MICROWAVE INDUCED BREAKDOWN SPECTROSCOPY FOR MATERIAL IDENTIFICATION USING BOLTZMANN-PLOT SUPER-RESOLUTION ALGORITHM

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Abstract. This paper presents a technique for identification of solid materials by localized microwaves. A small hotspot (~1-mm^3) created by thermal-runaway instability on the material surface is further radiated by the localized microwaves hence ejecting a plasma plume. Its atomic emission spectrum is detected and analyzed by an optical spectrometer for element identification, as in the known laser-induced breakdown spectroscopy (LIBS) technique. The conceptual feasibility of the microwave-induced breakdown spectroscopy (MIBS) as a low-cost substitute for the LIBS is demonstrated by experimental results. The proposed MIBS technique for material identification might be preferable in scenarios that permit direct contact with the identified material and its slight destruction.

1. INTRODUCTION

Atomic emission spectroscopy (AES) is used to detect the elemental composition of materials by identifying the unique spectral structure of each element, e.g. in laser-induced breakdown spectroscopy (LIBS) [1]. The LIBS is a mature technique exhibiting unambiguous detection capabilities. However, the laser apparatus might be too expensive and cumbersome for some applications, hence cheaper or simpler techniques might be of interest. Plasma characteristics are used to resolve LIBS uncertainties in line intensities emerged by short laser pulses with variable power levels [2].

Localized microwaves are used for "focused" heating of materials, which result in their local melting, evaporation and plasma ejection [3, 4]. Here we present an implementation of localized microwaves for detection of solids and liquids. The proposed technique applies the localized microwaves directly on the material's surface, as a substitute for the laser source in LIBS [5]. Advanced validation of the detected elements by a super-resolution technique using the plasma temperature evaluation by Boltzmann plot is presented.

2. LOCALIZED PLASMA EJECTION FOR MATERIAL IDENTIFICATION

The microwave-drill type applicator [3] plays the role of the laser beam in LIBS as shown in Fig. 1. The open-end applicator concentrates the microwave energy into a hotspot on the material surface by virtue of the localized thermal-runaway effect. The molten hotspot is further evaporated and ionized by the localized microwave field [4] for further AES analysis as illustrated in Fig. 1a. A plasmoid ejected from glass for instance in its identification process is shown in Fig. 1b.

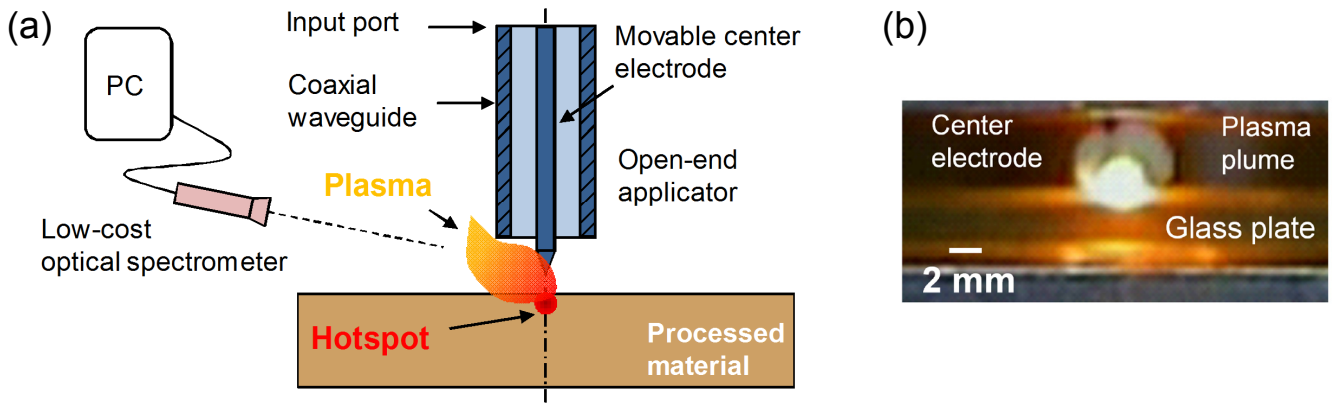

Figure 1. The localized-microwave based detection concept [5]. (a) An illustration of the setup required for localized plasma ejection for material identification. (b) An image of a plasmoid ejected from glass for its AES identification.

