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Evaluation of laser Induced Breakdown Spectroscopy for analysis of annealed Aluminum Germanium alloy at different temperatures

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Abstract. Laser Induced Breakdown Spectroscopy (LIBS) technique has been applied to study the annealing effect of Al-Ge alloy at 150, 175, 240, 280, 325 ^{0}C. LIBS spectra of all samples prepared at these annealing temperatures were recorded. The signal intensity of the Al and Ge spectral lines increases with increase in annealing temperature. This increase in the signal intensity is due to structural modification of Al-Ge sheets surface with annealing temperatures. This variation in intensity verifies the assessment of annealed materials which can be performed with LIBS technique.

1. Introduction

The Laser Induced Breakdown Spectroscopy (LIBS) technique is a suitable analytical tool for analyzing various types of sample such as solid, liquid and gas [1-15]. It is useful for on line, real time measurement and it is also suitable for field application in inaccessible environments owing to its advantages that include in situ, quick, and remote elemental analysis [1,2]. The technique utilizes atomic emission spectra directly collected from plasmas generated by the interaction of high-energy laser pulses and the target material. The line emission radiated from the plasma presents a spectral signature indicating the presence of constituents of the sample. The line emission intensity from the observed atomic emission spectra can be used for quantitative evaluation of the elemental composition.

LIBS technique has been used to measure the qualitative and quantitative composition of solid, molten materials and powder samples [16-18]. It has also been used to measure the composition of the molten materials. Only limited work has been carried out on LIBS application to thin film and thin

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sheets [19-21]. Recently, LIBS has been used to measure the elemental composition of thin sheets of copper. An interesting application of LIBS in variation of sample surface in polymer sheets has been reported [22].

In the present paper, we aimed to use LIBS technique for investigation of annealing effect at different temperatures on Al-Ge alloy thin sheets. Variation in the signal intensity of Al-Ge alloy samples annealed at different temperatures demonstrates the suitability of LIBS technique for assessment of level of annealing of the material. In addition impurities in the sample can also be identifies at the same time.

2. Experimental procedure

2.1. Samples

Al-Ge alloys preparation

Al-1.0 wt. % Ge alloy was prepared from pure elements 99.99% Al and Ge by melting in graphite crucible together with calcium chloride $CaCl_2$ flux to prevent oxidation. The ingot was homogenized at 823K for 48 hours. The ingot in the shape of rod was swaged into sheets of 2 mm in thickness for analysis with LIBS. The samples were annealed for 2 h at 773 K then quenched in iced water to obtain samples with the supersaturated - solid solution structure. Sheets of Al-Ge alloy samples were aged at temperature range (423- 598K) for 2h then quenched in iced water before applying the measurements.

2.2. The LIBS system

The schematic diagram of the LIBS experimental setup used in the present investigation is described elsewhere in details [16]. Briefly, the LIBS experiment was carried out with spectrolaser-7000 (Laser Analysis Technologies, Australia). The spectrolaser-7000 is an integrated system consists of excitation laser, optical spectrographs, sample chamber, focusing optics and data acquisition system equipped with charge coupled detector (CCD). The excitation laser is a high power (5-300 mJ variable) Nd:YAG laser having a 7 ns pulse duration at the fundamental wavelength of 1064 nm and operates in the Q-switched mode with a pulse repetition rate of 10 Hz. It also has the ability to focus on a fresh region of the sample through a short focal length lens for each successive laser pulse. In the present study, 100 mJ energy of the laser has been used with a varied delay time between 0.2 to 1μs (gate delay between the laser firing and the CCD detector). The laser radiation was focused by a convex lens with a focal length of about 48 mm onto a target to ablate material from the sample surface and produce a plasma cloud. A 600 μm diameter optical fiber was used to collect the radiation emitted by the generated plasma cloud. This collected light was then delivered to a high-resolution (0.1 nm FWHM) spectrometer equipped with a gated CCD camera. Each LIBS spectrum was recorded in the range of 190 – 1100 nm and an average of 10 points was taken to reduce the error due to laser fluctuation.

