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Nanosecond Pulsed Laser Color Marking of Titanium: Analysis of Oxide Layer Phase

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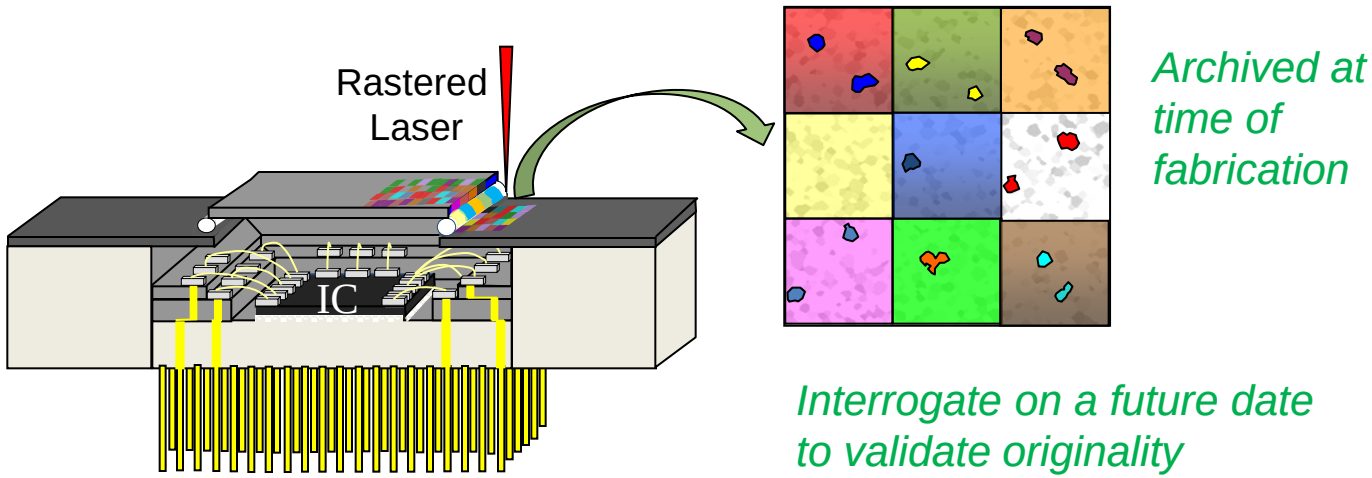
Motivation

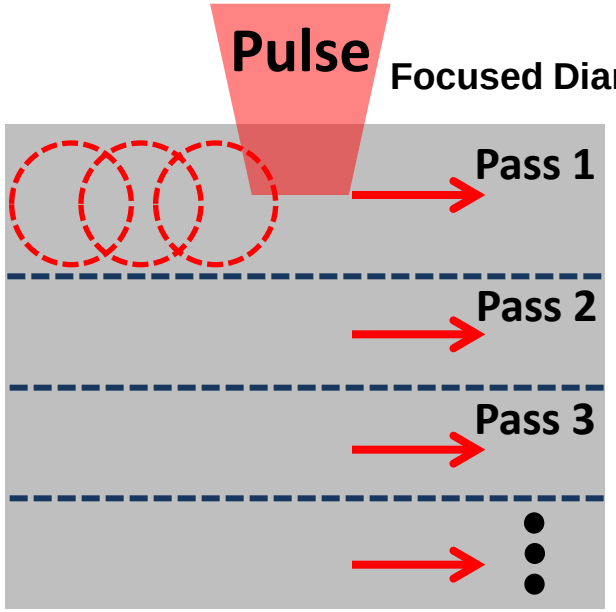
- Research how short (ns) and ultra-short (fs, ps) pulsed laser light interacts with the surfaces of different materials to create complex features and patterns at different scales (mm to nm) for use as passive indicators of interference and tamper.

  - Desire markings that are virtually impossible to duplicate and replicate.
  - Research fundamental physics and chemistry underlying feature definition.
  - Investigate long-term reliability of markings.

