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Deformation and Fracture of Pulsed Laser Oxides on 304L Stainless Steel

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Small Volume Plasticity and Scaling up to Macroscopic Behavior
Symposium in Honor of William W. Gerberich
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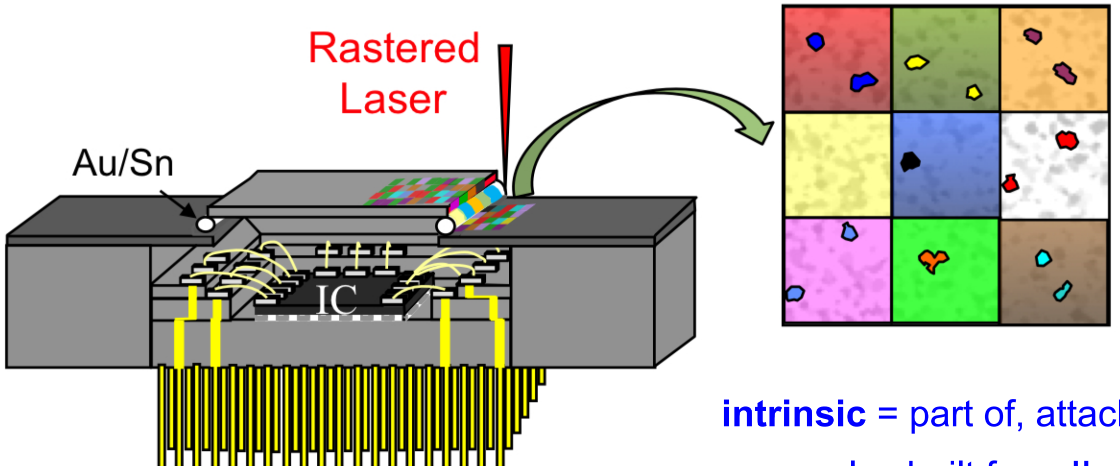
Pulsed laser oxides can create unique colored layers and patterns that can be used as passive indicators of interference

Short (ns) and ultra-short (fs, ps) pulsed laser light interacts with the surfaces of various materials to create complex color layers and patterns that can be used to identify, mark, and archive materials, components, and assemblies.

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



Archived

intrinsic = part of, attached to

also built from !!

We seek robust adherent markings that are impossible to duplicate and replicate.

Approach

Characterize deformation and fracture of pulsed laser light oxides on stainless steel substrates

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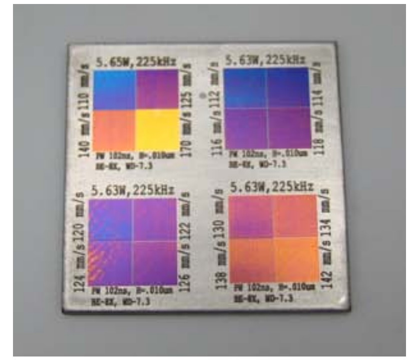
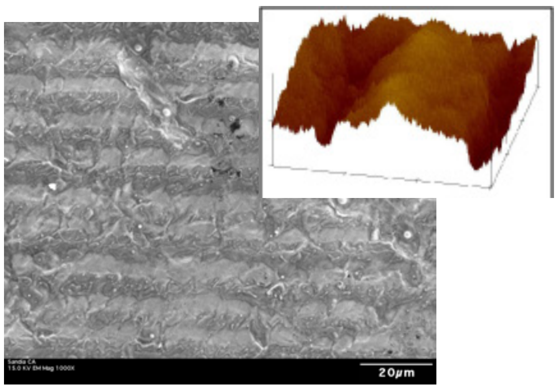
Tasks

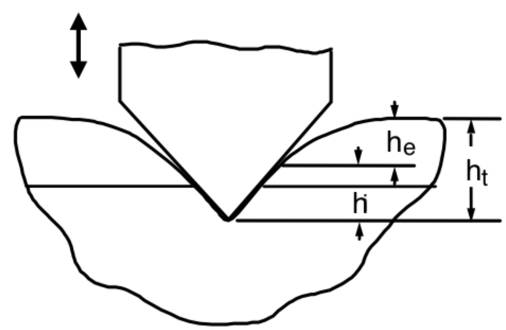
Employ pulsed laser light to create complex color layers and patterns at frequencies of 225, 250, 275, and 350 kHz and scan rates from 10-175 mm/s



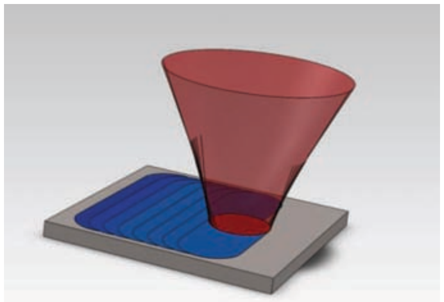


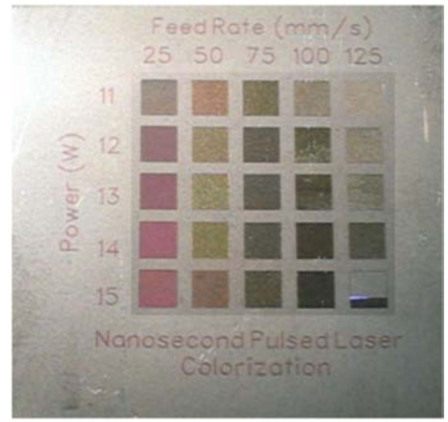
Use optical, atomic force, and scanning electron microscopy, and x-ray diffraction characterize oxide structure and composition

Determine mechanical behavior of the oxide patterns using nanoindentation and nanoECR techniques.



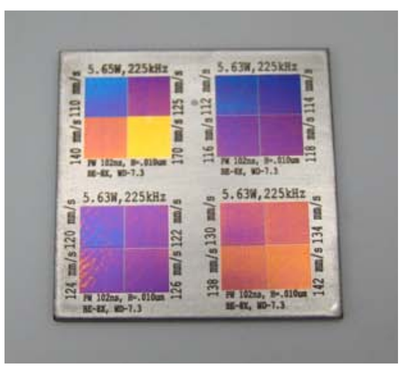
Patterns are formed by rastering a focused, ns-pulsed laser beam at constant power across a surface.



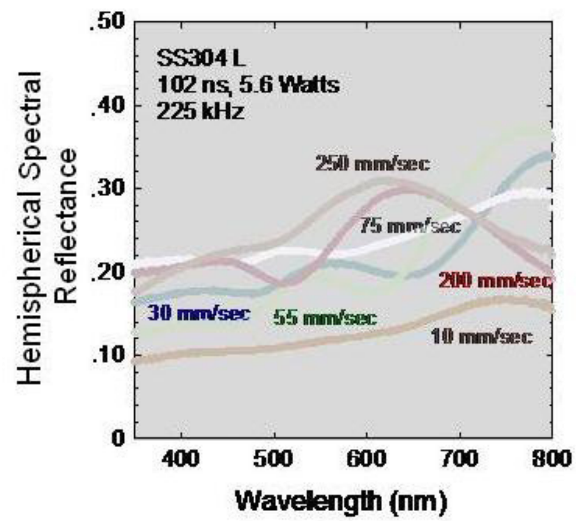


304L Stainless Steel

- Metal reacts with air to form a color layer (oxide)
- Color shifts with power and scan speed rate.
- A variety of colors are available with many materials.



