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

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Basic Research Technical Review

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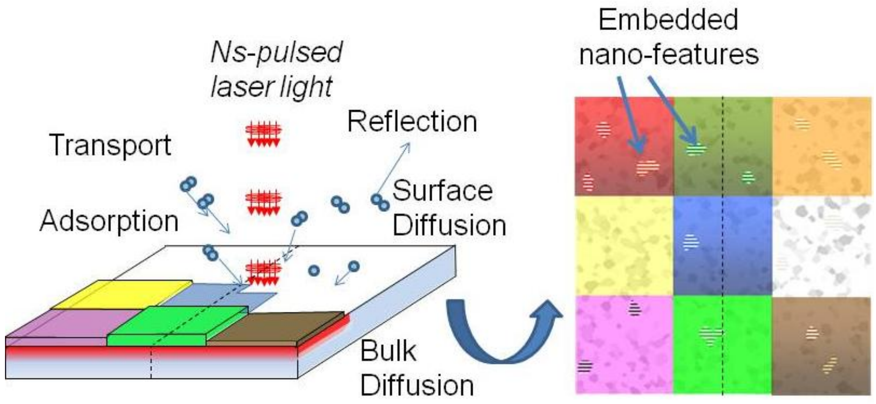
Basic Research of Intrinsic, Tamper-Indication Markings and Patterns Defined by Pulsed Laser Irradiation

PI: D.P. Adams, (SNL); Co-PI: Moody, Hobbs (SNL),

IACRO: 10-42571

Objective:
We will research how short and ultra-short laser pulses interact with the surfaces of various materials to create complex color layers and morphological patterns.

Relevance: Research will lead to novel methods for creating unique, passive indicators of interference (markings) that assist in monitoring compliance and regulating arms control. We seek markings that should be virtually impossible to duplicate and replicate.



Approach:
Investigate the basic physical and chemical processes underlying the formation of site-selective color patterns and surface morphological features during pulsed laser irradiation. Studies include embedding micro/ nano-scale morphology inside macro-scale color layers.

Personnel Support:
1 Tech. Staff (Sandia Labs) as PI
2 Tech. Staff (Sandia Labs) as co-PI
2 Graduate students (Univ. Michigan, Wash. State)

Results this year:

- Demonstrated controlled laser color marking of several materials (Stainless Steel, Ti, Kovar™)
- Investigated phase, composition, optical properties and through-thickness uniformity
- Researched mechanical properties (hardness, modulus) of laser-defined oxides on steel, Ti
- Retrofitted and qualified a sub-picosecond pump-probe optical microscope
- Investigated time evolution of ripple patterns formed during ultrafast laser irradiation

Funding:
Year 1: FY11-$349k, Year 2: FY12-$350k, Year 3: FY13-$350k

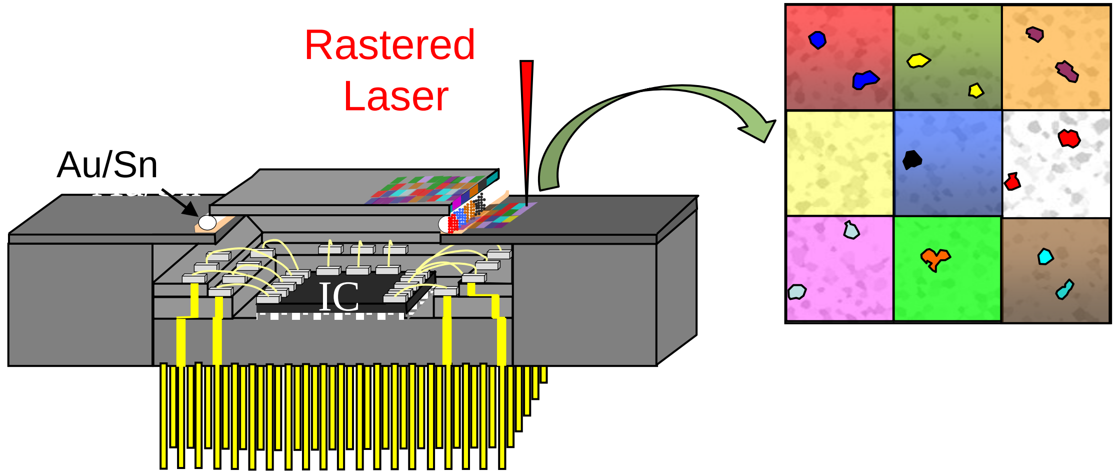
PI contact Information: David P. Adams, dpadams@sandia.gov, Phone: 505-844-8317

Program Objective

➢ We will research how short (ns) and ultra-short (fs, ps) laser pulses interact with the surfaces of various materials to create complex color layers, morphological patterns and other identifiable/archivable features at different scales.

- Research should lead to novel methods for creating unique, passive indicators of interference (markings) that assist in monitoring compliance and regulating arms control. *We seek markings that should be virtually impossible to duplicate and replicate.*

- The study of ultrashort and short pulsed laser-solid interactions is an active area of research.



Example: Wire bonded microelectronic IC in a Kovar^{TM} lid-sealed package.

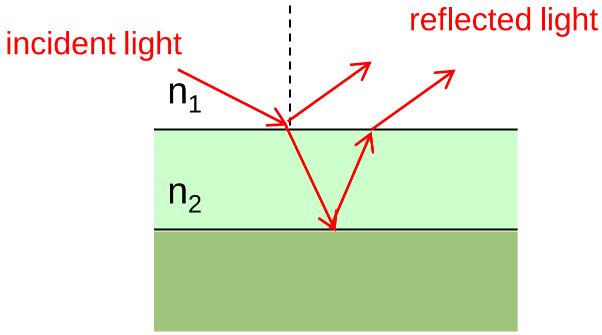
Background and Significance

Within the open literature we find that

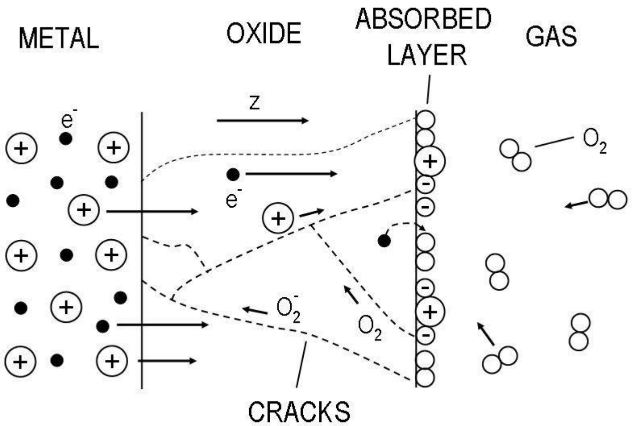
- Thin film interference can give rise to color.
- Continuous wave and pulsed laser irradiation can color the exposed surfaces of some materials (steel, copper) by forming metal oxides or metal nitrides.[1]
- Several potentially-important physical and chemical effects have been identified (e.g., change in %R with thickness)

- Pulsed laser irradiation can roughen the surfaces of many materials and form Laser Induced Periodic Structures (LIPS).
- Several mechanisms have been postulated to explain LIPS formation (interference with surface scattered waves[2], self-organization[3], Coulomb explosion[4]).
- However, a consensus has not been reached.