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



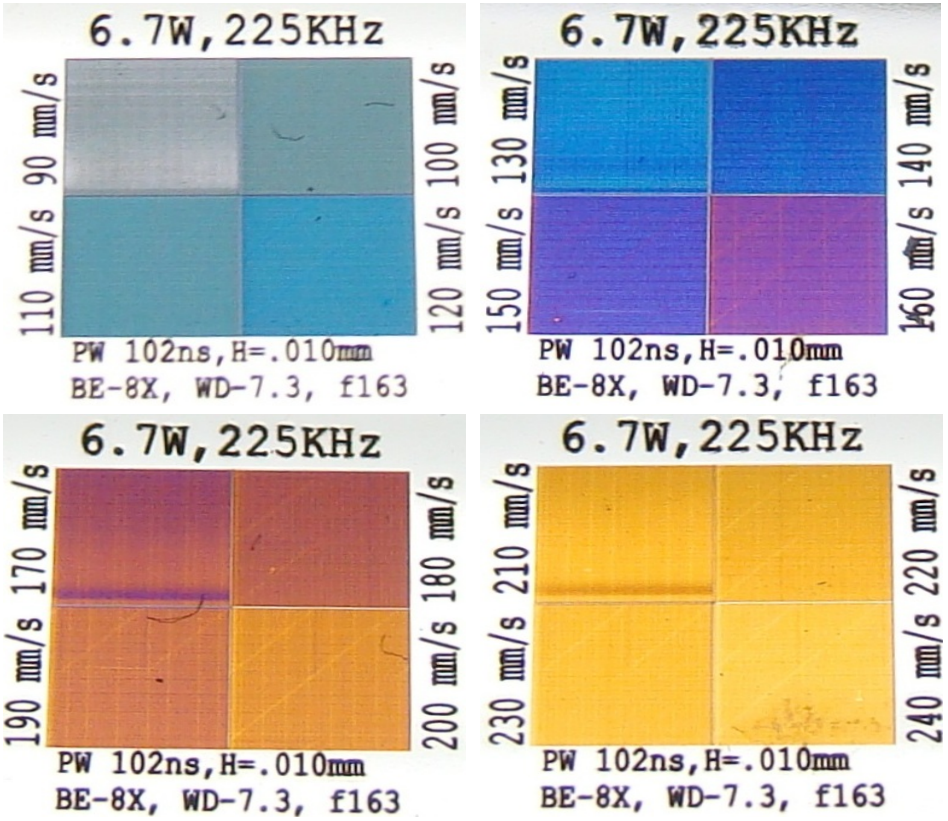
Laser Fluence Determines Colors



Laser induced surface melting + oxidation

- Color is similar for a given energy input (J/cm^2) – independent of laser scan rate.
- Colors form over a large range of scan rates and for different average powers.