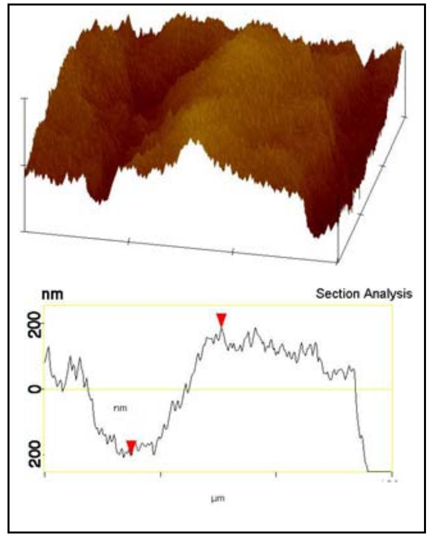
CP2 grade Ti

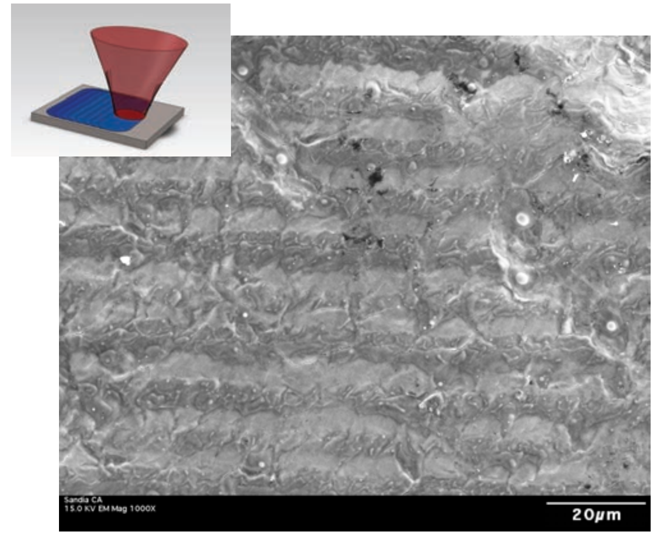


Probed with Cary 5000 Spectrophotometer

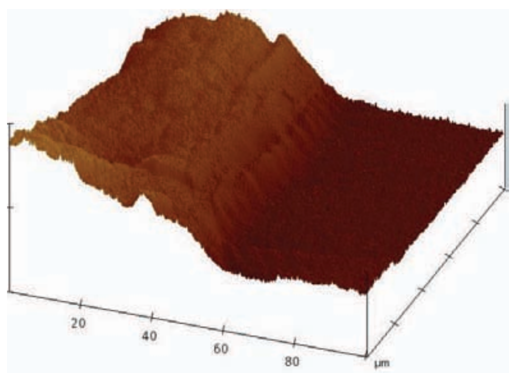
Surface structure showing pass roughness from raster overlap

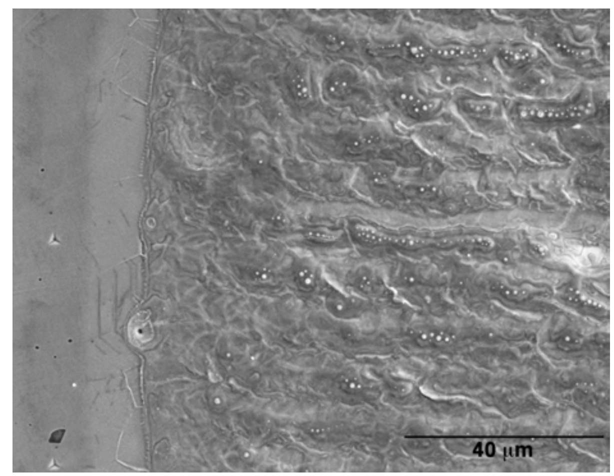
SEM and AFM of 90mm/s oxide ridges





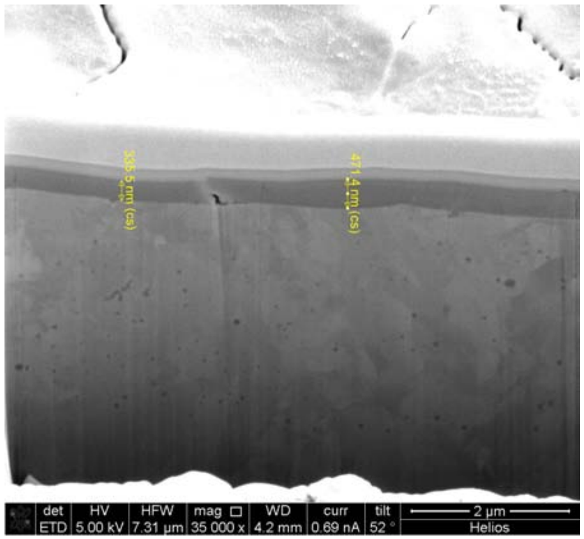
AFM and SEM images of 130mm/s oxide edge, rising from steel substrate.



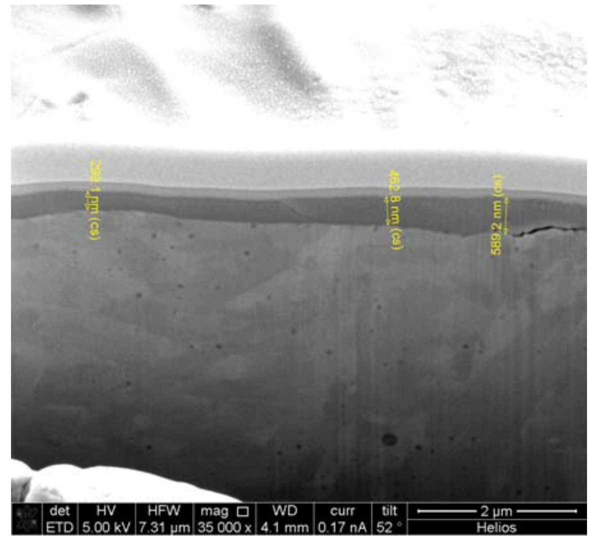


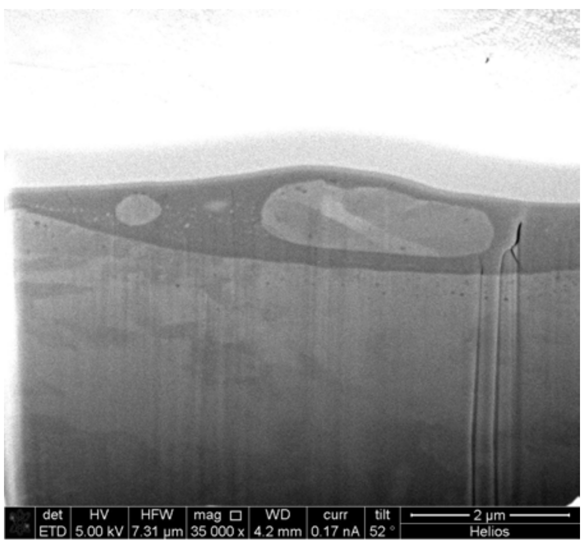
FIB cross sections reveal the complex structure of color layers with extensive channel cracking and instances of delamination