Thin film interference – optical path length differences (OPD) give rise effect (refractive index important)



Depiction of mechanisms that may play a role in laser coloring of metals (from Wautelet)



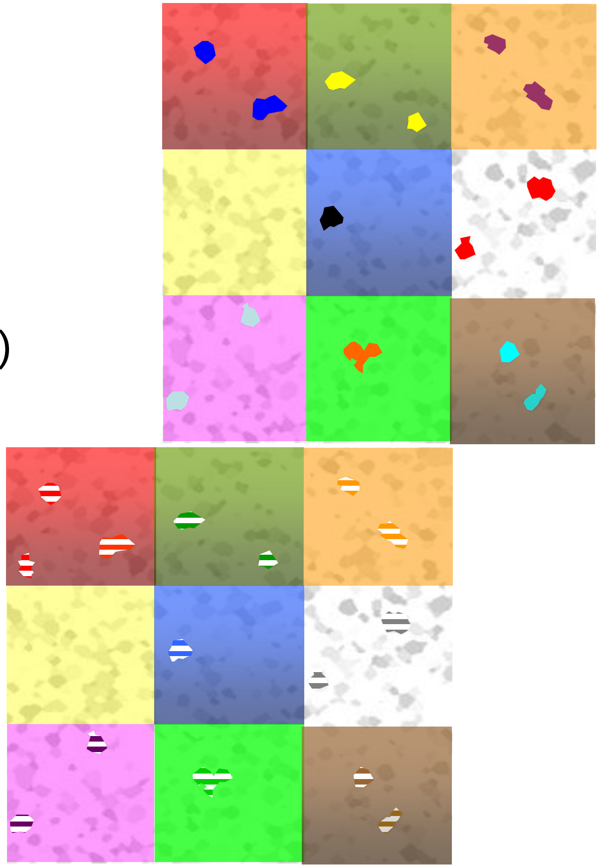
[1] M. Wautelet, Appl. Phys. A (1990).
[2] J. Bonse et al., J. Appl. Phys. (2009).
[3] J. Reif et al. Appl. Phys. A (2008).
[4] Y. Dong et al., Appl. Phys. Lett (2004).

Technical Approach: Research how intrinsic markings form at surfaces

Color layers

- physical and chemical mechanisms giving rise to color layer formation during pulsed, nsec laser irradiation
- site-specific coloring (intrinsic microscale marking)
- variety of materials (e.g., welds, solders)
- usefulness of psec domain (onset of thermal)
- detailed phase, microstructure, composition (and variations through thickness)
- mechanical integrity (hardness, toughness, adhesion)
- minimizing effects on component (reduced strain energy)
- long term stability of color markings (or metastability)

Two example intrinsic markings (macroscale color and microscale color or topography)



Expected interrogation method:
Macroscale : camera
Microscale : magnifying glass, microscope, diffractometer

Surface roughening

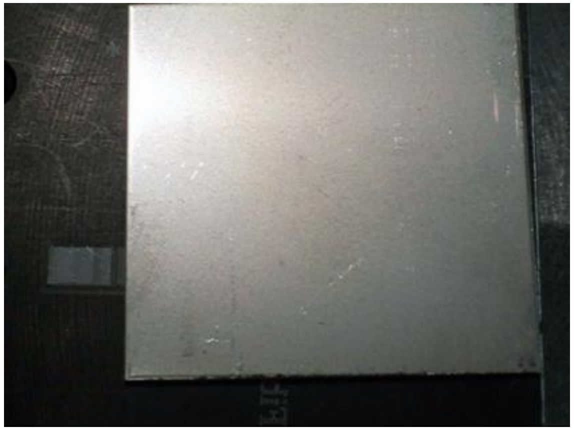
- mechanism(s) underlying ripple formation
- time evolution of surface ripples
- site-specific roughening (intrinsic microscale marking)
- integrity/stability of ripples over time

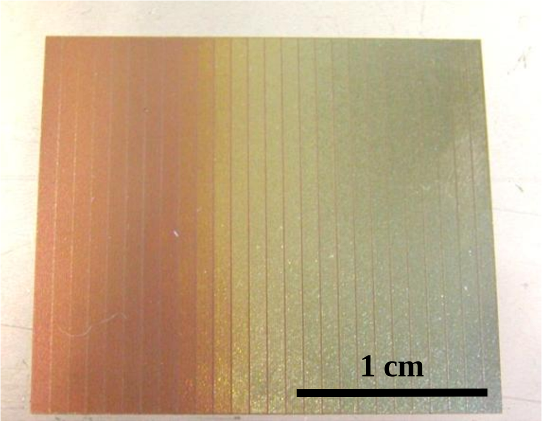
Hybrid approach

- embedding site-specific ripple patterns within macro color pattern and methods for making this

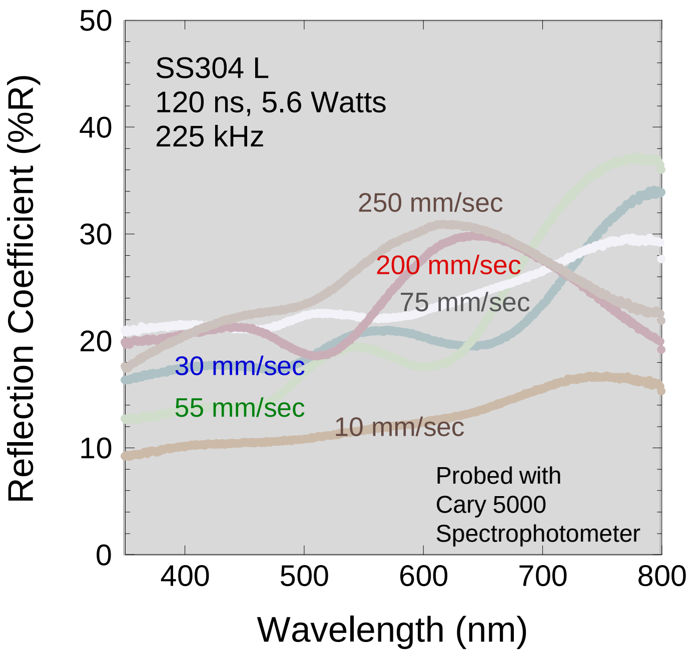
We have demonstrated feasibility of controlled, laser surface coloring (marking).

- Involves rastering a focused, nanosecond-pulsed laser beam (constant power) across a surface.
- Scan speed can be used to tailor color.
- Metal reacts with air to form a color layer (oxide) of characteristic thickness and refractive index.
- Compatible with a range of surface roughness.
- Variety of colors available with many materials.





Stainless Steel 304L



A variety of materials have been marked by our team to have complex color patterns.

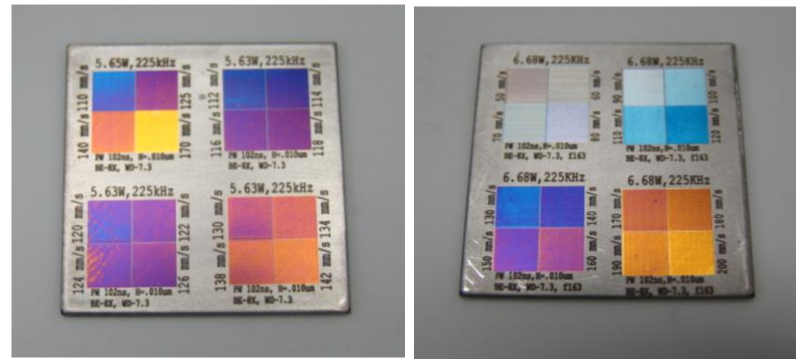
Materials colored (by our group) using 102 ns, 1064 nm diode laser (max. P_{avg} 20W):