Lower scan speeds

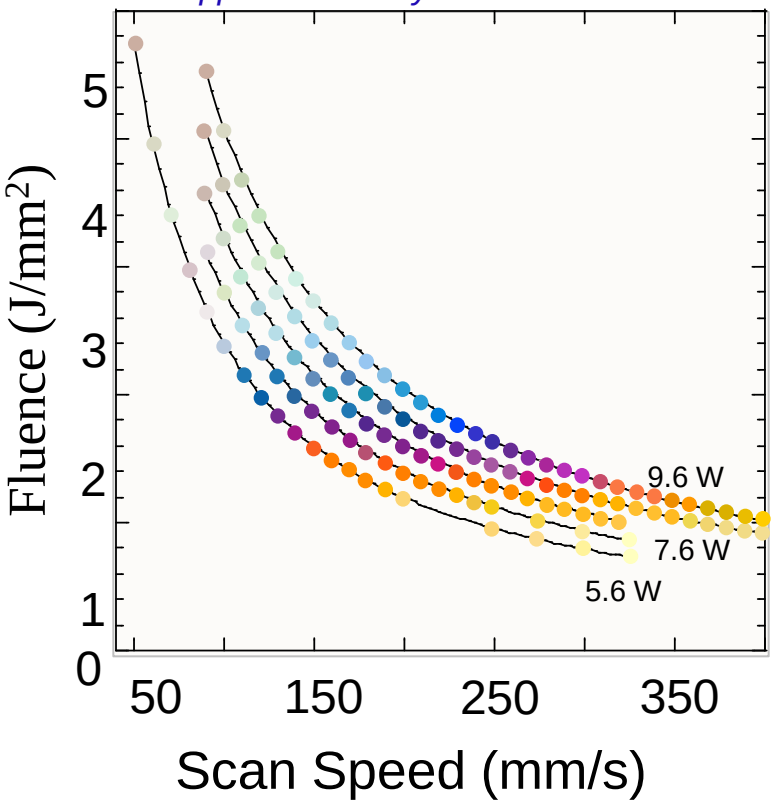


Higher scan speeds

Colors Consistent with Accumulated Fluence

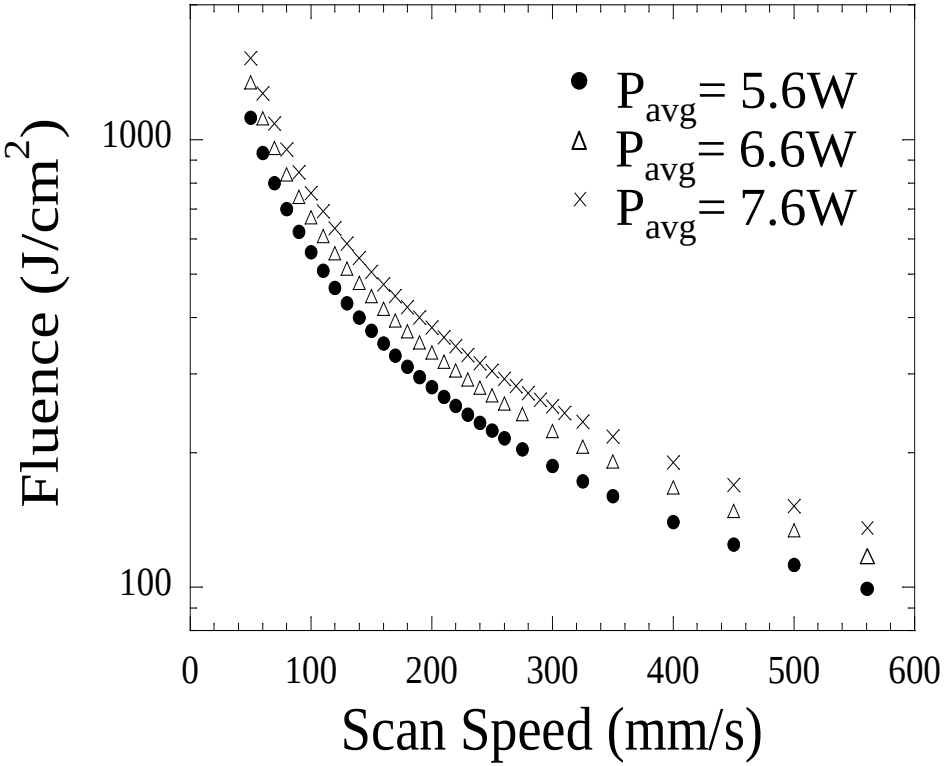
Laser-marked CP2 grade Ti
225kHz, 102 ns, 1064 nm

Color symbols are consistent with appearance to eye



The color order remains constant (e.g., orange at higher rate; blue at lower rate; pastels at very low rates) for a given P_{avg}.