3. Results and discussion

The observed LIBS spectrum of Al-Ge sheets without annealing from 200 nm to 900 nm is shown in Figure 1(a). The emission from LIBS plasma was recorded at a delay of t_{gate} = 1000 ns with respect to firing time of the laser at the target material and at a gate width of ΔT_{gate} = 2000 ns. Figure 1(a) reveals that the spectral emission lines from neutral atoms of aluminum and germanium dominate the LIBS spectrum over the whole spectral range from 200- 900 nm. The other impurities present in the samples are listed in Table 1. Actually, this is expected because Al and Ge are the main contents of the samples. Abundances of aluminum ions rather than germanium ions in the observed LIBS plasma were recognized due to the lower ionization potential of aluminum (IPAl = 5.98 eV) compare to germanium (IPGe = 7.89 eV). The observed aluminum transitions of 394 nm, and 396 nm have strong lines intensities and large self-absorption as expected since these represent aluminum resonance lines from ground states with high transition probabilities. The proper choice of the experimental conditions is therefore essential to overcome the effect of high number density and reduce the optical thickness of the plasma in a viable approach to minimize self-absorption. In doing so, the reduction of spectral lines intensity mitigates population number density of the species in the lower energy level of the transition. There are two ways to decrease the population number densities of low-lying energy levels: (A) By decreasing the laser pulse energy, the overall number of ablated species reduces, or (B) by studying the plasma during its early time of plume expansion (increased plasma temperature). Usually, the choice (A) is not very useful because the reduction of the laser energy not only reduces the number of ablated atoms but it also reduces the plasma temperature. On the other hand, the increase of temperature via the reduction of the gate delay (Condition B) is an efficient way to reduce the self-absorption as the temperature strongly reduces during the expansion of the laser-produced plasma. Thus, the optimized recording conditions are obtained when the observation time is early enough to limit the self-absorption and large enough to get a satisfactory signal-to-noise ratio. These conditions were achieved at 100mJ of laser energy, gate delay of t_{gate} = 1000 ns and gate width of Tgate = 2000 ns as mentioned earlier.

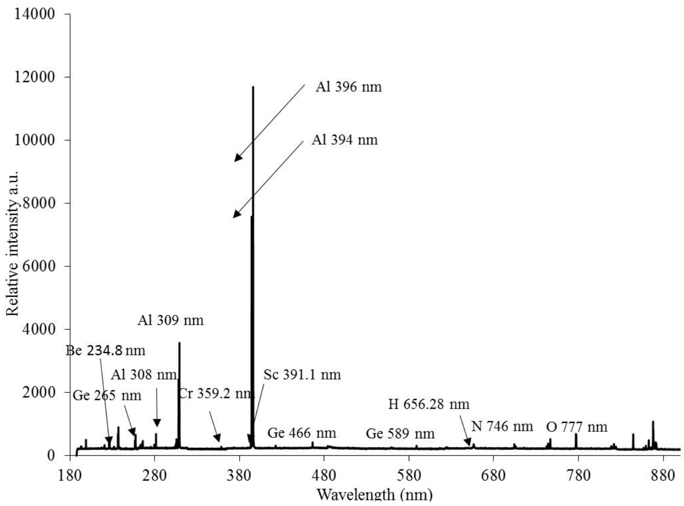

Figure 1(a). LIBS spectrum from 200-900 nm for Al-Ge sample without annealing.

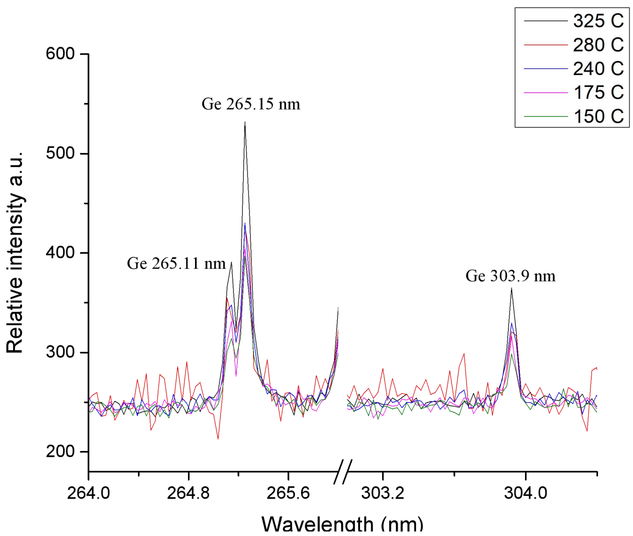

Figure 1(b). Expended LIBS spectra of Ge at different annealing temperatures.

Variations in the intensities of Ge lines at 265.15 nm, 446.35 nm and 285.16 nm observed in the LIBS spectra at different annealing temperatures are depicted in Figure 1(b). Similar effect in the Aluminum lines at wavelengths, 308.21 nm and 309.28 nm at different annealing temperatures was also observed which is shown in Figure 1(c).

Table 1. Spectroscopic data for trace elements.

Wavelength	Element	Elower	Eupper	A
194.295	Be I	21978.27	73429.32	1.30E+05
234.86	Be I	0	42565.4	5.60E+07
359.348	Cr I	0.00	27820.23	1.50E+07
391.181	Sc I	168.33	25724.67	1.80E+07
423.804	Sc I	16210.84	39799.98	7.10E+06
656.28	H I	82259	97492.3	4.40E+06
742.395	N I	83285.5	96751.7	6.00E+05
777.195	O I	73767.8	86631	3.70E+06
868.028	NI	83364.6	94881.8	2.50E+07