- Stainless steel 304L : R (ϕ = 0°) = 0.73
- Titanium CP2 grade: R (ϕ = 0°) = 0.57
- Titanium alloy Ti6Al4V: R (ϕ = 0°) = 0.37
- Kovar™ (FeNiCo): R (ϕ = 0°) = 0.63
- Georo™ (Au88Ge12): R (ϕ = 0°) = 0.74

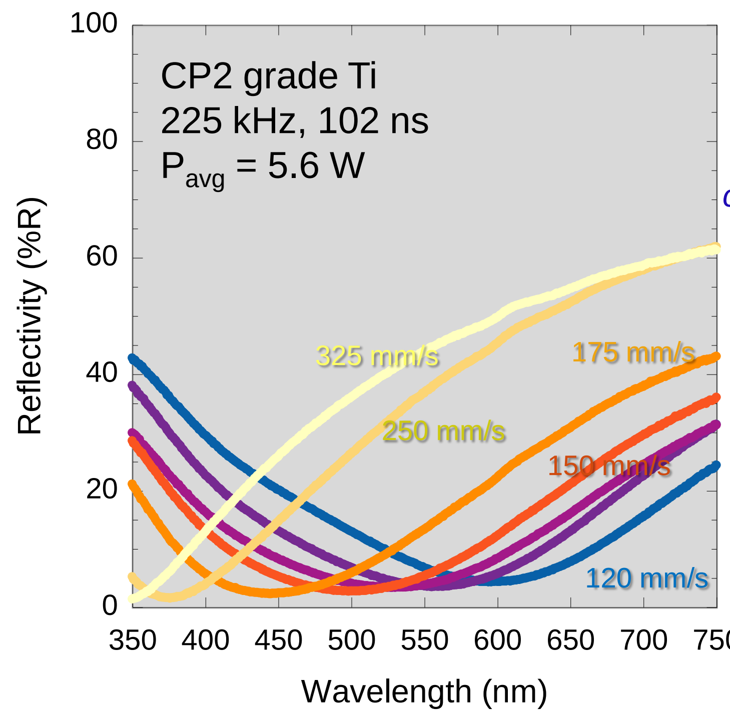
R_a varied from ~10 to ~10000 nm

Materials not colored (using 1064 nm):

- Copper: R (ϕ = 0°) = 0.97
- Aluminum: R (ϕ = 0°) = 0.95
- TiCuSil (braze): R (ϕ = 0°) = 0.96



1 cm

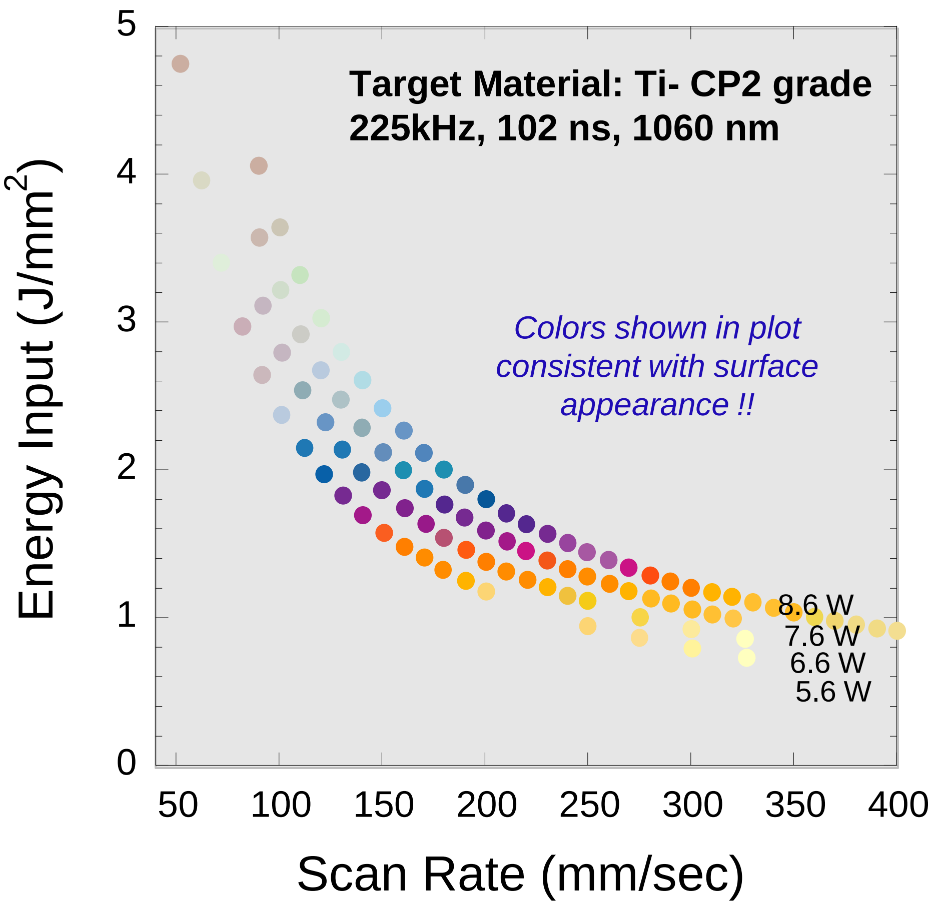


Colors shown in plot consistent with surface appearance !!

Probed with Cary 5000 spectrophotometer

For the range of process parameters used, the energy input determines the laser-defined colors.

- Colors form over a large range of scan rates and average power.
- Color is found to be similar for a given energy input (J/mm^2) independent of laser scan rate.
- For a given power the color order remains constant (e.g., orange at higher rate; blue at lower rate)
- Same general behaviors are exhibited by stainless steel and Ti6Al4V.
- Our next experiments will probe effects of pulse frequency (kHz).



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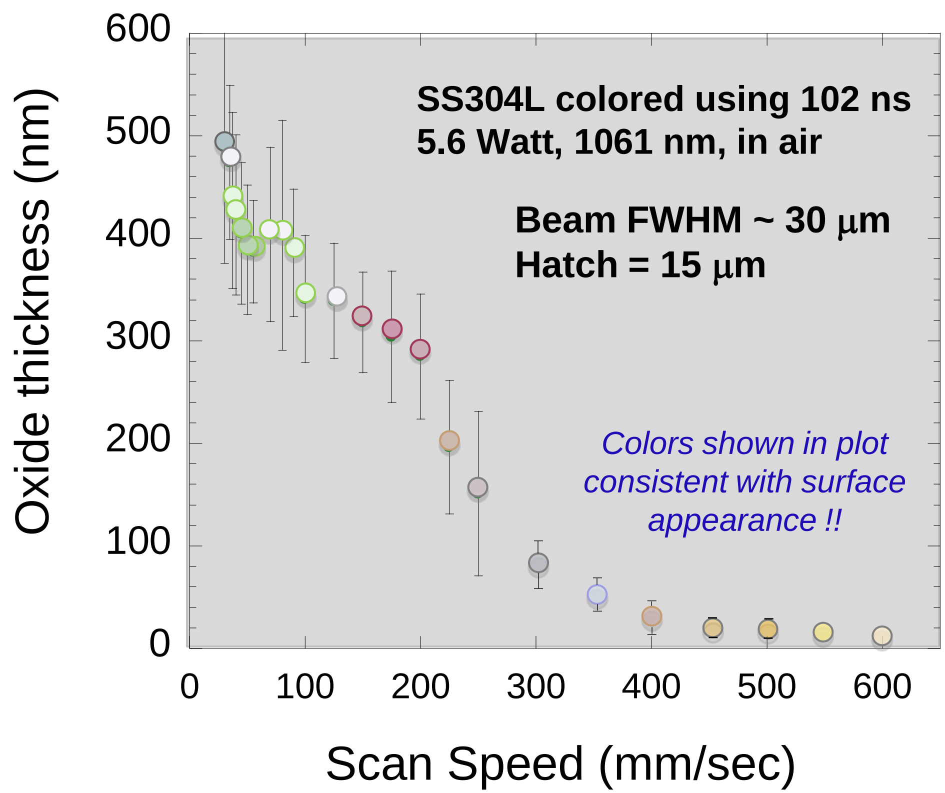
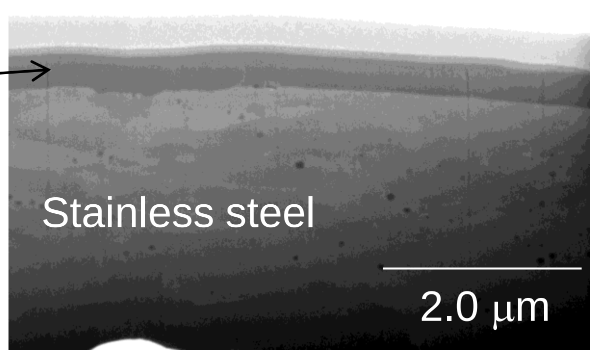
The observed colors vary with the laser-defined layer thickness.