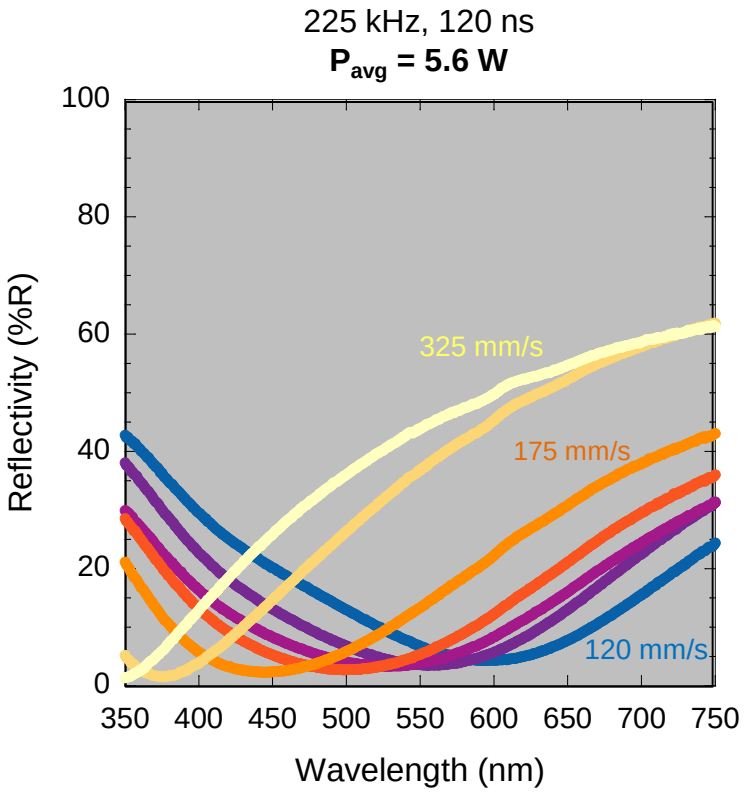
Accumulated Fluence



Color Information Archived in Several Forms

Reflectance Spectra

Represented color is consistent with appearance to eye

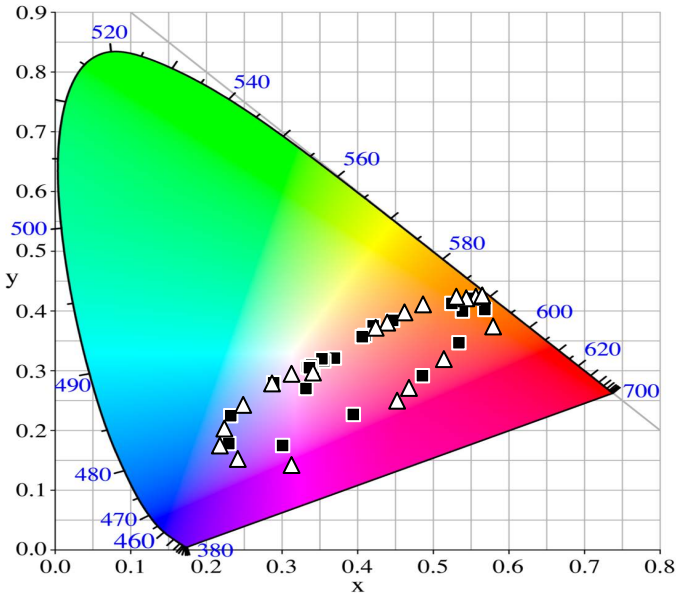


Chromaticity (obtained from individual pixels)