30 mm/s

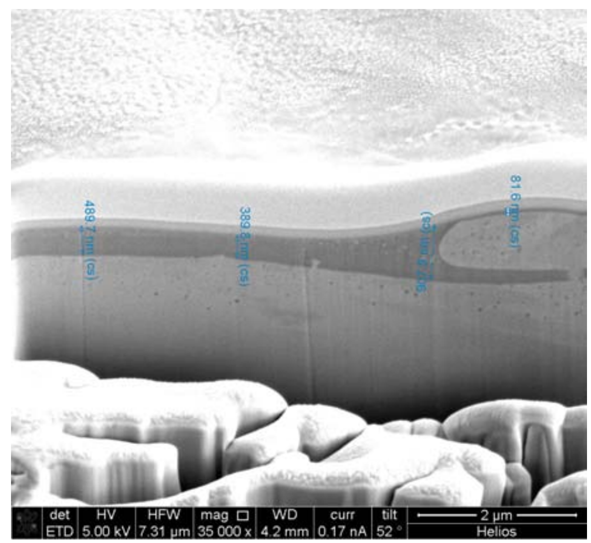


40 mm/s





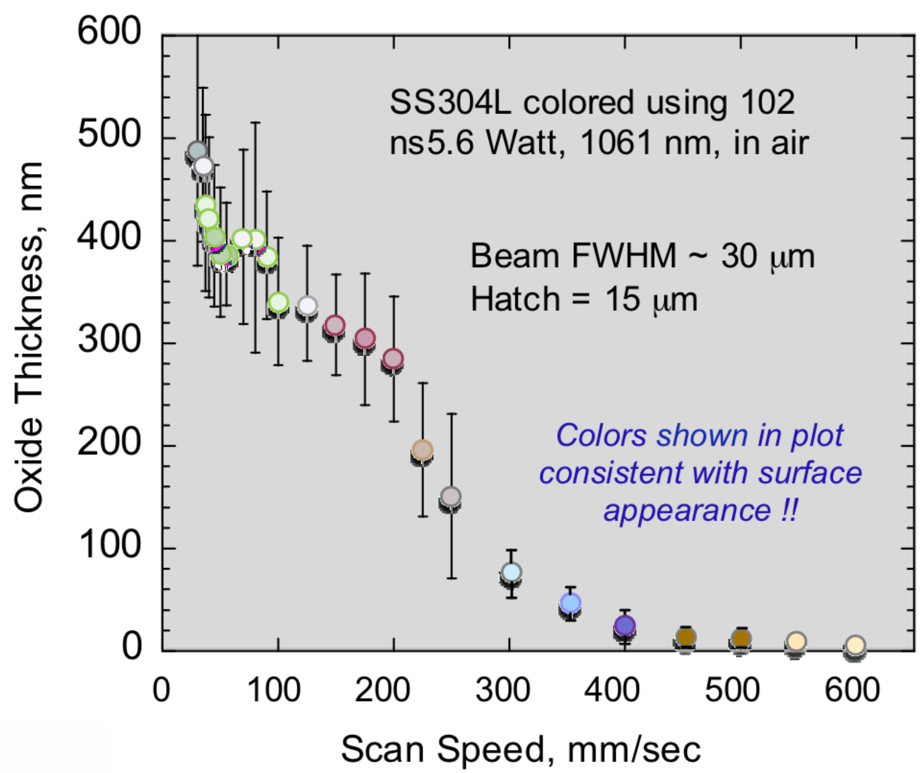
125 mm/s



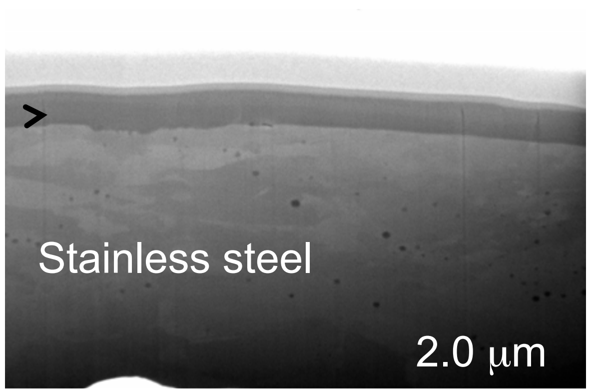
150 mm/s

The observed colors consistently vary with film thickness.

- Oxide thickness generally increases with decreasing scan rate (i.e., increasing heat input)
- Colors appear when oxide thickness is in the range of 15-500 nm.
- Large variation in oxide thickness for a given feature when using a beam overlap approach



Dark layer is laser-fabricated metal oxide

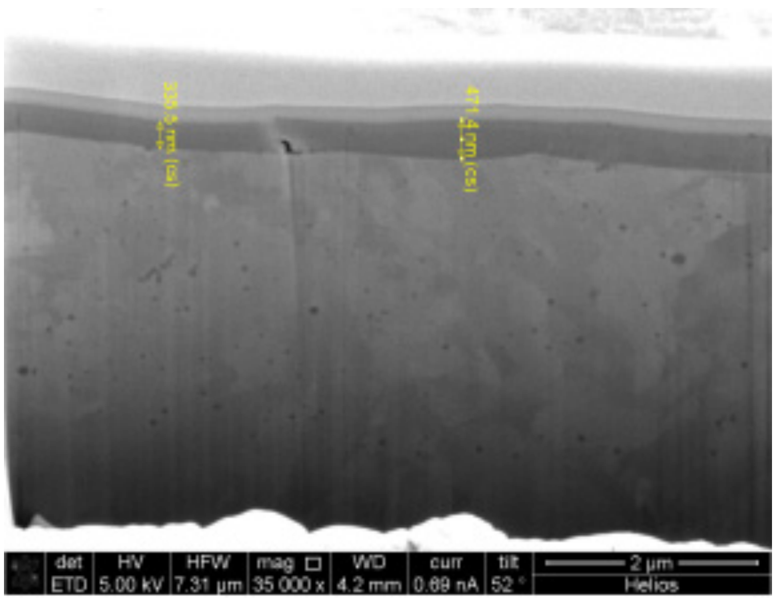


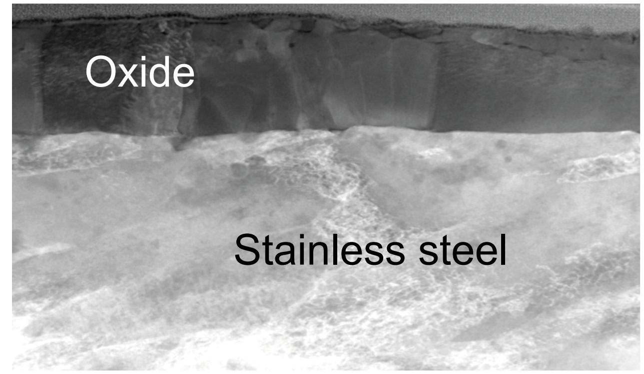
All measurements of thickness are obtained by XS-SEM after focused ion beam sectioning

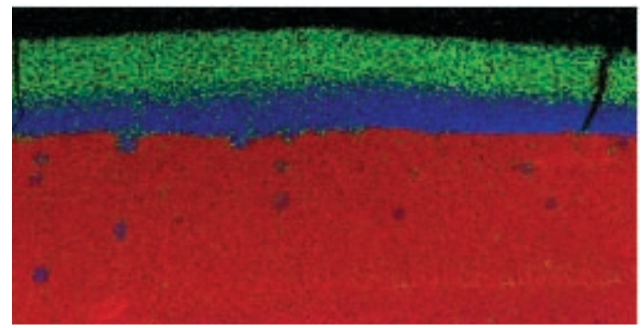
TEM and EDS reveal the complex structure and composition of color layers.

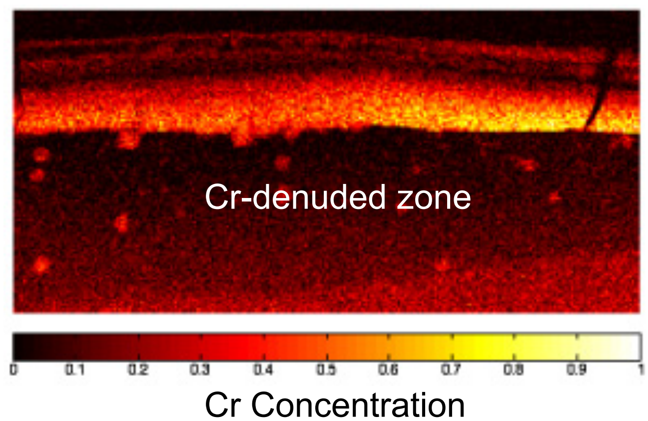
Oxides formed on SS 304L

- Form large grains
- Exhibit a composition gradient
- Contain Ni, Mn and Fe
- Create porous Cr denuded zone in the underlying stainless steel

