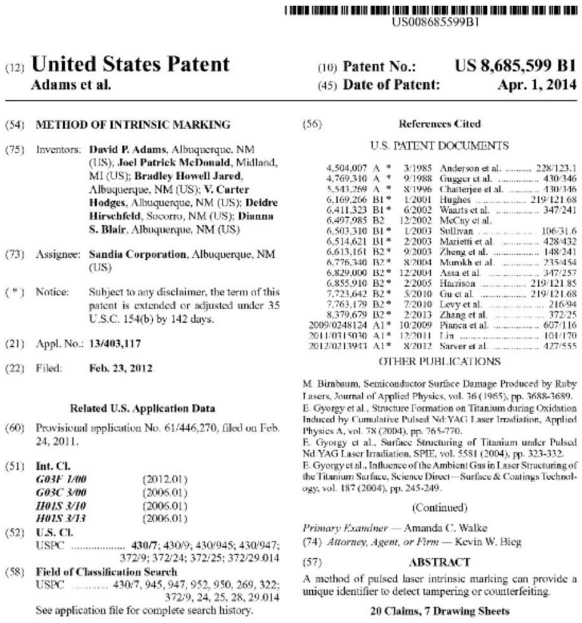
"Environmental resistance of oxide coatings grown on stainless steel 304L by pulsed laser irradiation in air", S.K. Lawrence et al. Corrosion Science, 2014. *Submitted*

"The effects of substrate and film composition on the optical properties of laser grown titanium oxide/oxynitride coatings, R.D. Murphy et al., Thin Solid Films, 2014. *Submitted*

"Nanosecond pulsed laser irradiation of titanium: oxide growth and effects on underlying metal", D.P. Adams et al. , Surface & Coatings Tech. 248 (2013) 38. *Published* (*Submitted* 2013)

"Pump probe imaging of laser induced periodic surface structures after ultrafast irradiation of Si", R.D. Murphy et al. Appl. Phys. Lett. 103 (2013) Article #: 141104. *Published* (*Submitted* 2013)

"Mechanical and electromechanical behavior of oxide coatings grown on stainless steel 304L by nanosecond pulsed laser irradiation", S.K. Lawrence et al. Surface & Coatings Tech. 235 (2013) 860. *Published* (*Submitted* 2013)



US008685599B1

(12) **United States Patent**
Adams et al.

(10) **Patent No.:** **US 8,685,599 B1**
(45) **Date of Patent:** **Apr. 1, 2014**

(54) **METHOD OF INTRINSIC MARKING**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 142 days.

(21) Appl. No.: **13/403,117**

(22) Filed: **Feb. 23, 2012**

Related U.S. Application Data

(60) Provisional application No. 61/446,270, filed on Feb. 24, 2011.

(51) **Int. Cl.**

G03F 1/00	(2012.01)
G03C 3/00	(2006.01)
H01S 3/10	(2006.01)
H01S 3/13	(2006.01)

(52) **U.S. Cl.**
USPC **430/7**; 430/9; 430/945; 430/947; 372/9; 372/24; 372/25; 372/29.014

(58) **Field of Classification Search**
USPC 430/7, 945, 947, 952, 950, 269, 322; 372/9, 24, 25, 28, 29.014
See application file for complete search history.

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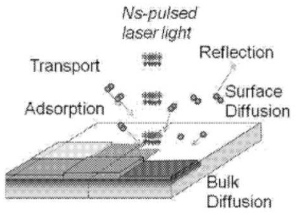
(57) **ABSTRACT**

A method of pulsed laser intrinsic marking can provide a unique identifier to detect tampering or counterfeiting.

20 Claims, 7 Drawing Sheets



Total Number of Publications for project (to date) = 13.

This technology can potentially benefit the warfighter.

•Intrinsic marking – no adhesive

•Applicable to various materials

•Color for easy recognition

•Advanced, encrypted barcoding

•Complex features that are virtually impossible to replicate

Now incorporate color and intrinsic surface ripples for added complexity.

Borrowed from website: Laser Photonics, Inc.

Scenario 1

- General asset protection (applied in the field)
- Enable rapid geolocation (with something as simple as cell phone)

This technology can potentially benefit the warfighter.

- Intrinsic marking – no adhesive
- Applicable to various materials
- Color for easy recognition
- Advanced, encrypted barcoding
- Complex features that are virtually impossible to replicate

Now incorporate color and intrinsic surface ripples for added complexity.

Borrowed from website: Laser Photonics, Inc.

Scenario 2

- Preventing counterfeit parts in the field
- Critical assets marked with non-transferable tag reduce risk of substitution.
- Archived microstructural features for unambiguous verification.