CIE1931 Color space

■ 5.6 W

△ 6.7 W



Visual photograph / micrograph

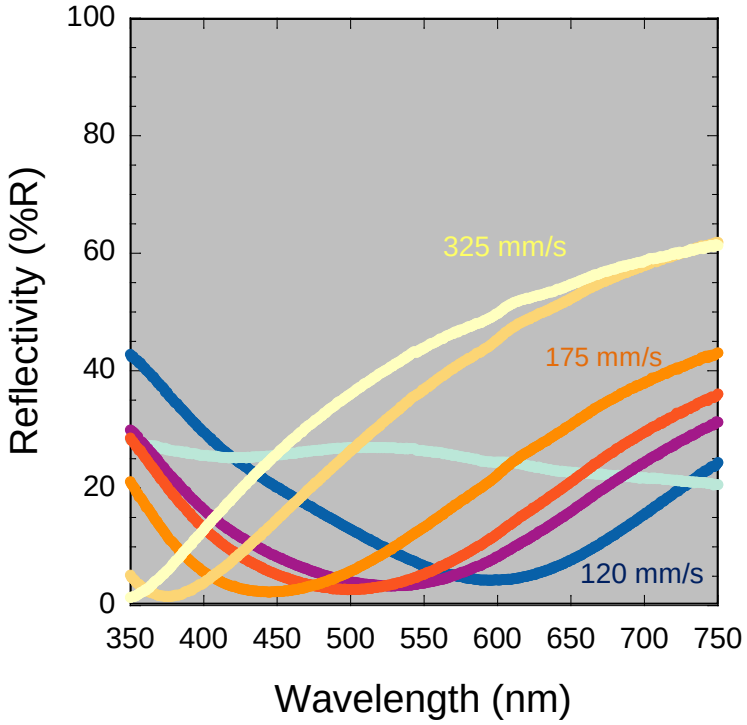
Spectral Response of Human Eye

CP2 grade Ti: 120 ns, 5.6 W 225kHz laser light

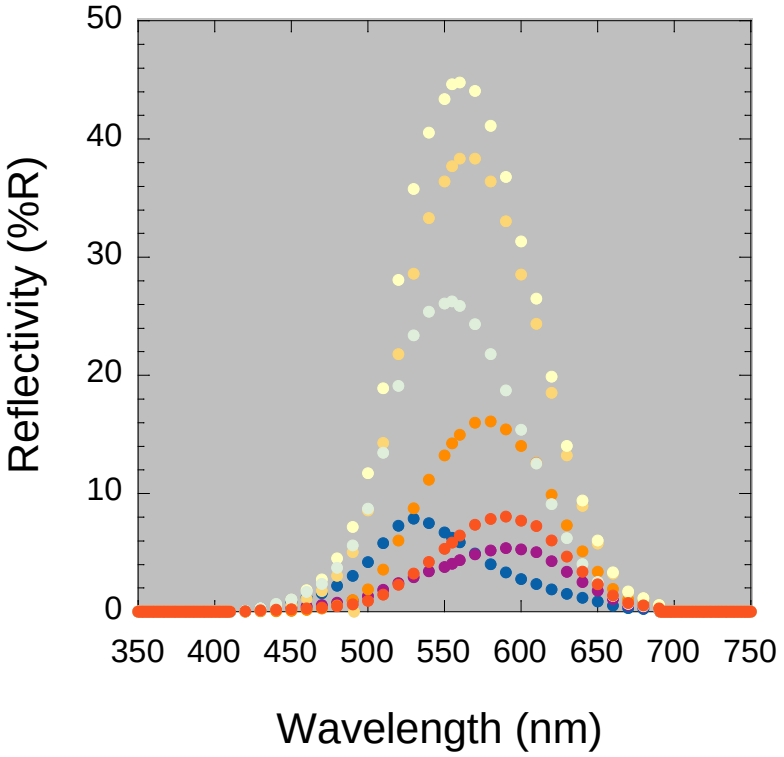
1.0 cm

Color symbols are consistent with appearance to eye

Response of unbiased Cary 5000 Spectrophotometer



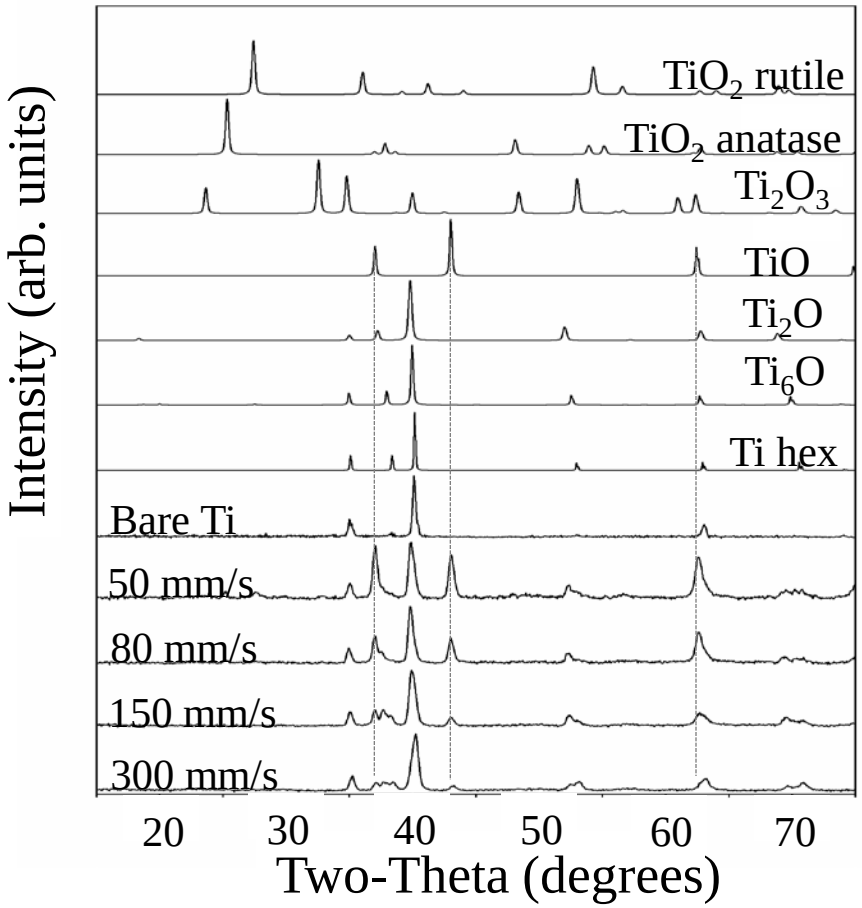
Corrected according to the luminosity function of the human eye