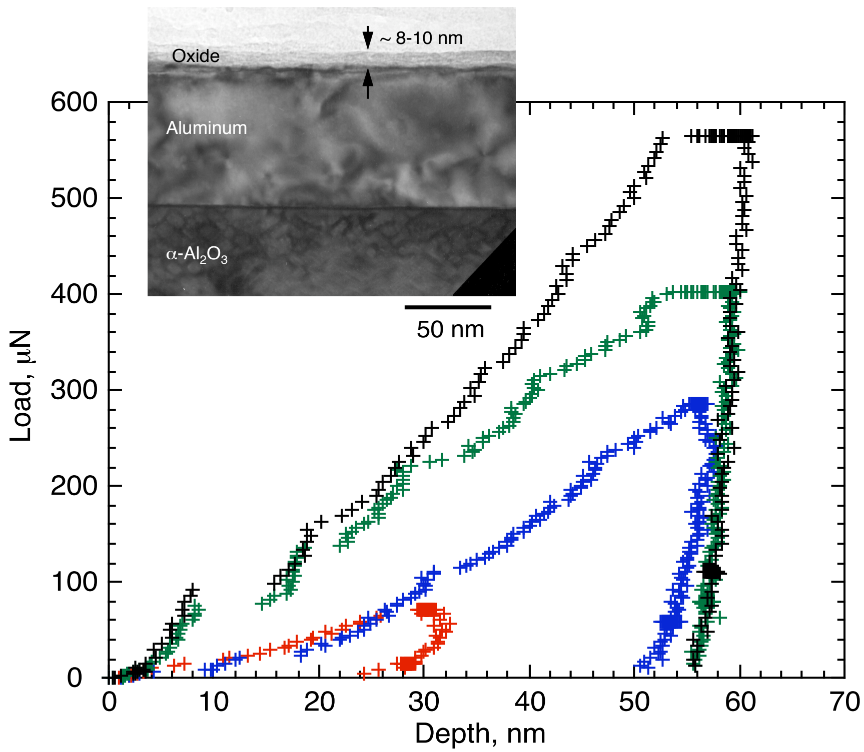


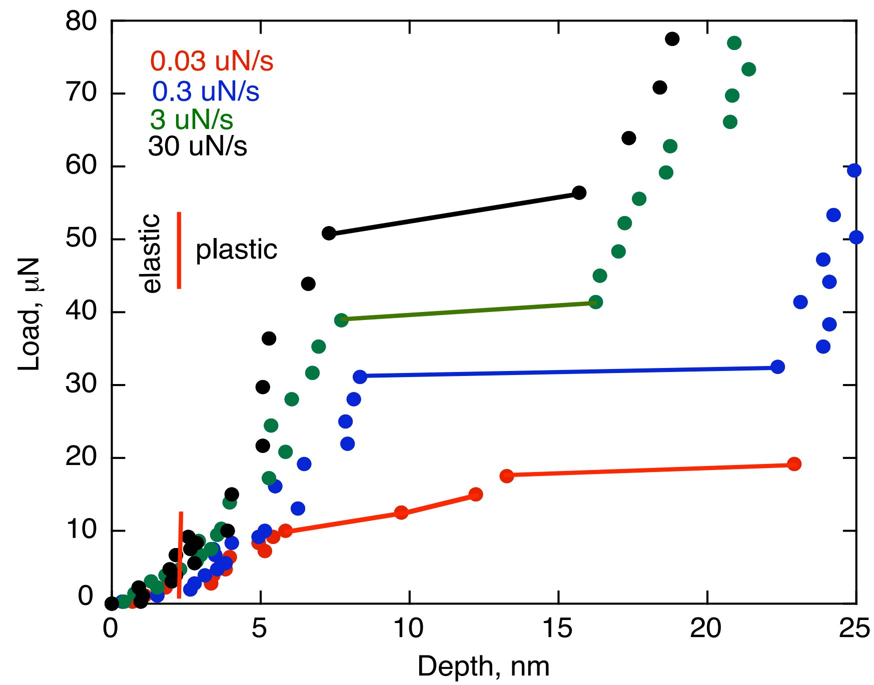






Work on thin aluminum films showed a strong rate dependence to indentation and large indentation excursions.

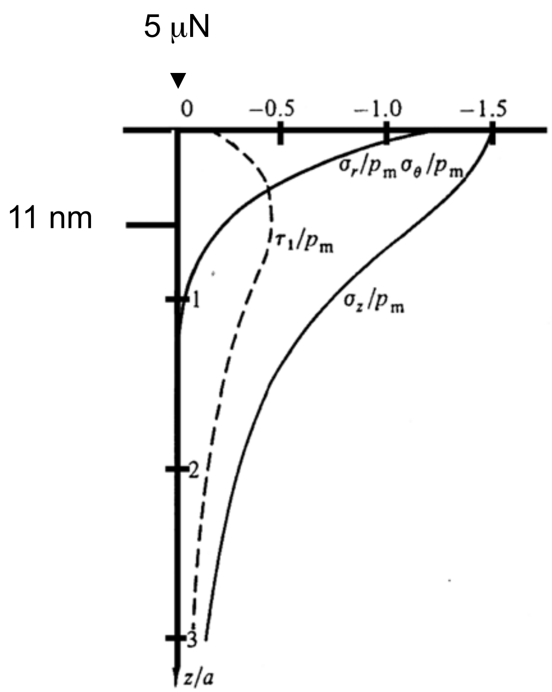


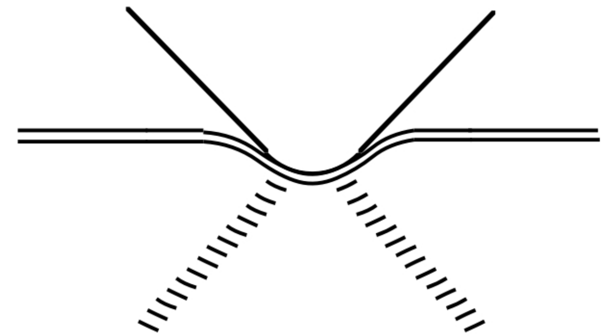


The behavior was attributed to effects of the surface oxide.

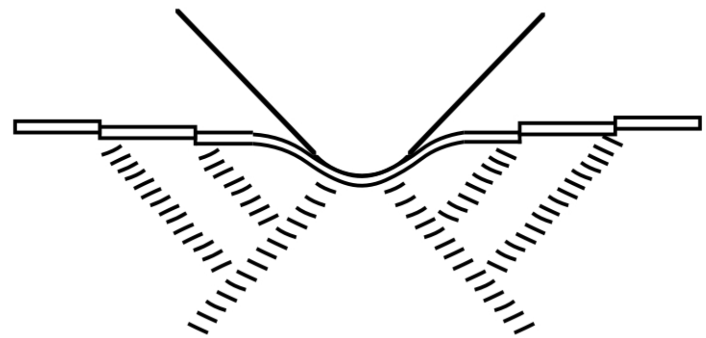
(Hoehn, Bahr, Moody, Gerberich, 1996)

The maximum elastic shear stress occurs near the surface oxide-aluminum interface indicating that the onset of rate dependence is due to dislocation emission