- Oxide thickness generally increases with decreasing scan rate (i.e., increasing heat input)
- Colors correspond to average oxide thickness in the range of 15-500 nm.
- Colors appear to form over a range of oxide thickness.
- Large variation in oxide thickness for a given feature when using this beam overlap approach; we expect to decrease variation with smaller hatch.



Dark layer is laser-fabricated metal oxide

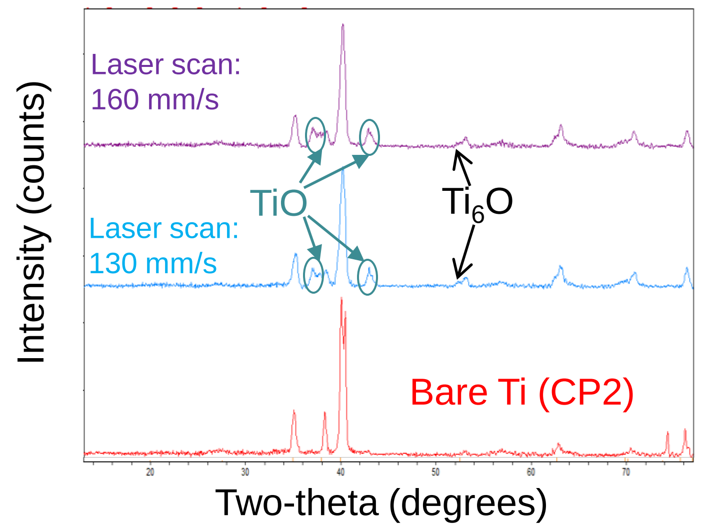


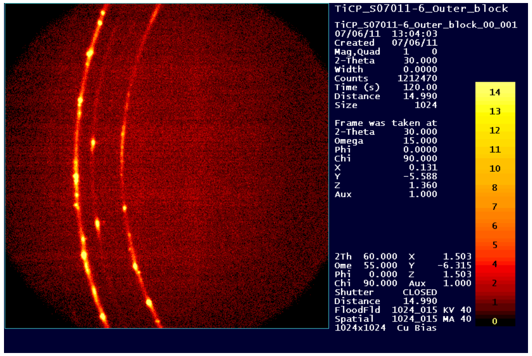
All measurements are obtained by XS-SEM after focused ion beam sectioning

The laser-defined colors are influenced by the layer thickness, composition and, hence, the laser process parameters.

- Oxides formed on SS 304L are characterized
  - $FeCr_2O_4$ spinel structure (when t exceeds100nm)*
  - composition gradient through thickness^

- Oxides formed on CP2 grade Ti develop as/with
  - TiO (wustite)†
  - Possibly Ti_6O (oxygen intercalation into hex Ti)
  - composition and phase gradient (thickness)^





Raw diffraction frame

**SS304L samples with thin oxides do not show crystalline phases.*

^ This suggests a complex refractive index.

† *There is no evidence for rutile or anatase TiO_2.*

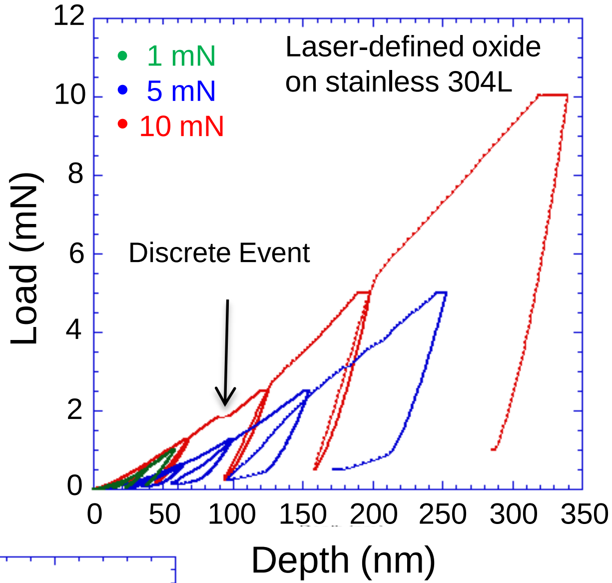
The mechanical properties of laser-defined oxides have been evaluated using nanoindentation techniques.

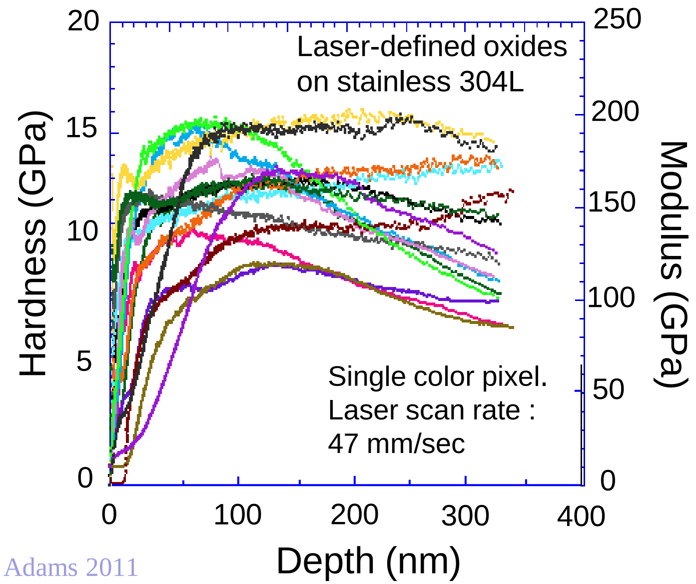
- Oxides defined on SS304L by laser irradiation have
  - an average modulus (E) of 160GPa and
  - an average hardness (H) of 11GPa.