Oxide Phase Formation

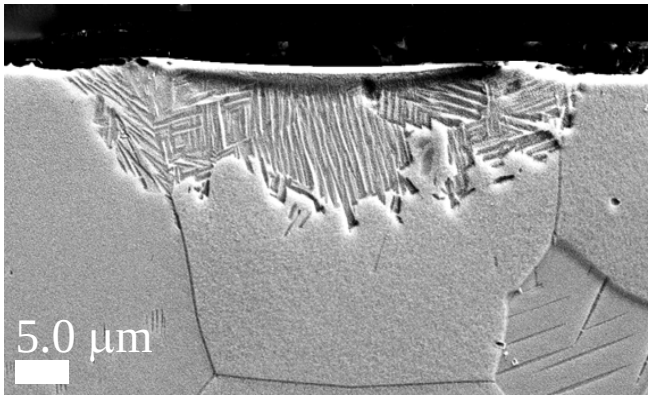
5.6 W Irradiation

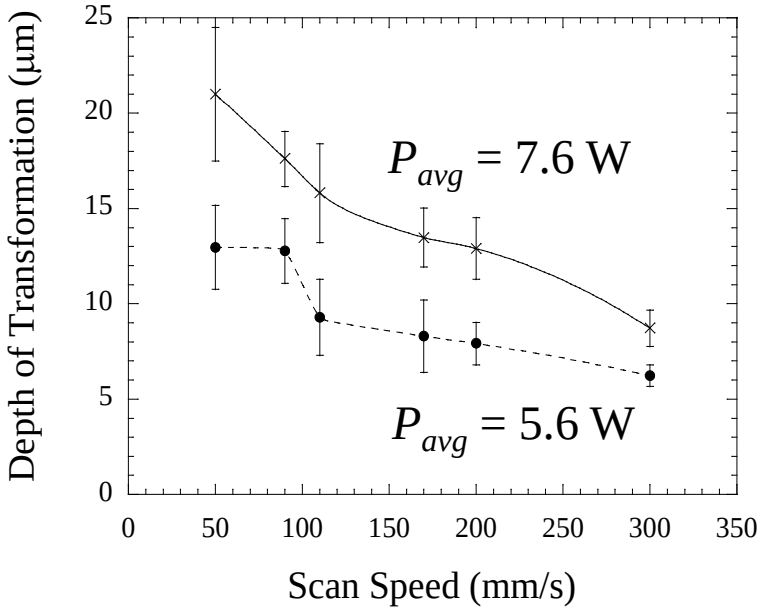
- TiO forms for all studied scan speeds.
- No evidence for crystalline TiO_2 formation.



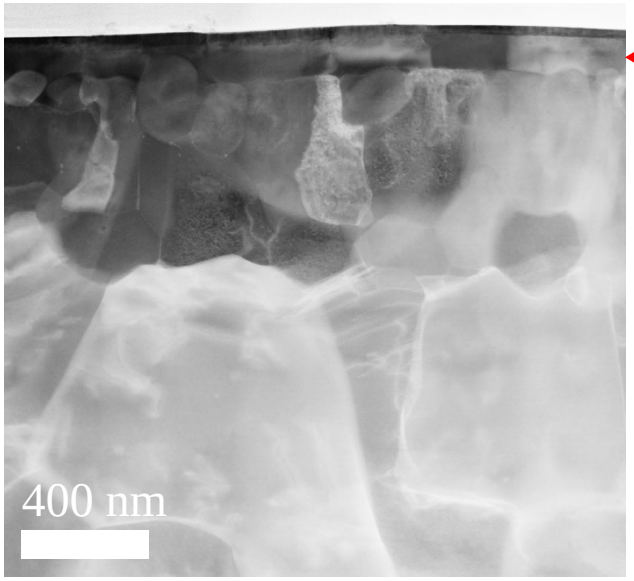
Cross-Section Studies

Bright-field transmission electron microscopy (TEM) image of laser affected region