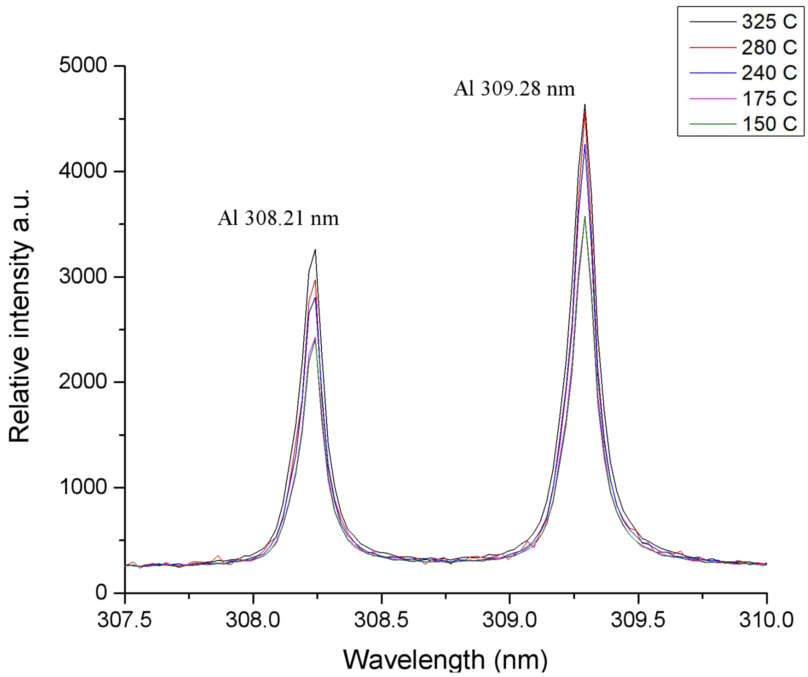

Figure 1(c). Al-Ge LIBS spectra of Al lines at different annealing temperatures.

When a sheet is annealed, the crystal structure is changed and as the annealing temperature increases, the energy band gap of the material decreases [23, 24]. Due to decrease in band gap less energy is required to excite and ionize the material. Since the energy in LIBS experiment was kept constant, therefore LIBS spectra of the sheet samples at higher annealing temperature are showing high intensity as compared to the samples annealed at lower temperatures.

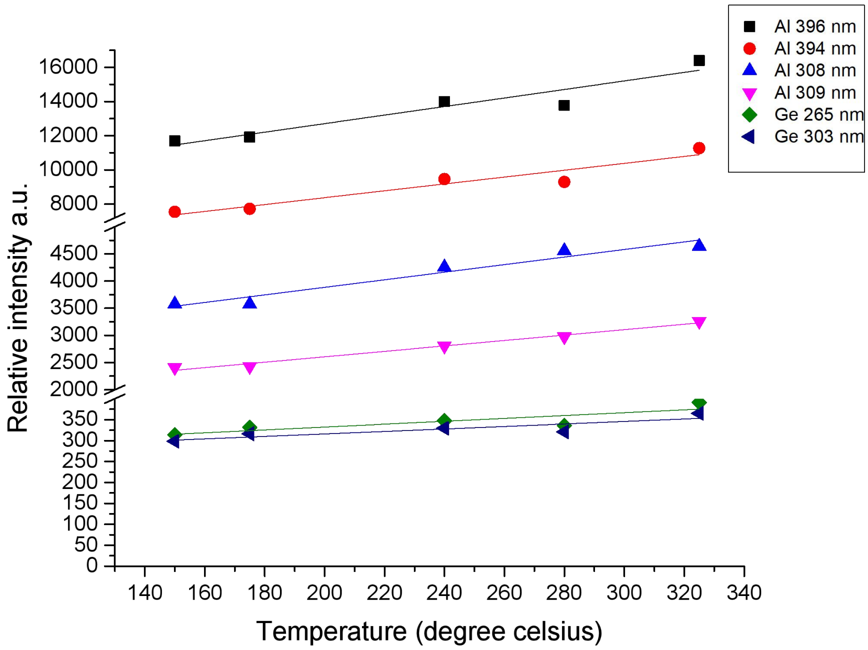

Figure 2. Variation of Al 309.28 nm line intensity with annealing temperature.

Variation in intensity of Aluminum lines at 396, 394, 309.28, 308.21 nm and Ge lines at 265, 303 nm in the LIBS spectra of Al-Ge samples annealed at different temperatures are depicted in Figure 2. This Figure reveals that the intensity variation in Al and Ge lines are linear with increasing temperature. This behavior indicates the structural modification due to laser interaction with materials, which may depends on the type of materials [25, 26] and on the thermal effects of the material. Such structural modifications due to thermal effects were discussed in the ref [27-29]. These results demonstrate that LIBS technique can be applied to assess the annealing effects in materials.

4. Conclusions

LIBS technique has proved to be a very good technique to study annealing effect in the form of variation in signal intensity of the respective material. It has been successfully applied to annealed Al-Ge alloy samples. It is demonstrated that signal intensity increases linearly with increasing annealing temperatures. This happens due to recrystallization of material with annealing temperatures. Moreover, impurities in the sample can be identified at the same time from LIBS spectra.

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