Summary

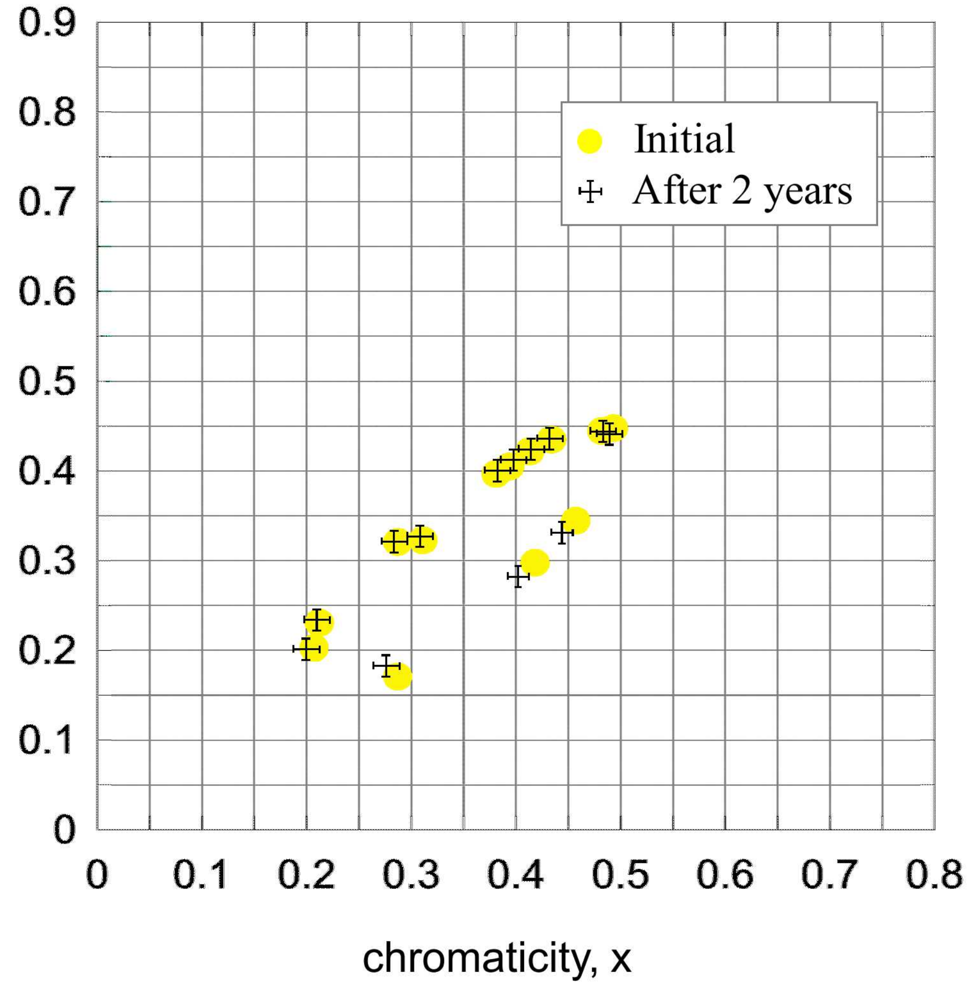
- Pulsed-laser color marking of oxidation of metals, alloys.
  - Aspects of complex, macro-scale color patterns can be tailored
    - average color, location, laser scan direction (for speckle analysis)
  - Other characteristics are formed spontaneously:
    - color islands, their different spectral reflectance, location
  - Large palette of colors (R, chromaticity) on different component materials
  - Detailed optical properties (n,k) measured >>> colors can now be predicted
  - Oxide coatings adhere well, are hard, and exhibit good wear resistance
  - Oxide coatings are stable over time and for moderate temperatures (250^{o}C for multiple hours)
  - All oxide coatings on Ti show good corrosion resistance (salt fog, local polarization testing)
  - Some oxide coatings on steels show good corrosion resistance (salt fog exposure)

- Nano-scale ripples are a second form of archivable marking.
  - Aspects of ripple markings are tailored (i.e., set by user)
    - average ripple wavevector is set by incident light polarization
  - Other characteristics are formed spontaneously:
    - ripple formation at local initial protrusions; period of ripples owes to plasmon excitation
  - Origin of ripple patterns identified (interference of scattered light with impinging light)
  - Time scales for surface ripple formation (~ 50 ps) demonstrated by ultrafast pump-probe microscopy

BACKUP SLIDES

Optical properties of color layers have not changed significantly over two years (normal aging).