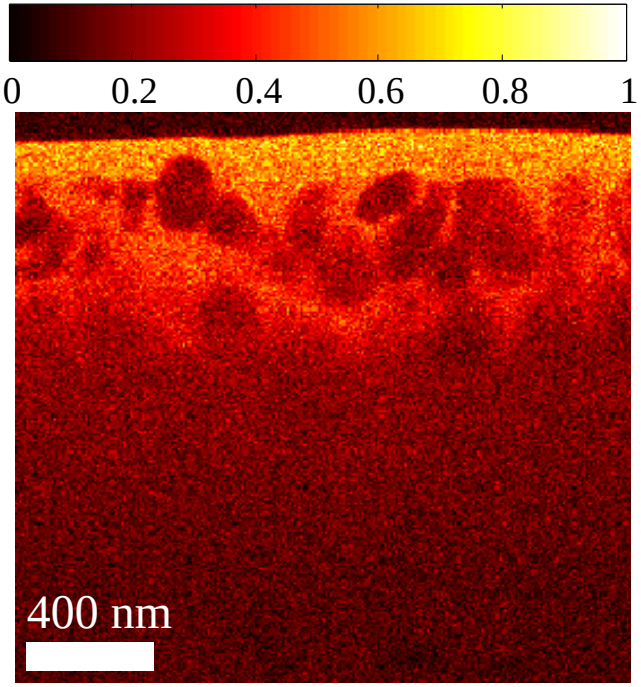


Scanning-TEM image of top layers

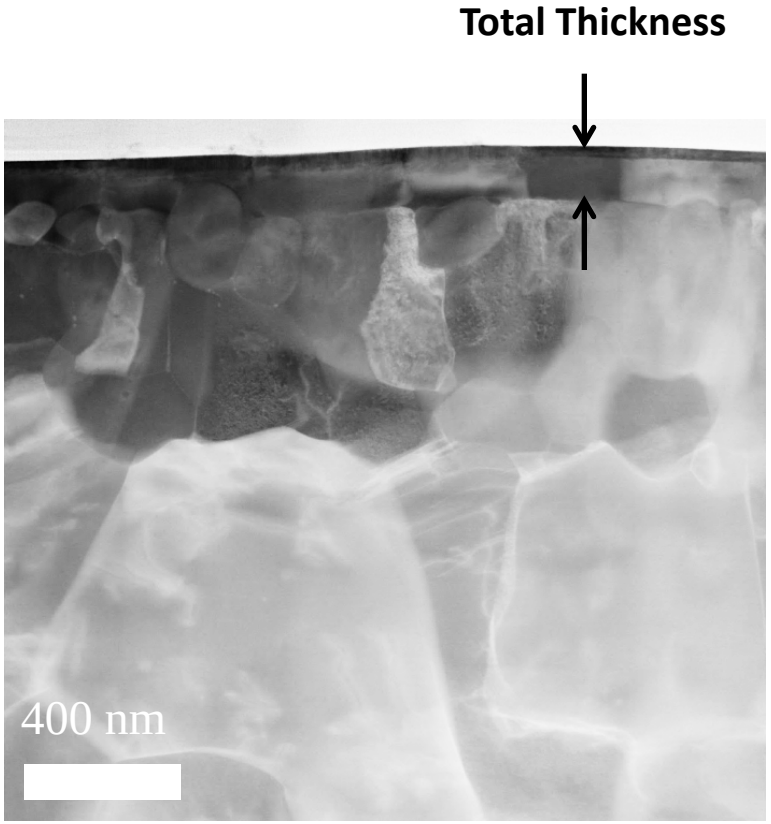


TiO Layer

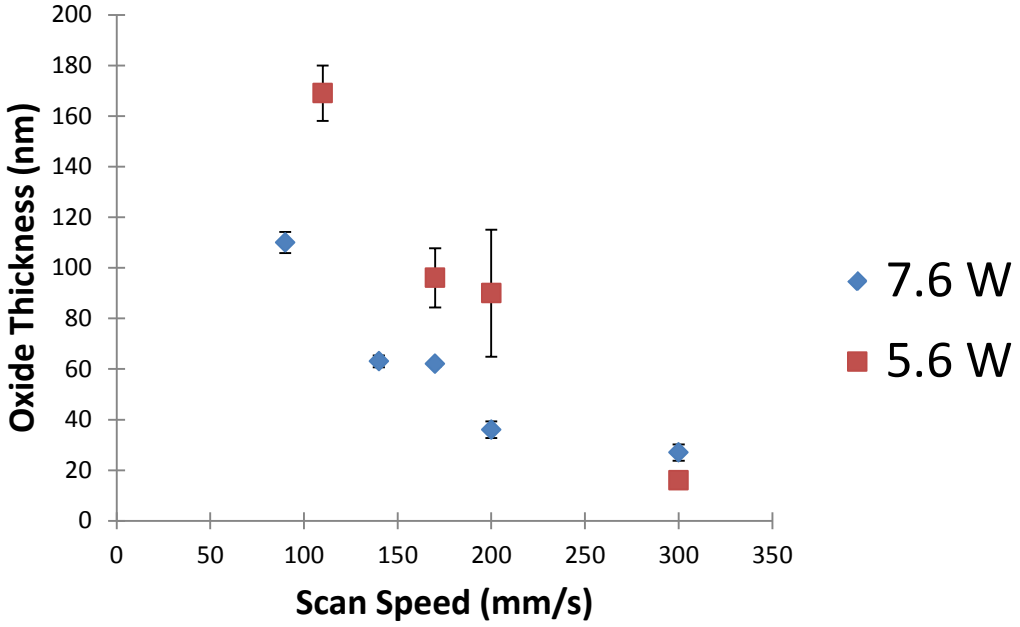
Oxygen distribution



Oxide Thickness



Oxide thickness increases as scan speed decreases.

