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APPLICATIONS OF FEMTOSECOND LASER-INDUCED BREAKDOWN SPECTROSCOPY

1. WHAT FEMTOSECOND LIBS IS

A. LIBS

i. LIBS ablates a material with a high-energy laser pulse, causing a small amount to form into a plasma. As the plasma condenses, it emits photons characteristic of the re-formation of compounds, which can be used to reconstruct the constituent elements.

ii. $$I_{pq} = \left(\frac{l}{4\pi}\right) n \left(\frac{g_p}{Z(T)}\right) A_{pq} \left(\frac{hc}{\lambda_{pq}}\right) \exp \frac{-E_p}{kT}$$ (Zorba, Mao, & Russo, 2010)

iii. It is considered non-destructive (due to the small volume ablated) and can be employed on a variety of samples with little or no preparation.

B. LIBS Configuration Considerations

i. Laser pulse duration—affects how local the deposition of energy is to the beam site (more below).

ii. Laser pulse energy—higher energies ensure that there is complete ionization, but also result in deeper craters and more extreme deposition outside of the crater (Zorba et al., 2010).

iii. Signal collection time—signal collection beginning too early is dominated by broadband continuum bremsstrahlung radiation. This continues until ~0.5μs after the pulse. Additionally, Stark broadening affects the peaks during this period. Contrarily, waiting too long after the ablation results in reduced signal to noise ratio (Wainner, Harmon, Miziolek, McNesby, & French, 2001).

C. Femtosecond-pulse LIBS

i. LIBS is limited by the formation of the plasma via ablation. If the energy is delivered over too long a period, the sample melts instead of ionizing. Avoiding this melting increases the spatial resolution of LIBS by shrinking the effective crater size from μm scale to ~100nm scale (Hwang, Jeon, Grigoropoulos, Yoo, & Russo, 2007).

ii. Femtosecond pulses deliver the energy more quickly, meaning that there is less time for phononic propagation to the rest of the material, resulting in less melting (vice plasma formation) (Zorba et al., 2010).

iii. The higher power/more intense pulse of femtosecond LIBS also means that the plasma ejecta does not have time to interact with the ablating pulse via inverse bremsstrahlung, improving signal-to-noise ratio (Hwang et al., 2007).

2. APPLICATIONS OF FEMTOSECOND-PULSE LIBS

A. Trace pollutant detection

i. This takes advantage of the portable nature of LIBS as well as the fact that little to no sample preparation is required (Wainner et al., 2001).

B. Semiconductor manufacture

i. The manufacture of microprocessors that use thin metallic film to conduct signal between semiconductor elements require precise information as to the thickness of metallic deposition. LIBS has the potential to determine this using repeated pulses as an analog for depth, given certain restrictions on the shape of the incident laser pulse (Galmed, Kassem, Von Bergmann, & Harith, 2011).

C. Trace explosives detection

i. The higher intensity of femtosecond pulses means that the total energy required to induce a plasma in a sample is smaller. This has potential advantages in portable (vice laboratory) systems where the total energy budget is limited (De Lucia, Gottfried, & Miziolek, 2009).

D. Bacteria identification

i. Because of the higher intensity/lower total energy available using femtosecond pulses, careful selection of pulse parameters can reduce the contributions of Oxygen and Nitrogen peaks (from the surrounding air) to the resultant spectrum. This facilitates analysis of the trace minerals that differentiate between different species of bacteria (Baudelet et al., 2006).

E. Measurement of isotopics in nuclear material

i. Cremers, et al, (Cremers et al., 2012) demonstrated the ability to measure isotopic shifts in Li and U using a portable LIBS apparatus. This has obvious applications to the field of nuclear security.

3. FUTURE DEVELOPMENT

A. Nonlinear optics

i. High energy femtosecond pulses have been demonstrated to have non-linear effects in atmosphere. This has allowed for the formation of “filaments” of plasma along which a both a second interrogating pulse and a returning signal can travel. This allows for long range (>90m) interrogation of samples without excessive degradation of the signal-to-noise ratio (Stelmaszczyk et al., 2004; Xu, Bernhardt, Mathieu, Roy, & Chin, 2007).