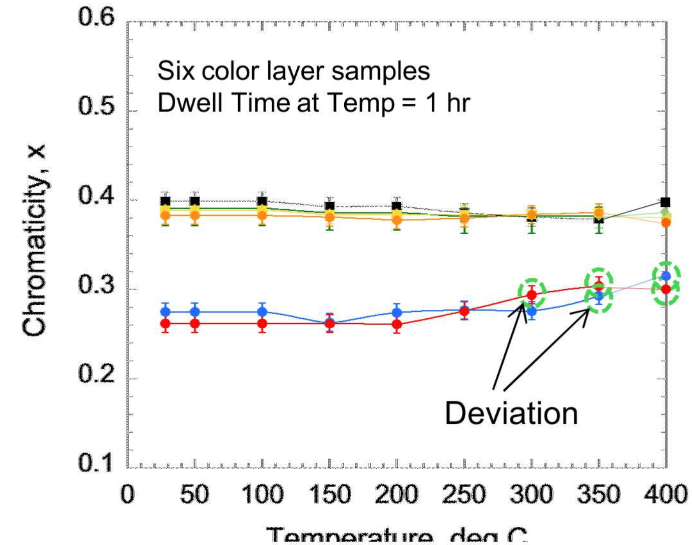
- 200 samples tested by aging at 75°F, 40% relative humidity, lighted room
- Tested samples were various oxide coatings made on SS304L, Ti
- No detectable change in chromaticity (within uncertainty)
- No detectable change in spectral reflectance (within uncertainty)



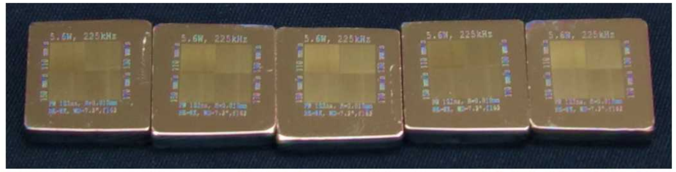
Also, there are no detectable changes in colored, micro-precipitates after 2 years.

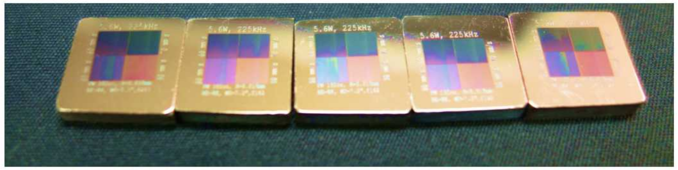
Accelerated aging at high temperature reveals high decomposition temperatures (~250^{o}C) for colored oxides.

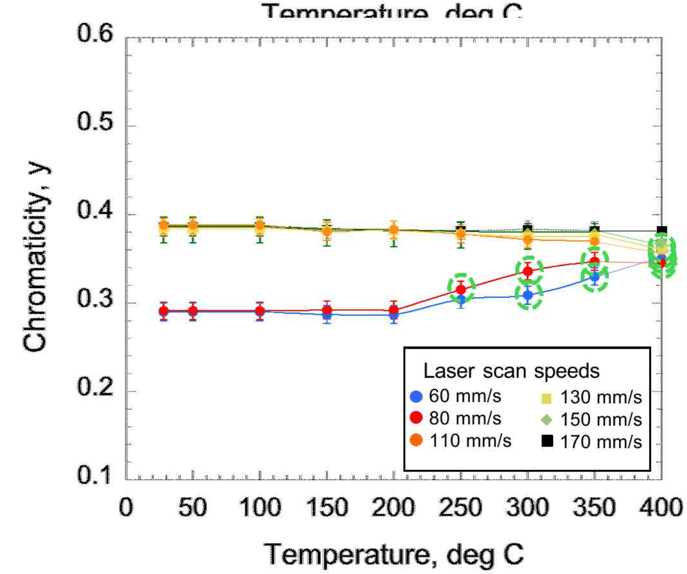
- No detectable change in chromaticity (x,y) up to 250^{o}C for multiple hours.
- No detectable change in spectral reflectance up to 200^{o}C for multiple hours.
- We turn to XRD for phase identification associated with transformation