Dislocation Emission

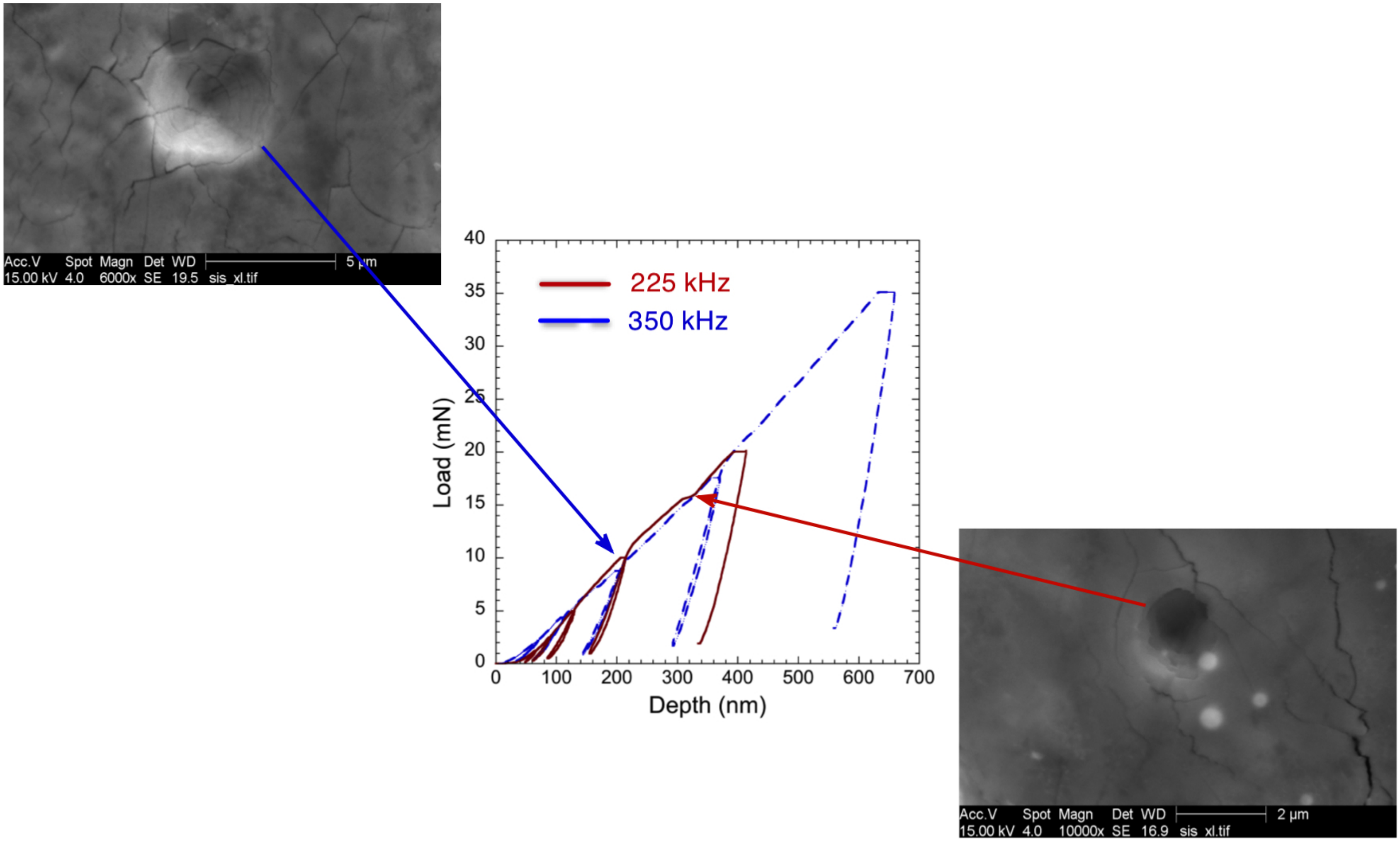


Oxide Fracture

The excursions are due to oxide fracture.

(W. W. Gerberich et al., Acta Metall. Mater., 1996)

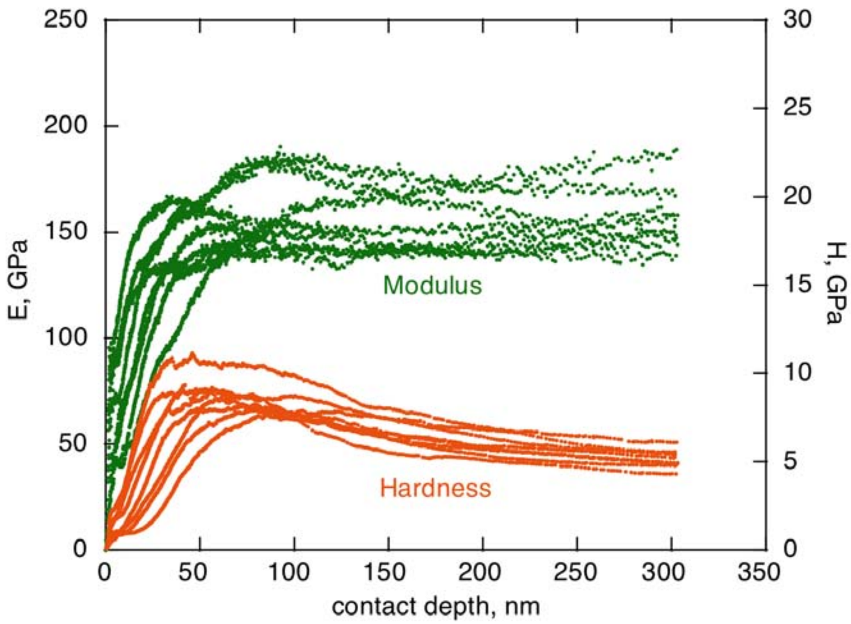
Indentation of laser oxides is accompanied by excursions in the load displacement plot.



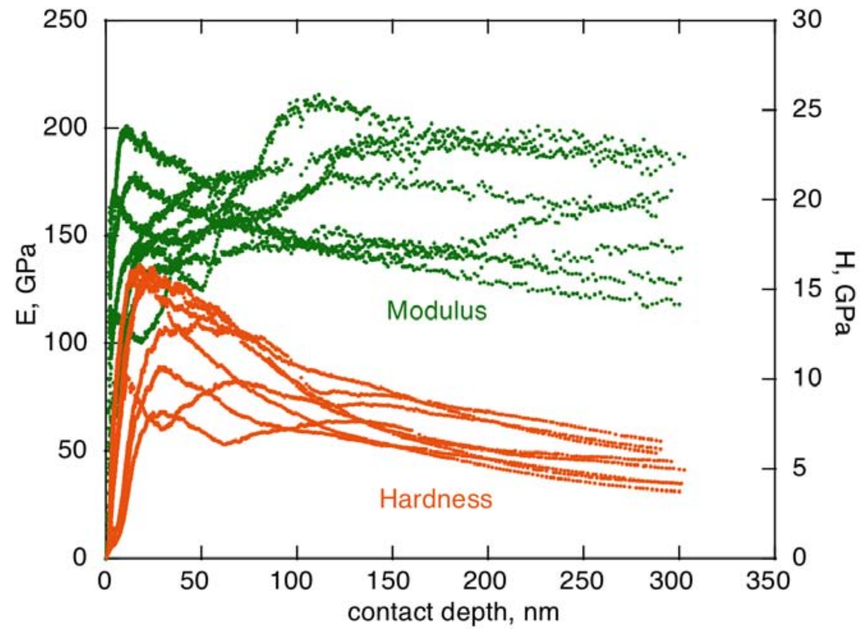
Excursions correlate to film cracking.