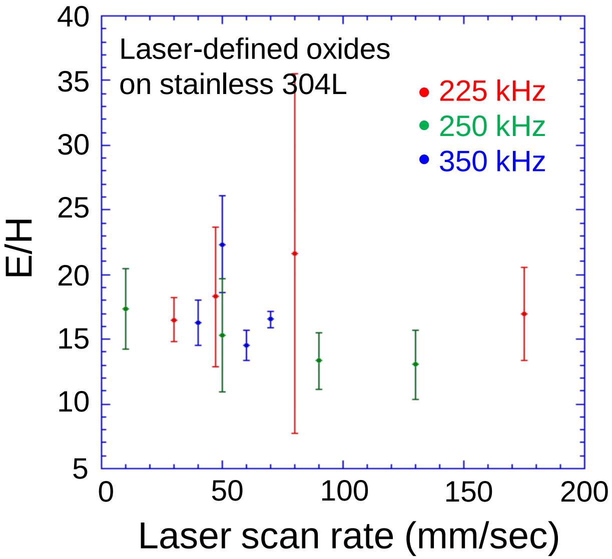
  compare w/ bare SS304L H=3GPa; E=120-200GPa

- Oxides produced using higher laser frequencies (250, 350kHz) exhibit distinctly larger H, E (although H/E is similar).

- Considerable scatter in measured properties – indicated by error bars





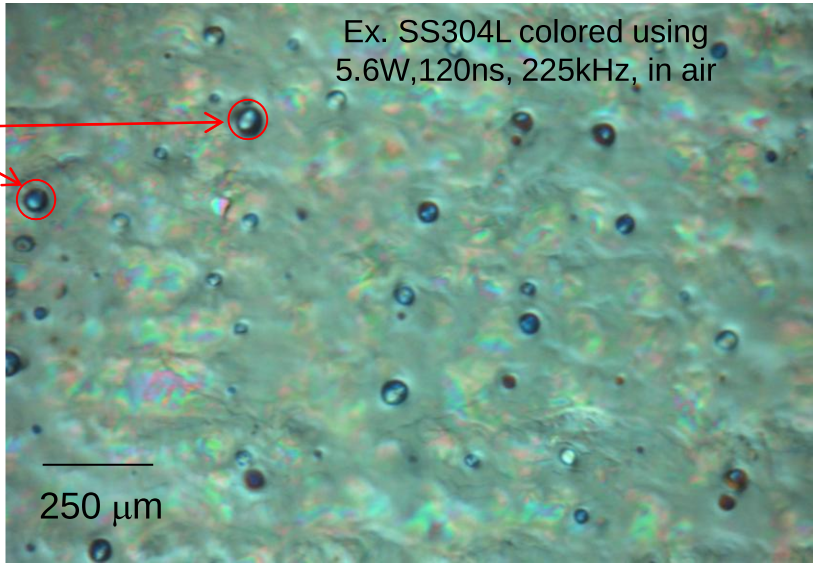


Our analysis follows the procedures by Oliver and Pharr J. Mat. Res. 1992

Laser-induced, site-specific colors and topography are intrinsic micro/nano-markings that would be virtually impossible to replicate.

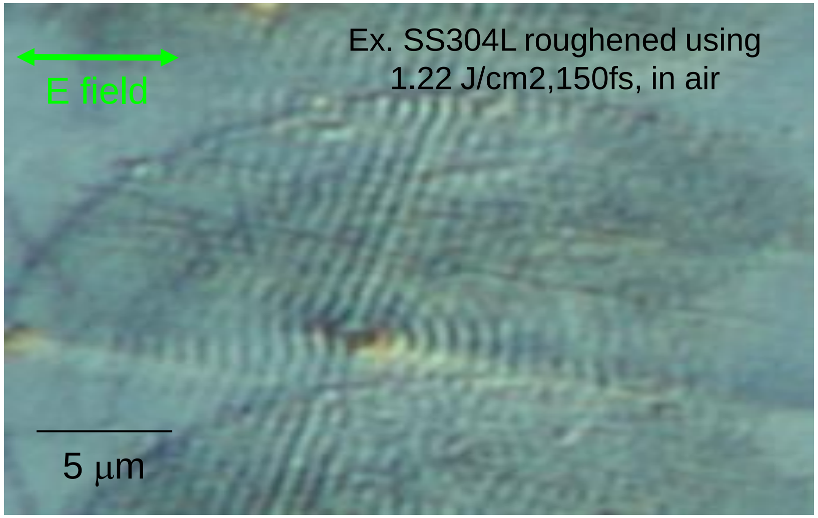
- Site-specific color formation at the (within a given macroscale color pixel) for a range of laser scan rates and macrocolors!!
  - Stainless steel 304L
  - Ti6Al4V

A look within a single color pixel



- Site-specific ripple formation at the microscale
  - All materials studied to date (SS304L, Si, Ti) exhibit site-specific ripples when irradiated with 100 fs laser light.
  - Formation around / near topographical features

Periodic ripple pattern formed about an initial surface defect



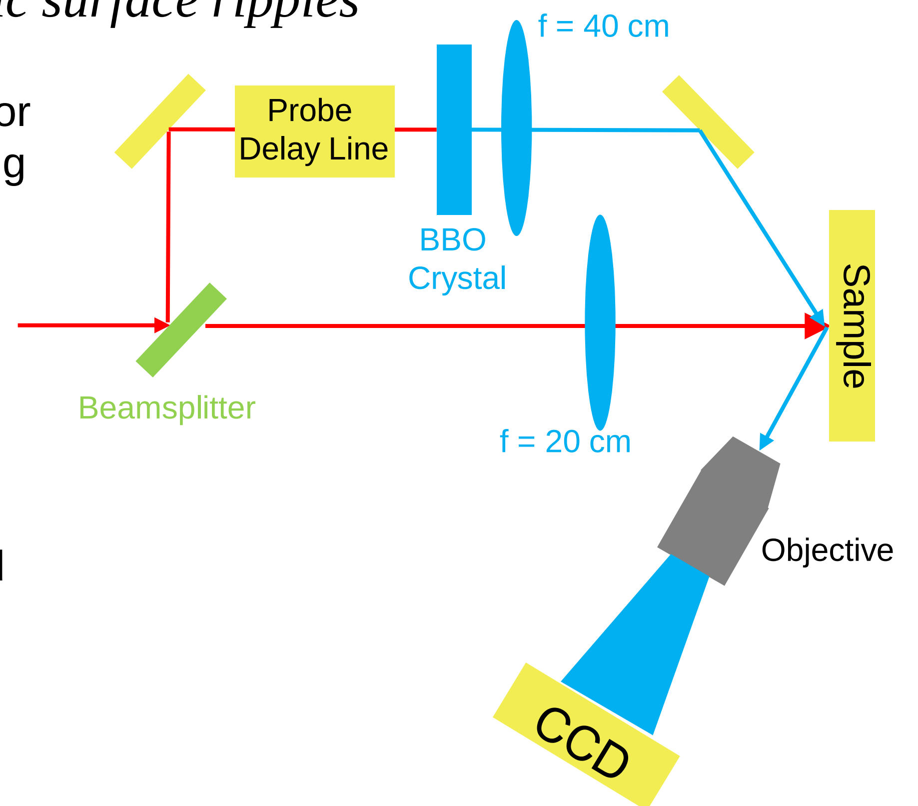
We are investigating the physical and chemical origins of site-specific markings.

