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Sub-microanalysis of solid samples with near-field enhanced atomic emission spectroscopy

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ABSTRACT

A novel approach, which we have chosen to name it as near-field enhanced atomic emission spectroscopy (NFE-AES), was proposed by introducing a scanning tunneling microscope (STM) system into a laser-induced breakdown spectrometry (LIBS). The near-field enhancement of a laser-illuminated tip was utilized to improve the lateral resolution tremendously. Using the hybrid arrangement, pure metal tablets were analyzed to verify the performance of NFE-AES both in atmosphere and in vacuum. Due to localized surface plasmon resonance (LSPR), the incident electromagnetic field is enhanced and confined at the apex of tip, resulting in sub-micron scale ablation and elemental emission signal. We discovered that the signal-to-noise ratio (SNR) and the spectral resolution obtained in vacuum condition are better than those acquired in atmospheric condition. The quantitative capability of NFE-AES was demonstrated by analyzing Al and Pb in Cu matrix, respectively. Submicron-sized ablation craters were achieved by performing NFE-AES on a Si wafer with an Al film, and the spectroscopic information from a crater of ~650 nm diameter was successfully obtained. Due to its advantage of high lateral resolution, NFE-AES imaging of micro-patterned Al lines on an integrated circuit of a SIM card was demonstrated with a sub-micron lateral resolution. These results reveal the potential of the NFE-AES technique in sub-microanalysis of solids, opening an opportunity to map chemical composition at sub-micron scale.

Keywords: Near-field enhanced atomic emission spectroscopy, LSPR, Sub-microanalysis, Imaging.

1. Introduction

LIBS is an attractive analytical technique with a wide range of applications due to its simplified operation, nearly non-invasive, minimal sample preparation and high speed of analysis, etc. LIBS imaging is of great importance for materials [1, 2], geological [3], life science [4-6], and so on. Significant successes in LIBS analysis from bulk analysis to spatially resolved chemical imaging have been achieved [7, 8]. In this research field, chemical imaging routinely achieves a lateral resolution of around 10-100 μm [1-7, 9, 10]. Efforts have been made to improve the lateral resolution of LIBS. Several groups have employed microscope objectives to generate tightly focused laser beam, of which pulsed energies are below 100 μJ, namely the micro-LIBS, resulting in lateral resolutions down to a few micrometers [11-13]. A micro-LIBS device had been applied to perform quantitative surface mapping, and the smallest ablation crater with the diameter of 3 μm was achieved for analytical purposes [11]. Alternatively, superior focusing ability down to submicron can be achieved by using femtosecond laser (fs-laser) light, by which 450-700 nm craters (Full width at half maximum) can be generated with detectable spectral emission signals

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