Modulus and hardness exhibit significant scatter within each oxide pattern consistent with variable thickness

250 kHz 10 mm/s

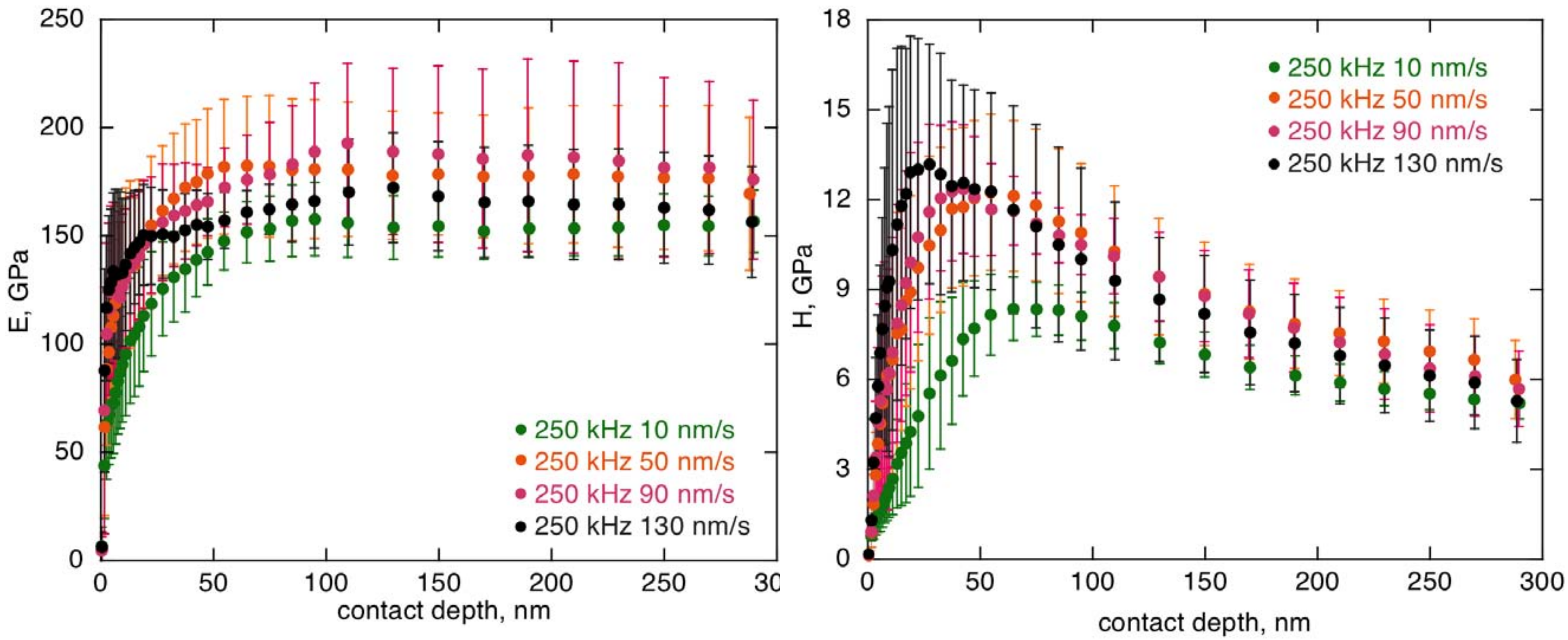


250 kHz 130 mm/s



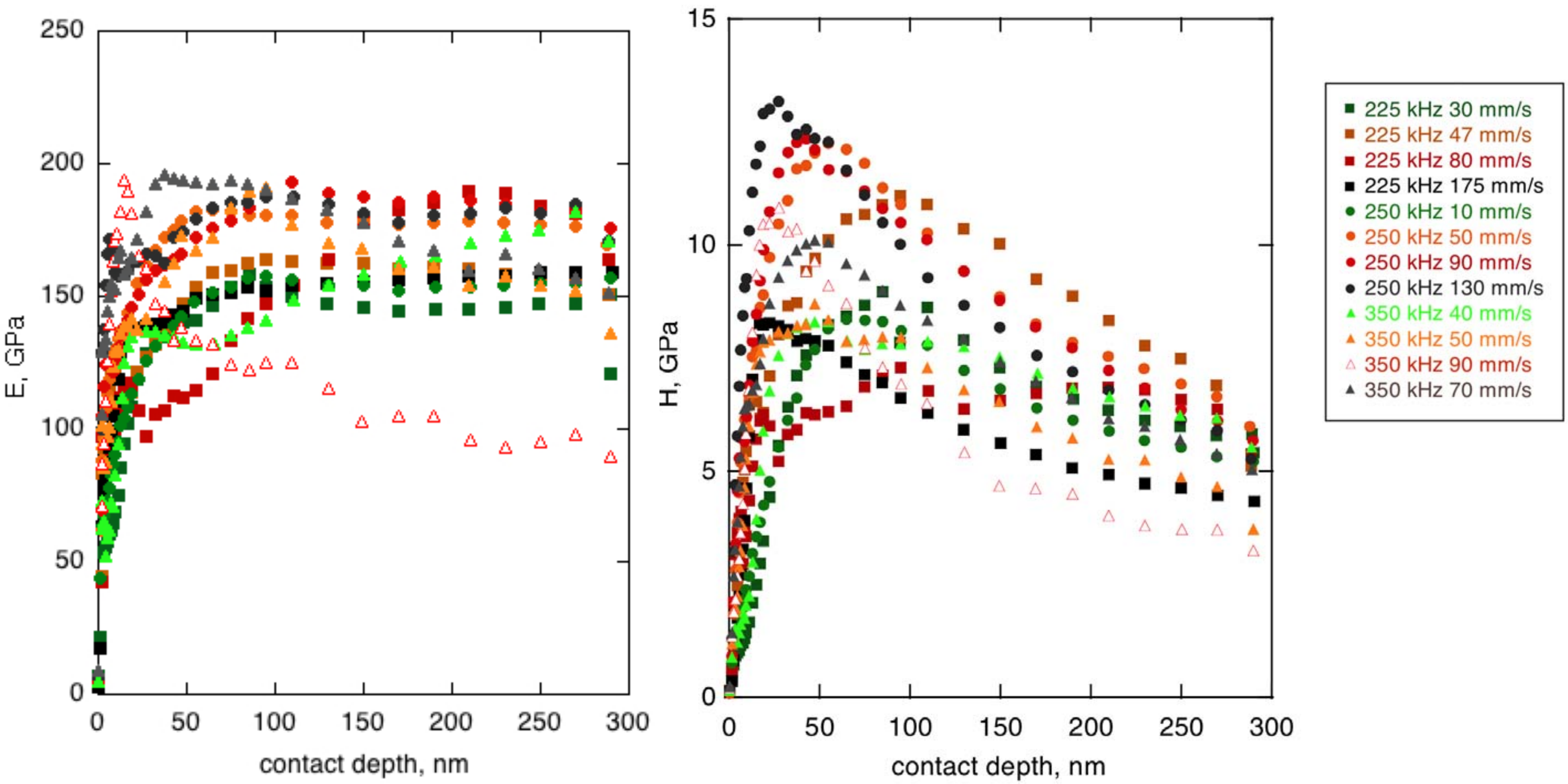
The spike in the curves correlates with oxide fracture