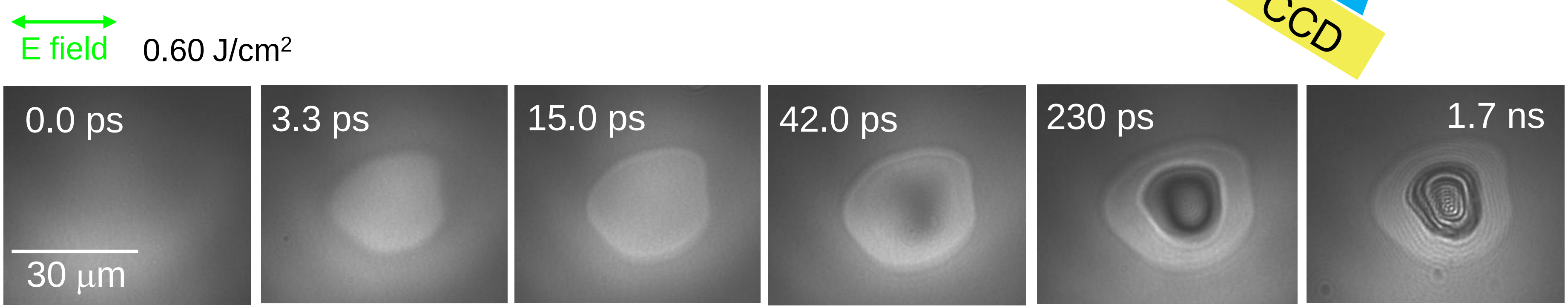
Ex. Site-specific surface ripples

- Pump-probe optical investigation of timescales for ripple formation (considered critical for identifying underlying mechanisms)

- Pump-probe microscope has been built, tested.
  - capable of sampling surface morphology
  - 33 femtosecond temporal resolution

- Experiments completed with Si (model system) demonstrate that long λ (1-2 μm) Laser Induced Periodic Structures (LIPS) form 40 picoseconds after absorption of the pump pulse.





This will be discussed in greater detail by Ryan Murphy in Wednesday's poster session!!

Accomplishments

<u>Presentations</u> *(Full or Partial DTRA support)*

Contributed: Fall 2011 Materials Research Society Symposium (Murphy et al., Time Evolution of Periodic Structures induced by Femtosecond Laser Pulses, Session EE: Self Organization and Nanoscale Pattern Formation) - *Full*

Contributed: Fall 2011 Materials Research Society Symposium (Lawrence et al., Deformation and Fracture of Pulsed Laser Oxides, Session SS: Nanomechanics of Material Behavior) - *Partial*

Invited: January 2012 18^{th} International Symp. Plasticity (Moody et al., Mechanical Properties of Pulsed Laser Oxides) - *Full*

<u>Publications</u>

Proceedings of the Materials Research Society, "The Time Evolution of Periodic Structures Induced by Femtosecond Laser Pulses", R.D. Murphy, M.J. Abere, B. Torralva, D.P. Adams and S.M. Yalisove – *in progress*, due at meeting, Nov. 2011. - *Full*

Proceedings of the Materials Research Society, "Deformation and Fracture of Pulsed Laser Oxides on 304L Stainless Steel", S.K. Lawrence, D. Stauffer, D.P. Adams, W.W. Gerberich, D.F. Bahr, and N.R. Moody – *in progress*, due at meeting, Nov. 2011. - *Partial*

<u>Patent Application</u>

US, "Method of Intrinsic Marking", Adams, Blair, Jared, McDonald (filed through Sandia Labs, 2011)

<u>Graduate Students</u>

Two – See next slide

University Collaborations

- Sub-contract placed with Univ. of Michigan
  (finalized: November, 2010, PO: 1081780)
- Ryan Murphy (Applied Physics)
  Expected PhD date: 6/2012, 100% time commitment
- Basic research of surface roughness evolution during pulsed laser irradiation involving ultrafast pump-probe microscopy

- Sub-contract placed with Washington State Univ.
  (finalized: March, 2011, PO: 1127609)
- Samantha Lawrence (Materials Science & Engineering
  Expected PhD date: 2016, 25% time commitment
- Research of the mechanical properties of laser-fabricated metal oxides (includes study of hardness, adhesion, phase, variations through thickness)

Students and professors are US citizens

Conclusions

- Pulsed (100 nanosecond) laser irradiation is an accommodating, reproducible method for marking different materials with colored oxide layers at the macroscale.
  - Large palette of readily-identifiable colors for all materials tested to date
  - Accomodates different surface polish, some curvature; ultimately field-deployable
  - Complex patterns possible

- Color layers created by pulsed laser irradiation (100 ns) are often mixed, crystalline metal oxide phases that have a compositional variation through thickness. Oxide thicknesses are in the range of 100-500 nm.

- Two forms of site-specific (random) markings have been created by pulsed laser irradiation:
  - Local oxides with distinct colors (different than surrounding areas) - 100 ns pulses
  - Ripple patterns with small distribution of frequencies form near initially rough morphologies (virtually all materials) – 100 fs pulses

- The time scales for surface ripple formation during 100 fs pulse laser irradiation have been identified using a model material system (Si).

Future Directions

COLOR LAYERS

- Color layer formation (chemical kinetics, phase formation, modeling heat affected zone)
- Mechanical properties of oxide layers (layer toughness and adhesion).
- Site-selective color formation
- Techniques for minimizing strain (goal: prevent oxide cracking, eliminate warpage)
- Growing the list of materials that can be patterned-

SURFACE RIPPLES

- Mechanisms underlying surface ripple formation – pump-probe optical microscopy, transmission electron microscopy
- Site-specific ripple formation in relevant materials (e.g., stainless steel)

EMBEDDING MORPHOLOGY WITHIN COLOR LAYERS

- Research methods that combine surface morphology and color layer formation (a potentially complex marking)

OTHER

- Consider other methods of intrinsic information (magnetic domains)

EXTRA SLIDES

Equipment used in this study

Nanosecond fiber laser @ 1064 nm (SPI, Inc. Nd:YAG)
Femto/pico-second laser (Spectra Physics Ti:sapphire)
  and optical parameteric amplifier for access to different λ
Nanosecond laser @ 532 (JDSU)

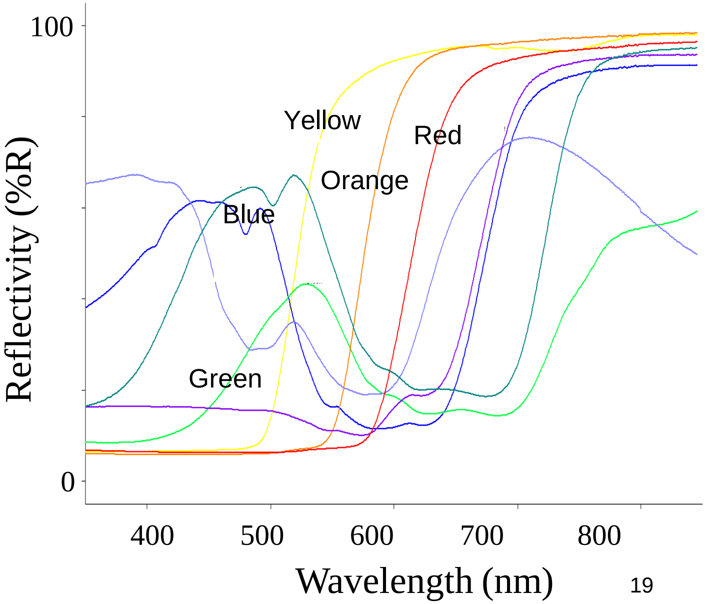
UV-Vis-IR spectrophotometer (Varian Cary 5000)
Spectroscopic Ellipsometer (Woolam)
High speed imaging device (Vision Research Phantom)

Scanning electron microscopes (FEI) with EDS
Transmission electron microscopes (FEI) with EDS
X-ray diffractometers (numerous)
Auger electron spectroscopy (several)
Focused ion beam sectioning tool (FEI, Ga LMIS)

Custom-built sub-psec pump-probe microscope

Nanoindenter XP
Nanoindenter Ubi1 (Hysitron)
Nanoscope (Digital Instruments IIA)