Ex. Oxides made on Ti6Al4V were aged at high temperature







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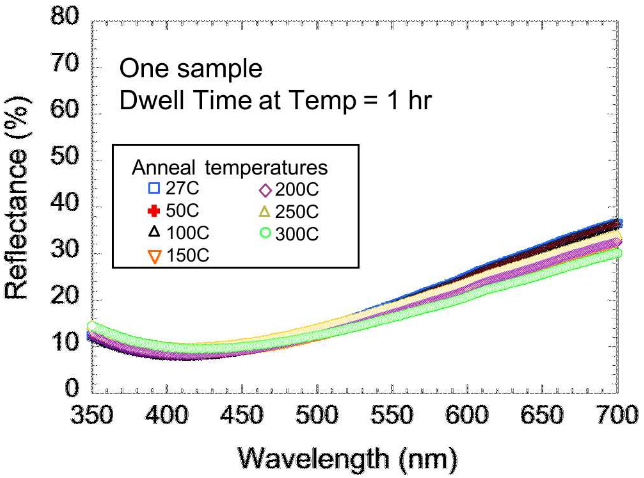

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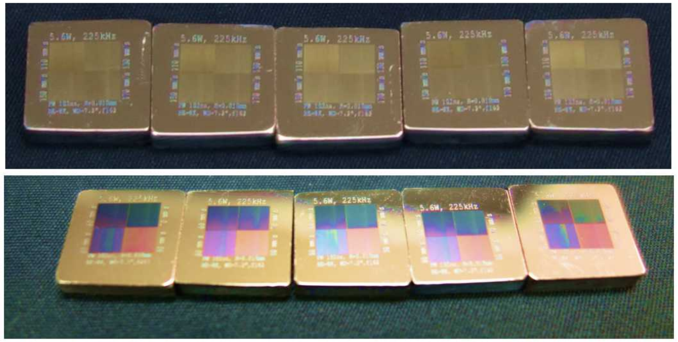
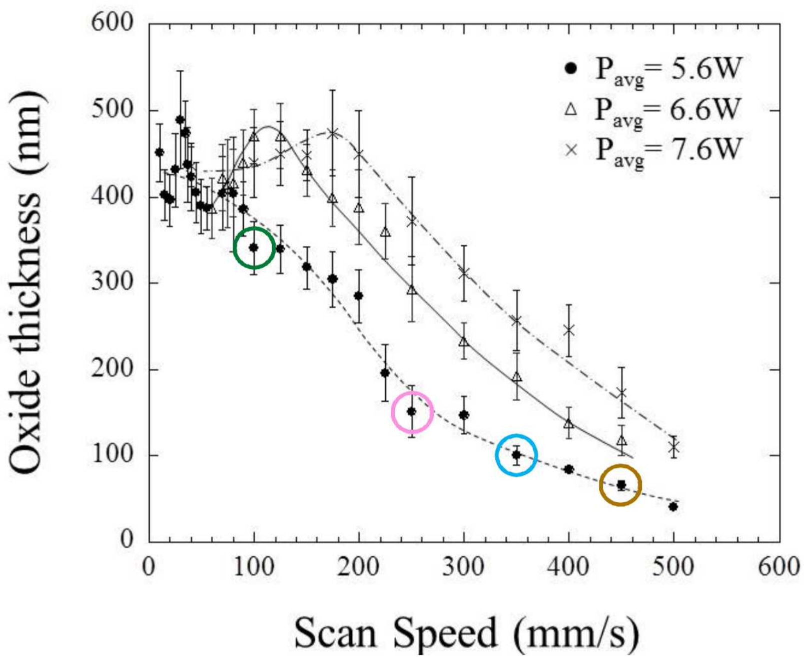


D.P. Adams 2013

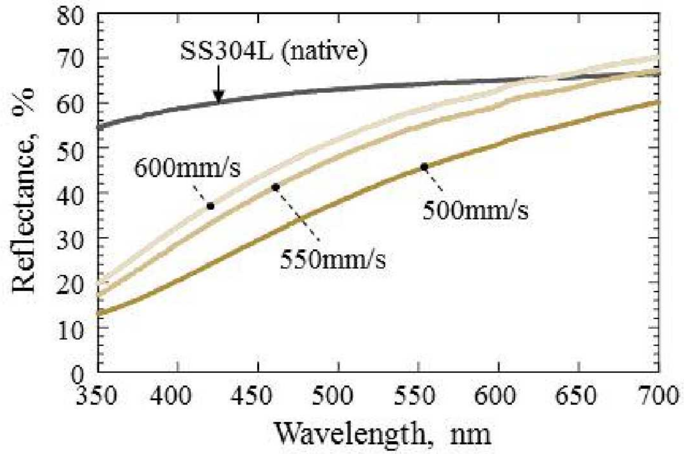
Oxide thickness, in part, determines color.

- Scanning electron microscopy shows oxide layers are ~ 10 - 500 nm.
- Thickness generally increases with fluence or decreasing scan speed (at fixed P_{avg}).