Modulus and hardness increase with increasing scan rate



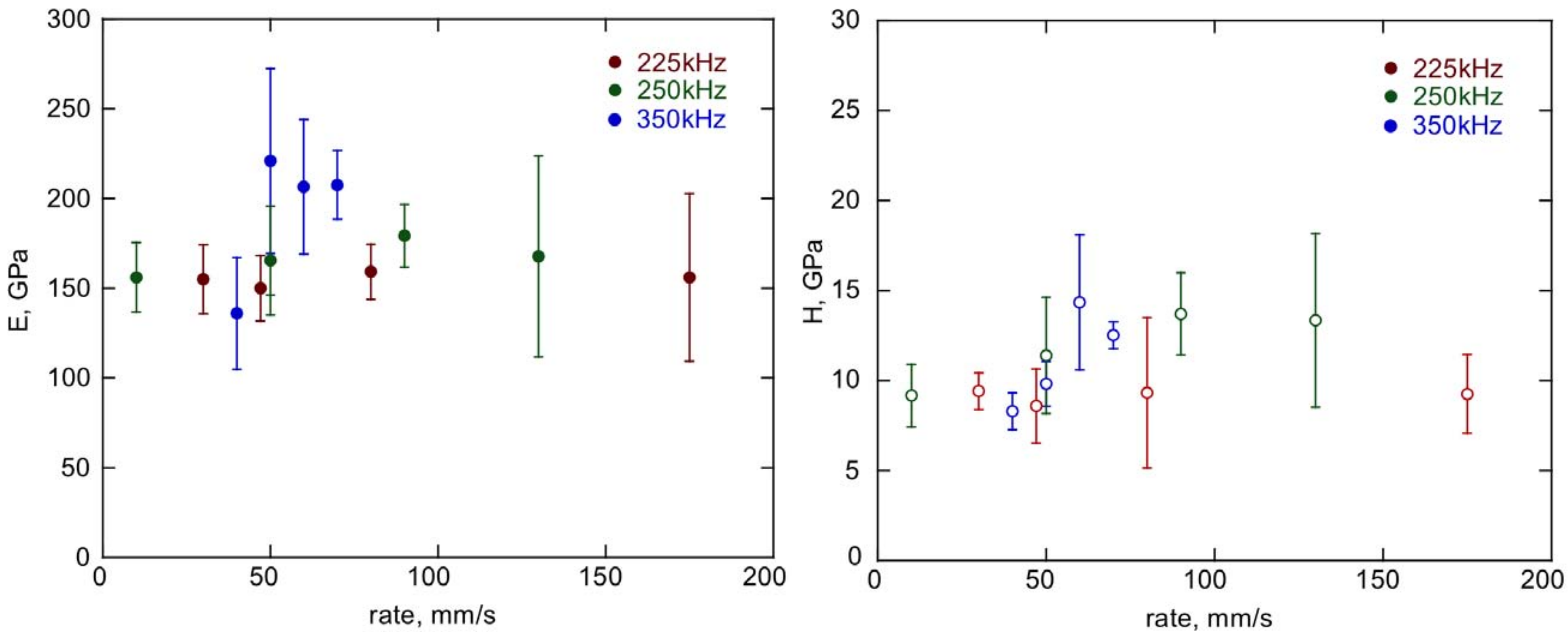
The depth at fracture decreases with scan rate

Modulus and hardness also increase with increasing frequency



The difference is most pronounced between the 225 kHz and 350 kHz oxides

Modulus and hardness at fracture suggests that changing frequency may have a stronger effect than changing scan rate



Summary of measured mechanical properties indicates that frequency and scan rates increase modulus and hardness.

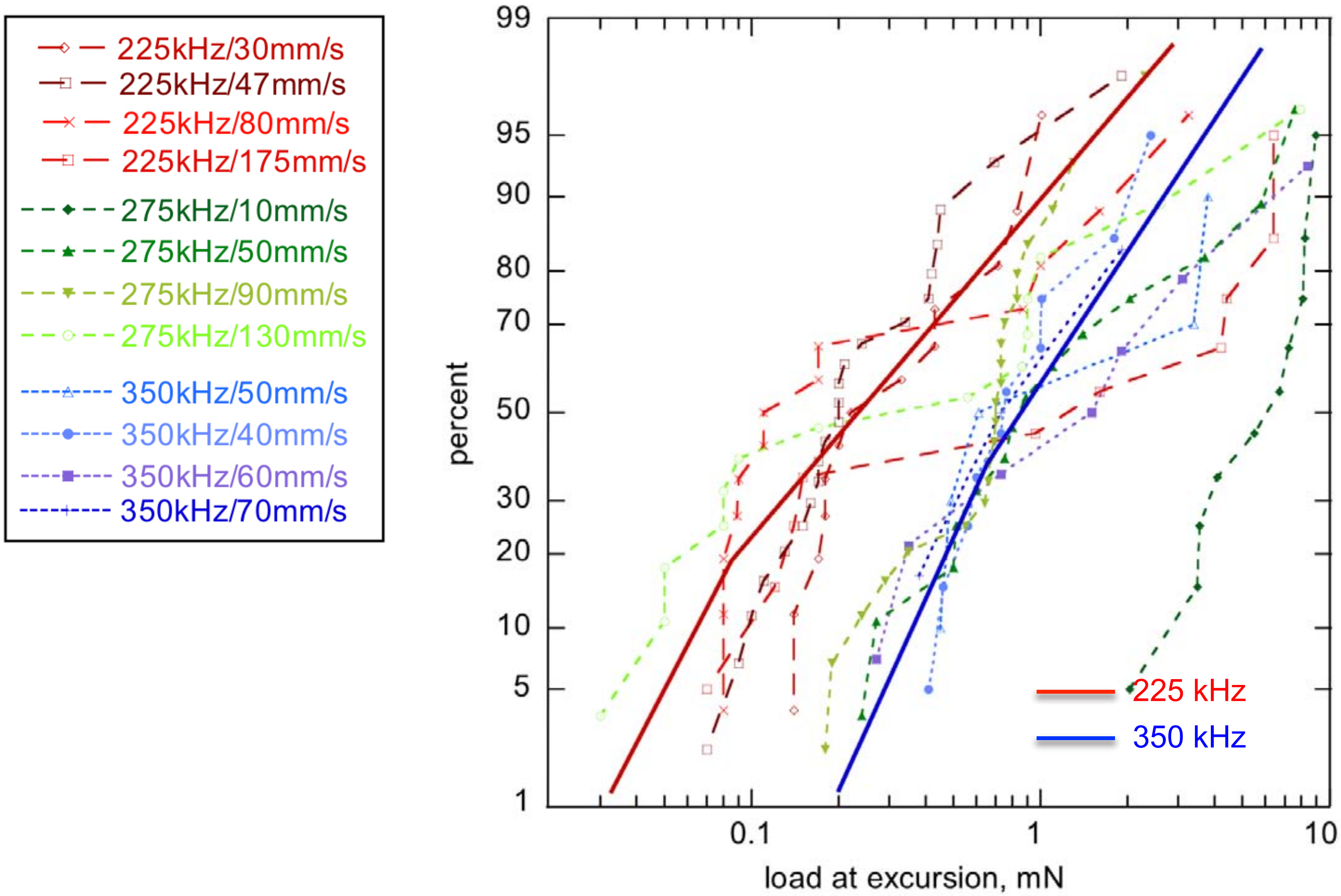
Laser Scan Rate (mm/s)	Laser Pulse Frequency (kHz)	Average Hardness (GPa)	Average Modulus (GPa)
30	225	9.2±1.0	155±20
47	225	8.5±2.0	150±20
80	225	9.0±4.0	160±15
175	225	9.2±2.0	155±40
10	275	9.0±2.0	158±23
50	275	11.3±3.3	165±20
90	275	14.0±2.5	180±15
130	275	13.5±5.0	170±55
40	350	8.0±1.0	137±32
50	350	9.5±1.0	220±50
60	350	14.5±4.0	206±40
70	350	12.3±1.0	208±20

(Test were run at 250 and 275 kHz using the same scan rates. Results were essentially the same.)