3. MATERIAL IDENTIFICATION AND VALIDATION ALGORITHM

The peaks above a selected threshold are detected by the parsed AES data. The algorithm employs the atomic database [6], including the wavelength λ_{ki}, the transition probability A_{ki} of the upper E_k to the lower E_i energy level, and the upper level degeneracy g_k of each atomic emission line. The detected lines are compared to the database in order to identify the element content. The threshold and the database are updated until sufficient lines are detected. Usually, if multiple lines exist within the spectral resolution of the spectrometer, they can not be identified. Here we use Boltzmann plot fitted for each option by

$$\ln\left(\frac{I_{ki}\lambda_{ki}}{g_k A_{ki}}\right) = -\frac{E_k}{k_B T_{exc}} + const., \tag{1}$$

where I_{ki} is the peak intensity, and T_{exc} is the plasma excitation temperature. If any optional element within the multiple line results in a significantly low R^2 in the fit, this option is omitted as presented in the algorithm flowchart in Fig. 2. Since a spectrometer with higher resolution could have resolved this ambiguity, the distinction between the lines is considered as a super-resolution detection algorithm.

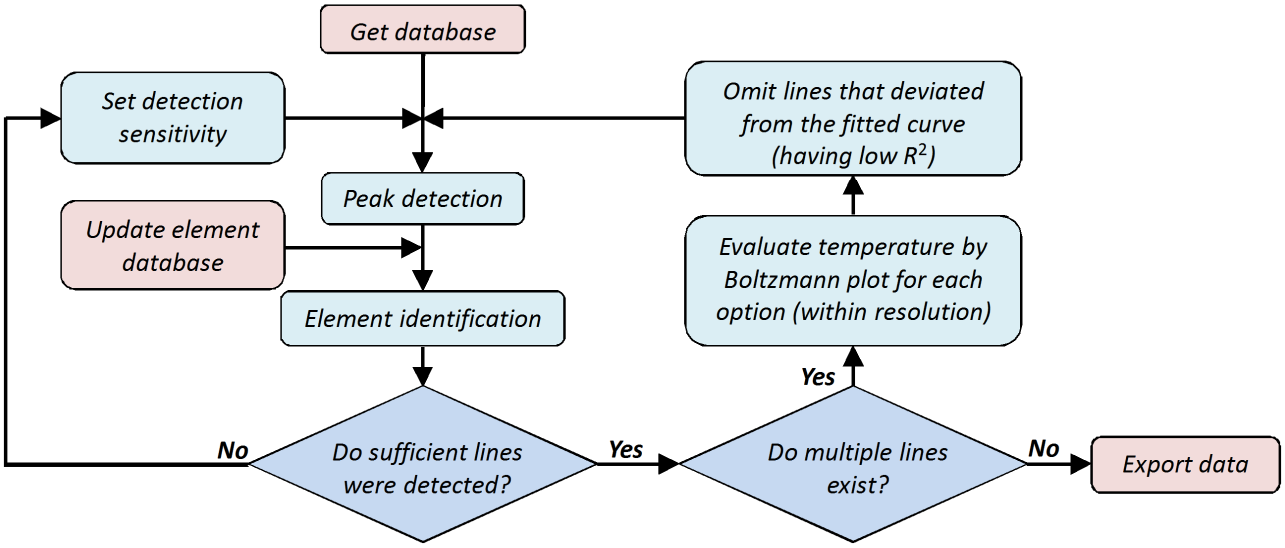

Figure 2. A flowchart of the MIBS detection and validation using a super-resolution algorithm.

3.1. The required microwave power

The localized microwave technique is applicable for materials with sufficient dielectric losses or electric resistively to absorb the microwave energy. Low power localized microwaves can be used for material identification enabling a compact, battery-operated system [7]. The lower limit D for the absorbed microwave-power density is given heuristically for dielectric and metals by

$$D_M = 1.4 k_{th}\sqrt{\omega\mu_0\sigma}\,\Delta T d_{hs}^2, \tag{2}$$

$$D_D = 2.5 k_{th}\, d_{hs}\Delta T / \Delta\varepsilon_r'', \tag{3}$$

respectively, where ω is the microwave angular frequency, μ_0 is the vacuum permeability, k_{th} and σ are the material's thermal and electric conductivity, d_{hs} is the hotspot width, and $\Delta\varepsilon_r''$ is difference of the imaginary part of the permittivity between the melting and room temperature difference ΔT.