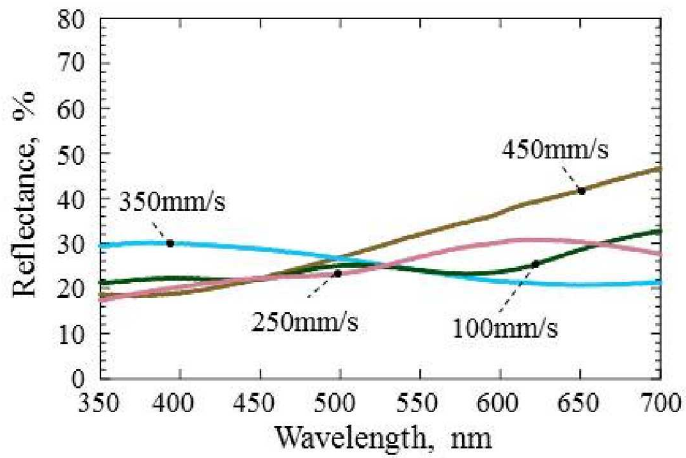
Example: Oxides on Stainless Steel 304L



- For t_{ox} < ¼ λ of visible light, attenuation.



- For t_{ox} > ¼ λ of visible light, attenuation and interference.



D.P. Adams 2012

University Collaborations in 2013

- Sub-contract extended with Univ. of Michigan

- Ryan Murphy (Applied Physics grad. student)
  Graduated with PhD : 2/2013 (100% commitment)
  Now a post doc at Sandia working with this team

- Basic research of surface roughness evolution
  during pulsed laser irradiation involving ultrafast
  pump-probe microscopy

- Sub-contract extended with Purdue Univ.

- Samantha Lawrence (Materials Science & Engineering
  Expected PhD date: 2014, 25% time commitment

- Research of the mechanical properties of laser-fabricated
  metal oxides (includes study of hardness, adhesion,
  phase, variations through thickness)

All students and professors are US citizens

Technical Objectives for FY11 have been completed

- Research pixel-by-pixel control of laser color features using 10-200 ns light
- Research effects of pulse frequency on color layer formation
- Investigate microstructure, composition, optical properties of color layers
- Research hardness and modulus of color layers (nanoindentation)
- Implement a thermal modeling code to simulate the effects of laser irradiation (fixed position, varies pulse duration, rate, energy per pulse, wavelength)
- Qualify ultrafast pump-probe instrument (Univ. of Michigan)
- Research temporal evolution of laser-induced periodic surface structures

Sandia National Laboratories

Technical Objectives for FY12 have been completed

Research includes

- the physical and chemical properties of laser color layers
- micro-color centers forming at selective sites within macro-scale patterns
- the toughness of laser-fabricated color layers
- heat-affected zones via thermal modeling
- feasibility of picosecond and single nanosecond laser coloring of metals
- the temporal evolution of laser-induced periodic structures
- the origin of laser-induced surface ripples
- site-selective formation of periodic surface topographv

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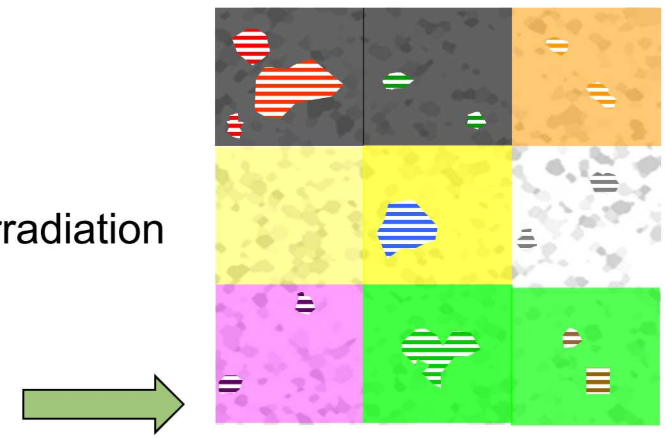
Technical Objectives of FY 13

<u>Research of</u>

- Stability of laser-fabricated markings
  - Normal aging (room temperature, multiple years)
  - Accelerated thermal aging (elevated temperature, short time)
- Mechanical properties of laser-defined color oxide layers
  - Toughness
  - Coefficient of friction
- Modeling heat affected zones assoc. with scanned, ns irradiation
  - Thermal modeling of pulsed heat input
  - Multiple substrates
- Complex markings that combine periodic ripples, colors
  - All-in-one process involving ns irradiation
  - Two step process involving ns and fs irradiation



Hypothesis: colors and morphology

An additional Year 3 task involved publishing results from Year 2.