Spectrochimica Acta Part B 111 (2015) 80–86

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

On the use of laser induced breakdown spectroscopy to characterize the naturally existing crystal in Pakistan and its optical emission spectrum

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A R T I C L E I N F O

Article history:
Received 27 August 2014
Accepted 2 July 2015
Available online 11 July 2015

Keywords:
LIBS
Quartz
Silicon
Plasma temperature
Electron number density

A B S T R A C T

We have used the Laser Induced Breakdown Spectroscopic (LIBS) technique to qualitatively identify the naturally existing transparent crystal as a pure quartz (SiO_2) by observing its optical emission spectra using a Q-switched Nd:YAG laser, fundamental wavelength at 1064 nm and second harmonic at 532 nm. The spectra were registered using a set of five miniature spectrometers covering the spectral range from 200 nm to 720 nm. The plasma temperature has been calculated in the range from 8500 K to 10,200 K and the electron densities determined from the Stark broadened spectral lines in the range of 1.0×10^{17} cm^{-3} to 6.0×10^{17} cm^{-3}. We report here the full widths at maximum of the spectral lines associated with the 3p4s $^3P_{0,1,2} \rightarrow 3p^2\ ^3P_{0,1,2}$, $^1S_0$, $^1D_2$ transitions in Si and four multiplets of singly ionized silicon.

1. Introduction

Silicon is a nonmetallic element and an important semiconductor material which is being used to manufacture power transistors, semiconductor devices, integrated circuits and solar cells. Silicon dioxide is the most common compound that is the constituent of minerals and rocks. The transparent quartz crystals are used to manufacture mercury vapor ultraviolet (UV) lamps and optical instruments due to their excellent transmission property up to the vacuum ultra violet (VUV) region. Interestingly, a beautifully cut transparent quartz crystal is found in abundant in the Northern Areas of Pakistan. In order to characterize this naturally obtainable material, we used the Laser Induced Breakdown Spectroscopic (LIBS) technique which is a simple and a non-contact technique being extensively used for the elemental analysis of samples that may be a solid, liquid or gas. In this technique, a high power laser beam is focused on the surface of a sample which generates plasma by the ablation, excitation and ionization processes. The plume of the laser produced plasma contains atoms and ions of the constituent elements whereas the emitted radiation yields detailed information about the structure of the elements. The emission spectra are used for the diagnostics of plasma to extract electron number density and plasma temperature [1–6].

Much attention has been paid to study the laser induced silicon plasma. Wolf [7] studied the plasma properties of laser ablated SiO_2 by irradiating the sample by a Nd:YAG laser 1064 nm at a flux of 7×10^{10} W/cm^2 and reported the plasma temperature ≈3.4 eV and electron density ≈7.6×10^{16} cm^{-3} and determined the Stark broadening line widths of five singly ionized silicon lines. Liu et al. [8] studied the silicon plasma generated by a nanosecond (ns) Nd:YAG laser at 266 nm and reported the plasma temperature in the range of 20,000–70,000 K whereas the electron density determined from the Stark broadening of the Si I line at 288.16 nm was in the range of 10^{18}–10^{19} cm^{-3}. Milan and Laserna [9] observed the silicon ablation using a Nd:YAG laser (532 nm) and reported the electron temperature in the range of 6000–9000 K and the electron number density of the order of 10^{18} cm^{-3}. Samek et al. [10] investigated the spatial and temporal behavior of laser ablation of silicon using a femtosecond (fs) laser; 170–200 fs pulse width. Conde et al. [11] studied the effects of the number of laser pulses on the surface roughness and ablation depth of silicon and copper samples. Zeng et al. [12] studied the ablation efficiencies of silicon using a fs laser (Ti: Sapphire, 100 fs pulse width) and a ns Nd:YAG laser (3 ns pulse width) and inferred that the ablated crater created by the fs laser is nearly twice deeper than that with the ns laser. Amal et al. [13] studied the laser produced plasma on the surface of silicon at different ambient pressures using single and double pulse LIBS technique. Torrisi et al. [14] studied the ablation of silicon using a 3 ns Nd:YAG laser coupled with a mass quadrupole spectrometer to monitor the emission of neutral and ionic species. The time resolved plasma properties for the double pulse laser induced breakdown spectroscopy of silicon was reported by Mao et al. [15] using two laser pulses

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http://dx.doi.org/10.1016/j.sab.2015.07.004
0584-8547/

at 1064 nm and studied the plasma properties as a function of delay between the laser pulses and inferred an increase in the plasma properties and crater dimensions. Camacho et al. [16] reported the laser induced breakdown spectroscopy of trisilane (Si_3H_8) using infrared CO_2 laser pulses and observed strong emission due to Si and ionic fragments Si^+, Si^{2+}, and Si^{3+}. The excitation temperature determined from the singly ionized silicon lines was 26,000 ± 3000 K and that from the hydrogen atomic lines as 5600 ± 300 K whereas the electron density around 1.44×10^{16} cm^{-3} was estimated from the Stark broadened H_β line profile. Khaleeq-ur-Rahman et al. [17] captured the images of the time-integrated silicon plasma produced by a Nd:YAG (1064 nm) laser and studied shot-to-shot variation in the emission signal. The effect of ambient pressure on the laser induced silicon plasma temperature, density and its morphology has been studied by Cowpe et al. [18, 19] using a 532 nm Nd:YAG laser and reported the electron densities in the range 2.79×10^{16} to 5.59×10^{19} cm^{-3} and excitation temperatures of 9000–21,000 K. Recently, El Sherbini and Al Aamer [20] reported the plasma parameters from the emission lines of the laser produced silicon plasma and also reported, using double laser pulses of same energy, a signal enhancement by a factor of about 30 for the neutral silicon line at 288.16 nm and 100 for the doubly charged aluminum line at 281.62 nm. The electron density in the range of 4×10^{17}–2×10^{18} cm^{-3} and the plasma temperature in the range of 0.95 eV–1.25 eV were reported. More recently, Shakeel et al. [21] characterized the laser ablated silicon plasma using the first and second harmonics of a Nd:YAG laser at a laser irradiance of 2–16 GW cm^{-2} and reported the electron temperature in the range of 6350 K–8200 K and electron density in the range 3.42×10^{16} cm^{-3}–5.10×10^{16} cm^{-3}.

