Fast Atomic Mapping of Heterogeneous Surfaces Using Microline-Imaging Laser-Induced Breakdown Spectrometry

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A new approach for quick simultaneous and multielemental characterization of heterogeneous solid samples using laser-induced breakdown spectrometry (LIBS) is presented. The basic idea relies on focusing the incident laser beam with a cylindrical lens to produce a long and narrow microline plasma. The emitted light is then projected along the spectrograph slit, where each ablated location on the sample generates a signal at a defined height, and acquired with a charge-coupled device (CCD) detector. The method has been tested for compositional mapping of solar cells, enabling a 25-fold increase of analysis speed as compared to conventional LIBS configuration.

Index Headings: Laser-induced breakdown spectrometry; LIBS; Chemical imaging; Materials analysis.

INTRODUCTION

Materials characterization is a vast field where different scientific disciplines and techniques cohabit in the common effort to provide a complete description of the sample of interest from different points of view. Concerning direct chemical elemental analysis, there are many alternatives capable of determining the elements present in a given sample. However, most of them require working under moderate or high vacuum conditions, or they present some restrictions in terms of sample type, shape, or conducting properties. Laser-induced breakdown spectrometry (LIBS) is considered a promising technique in terms of the outstanding capabilities of performing fast and accurate analysis in air at atmospheric pressure without limitations in sample size or nature. In spite of these unique advantages, LIBS is still affected by several drawbacks derived from the lack of standardization and different matrix effects (selectively vaporization, sample fractionation), which limit real quantitative approaches. Several books and review articles provide a complete description of theoretical fundamentals and recent applications in different industrial and analytical situations. 1–5 Recently, LIBS has been explored as an alternative technique in surface analysis 6 due to its capabilities of furnishing information on the lateral 7,8 and in-depth 9–11 distribution of the constituent elements of a sample at the micrometric level. As a result of major progress in the performance of the technique, depth-resolved measurement at the nanometric range has also been achieved. 12

A new approach within the capabilities of LIBS for materials characterization is compositional mapping. 13–17 In this instance, a selective image of the sample, depicting the distribution of a given element, is obtained by delivering consecutive laser pulses over a fixed position and rastering the laser through a defined path over the analyzed area. When a multidimensional detector is used, a complete spectrum covering a selected range of useful wavelengths is obtained for each laser event. After selection of the desired emission lines, the spatial distribution of the element present in the sample may be mapped out. To date, detailed spatial information by the so-called imaging-mode LIBS has been achieved by point-to-point mapping using a spherical lens focusing system, at the cost of increased measurement time and data storage requirements. For instance, with a N₂ laser, 800 sampling points are required to describe a 3 × 3 mm² area with 80 and 150 μm resolution (for the X and Y directions, respectively). 18 Many other laser-based imaging techniques also share the problems mentioned, in particular Raman microscopy 19,20 where the sample is to be analyzed by rastering the laser or by moving the sample through defined paths. In these cases, different strategies using cylindrical lenses or scanning mirrors have been developed to maintain a compromise between spatial resolution and analysis time to a workable regime. 21

An alternative approach for obtaining images using LIBS involves exploring the two-dimensional capability of charge-coupled device (CCD) detectors. In these types of systems, one dimension of the detector is reserved for light dispersion (providing spectral information), while emission from different locations on the surface is effectively focused onto the second dimension of the CCD (providing spatial information). Full advantage of this approach can be obtained if the laser is focused to a microline at an energy exceeding the plasma threshold fluence along the full microline, and the plasma formed in a direction parallel to the spectrometer entrance slit is collected. With the use of this focusing and detection system, each ablated location in the sample will generate a signal at a defined height in the slit. In the present paper this proposed microline-imaging LIBS is presented, and performance parameters for generation of surface chemical images are discussed.