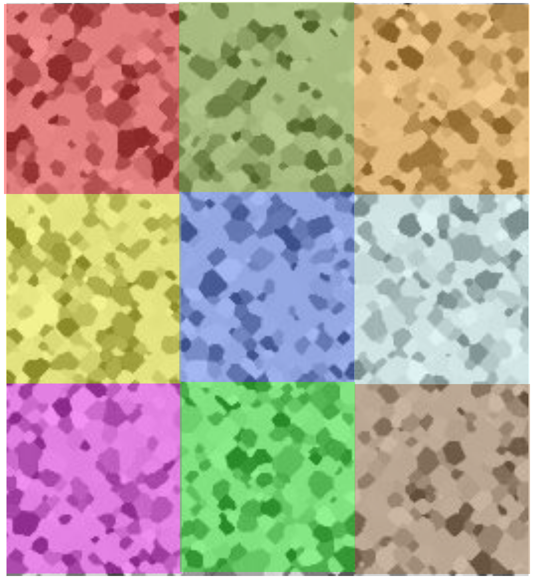
Cary 5000 (Varian Inc.) spectrophotometer with integrating sphere and data obtained with this (color standards from Labsphere)



Site-specific coloring at the microscale should be an advantageous intrinsic marking.

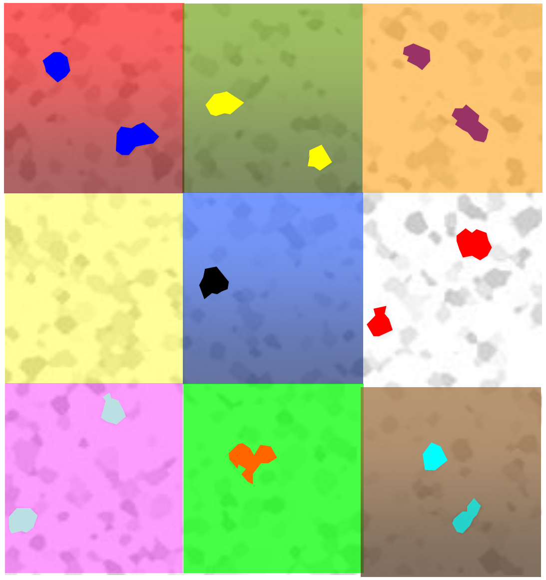
Colored pixels with somewhat visible underlying grain structure.

Disadvantage: While intrinsic to part, there are no intrinsically-random features.



Colored pixels with site-specific, different colors at microscale.

Advantage: Local color formed at certain microstructural features. This is virtually impossible to replicate or duplicate.

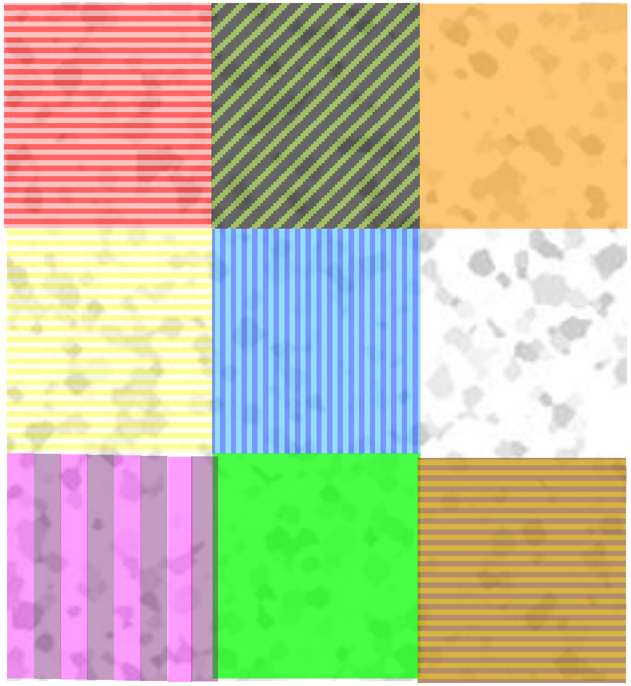


We have found evidence of this in alloys. Most likely due to differences in refractive index or oxide thickness or both.

Periodic surface shapes superposed within colored pixels offer additional complexity to an archivable pattern.

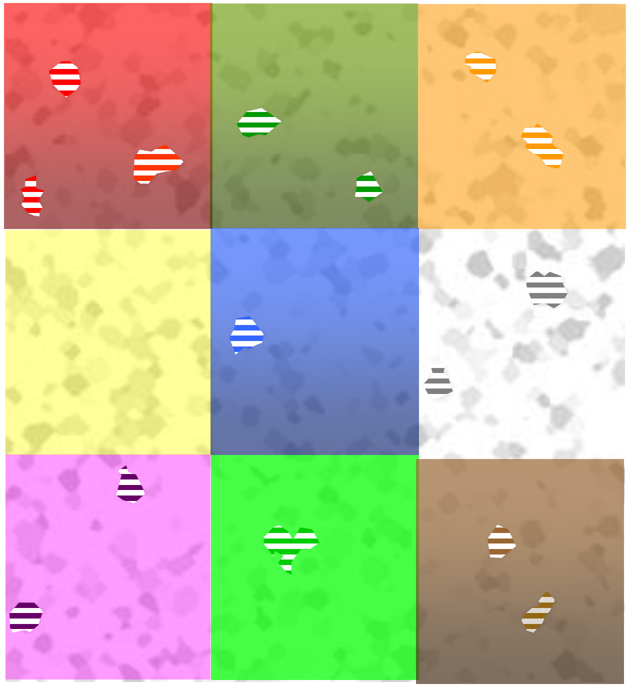
Color pattern with tailored roughness formed by laser scans.

Disadvantage: While intrinsic to part, there are no intrinsically-random features.



Color pattern with random roughness.

Advantage: Roughening keys off certain microstructural or morphological features. Virtually impossible to duplicate or replicate.



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Specific Technical Objectives FY11

Research pixel-by-pixel control of color using 10-200 ns light

Research effects of pulse frequency on color layer formation

Investigate the microstructure, composition, optical properties of color layers

Research hardness and modulus of color layers (nanoindentation)

Implement a thermal modeling code that simulates the effects of laser irradiation (pulse duration, repetition rate, energy per pulse, wavelength)

Qualify pump-probe instrument (Univ. of Michigan)

Research the temporal evolution of laser-induced periodic surface structures

Specific Technical Objectives FY12

Research site-selective laser coloring (with scanned, pulsed lasers)

Investigate the microstructure / composition origin of site-selective coloring

Research feasibility of picosecond to nanosecond laser coloring of metals

Research the through-thickness toughness of color layers (as a function of laser process parameters)

Complete thermal modeling of heat-affected zones created during pulsed laser processes

Complete research of the temporal evolution of laser-induced periodic surface structures