The present work was started with two objectives; to exploit the LIBS technique to characterize the naturally existing transparent crystal in Pakistan. Secondly, to study the optical emission spectrum of the laser produced plasma to determine the plasma parameters and line widths. The observed lines have been identified as transitions from the upper levels associated with the 3p4s and 3p3d configurations to the lower levels attached with the $3p^2$ ground state configuration of silicon. All the dipole allowed transitions associated with the $3p4s \rightarrow 3p^2$ transitions have been observed and their widths have been deduced by Lorentzian fit to the experimentally observed line profiles. Besides, four multiplets of singly ionized silicon have been observed and their FWHM has also been determined.

2. Experimental setup

The LIBS apparatus used in the present study is the same as described in our earlier papers [22–25]. In brief, it consists of a Q switched Nd:YAG laser (Brilliant, Quantel France), 5 ns pulse duration and 10 Hz repetition rate. The laser is capable of delivering 400 mJ at 1064 nm and 200 mJ at 532 nm. The laser pulse energy was varied by the flash lamp Q-switch delay and its energy was measured by an energy meter (Nova-Quantel). The (160–250) mJ laser beam was focused on the sample, placed in air at atmospheric pressure, through a lens of 20 cm focal length. The spot diameter at the target surface was about 0.5 mm and the corresponding power density at 200 mJ laser energy is about 2×10^{10} W cm^{-2}. The sample was fixed on a holder, which was rotated continuously to provide a fresh surface for each laser shot. The emission from the plasma plume was registered through an optical fiber (high-OH, core diameter: 600 μm) having a collimating lens (0–45°), coupled with the LIBS2000 (Ocean Optics. Inc, USA) system that is equipped with five spectrometers, 2400 lines/mm gratings to cover the wavelength range from 200 to 400 nm and 1800 lines/mm gratings to cover the range from 400 to 720 nm. Each spectrometer installed in the LIBS2000 detection system is outfitted with 5 μm slit, 2048 element linear CCD array and its spectral resolution is ≈0.06 nm. To record the emission spectrum, the detection system and the Q-switch of the Nd:YAG laser were synchronized through a four-channel digital delay/pulse generator (SRS DG 535). The energy of the laser pulse was varied through the OOILIBS software. The data were acquired at a delay time of about 3 μs between the laser firing and the opening of the detection system to eliminate the contribution of the continuum radiation. The spectra were recorded at different distances, perpendicular to the target surface along the plume expansion, to monitor the spatial variation in the line intensities. The output data were averaged for 10 laser shots to minimize the statistical errors. All the five spectrometers installed in the LIBS2000 are manufacturer calibrated in efficiency using the DH-2000-CAL standard light source. The data acquired simultaneously by all the five spectrometers were stored on a computer through the OOILIBS software for subsequent analysis. The recorded signal was corrected by subtracting the dark signal of the detector through software.

3. Results and discussion

3.1. Characteristics of the crystal

In Fig. 1 we show a photograph of the naturally existing transparent crystal, as found in the Northern Areas of Pakistan. It looks very sharply cut with perfect edges. We compared this photograph with the crystal pictures available in the literature and came to the conclusion that it is quartz (SiO_2) which is the most abundant mineral on Earth and serves as a significant component of sedimentary rocks.

In order to confirm qualitatively the elemental composition of this naturally existing transparent crystal, we focused the 1064 nm laser beam on its surface to produce a plasma and recorded the emission spectrum of the plume. The spectrum reveals all the prominent spectral lines of silicon. Subsequently, we recorded the emission spectrum of the laser produced plasma on the pure silicon sample. Both the spectra were identical, however the intensities of the spectral lines were higher in the pure silicon spectra when recorded at the same laser irradiance of 5×10^6 Wcm^{-2}. Interestingly, no additional lines of any other element, which might be present as an impurity, have been detected in the emission spectrum. This assures that this natural crystal is spectroscopically pure SiO_2. We also recorded the absorption spectrum of this transparent crystal which is opaque up to the UV region and begins to absorb below 200 nm, a characteristic of quartz windows that are commonly used in the optical instruments for the VUV region. Zhen-Guo et al. [26] determined the oxygen concentration in the heavily doped silicon wafer using the LIBS technique. The neutral oxygen line which can be detected in LIBS lies at 777.31 nm. The longest wavelength detectable in our detection system is 720 nm that is why we are unable to comment on the liberation of oxygen in the present studies.

In Fig. 2, we show the emission spectra of the laser produced plasma on the sample covering the spectral range from 400 nm to 515 nm recorded at different laser energies. It is evident from the figure, as the

Fig. 1. Photograph of the naturally existing transparent crystal (SiO_2) in Pakistan.