(Average values determined from 10 or more indents per specimen)

In general the 350 kHz oxides are stronger than the 225 kHz oxides

Normal probability plot of load at discrete events

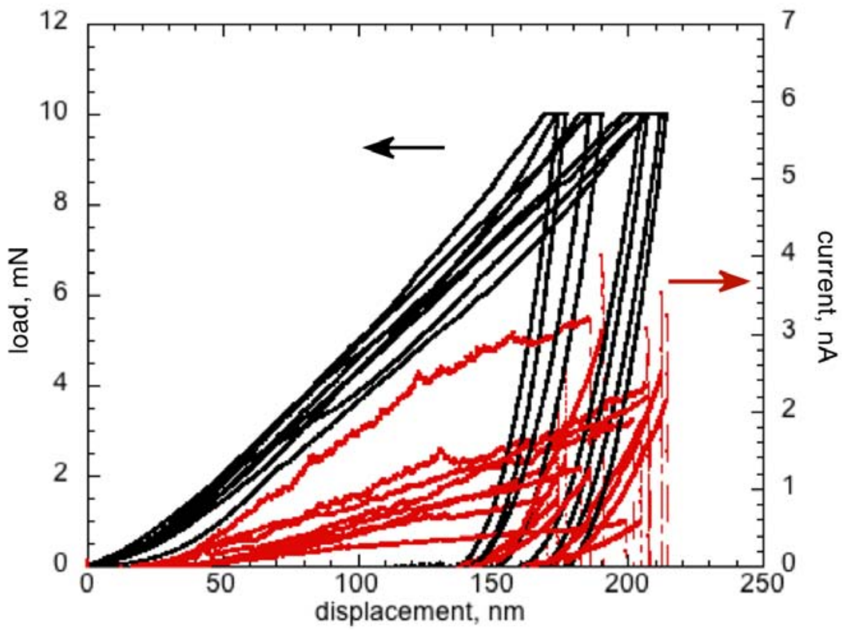


(Lawrence et al. MRS Proceedings, 2011)

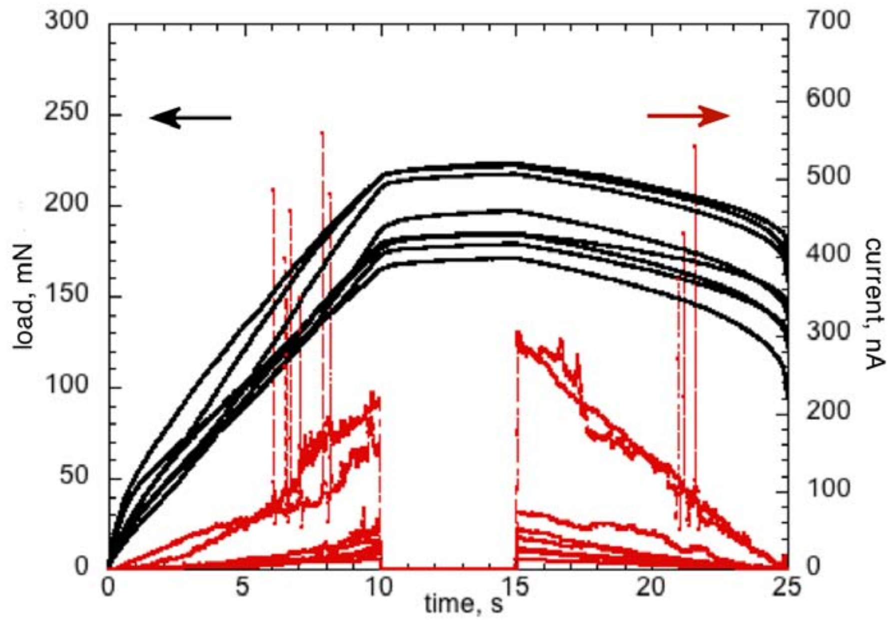
The highest excursion loads are observed on the higher scan rate films.

Conducting indentation shows conductivity increases markedly in oxides formed at higher scan rates.

250 kHz 10mm/s

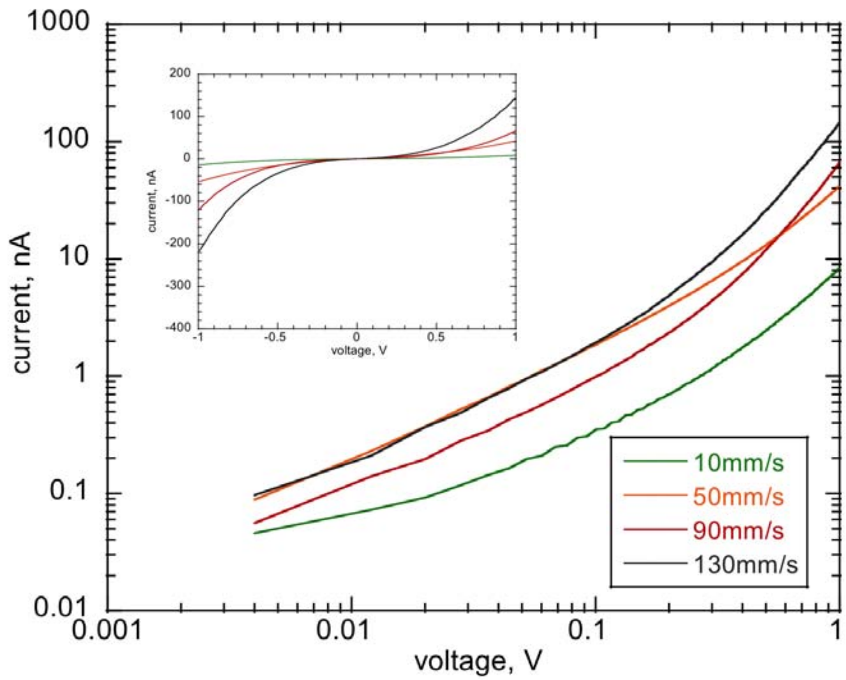


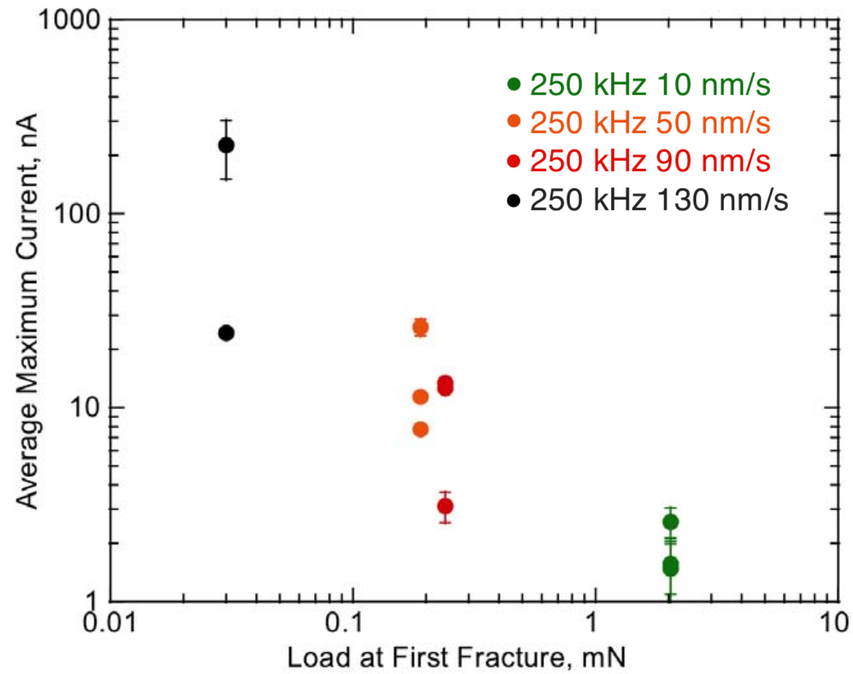
250 kHz 130mm/s



Conducting indentation also enables comparison of load/current at discrete events such as dislocation nucleation or oxide fracture.

Faster scan rates correlate with higher film conductivity suggesting a higher defect concentration in oxides formed at higher scan rates





Oxides with a higher fracture load have lower conductivity consistent with a lower defect concentration

Conclusions

Oxide films have an undulating surface topography and a thickness around 400nm. Channel cracking is prevalent on the surface of all oxides. Some delamination occurs at the interface of the substrate and oxide.

The oxides are composed mainly of Fe_3O_4 and an Fe-Ni-Cr oxide.

While there is considerable scatter in mechanical property data, the average modulus of the films is ~160GPa and the average hardness is ~11GPa

Nanoindentation demonstrates that faster laser scan rates lead to tougher films and that higher laser frequencies result in oxides which fracture at higher loads.

Faster scan rates and lower frequencies correspond with higher conductivity, likely due to the presence of defects.

Suggest that performance that reliability can be tailored through processing

Acknowledements

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