EXPERIMENTAL

Instrumentation. The diagram of the setup is shown in Fig. 1. A Q-switched Nd:YAG laser (Continuum, Model Surelite SLI-20, pulse width 5 ns) operating at the 1064 nm wavelength was used to irradiate the samples. The energy output was varied in the range between 21 and 88 mJ/pulse by controlling the flash lamp voltage and the Q-switch delay. No appreciable changes in the spatial distribution of the laser beam were observed in the working range. The energy output was monitored daily with a pyroelectric joulemeter (Gentec, Model ED-200). The beam was delivered with the use of quartz
prisms and focused at normal incidence onto the sample surface with a 90 mm focal length cylindrical lens (CL). In this way, a microline plasma [5.8 mm (h) × 0.015 mm (w)] was formed at the focal point. The length of the cited line was equal to the diameter of the incident laser beam. The relative orientation of the sample and the CL enables the plasma light formed to be colinear with the spectrograph slit, typically set at 30 μm. The plasma light was always collected from regions close to the sample surface and was brought to the entrance slit of a 0.5 m focal length spectrograph (Chromex, Model 500 IS) by a planoconvex quartz lens (100 mm focal length). Light was dispersed by using 2400 and 300 grooves mm⁻¹ gratings with reciprocal linear dispersion values of 2.5 and 20 nm mm⁻¹, respectively. An intensified charge-coupled device (ICCD) detector (Stanford Computer Optics, Model 4Quik 05) was used to detect the dispersed plasma light. The experiment timing was performed through a TTL signal from the Q-switch output of the laser. This output was measured as being delayed ~200 ns from the laser firing by using a 2 ns rise time photodiode (Thorlabs) and a 100 MHz oscilloscope (Textronik). Each spectrum was corrected by subtracting the dark signal of the detector, which was measured separately.

**Samples.** Photovoltaic converters used as solar cells provided by Isofotón S. A. (Málaga, Spain) were employed as samples. These devices present a well-defined structure consisting of silicon wafers covered by a 40 nm thickness TiO₂ layer (acting as an antireflection coating) and an array of silver fingers (acting as charge collectors) periodically spaced at 2 mm intervals. The average width and thickness of the silver fingers are about 200 μm and 30 μm, respectively.

**RESULTS AND DISCUSSION**

The method was initially tested in solar cells, a sample well-characterized previously by the authors using con-

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**Fig. 1.** Schematic diagram of the microline-imaging LIBS. (A) Nd:YAG laser; (B) cylindrical lens; (C) sample; (D) X-Y-Z translational stage; (E) collection lens; (F) sample image on the spectrograph slit; (G) spectrograph; (H) CCD detector; (I) optical table.

**Fig. 2.** (A) Representation of the surface of a solar cell portion after the exposition to the line-focused laser beam. (1) Ag fingers. (2) Crater produced by laser ablation. (B) CCD image of the laser-ablated plasma across three fingers. It should be noted that only a section of the whole image has been shown. (C) Ag(I) 328.01 nm emission profile along the sampling line indicated in Fig. A2.
FIG. 3. FWHM of the profile of a silver finger along the microline vs. pressure.

FIG. 4. Micrography of two craters on a photovoltaic cell. The inset is a micrographic image obtained by a backscattered-electrons detector of the region limited by the dashed line.

A scheme of the path followed to perform the analysis is shown in Fig. 2. The sample, showing the typical arrangement of silver fingers and the anti-reflective coating (TiO$_2$), was analyzed by focusing the incident laser beam into a microline in a zone covering three silver fingers (Fig. 2A). After being focused at the entrance slit of the spectrograph (fitted with a 300 grooves/mm grating and centered at 300 nm), the CCD acquires an image containing spatial and spectral information (Fig. 2B). As shown, three bright points are clearly visible in the CCD image corresponding to the spatial location of the silver fingers. These points unquestionably correspond to Ag, as the CCD matrix was partially closed to read the spectral window between 324 nm and 331 nm, where the intense Ag emission at 328.01 nm is located. Obviously, by increasing the spectral window observed, simultaneous and multielemental images were also taken, where the complementary pattern for Ti was apparent (see below).