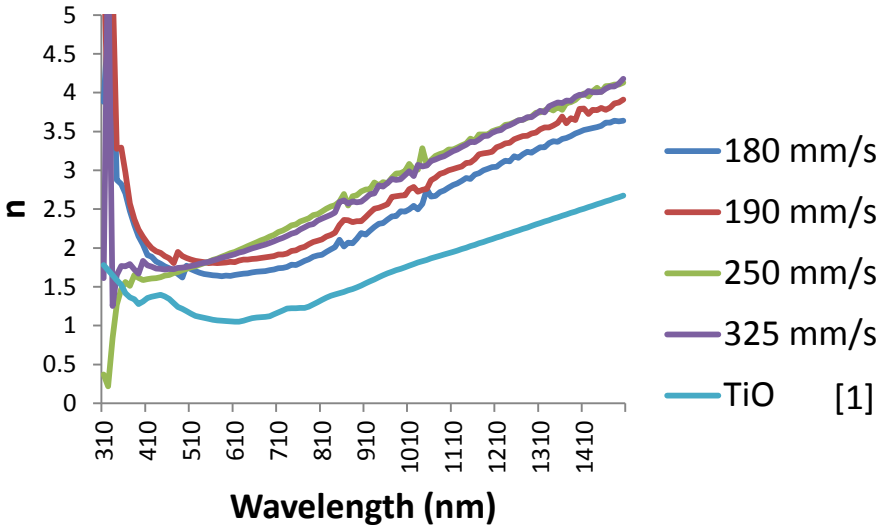


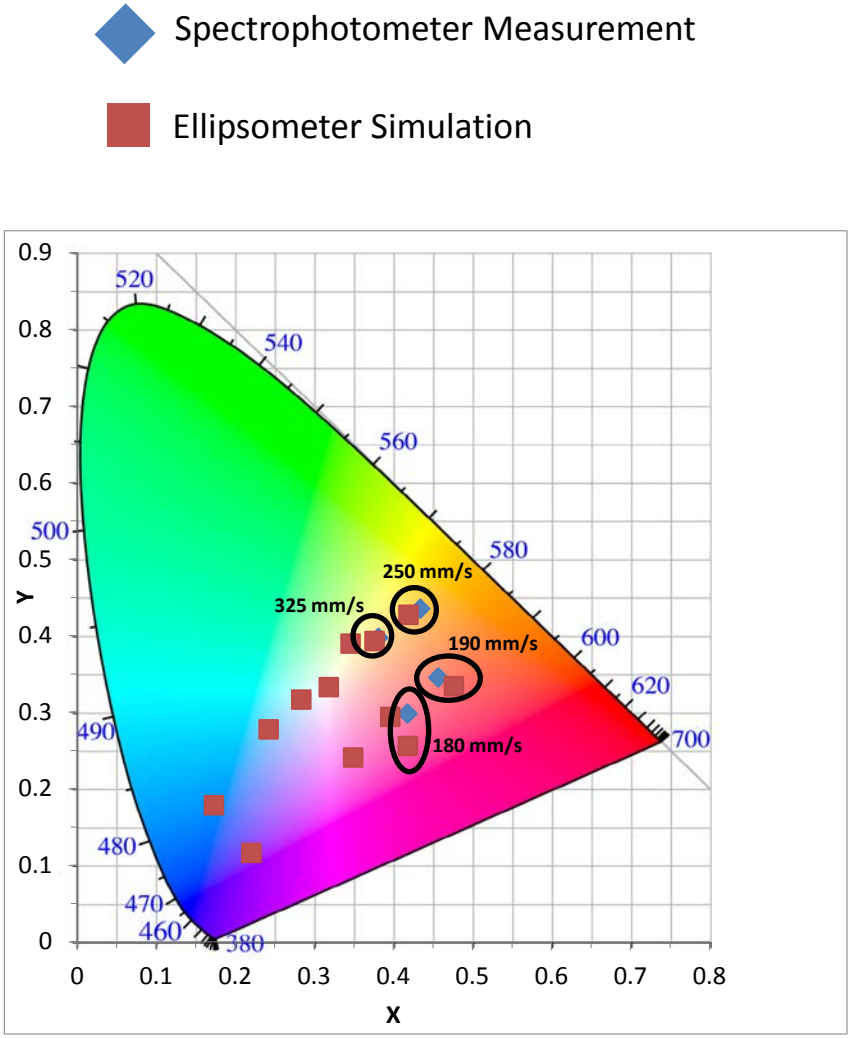
Prediction of Oxide Thickness and Color

Ellipsometric Model

Fit TiO_2 thicknesses: 10 nm - 19 nm

Substrate Fitting





[1] O. Banakh, et. al., Surface and Coatings Technology **151-152**, 272 (2002).

Conclusions

- Ns laser irradiation of Ti substrates forms colors
- Varying scan speed has largest affect on color formation
- TiO thickness increases with decreasing scan speed
- Ellipsometric fit suggests a thin, amorphous TiO_2 phase forms
- TiO_2 layer is likely responsible for color formation
- Better correlation between TEM cross-sections and ellipsometric model is needed