4. EXPERIMENTAL DEMONSTRATION

The experimental setup employs a 2.45 GHz automatically tuned generator in the range 0-800 W. The microwave energy is focused by an open-end coaxial applicator into the detected material surface. An optical spectrometer (Avantes AvaSpec-3648) with ~0.3 nm resolution and 14 Hz sampling rate is used to detect the spectral emission from the plasma ejected from the surface.

4.1. Identification of elements

The identification process is demonstrated here on a copper substrate as shown in Fig. 3. The lines identified are of copper and chromium as an impurity marked in Fig. 3a. The inset shows the plasma emission used for the analysis. One multiple line at 324 nm is not identified decisively, since it can be referred to Cu I or Cr I line as shown in Fig. 3b (note the question mark in Fig. 3a). The spectral resolution of the spectrometer employed here is insufficient for the distinction between the two lines.

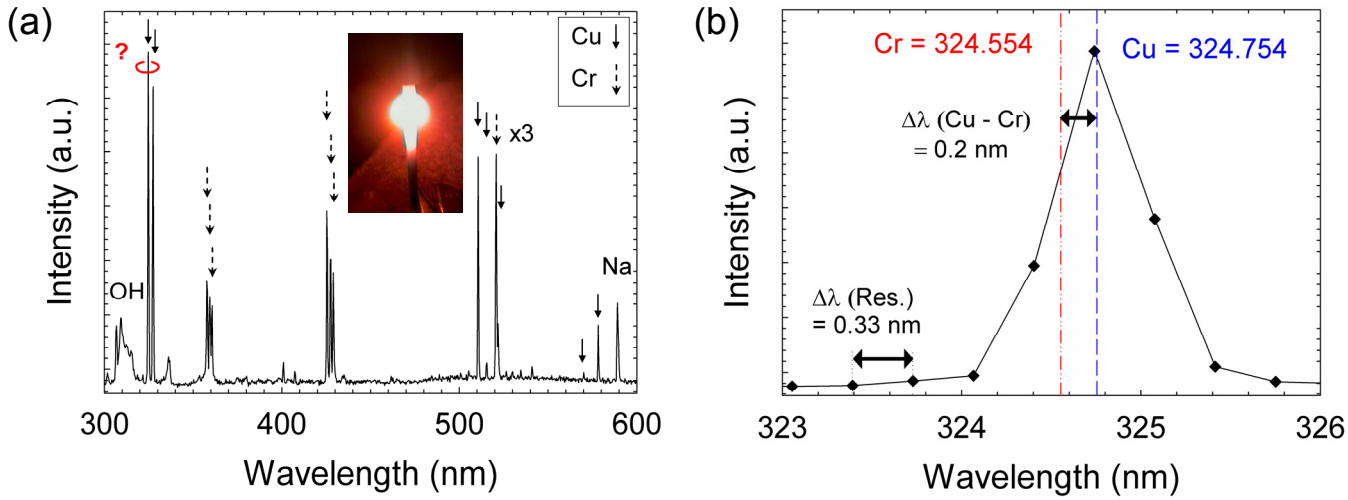

Figure 3. Experimental identification of copper by localized microwaves. (a) A typical spectrum of copper excited by localized microwaves. The inset shows the plasma ejected. (b) The unidentified 324 nm line enlarged.

4.2. Super-resolution detection of multiple spectral lines

In order to attribute the detected peak to the relevant element, the plasma temperature is evaluated. This can be done for instance by evaluating the rotational temperature of the OH emission ($A^2\Sigma^+ - X^2\Pi$), which is equal to the excitation temperature under local thermal equilibrium (LTE) conditions, as demonstrated in Fig. 4. The simulated temperature is fitted to the measured spectrum by the LIFBASE simulation [7], which results in ~0.4 eV as shown in Fig. 4a.