The use of a single cylindrical lens to focus a laser beam may present certain disadvantages derived from the quasi-Gaussian energy distribution. This fact has been overcome by different methods in the development of X-ray lasers by splitting the beam in several parts (using cylindrical lens arrays or segmented wedges) and focusing each component at the same position, forming a common line focus. Recently, the use of the so-called Powell lens has also been shown to be a powerful instrument to obtain laser beams with a highly uniform line shape. The effect of using a noncorrected cylindrical focusing system is observed in Fig. 2C, where the profile along the microline of the Ag(I) emission at 328.01 nm is plotted. As shown, the intensity decreases symmetrically...
Fig. 5. Normalized intensities profiles of Ag (solid line) and Ti (dashed line) along the microline. Data for silver fingers of increasing width were plotted against pixel number, in the CCD spatial direction. Silver finger width: (A) 1000 μm, (B) 1400 μm, and (C) 1800 μm. See text for more details.

from the beam center to the edges, in accordance with the Gaussian intensity profile of the laser.

The real 1:10 aspect ratio between Ag fingers (~200 μm width) and Ti coating (~2000 μm) in the solar cell does not match that obtained by this approach, as evidenced by comparison of Figs. 2A and 2C. This effect must be due to the different factors affecting the magnification of the image: collection optics, spectrograph aberrations, imperfect electron transfer in the intensifier, and others. However, with the cited factors regarded as constant, the effect of plasma expansion was also studied. In order to check for this effect, different strategies were followed. In the first approach, the plasma was monitored at an early time. For these purposes, the acquisition time in the detector was set at 50 ns while the delay time in the acquisition was varied between 100 and 500 ns. The pulse energy range was 28–88 mJ. Although no noticeable effect on the aspect ratio was observed in the time range studied, the best compromise between the signal intensity and aspect ratio was obtained at 300 ns and low pulse energy. Second, the effect of over-pressure was checked as a way to confine the plasma and avoid its free expansion. To carry out the experiments, we enclosed the sample in a pressurized chamber and applied pressures between 1 and 8 bar while monitoring plasma emission. Higher pressures were not studied due to leaks in the system used. In this working range, the full width at half-maximum (FWHM) of the finger profile decreases with increasing pressure. This effect is shown in Fig. 3 and indicates a clear deformation of the profile as the plasma expands. Although the experiments have been performed at atmospheric pressure due to its flexibility, work is in progress to fully describe the effect of pressure on the proposed method.

Once the experimental conditions were established (integration time: 50 ns; delay time: 300 ns; energy per pulse: 28 mJ), further experiments were conducted to demonstrate the capability of the method to reflect the compositional differences of a given sample. As noted, while with the use of a spherical lens the lateral resolution is given by the crater diameter, in the microline configuration the lateral resolution will be defined by the width of the rectangular crater generated (easily measured by optical microscopy), and by the capability of the detection system to resolve an image generated in the slit.

The lateral resolution for the microline-imaging LIBS due to the width of the crater generated may be seen in Fig. 4 where two craters, showing a 20 μm width and spaced at 250 μm, were photographed. With this lateral resolution, 40–50 lines per millimeter could be analyzed without evident overlapping. As observed in the figure, the microline completely crosses a silver finger (in the center of the figure). The pyramid-shaped structures also observable correspond to the textured-silicon surface, as the TiO₂ is not visible under the electron microscope. Although the structure is rather symmetrical, Fig. 4 shows some irregularities between phases. This fact is more evident in the inset, where detailed micrography of the boundary using the backscattered-electrons detector (to maximize the differences due to different composition) was taken. As shown, the interface, far from being sharply defined, shows irregularities in a range of about 30 μm.