Investigate site-selective formation of periodic surface roughness

Specific Technical Objectives FY13

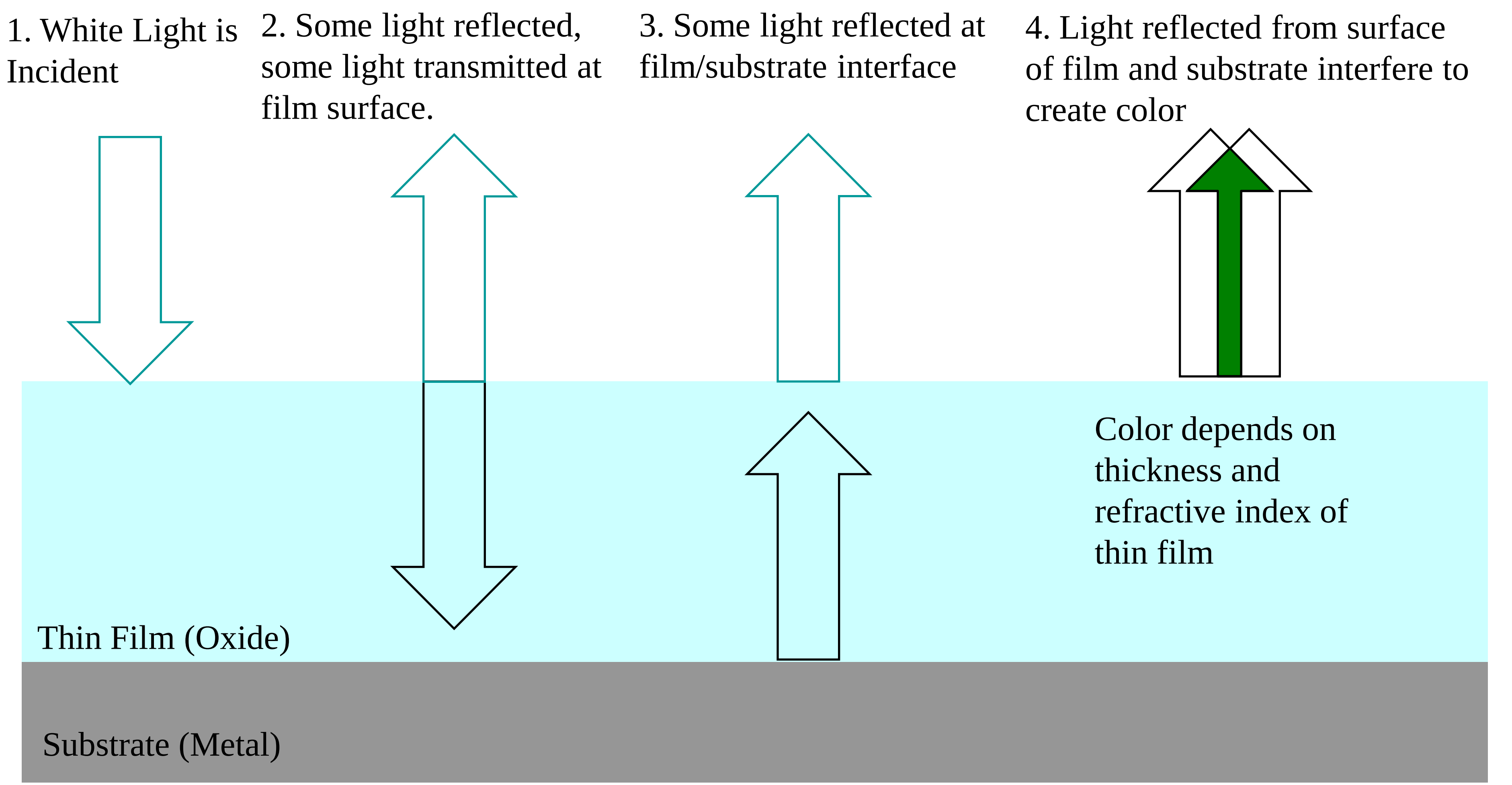
Research processes that embed periodic surface roughness within color patterns (single step and two step techniques)

Research the stability of laser-fabricated color layers and periodic surface roughness (accelerated aging methodologies)

Research the interfacial toughness of laser-fabricated color layers (stressed superlayer methods or four-point bend techniques)

Complete thermal modeling of laser coloring processes applied to monolithic and multiphase materials

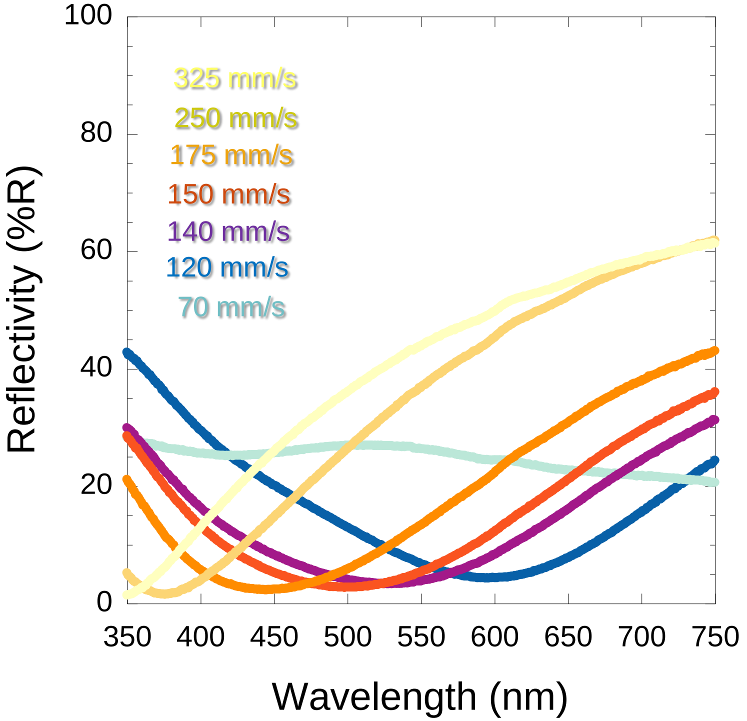
Thin Film Interference gives rise to Color Change



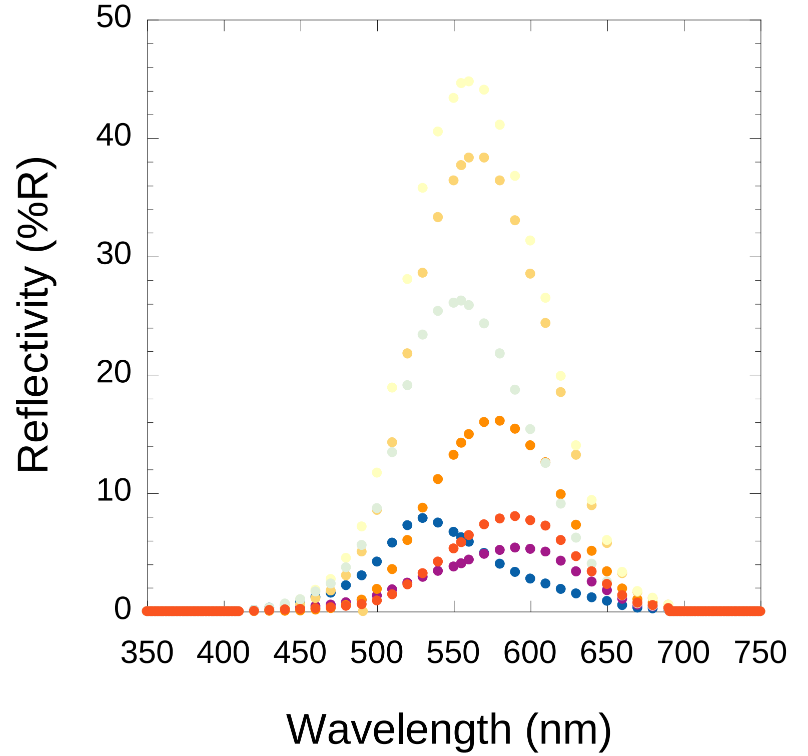
Differences in signal detected by spectrophotometer and human eye

Ex. CP2 grade Ti patterned by 102 ns, 225kHz laser light

Response of unbiased Cary 5000 Spectrophotometer



Corrected according to the luminosity function of the human eye



Colors consistent with appearance of surface (to eye)