The excitation temperature of the plasma can be estimated by Boltzmann plot fit for each element according to (1). The plasma excitation temperature is determined therefore by the slope of the linear fitted curve. The detected lines are used to evaluate the plasma temperature by the Boltzmann plot applied to copper and chromium, as presented in Fig. 4b. The lines fitted by linear curves show temperature in the range 0.3-0.6 eV with significance R^2 in the order of 0.6. In case that the unidentified line is referred to Cu, the results are slightly changed as presented in Fig. 4b. However, if attributed to Cr, the 324 nm line is significantly deviated from the fit by R^2 of 0.03, resulting a negative plasma temperature (-6 eV), thus the option of a chromium line is declined.

This example demonstrates the use of the statistics factors of the Boltzmann plot using the line intensity in order to validate the detected lines. Calibration of the intensity measured by the spectrometer can increase the R^2 coefficient of determination above the 0.6 significance measured here to enhance the elimination process exampled. This method can be applied to reject lines that result in bad fits, though it

can not approve the revealed line. Other validations can be done in case of ion lines detected, by using Saha equation for the electron density calculation.

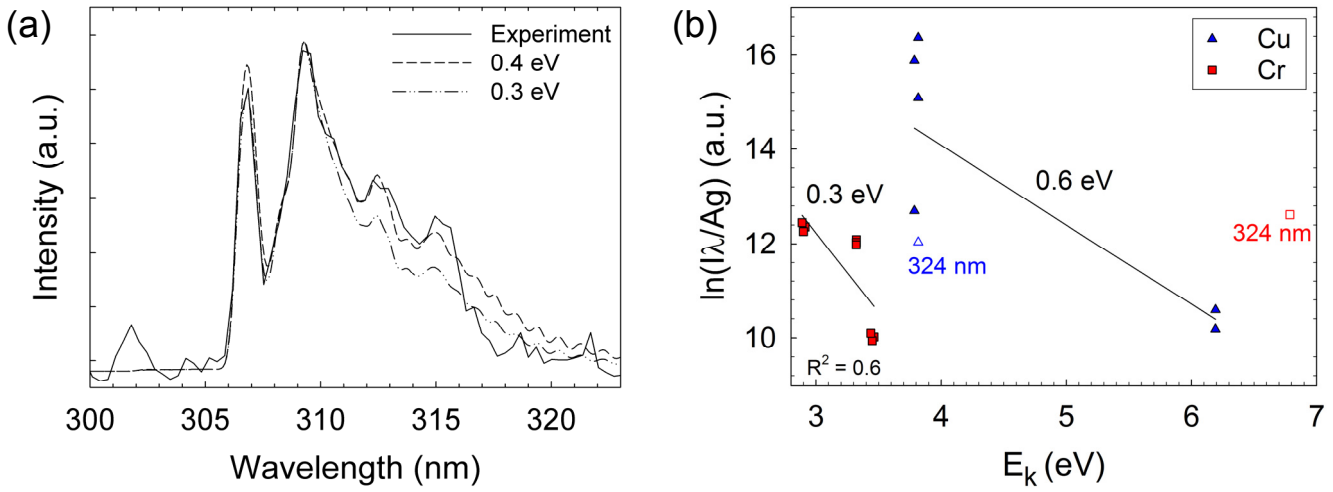

Figure 4. Plasma temperature evaluation for super-resolution detection. (a) OH radical emission used for the temperature estimation. (b) Boltzmann plot employed to attribute the ambiguous spectral lines to Cu or to Cr.

5. CONCLUSION

Localized microwaves are employed in order to detect and identify materials. The method is applicable when a direct physical contact with the detected material and its slight destruction are allowed. The super-resolution method is utilized to distinguish between different elemental spectral lines that are close to each other within the spectrometer resolution limit. This technique enables the use of a low-cost spectrometer with an inferior spectral resolution for material identification in the field. This simplification is accompanied by low-power solid-state microwave applicator [8] for the plasma ejection from the surface. The integration of low-power compact microwave generator and low-end spectrometer with super-resolution processing may provide a conceptual solution for portable battery-operated systems for MIBS applications in the field.

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