With respect to the lateral resolution due to the projected image in the slit, it will be defined by the pixel-limited sampling of the CCD camera and the magnification of the projected image. As noted, there are several factors affecting the magnification of the image such as imperfections in the collection optics, spectrograph aberrations, and imperfect electron transfer in the intensifier, as well as the studied plasma turbulences or radial expansion. The overall effect will be a distortion of the real image as seen by the detector. The use of patterned targets such as the USAF 1951 may help to estimate the
Fig. 6. (Left panel) Distribution map of silver in a photovoltaic cell using the microline-imaging LIBS. The surface of the sample was rendered from the emission of the Ag(I) line at 328.01 nm. (Right panel) Scanned image of the analyzed sample, showing the pattern of white and black areas (corresponding to the silver fingers and the TiO$_2$ coating, respectively). Both images are shown to scale.

Checking for the dependence of this lateral resolution value with respect to sample size, we analyzed silver fingers of increasing width (between 1000 and 1800 μm). In this instance, and in order to demonstrate the multielemental capability of the method, the CCD readout zone was modified to simultaneously monitor the Ag(I) signal at 328.01 nm and the Ti(II) signal at 252.46 nm. Once the spectral image was captured, the data were post-processed for both elements, and the intensity profiles of Ag and Ti along the microline were plotted together as a function of the pixel number, that is, slit height. The results are shown in Figs. 5A–5C as normalized intensities. As expected, the maximum of the Ag profile coincides with the minimum of the Ti profile showing the alternation pattern between Ag fingers and TiO$_2$ coating in the sample. The FWHM of these profiles increases with Ag finger width: its value for the 1000, 1400, and 1800 μm width silver finger was 108, 138 and 184 pixels, respectively.

It must be noted that the shape of the Ag intensity profile does not seem to follow a Gaussian profile. This fact, apparently in contradiction to comments about Fig. 2, is somehow logical taking into account that signals from consecutive points will tend to convolute as a consequence of the radial expansion. This fact was tested with pure foils of different metals, and the result was identical. In the solar cell, as the Ag fingers are spaced by the TiO$_2$ layer, the effect of the Gaussian profile is noticeable.

Once the experimental conditions were established, a complete three-dimensional (3D) analysis of a 6 × 2 mm$^2$ solar cell area was performed. The distance between consecutive microlines was set at 50 μm, the minimum allowed by the translational stage used. The rendered image is observed in Fig. 6A, while Fig. 6B shows the scanned image of the solar cell. Both images were touched up with the use of commercial programs in order to use the same color code and gray levels. The gray-level scale was established by assigning black to the level of the signal-to-background ratio (SBR) of Ag signal lower than 3, and white to the level of maximum SBR value, with several gray levels in between. Dark zones indicate a deficiency of Ag, while the brightest zones indicate the spatial location of Ag. As shown, the LIBS image represents quite accurately the solar cell structure. However, the aspect of the final image was contrast-dependent, in accordance with other line imaging applications. It should be stressed that only 40 laser events were necessary to completely map the area of interest, while 1000 laser events were required to map the same area using a conventional LIBS configuration. The spacing between craters is also improved: 20 μm using mi-
croline-imaging LIBS as compared to 80 and 150 μm (X and Y directions, respectively) with a conventional LIBS configuration. Consequently, the speed of analysis including both spectra acquisition and data processing is increased by 25-fold when this studied configuration is employed.

**CONCLUSION**

A new approach to the capabilities of LIBS for materials characterization and compositional mapping has been discussed and evaluated. The new method is an alternative to conventional LIBS where the laser beam is tightly focused on the sample surface and the distribution of a given element is obtained by rastering the laser through a defined path. The method relies on using a cylindrical lens to produce a long, narrow plasma (microline plasma). The light is projected along the spectrograph slit of an imaging spectrograph, where each ablated point in the sample generates a signal at a defined height, and then acquired in a charge-coupled device detector. Thus a monodimensional image of the sample surface is obtained for each laser shot. The method has been successfully tested for compositional mapping of solar cells, enabling high-speed elemental characterization of heterogeneous materials with micrometric lateral resolution. The system, in the present state, is a promising alternative for fast imaging or determination of inclusions; however, additional work is required to determine the optical and experimental parameters affecting the spatial resolution.

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